

**Thermally induced intramolecular hydrogen atom transfer and the study
of the flash vacuum pyrolysis of various cyclic and non-cyclic organic
molecules related to, and including, *o*-allyltoluene**

by

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CHAPTER 1. GENERAL INTRODUCTION

Explanation of Dissertation Format

This dissertation consists of eight chapters, the first being this introduction. Chapter two is a literature review covering previous work related to the material found in the following five chapters. Chapters three and four consist of two complete papers in the style suitable for publication in journals published by the American Chemical Society. Chapters five through seven are also presented in the style suitable for publication in journals published by the American Chemical Society but will not be submitted for publication. Chapter eight is a general conclusion chapter. Detailed analytical data and/or spectra are contained in appendices at the end of the dissertation.

The research described in the results and experimental sections of each paper was performed by the author with the following exceptions. In the first paper (Chapter 3), the FVP and product analysis of *o*-allyltoluene (non-deuterated) is part of the Ph.D. dissertation of James L. Malandra (Iowa State University, 1993), while the FVPs and product analyses of *o*-(1-methylallyl)toluene, 2,2-dimethylindan, *o*-allylethylbenzene, *o*-allylcumene, *o*-(3-butenyl)toluene, and *o*-(4-pentenyl)toluene are part of the Ph.D. dissertation of John M. Ferguson (Iowa State University, 1995). In the second paper (Chapter 4), the FVP's and product analyses of *o*-allylphenol and *o*-(1-methylallyl)phenol are also part of the Ph.D. dissertation of John M. Ferguson (Iowa State University, 1995), while the FVP and product analysis of *o*-(ethenyloxy)toluene is part of the MS thesis of Fang Li (Iowa State University, 1995).

Background

Over the past two decades, workers in the Trahanovsky group have directed a large part of their studies toward the understanding of the gas-phase thermal reactions of simple organic molecules, such as hydroaromatic hydrocarbons and various alkylaryl olefins. In the process of studying the flash vacuum pyrolysis (FVP) of tetralin, evidence was observed consistent with the secondary pyrolysis of one of the products, *o*-allyltoluene. During further studies on the FVP of *o*-allyltoluene, we observed a rearrangement that appears to involve diradicals formed by an uncommon thermally induced intramolecular hydrogen-atom transfer.

In our desire to study the scope of this rearrangement, we have studied the FVPs of several related alkylaryl olefins including *o*-allyltoluene- α,α,α - d_3 , (*E/Z*)-*o*-(1-propenyl)toluene, *o*-(1-methylallyl)toluene, *o*-allylethylbenzene, *o*-allylcumene, *o*-(3-butenyl)toluene, *o*-(4-butenyl)toluene, and 2-methylstyrene. These results, as well as the initial work on *o*-allyltoluene, are presented in the first paper (Chapter 3). In the second paper (Chapter 4), parallel studies on the phenol and aniline analogs of *o*-allyltoluene are presented. The remaining three papers present the results of FVPs on some cyclic and heterocyclic analogs of *o*-allyltoluene, including 3-(*o*-tolyl)propene oxide (Chapter 5), *o*-cyclopropylmethyltoluene (Chapter 6), and *o*-cyclohexyltoluene (Chapter 7).

CHAPTER 2. LITERATURE REVIEW:

Gas-Phase Thermal Rearrangements of Various Cyclic and Non-Cyclic Molecules Related to, and including, *o*-Allyltoluene; and the Formation of Diradicals and Radical Pairs by Hydrogen Atom Transfer

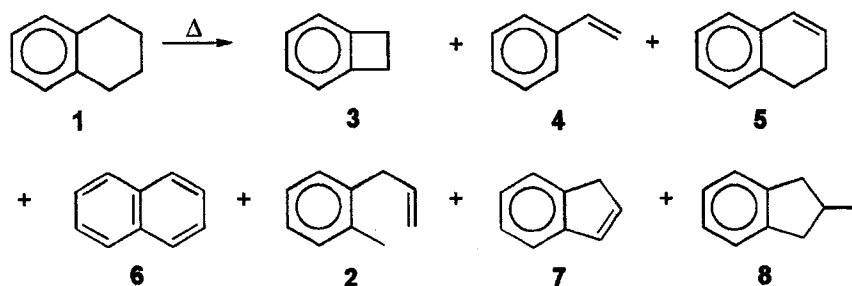
Introduction

The following chapters of this dissertation comprise five papers presenting the results of a series of flash vacuum pyrolyses (FVP's) on selected aromatic hydrocarbons, epoxides, and medium to small ring hydrocarbon systems. In the process of discussing these results the work of numerous researchers will be cited. In this chapter, references from the following five chapters related to gas phase thermal rearrangements will be reviewed in greater detail. In addition, several recent (2000 – present) articles regarding the gas phase thermal rearrangements of molecules structurally related to those in the dissertation are also reviewed. The contents of this chapter are divided by specific molecule or functional group type. A short section on the formation of diradicals and radical pairs by hydrogen atom transfer is also included.

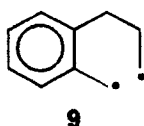
1. *o*-Allyltoluene and Related Molecules

1.1. Tetralin (1)

Our study of the FVP of *o*-allyltoluene (2) was precipitated by previous work in our group with the FVP of tetralin (1).¹ Earlier work by Bergman and Moore under FVP and laser excitation conditions established that the FVP of 1 involves two major decomposition pathways: (a) loss of ethylene to give benzocyclobutene (3) and styrene (4) and (b) loss of hydrogen to give 1,2-dihydronaphthalene (5) and naphthalene (6).² Along with these major



products many other minor products are observed including *o*-allyltoluene (**2**), indene (**7**), and 2-methylindan (**8**). A third, minor, pathway involving intramolecular disproportionation of diradical **9** is proposed to explain the formation of **2**. Work by Malandra and others in our



group revealed that at higher pyrolysis temperatures the yield of **2** decreased but the yield of **7** increased. It was this evidence for possible secondary pyrolysis products of **2** that motivated our direct FVP studies of **2**.

Recently, Poutsma, Marquiere, and Dominé have reviewed progress in understanding the thermal decomposition mechanisms of **1**.³ However, none of the mechanisms presented invoke diradicals.

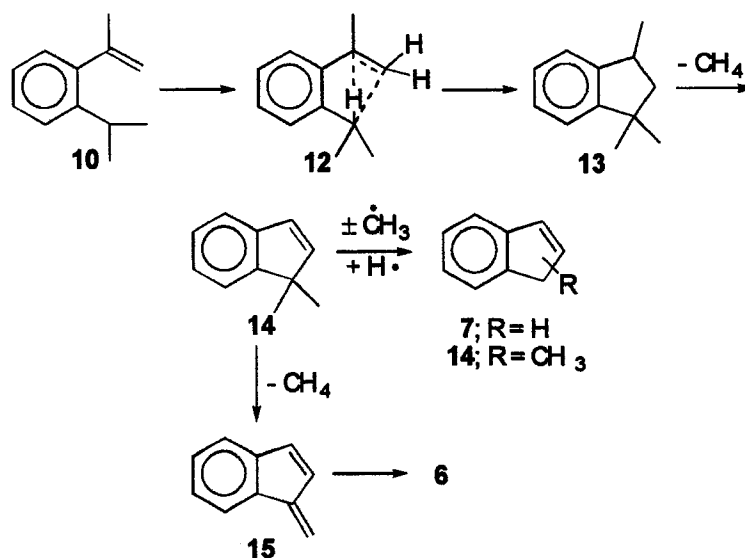
1.2. *o*-Allyltoluene (**2**)

In our FVP studies of **2** at 700-900 °C we observed **7** and **8** as the main products.⁴ Previous gas-phase pyrolyses of **2** yielded different results. Lambert and co-workers carried out the static gas-phase pyrolysis of **2** at 350-400 °C. They reported *o*-tolylpropene, methylindan (isomer not specified), and tetralin as major products.⁵ *o*-Xylene, *o*-ethyltoluene, *o*-methylstyrene, *o*-propyltoluene and naphthalene were reported as “possible minor products”. No toluene was detected and no mention of **7** was made. Hurd reported that under

flow pyrolysis conditions at 650-700 °C, **2** gives *o*-xylene, toluene, naphthalene, and unchanged starting material.⁶

1.3. *o*-Isopropyl- α -methylstyrene (**10**)

Brown and coworkers have pyrolyzed *o*-isopropyl- α -methylstyrene (**10**) under FVP conditions (800 °C, 0.01 torr), observing **6**, **7**, and partly characterized mono-methylindenes (**11**) as major products.⁷ A transition state (**12**) of “diradical character” is proposed as the initial step, yielding 1,1,3-trimethylindan (**13**), which is not observed in the product mixture but is proposed as an intermediate species. From this point, a series of steps involving methyl radical and/or hydrogen atom loss and the formation of undetected intermediates **14**, and **15**, are proposed to explain the observed products (Scheme 1). The conversion of **14** into



Scheme 1

7 does not take place by a unimolecular process. Compounds **13**, **14**, and **15**, when pyrolyzed separately, yield products consistent with their position in Scheme 1.

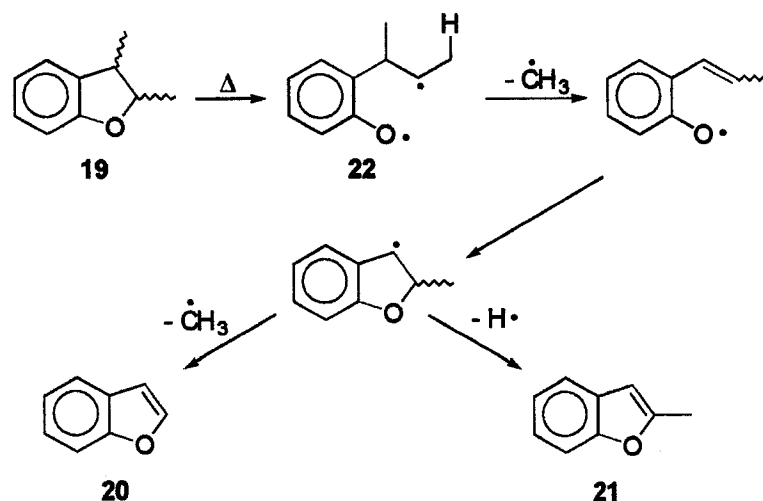
While Brown and co-workers were unable to detect **13** in their FVP product mixtures, our pyrolyses of *o*-methylstyrene (**16**) and *E/Z*-*o*-(1-propenyl)toluene (**17**), under similar con-

condition, yielded significant amounts of indan (**18**) and 2-methylindan (**8**), respectively, with indene as the main product in both cases.⁴



2. *cis*- and *trans*-2,3-Dimethyl-2,3-dihydrobenzofuran (**19**)

van Meurs and coworkers have carried out flow pyrolysis on a mixture of *cis*- and *trans*-2,3-Dimethyl-2,3-dihydrobenzofuran (**19**), observing the formation of benzofuran (**20**) and 2-methylbenzofuran (**21**) as the main products at 700 °C.⁸ They propose the formation of diradical **22**, by homolytic C-O bond fission, followed by a series of methyl radical and hydrogen atom losses to explain the production of **20** and **21** (Scheme 2).



Scheme 2

In our studies on the FVP of *o*-allylphenols we have proposed diradical **22** as the intermediate, resulting from intramolecular hydrogen atom transfer, between *o*-(1-methylallyl)phenol (**23**) and the main product **19** at 600 °C.⁹ At higher temperatures, 700-800 °C, we too observe **20** and **21** as the main products.

3. Terminal Epoxides

In our FVP of 3-(*o*-tolyl)propene oxide we have observed the selective rearrangement to 3-(*o*-tolyl)propionaldehyde.¹⁰ Previous work with the pyrolysis of terminal epoxides has yielded significantly different results.

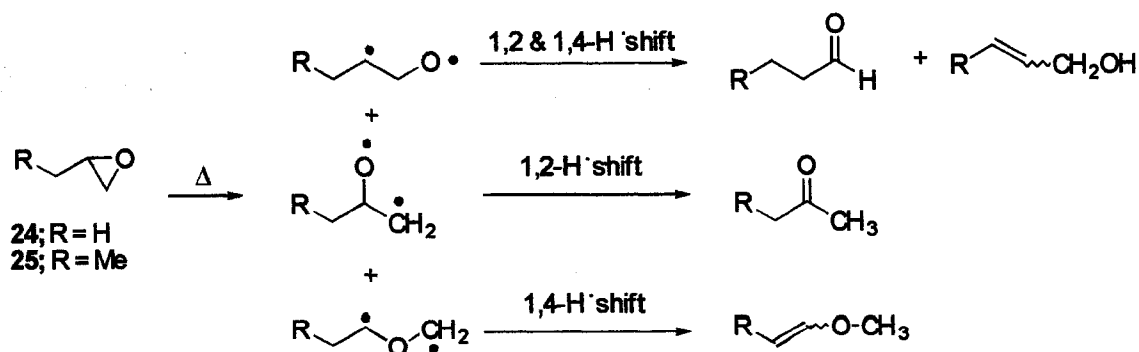
3.1. Propene Oxide (24)

During the past thirty years there have been four major studies of the gas-phase pyrolysis of propene oxide (24).¹¹ In the earliest study, Hardwick pyrolyzed 24 in the presence of toluene (radical scavenger) in a small stainless steel pressure vessel at 402-459 °C.^{8a} The main isomerization products were propionaldehyde (60-70 %) and acetone (14 %) along with minor amounts of non-specified decomposition products. Hardwick suggests that unimolecular rearrangement of 24 results in an intermediate (not specified) that then either rearranges to the aldehyde and ketone isomers or fragments into free radicals. Studies that followed by Blades^{11b} and Flowers^{11c} yielded additional isomerization products including allyl alcohol and methyl vinyl ether, respectively. Both studies were carried out in surface-treated static systems in the absence of toluene. More recently, Lifshits has employed shock tube pyrolysis in studying the thermal gas-phase reactions of 24, observing the same products as Blades and Flowers.

3.2. 1,2-Epoxybutane (25)

Prior to his work with propene oxide, Flowers studied the static pyrolysis of 1,2-epoxybutane (25), observing products parallel to those he would later report for the similar pyrolysis of 24.¹² Flowers proposed three parallel two-step mechanisms in which ring

scission to one of three possible diradicals is followed by 1,2- and/or 1,4-hydrogen shifts (Scheme 3). This mechanism also explains the pyrolysis results of **24**.

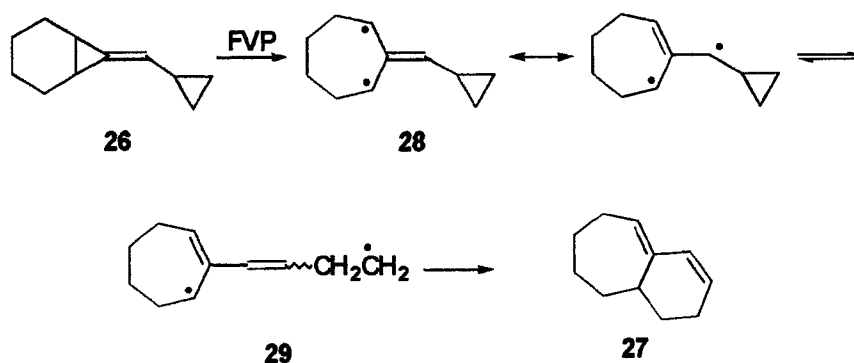


Scheme 3

4. Small Ring Hydrocarbon Gas Phase Pyrolyses

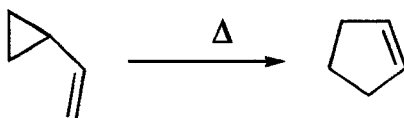
4.1. Cyclopropyl Thermal Ring Opening

Cohen and co-workers have employed FVP induced double ring expansions of cyclopropylalkylidenecyclopropanes in a novel route to six-membered rings.¹³ In the most fundamental example, they carried out the FVP of cyclopropylmethylidenecyclopropane (**26**) at 550 °C and 0.01 Torr, producing the double ring expanded diene (**27**) in 92 % yield. The formation of **27** is explained by the initial homolytic cleavage of the strained doubly allylic bond followed by rearrangement of the resulting trimethylenemethane diradical (**28**) into the



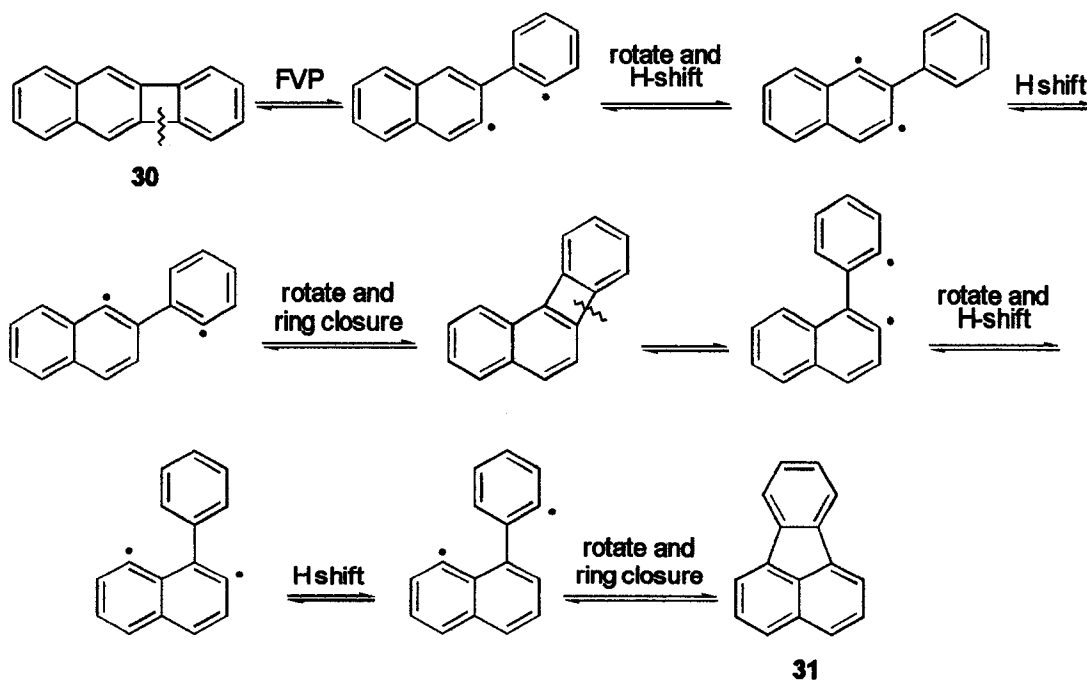
Scheme 4

homoallylic radical (**29**) (Scheme 4). Closure of diradical **29** would then result in **27**. Recently, Baldwin has reviewed the thermal rearrangements of vinylcyclopropanes to cyclopentenes.¹⁴



4.2. Cyclobutyl Thermal Ring Opening

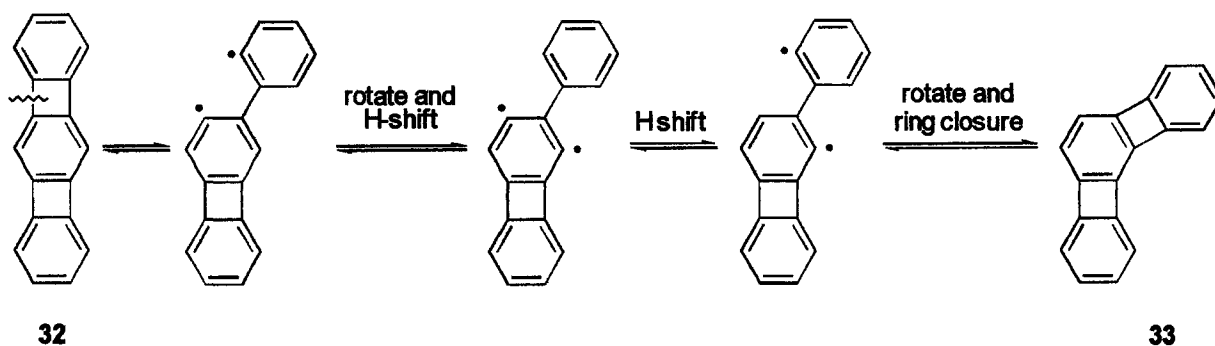
Recently, Scott and co-workers have observed the conversion of benzo[*b*]biphenylene (**30**) into fluoranthene (**31**) as the major product under FVP conditions at 1100 °C.¹⁵ The process appears to proceed from phenyl group migration around the perimeter of the poly



Scheme 5

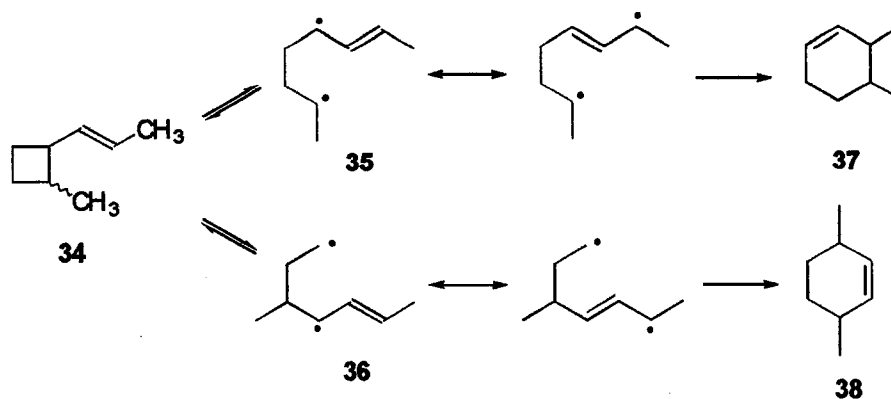
cyclic ring system and is explained by a series of homolytic bond breaking and forming steps and 1,5- and 1,6-hydrogen atom transfers, as shown in Scheme 5. These results provide a mechanistic link between alternant and nonalternant polycyclic aromatic hydrocarbons (PAHs) at high temperatures.

Vollhardt and co-workers, in explaining the isomerization of linear (32) to angular [3]phenylene (33) under FVP conditions at 1000 °C, have proposed a mechanism parallel to Scott's explanation for the isomerization of 30 to 31 (Scheme 6).¹⁶



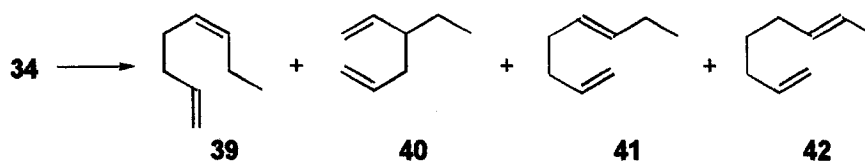
Scheme 6

In recent non-PAH related work Baldwin and co-workers have studied the thermal gas-phase rearrangements and fragmentations of *cis*- and *trans*-1-(*E*)-propeny-2-methylcyclobutane (34) in a static reactor at 275 °C.¹⁷ It was shown that 34 undergoes standard pericyclic isomerizations as well as other thermal isomerizations involving diradicals 35 and

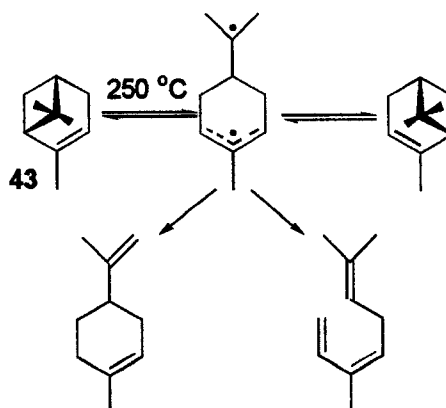


Scheme 7

36, resulting from cleavage of C1-C2 or C1-C4, respectively. The two diradicals give rise to *cis*/*trans* isomerization of **34** as well as the products *cis*- and *trans*-3,4-dimethylcyclo-hexene (**37**) and *cis*- and *trans*-3,6-dimethylcyclohexene (**38**) (Scheme 7). The pericyclic isomerizations give rise to 1,5-(*Z*)-octadiene (**39**), 3-ethylhexa-1,5-diene (**40**), 1,5-(*E*)-octadiene (**41**), and 1,6-(*E*)-octadiene (**42**).

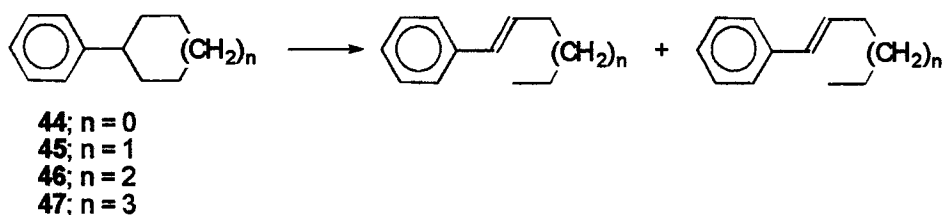


Recently, Gajewski has also reported non-PAH related work in which the mechanism for the pyrolysis mediated isomerization of α -pinene (**43**) is studied.¹⁸

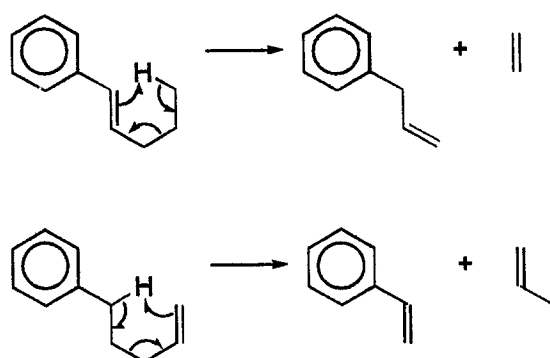


5. Medium Ring Hydrocarbon Gas Phase Pyrolyses

Zimmermann and co-workers have pyrolyzed phenylcyclopentane (**44**), phenylcyclohexane (**45**), phenylcycloheptane (**46**), and phenylcyclooctane (**47**) from 700-780 °C in a



static reactor in the presence of steam.¹⁹ While they observed numerous decomposition products, they propose that initially the starting materials undergo either dehydrogenation to the corresponding phenylcycloalkene or isomerization to the corresponding 1-phenyl-1-alkene and/or ω -phenyl-1-alkene. They postulate that fragmentation of the isomeric products by retro-ene reaction yields the corresponding major products of ethylene and styrene, as shown below for the isomerization products of **44**.

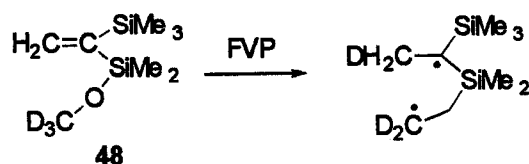


6. Formation of Diradicals and Radical Pairs by Transfer of a Hydrogen Atom

In the second chapter of this dissertation the concept of formation of a diradical by thermally-induced intramolecular transfer of a hydrogen atom is introduced.⁸ We are aware of only one report which proposes this mechanism, and this is for the cyclization of an organosilicon compound. There are, however, examples of the formation of diradicals by transfer of a hydrogen atom in intramolecular photochemical reactions. Radical pairs have also been reported in a few intermolecular thermal reactions.

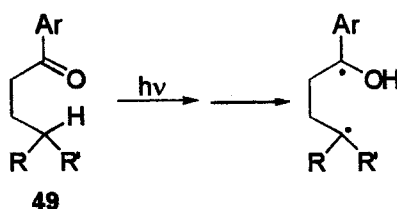
6.1. Thermally Induced Intramolecular Hydrogen Atom Transfer

Barton and co-workers have proposed the formation of a 1,4-diradical by thermally induced intramolecular hydrogen atom transfer in the FVP of alkoxyvinylsilane **48**²⁰ They observed a deuterium isotope effect consistent with C-H(D) cleavage in the transition state.

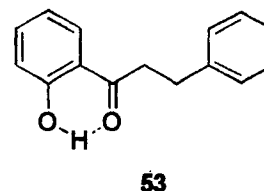
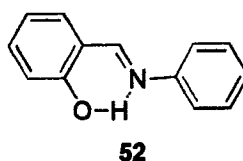
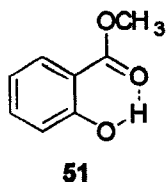
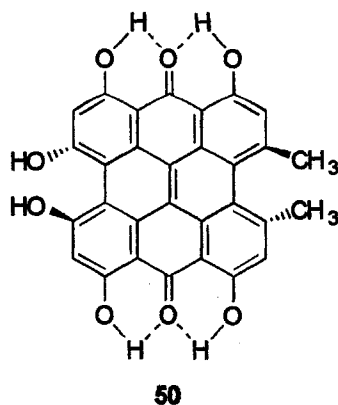


6.2. Photochemically Induced Intramolecular Hydrogen Atom Transfer

Johnston and Scaiano, in their review of solution phase biradical reactions, have included a section on photochemically induced intramolecular hydrogen atom transfer.²¹ The Norrish Type II reaction, a common photochemical reaction leading to biradicals, occurs from the triplet state as illustrated below for aryl alkyl ketone **49** More recently photochemi-

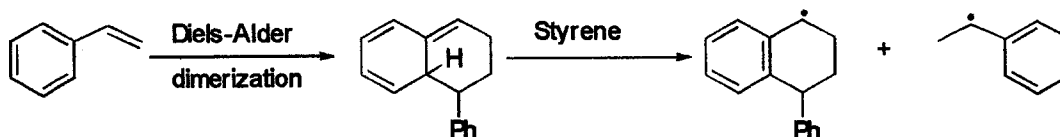


cally induced excited-state intramolecular hydrogen atom transfers have been studied by Kraus and Petrich in the naturally occurring polycyclic quinone hypericin (**50**)²² and by Arai in methyl salicylate (**51**), *N*-salicylideneamine (**52**), and 2'-hydroxychalcone (**53**).²³

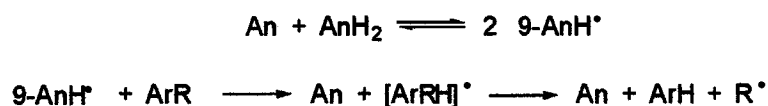


6.3. Thermally Induced Intermolecular Hydrogen Atom Transfer

Intermolecular hydrogen-atom transfer has long been proposed as a key step in the mechanism for spontaneous initiation of styrene polymerization.²⁴ Proposed by Mayo, it involves the removal of a hydrogen atom from the initially formed Diels-Alder dimer. A few



recent examples of diradicals generated by thermally induced intermolecular hydrogen atom transfer have been reported. Arends and co-workers have studied the hydrogen shuttling reactions of naphthalene derivatives (ArR) in anthracene (An)/9,10-dihydroanthracene (AnH₂) mixtures, observing desubstitution of the derivatives by radical hydrogen transfer through 9,10-dihydroanthracene radicals (9-AnH).²⁵ Rüchardt and



co-workers have recently reported that the transfer of hydrogen from AnH₂ to α -methylstyrene is catalyzed by the addition of a stoichiometric amount of a hydrocarbon with weaker C-H bonds than AnH₂.²⁶

Conclusions

While much of the work highlighted in this chapter parallels, and in some cases has inspired, the work presented in the preceding chapters, some of the results are significantly different from those observed in our studies. Observations made when expanding on previous tetralin pyrolysis work motivated our study of the FVP of *o*-allyltoluene. Our results

from the FVP of *o*-allyltoluene, however, vary greatly from previous work. Most significantly, previous research yields no evidence for the indene obtained as a major product in the FVP of *o*-allyltoluene. Work by van Meurs on the pyrolysis of dihydrobenzofurans coincides very well with our work in the FVP of *o*-allylphenols. Possibly the most significant difference between our studies and previous studies involves the thermal rearrangement of terminal epoxides. Previous pyrolyses of terminal epoxides have yielded numerous isomerization products including aldehydes, ketones, allyl alcohols, and methyl vinyl ethers. Our selective isomerization of 3-(*o*-tolyl)propene oxide to 3-(*o*-tolyl)propionaldehyde is therefore surprising.

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CHAPTER 3. Flash Vacuum Pyrolysis of *o*-Allyltoluene. Generation of Diradicals by Intramolecular Hydrogen-Atom Transfer

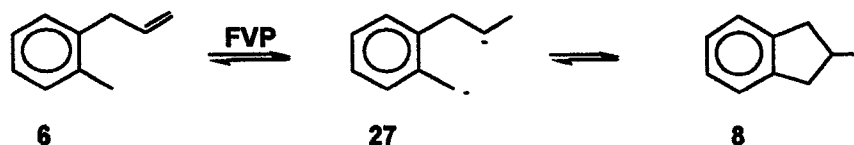
A paper to be submitted to the Journal of Organic Chemistry

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Abstract

The flash vacuum pyrolysis (FVP) of *o*-allyltoluene (**6**) at 700 °C and 800 °C gives 2-methylindan (**8**) as the major product. At 900 °C, **8** is still produced but indene (**7**) is the major product along with several minor products. It is proposed that **8** is produced by a two-step mechanism involving a diradical (**27**) formed by a reversible intramolecular hydrogen-atom transfer. The production of indene (**7**) at higher temperatures is explained by

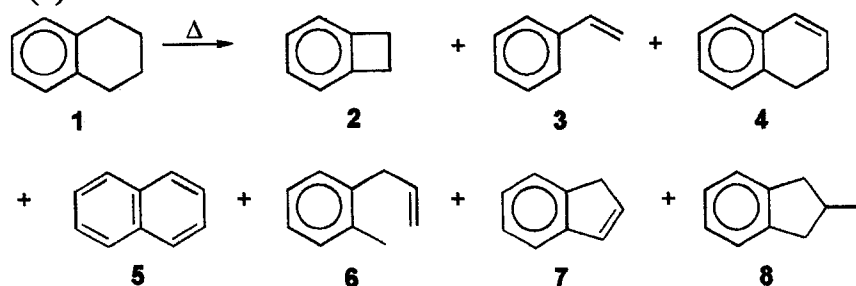


conversion of **27** to **7** by a series of reactions involving the loss of a methyl group and a hydrogen atom. The FVP's of several related molecules, *o*-allyltoluene- α,α,α - d_3 (**6- d_3**), 2-methylindan (**8**), (*E/Z*)-*o*-(1-propenyl)toluene (**9**), *o*-(1-methylallyl)toluene (**10**), 2,2-dimethylindan (**11**), *o*-allylethylbenzene (**12**), *o*-allylcumene (**13**), *o*-(3-butenyl)toluene (**14**),

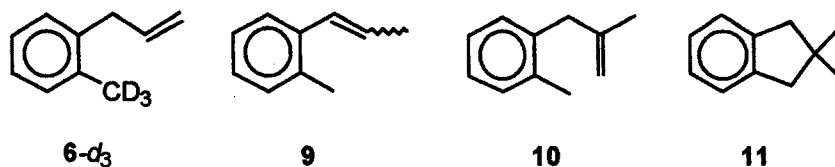
o-(4-pentenyl)toluene (15), 2-methylstyrene (16), and indan (17) were also studied to probe the mechanism and scope of this transformation.

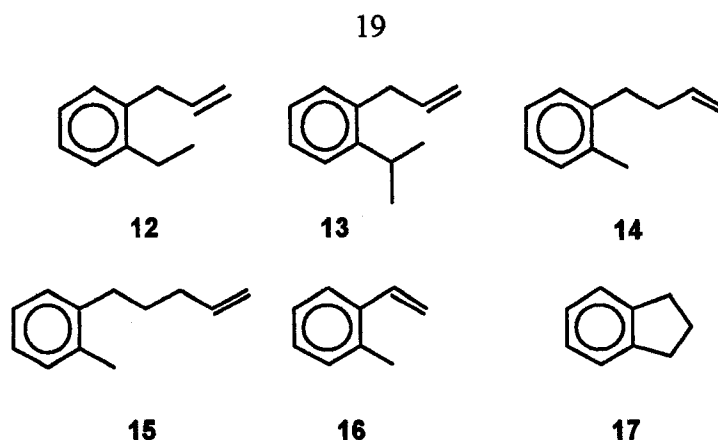
Introduction

The gas-phase pyrolysis of tetralin (1) involves two major decomposition pathways: (a) loss of ethylene to give benzocyclobutene (2) and styrene (3) and (b) loss of hydrogen to give 1,2-dihydronaphthalene (4) and naphthalene (5).^{1,2} Along with these major products, there are many other minor products, including *o*-allyltoluene (6), indene (7), and 2-methylindan (8).¹



While studying the effects of the pyrolysis temperature on the yields of products obtained by the flash vacuum pyrolysis (FVP) of **1**, we noted that as the pyrolysis temperature increases, the yield of **6** decreases, but the yield of **7** increases. To check the possibility that **6** was the source of **7**, we studied the FVP of **6** itself. We now report that indeed **7** and **8** are the major products of the FVP of **6**, which differs from results previously reported for the gas-phase reactions of **6**.^{3,4} The FVP's of several related molecules, *o*-allyltoluene- α,α,α -*d*₃ (**6-d**₃), 2-methylindan (**8**), (*E/Z*)-*o*-(1-propenyl)toluene (**9**), *o*-(1-methylallyl)toluene (**10**), 2,2-dimethylindan (**11**), *o*-allylethylbenzene (**12**), *o*-allylcumene (**13**), *o*-(3-butenyl)toluene (**14**), *o*-(4-pentenyl)toluene (**15**), *o*-methylstyrene (**16**), and indan (**17**) were also studied.

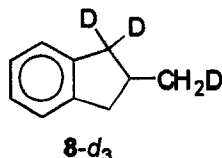




Results

The results of the FVP of *o*-allyltoluene (**6**) at 0.10 torr (700-900 °C) are presented in Table 3.1. The major products are 2-methylindan (**8**) (4.1-25.3%) and indene (**7**) (0.8-32.0%). Low yields of tetralin (**1**), 1,2-dihydronaphthalene (**4**), naphthalene (**5**), and *o*-methylstyrene (**16**) are also produced. At 800-900 °C, small amounts of (*E*)-*o*-(1-propenyl)toluene (**9-E**) are produced.

The deuterium labeled *o*-allyltoluene **6-d₃** was pyrolyzed under similar conditions. At 725-750 °C the only product observed by ¹H and ²H NMR spectroscopy is **8-d₃**. Deuterium atoms are detected at one benzylic position (two broad singlets at δ 3.05 ppm and 2.54 ppm) and on the methyl position (multiplet δ 1.3-1.1 ppm). The 850 °C FVP product mixture shows stronger deuterium signals for **8-d₃** and additional weak signals, which were not assigned, in the aromatic and olefinic regions.



The FVP of 2-methylindan (**8**) at 0.05 torr (700-900 °C) yields products similar to those produced by the FVP of **6**. The main product is **7** (0.8-26.4%) with small amounts of **5**, **6**, **9-(E)**, 3-methyl-1*H*-indene (**18**), 2-methyl-1*H*-indene (**19**), and 1,2-dihydronaphthalene (**4**) also being produced. These results are presented in Table 3.2.

Table 3.1. Products and Recovered Starting Material from the FVP of *o*-Allyltoluene (6) at Various Temperatures ^{a,b}

entry	yield, % ^c		
	700 °C	800 °C	900 °C
<i>o</i> -allyltoluene (6) ^d	91	45	6.6
<i>o</i> -methylstyrene (16)	1.1	3.3	5.8
indene (7)	0.8	6.9	32
2-methylindan (8)	4.1	25	14
(<i>E</i>)- <i>o</i> -(1-propenyl)toluene (9- <i>E</i>)	—	2.9	3.5
tetralin (1)	0.3	2.7	3.3
3-methyl-1 <i>H</i> -indene (18)	—	0.7	3.5
2-methyl-1 <i>H</i> -indene (19)	—	0.4	0.7
1,2-dihydronaphthalene (4)	0.6	1.4	1.1
naphthalene (5)	—	1.0	8.1
other products	3.3 ^e	10 ^e	21 ^e
recovery ^f	84	89	73
conversion ^g	9.1	55	93

^aFVP conditions: system pressure = 0.10 torr, sample temperature = 0 °C.

^b Amounts determined by GC with a known quantity of biphenyl added as standard. Data represent the average of triplicate runs with a standard deviation of 0.9%. Products identified by comparison with authentic samples by retention time and GCMS are indicated by name.

^c Moles of product divided by total moles of recovered material X 100. ^d Starting material purity as determined by FVP at RT is 97 %. ^e See Table A-1 in Appendix A for a more detailed analysis. ^f Total moles of recovered material divided by moles of starting material used X 100. ^g Total moles of recovered material minus moles of recovered starting material divided by total moles of recovered material X 100.

Table 3.2. Products and Recovered Starting Material from the FVP of 2-Methylindan (8) at Various Temperatures ^{a,b}

entry	yield, % ^c		
	700 °C	750 °C	850 °C
2-methylindan (8) ^d	97	92	48
<i>o</i> -methylstyrene (16)	—	0.1 ^e	0.7 ^e
<i>o</i> -allyltoluene (6)	0.5	1.6	3.6
indene (7)	0.8	2.4	26
(<i>E</i>)- <i>o</i> -(1-propenyl)toluene (9- <i>E</i>)	—	0.3	2.2
3-methyl-1 <i>H</i> -indene (18)	1.0	1.6	3.4
2-methyl-1 <i>H</i> -indene (19)	—	—	0.7
1,2-dihydronaphthalene (4)	—	0.2	0.7
naphthalene (5)	—	0.3	3.6
other products	0.4 ^f	1.4 ^f	13 ^f
recovery ^g	84	94	95
conversion ^h	2.5	8.1	52

^a See Table 3.1, note *a*. ^b See Table 3.1, note *b*. ^c See Table 3.1, note *c*. ^d Starting material 80 mole % pure by ¹H NMR spectroscopy quantification against durene. ^e The *o*-methylstyrene (16) peak in the chromatogram also contains an unknown of MW = 136 (see Figures A-8 and A-9 in Appendix A for GC-MS analysis of this peak). The area of the peak was divided in half for calculations, making the results for 16 approximate. ^f See Table A-2 in Appendix A for a more detailed analysis. ^g See Table 3.1, note *f*. ^h See Table 3.1, note *g*.

The results of the FVP of (*E/Z*)-*o*-(1-propenyl)toluene (**9**) at 0.02 torr (900-1000 °C) are presented in Table 3.3. The main products at 900 °C are indene (**7**) (36.5%) and *o*-methylstyrene (**16**) (9.9%). Small amounts of naphthalene (**5**), 2-methylindan (**8**), 3-methyl-1*H*-indene (**18**), and *o*-allyltoluene (**6**) are also produced. At 1000 °C the main products are **7** (53.5%) and **5** (17.2%). Small amounts of **16** and **18** are produced along with very small amounts of **6** and **8**.

The results of the FVP of *o*-(1-methylallyl)toluene (**10**) at 0.10 torr (700-900 °C) are presented in Table 3.4. The major product at 700-850 °C is 2,2-dimethylindan (**11**) (4.0-31.7%). Small amounts of **5**, **7**, **18**, **19**, and 1-(*o*-tolyl)-2-methylpropene (**20**) are formed. At 900 °C, the major products are **5** (18.8%) and **7** (16.6%), accompanied by small amounts of **11**, and **18-20**.

2,2-Dimethylindan (**11**) was pyrolyzed at 900 °C and affords products (Table 3.5) similar to those produced by the FVP of *o*-(1-methylallyl)toluene (**10**) at 900 °C. The major products are **5** (24.0%) and **7** (21.7%), along with low yields of **10**, and **18-20**.

The results of the FVP of *o*-allylethylbenzene (**12**) at 0.10 torr (700-800 °C) are presented in Table 3.6. At 700 °C, low yields of compounds **18**, **19**, *o*-ethylstyrene (**21**) (*E*)-*o*-(propenyl)ethylbenzene (**23**), and *o*-propylstyrene (**22**) are produced as well as a small amount of an unknown compound of *m/z* = 146. At 750-800 °C, the major products are **5** (5.7-19.3%) and **7** (6.9-22.8%). Small amounts of **18-23** are produced as well as many minor products.

The results of the FVP of *o*-allylcumene (**13**) carried out under similar conditions are presented in Table 3.7. At 700 °C, low yields of naphthalene (**5**), indene (**7**), and *o*-methylstyrene (**16**) are obtained, along with small amounts of two compounds of molecular weight 160. At 750 °C, larger amounts of **5** (17.7%), **7** (6.0%), and **16** (8.2%) are formed as well as many minor compounds.

**Table 3.3. Products and Recovered Starting Material from the FVP of
(*E/Z*)-*o*-(1-Propenyl)toluene (9) at Various Temperatures ^{a,b}**

entry	yield, % ^c	
	900 °C	1000 °C
(<i>E</i>)- <i>o</i> -(1-propenyl)toluene (9- <i>E</i>) ^d	16	2.3
<i>o</i> -methylstyrene (16)	9.9	4.3
(<i>Z</i>)- <i>o</i> -(1-propenyl)toluene (9- <i>Z</i>) ^d	8.0	0.7
<i>o</i> -allyltoluene (6)	1.1	0.2
indene (7)	36	53
2-methylindan (8)	4.7	0.8
3-methyl-1 <i>H</i> -indene (18)	4.3	5.1
1,2-dihydronaphthalene (4)	0.5	—
naphthalene (5)	5.6	17
other products	13 ^e	16 ^e
recovery ^f	84	53
conversion ^g	76	97

^a See Table 3.1, note *a*. ^b See Table 3.1, note *b*. ^c See Table 3.1, note *c*. ^d Starting material 86 mole % pure by ¹H NMR spectroscopy quantification against triphenylmethane: (*E/Z*) = 0.95. ^e See Table A-3 in Appendix A for a more detailed analysis. ^f See Table 3.1, note *f*. ^g See Table 3.1, note *g*.

Table 3.4. Products and Recovered Starting Material from the FVP of *o*-(1-methylallyl)toluene (10) at Various Temperatures ^{a,b}

entry	yield, % ^c			
	700°C	800 °C	850 °C	900 °C
<i>o</i> -(1-methylallyl)toluene (10) ^d	90	30	22	6.2
indene (7)	—	2.7	5.9	17
2,2-dimethylindan (11)	4.0	32	24	9.8
1-methyl-2-(<i>o</i> -tolyl)propene (20)	0.7	6.0	6.6	4.7
3-methyl-1 <i>H</i> -indene (18)	0.2	3.3	4.5	5.2
2-methyl-1 <i>H</i> -indene (19)	0.4	3.5	4.4	4.0
naphthalene (5)	0.1	4.1	6.6	18.8
other products	4.5 ^e	16 ^e	21 ^e	23 ^e
recovery ^f	89	84	81	67
conversion ^g	10	70	78	94

^a See Table 3.1, note *a*. ^b See Table 3.1, note *b*. ^c See Table 3.1, note *c*. ^d Starting material purity = 94 area % by GC assay. ^e See Table A-4 in Appendix A for a more detailed analysis. ^f See Table 3.1, note *f*. ^g See Table 3.1, note *g*.

Table 3.5. Products and Recovered Starting Material from the FVP of 2,2-Dimethylindan (11) at 900 °C *a,b*

entry	yield, % <i>c</i>
2,2-dimethylindan (11) <i>d</i>	11
indene (7)	22
<i>o</i> -(1-methylallyl)toluene (10)	4.8
1-methyl-2-(<i>o</i> -tolyl)propene (20)	5.4
3-methyl-1 <i>H</i> -indene (18)	7.4
2-methyl-1 <i>H</i> -indene (19)	5.4
naphthalene (5)	24
other products	26 <i>e</i>
recovery <i>f</i>	60
conversion <i>g</i>	89

a See Table 3.1, note *a*. *b* See Table 3.1, note *b*. *c* See Table 3.1, note *c*. *d* Starting material purity = 97 area % by GC assay. *e* See Table A-5 in Appendix A for a more detailed analysis. *f* See Table 3.1, footnote *f*. *g* See Table 3.1, footnote *g*.

Table 3.6. Products and Recovered Starting Material from the FVP of *o*-Allylethylbenzene (12) at Various Temperatures *a,b*

entry	yield, % <i>c</i>		
	700 °C	750 °C	800 °C
<i>o</i> -allylethylbenzene (12) <i>d</i>	74	49	15
<i>o</i> -ethylstyrene (21)	2.6	5.2	5.5
indene (7)	1.9	6.9	23
ED-146 [C ₁₁ H ₁₄] <i>e</i>	3.9	3.6	2.6
3-methyl-1 <i>H</i> -indene (18)	1.8	4.7	6.7
<i>o</i> -propylstyrene (22)	—	1.7	3.6
2-methyl-1 <i>H</i> -indene (19)	1.2	3.6	4.5
(<i>E</i>)- <i>o</i> -(propenyl)ethylbenzene (23)	1.4	2.2	2.1
naphthalene (5)	1.6	5.7	19.3
other products	7.2 <i>f</i>	12 <i>f</i>	14 <i>f</i>
recovery <i>g</i>	79	79	71
conversion <i>h</i>	26	52	85

a See Table 3.1, note *a*. *b* See Table 3.1, footnote *b*. *c* See Table 3.1, note *c*. *d*

Starting material purity = 96 area % by GC assay. *e* Products identified by GCMS only are indicated by code: XY-nnn, where 'X' corresponds to the system where first observed (E = 11, C = 12), 'Y' to the individual unknown product (A, B, C, etc.), and 'nnn' to the nominal mass. *f* See Table A-6 in Appendix A of for a more detailed analysis. *g* See Table 3.1, footnote *f*. *h* See Table 3.1, footnote *g*.

Table 3.7. Products and Recovered Starting Material from the FVP of *o*-Allylcumene (13) at Various Temperatures ^{a,b}

entry	yield, % ^c	
	700 °C	750 °C
<i>o</i> -allylcumene (13) ^d	54	20
indene (7)	1.7	6.6
CC-160 [C ₁₂ H ₁₆] ^e	4.4	3.4
3-methyl-1 <i>H</i> -indene (18)	3.6	8.2
CG-160 [C ₁₂ H ₁₆]	2.5	5.1
naphthalene (5)	5.1	18
other products	30 ^f	39 ^f
recovery ^g	83	73
conversion ^h	46	80

^a See Table 3.1, note *a*. ^b Amounts determined by GC with a known quantity of biphenyl added as standard. Data for 700 °C represent the average of duplicate runs. Data for 750 °C represent the average of triplicate runs. ^c See Table 3.1, note *c*. ^d Starting material purity = 92 area % by GC assay. ^e See Table 3.5, note *e*. ^f See Table A-7 in Appendix A of for a more detailed analysis. ^g See Table 3.1, footnote *f*. ^h See Table 3.1, footnote *g*.

The results of the FVP of *o*-(3-butenyl)toluene (**14**) at 0.010 torr (700-900 °C) are presented in Table 3.8. Good yields (*ca.* 40%) of 1,2-di(*o*-tolyl)ethane (**24**) are obtained at 700-800 °C. At 900 °C, significant amounts (10-20%) of *o*-xylene (**25**), benzocyclobutene (**2**), *o*-ethyltoluene (**26**), and styrene (**3**) are formed.

The results of the FVP of *o*-(4-pentenyl)toluene (**15**) at 0.010 torr (600-800 °C) are presented in Table 3.9. The major product at 700-800 °C is *o*-methylstyrene (**16**) (30.6-59.8%). Numerous side products, each produced in small amounts, are formed at high conversion (900 °C).

The FVP of *o*-methylstyrene (**16**) at 0.01 torr (950 °C) results in a 59.3% conversion to indan (**17**) (15.4%) and indene (**7**) (30.0%). Indan (**17**) when pyrolyzed under similar conditions produces primarily **7** and **16** in a 5.8 to 1 ratio, with the ratio of 1.1 to 1 for **17** to **7**.

The results of the liquid-phase thermolysis of *o*-(1-methylallyl)toluene (**10**) in phenyl ether (240 min, 400 °C) are presented in Table 3.10. At a higher starting concentration of **10**, the major product is 1-methyl-2-(*o*-tolyl)propene (**20**), the double-bond isomer of **10**. Small amounts of naphthalene (**5**), 2,2-dimethylindan (**11**), 3-methyl-1*H*-indene (**18**), and 2-methyl-1*H*-indene (**19**) are also formed. When the initial concentration of **10** is lowered 5-to 20 % of its initial value, the conversion to **20** is lower. The percentages of **5**, **11**, **18**, and **19** do not change significantly.

Table 3.8. Products and Recovered Starting Material from the FVP of *o*-(3-Butenyl)toluene (14) at Various Oven Temperatures ^{a,b}

entry	yield, % ^c		
	700 °C	800 °C	900 °C
<i>o</i> -(3-butenyl)toluene (14) ^d	64	42	16
<i>o</i> -xylene (25)	0.4	4.7	19
styrene (3)	—	0.5	6.8
benzocyclobutene (2)	0.4	3.5	15
<i>o</i> -ethyltoluene (26)	—	3.0	10
1,2-di(<i>o</i> -tolyl)ethane (24)	34	39	7.6
other products	0.6 ^e	7.3 ^e	26 ^e
recovery ^f	98	89	100
conversion ^g	36	58	84

^a See Table 3.1, note *a*. ^b See Table 3.1, note *b*. ^c See Table 3.1, note *c*. ^d Starting material purity as determined by FVP at RT is >99 %. ^e See Table A-8 in Appendix A for a more detailed analysis. ^f See Table 3.1, note *f*. ^g See Table 3.1, note *g*.

Table 3.9. Products and Recovered Starting Material from the FVP of *o*-(4-Pentenyl)toluene (15) at Various Oven Temperatures ^{a,b}

entry	yield, % ^c		
	600 °C	700 °C	800 °C
<i>o</i> -(4-pentenyl)toluene (15) ^d	90	53	3.0
<i>o</i> -methylstyrene (16)	1.5	31	60
other products	8.1 ^e	16 ^e	37 ^e
recovery ^f	96	87	70
conversion ^g	9.6	47	97

^a See Table 3.1, note *a*. ^b See Table 3.1, note *b*. ^c See Table 3.1, note *c*. ^d Starting material purity as determined by FVP at RT is 92 %. ^e See Table A-9 in Appendix A for a more detailed analysis. ^f See Table 3.1, note *f*. ^g See Table 3.1, note *g*.

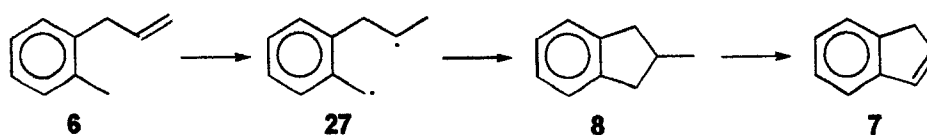
Table 3.10. Products and Recovered Starting Material from the Liquid-phase Thermolysis of *o*-(1-Methylallyl)toluene (10) in Phenyl Ether at Various Concentrations ^a

entry	yield, % ^b	
	0.0724 mol L ⁻¹	0.0145 mol L ⁻¹
<i>o</i> -(1-methylallyl)toluene (10) ^c	14	50
2,2-dimethylindan (11)	3.6	3.9
1-(<i>o</i> -tolyl)-2-methylpropene (20)	58	27
3-methyl-1 <i>H</i> -indene (18)	6.1	7.3
2-methyl-1 <i>H</i> -indene (19)	4.5	2.2
naphthalene (5)	4.7	1.2
other products	9.4 ^c	8.7 ^c

^a Thermolysis conditions: 0.5 mL of degassed phenyl ether solution was sealed in a glass tube and then heated to 400 °C for 240 min. ^b See Table A-9 in Appendix A for a more detailed analysis. ^c Starting material purity = 95 area % by GC assay.

Discussion

The FVP of *o*-allyltoluene (**6**) at 700 °C and 800 °C produces as the major product 2-methylindan (**8**). At 900 °C, **8** is still obtained, but indene (**7**) is the major product along with several minor products, including tetralin (**1**), 1,2-dihydronaphthalene (**4**), naphthalene (**5**), (*E*)-*o*-(1-propenyl)toluene (**9-E**), *o*-methylstyrene (**16**), 3-methyl-1*H*-indene (**18**), and 2-methyl-1*H*-indene (**19**). We propose that **8** is produced by a two-step mechanism involving diradical **27** formed by an intramolecular hydrogen-atom transfer. Although there are



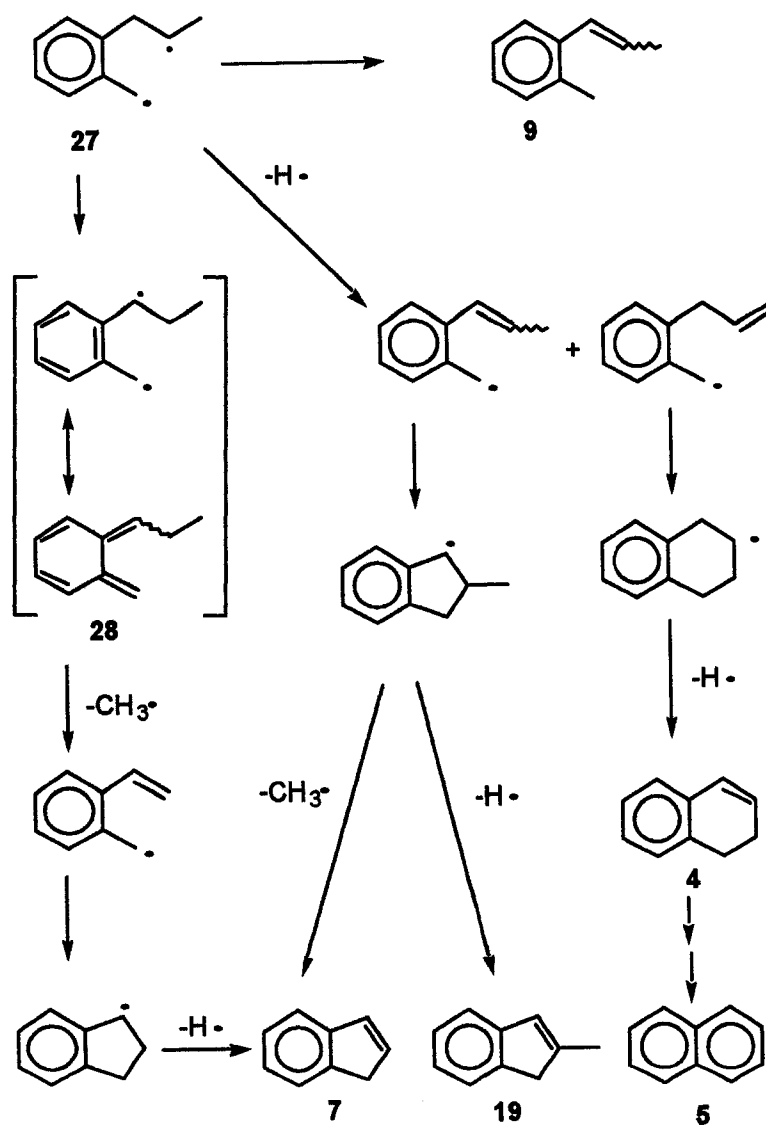
examples of the formation of diradicals by transfer of a hydrogen atom in intramolecular photochemical reactions⁵ and examples of the formation of radical pairs in a few intermolecular thermal reactions,^{6,7,8} we are aware of only one report which proposes the formation of a diradical by thermally-induced intramolecular transfer of a hydrogen atom and this is for the cyclization of an organosilicon compound.⁹

The generation of diradical **27** by a thermally-induced intramolecular hydrogen-atom transfer of **6** is simply the reverse of an intramolecular disproportionation reaction¹⁰ of diradical **27** and is reasonable based on estimated enthalpy changes. The estimated ΔH^0 value for the conversion of **6** to **27**, using Benson's method,¹¹ is 45 kcal/mol. With the assumption that the corresponding ΔH^\ddagger value lies within 2-3 kcal/mol of the ΔH^0 value, the conversion of **6** to **27** is not unreasonable at temperatures ≥ 700 °C.

The proposed mechanism involving diradical **27** for the formation of **8** from **6** is consistent with the results of the FVP of *o*-allyltoluene- α,α,α -*d*₃ (**6-d**₃) which shows that a methyl hydrogen atom is transferred to the terminal olefinic carbon atom. Moreover, many of the other products obtained from the FVP of **6** can be derived from diradical **27** (Scheme 1). Intramolecular disproportionation¹⁰ accounts for **9** and it is reasonable that diradical **27** gives

more **8** than **9**, since calculated¹¹ ΔH_f^0 values show that **8** is 16 kcal/mol more stable than **6** and 11 kcal/mol more stable than (**9-E**). A series of 1,2-hydrogen-atom shifts^{12,13} and β fragmentations¹² lead to most of the remaining products.

Scheme 1

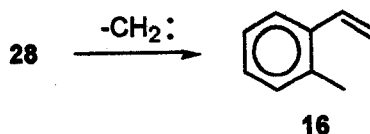


The formation of **18** is accounted for by the interconversion of **19** to **18** by a series of 1,5-hydrogen and 1,5-methyl shifts, which is analogous to the known interconversion of

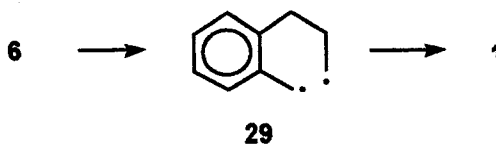


phenyl substituted indenenes.¹⁶

o-Methylstyrene (16) is explained by the loss of a methylene group from 28, a reaction which we discuss below.

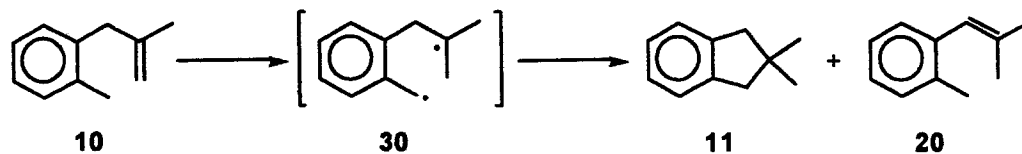


Tetralin (1) cannot be obtained directly from diradical 27, but conversion of 6 to diradical 29 by a hydrogen-atom transfer to the internal olefinic carbon atom, followed by intramolecular coupling of 29 is a reasonable route to 1.



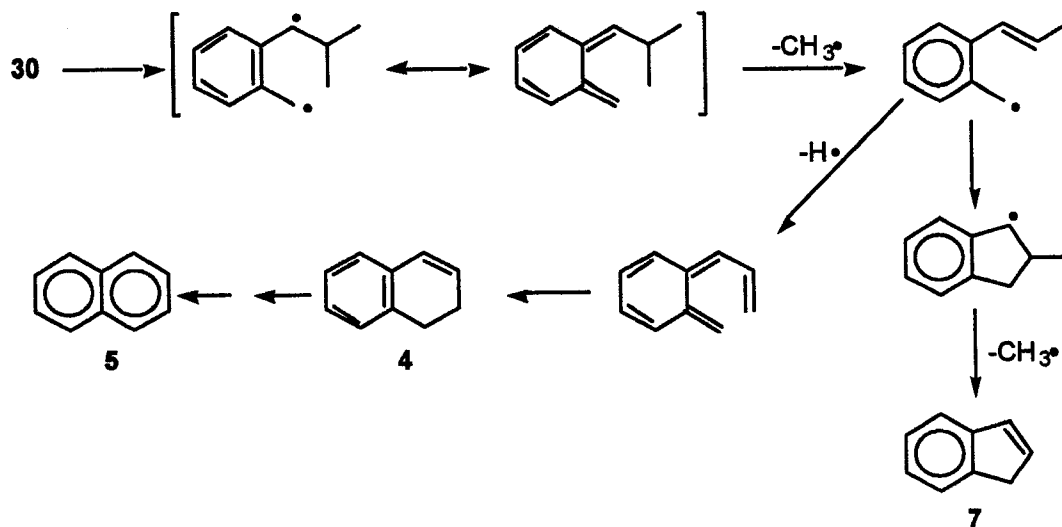
The reversibility of the conversion of 6 to 2-methylindan (8) via diradical 27 is supported by the products of the FVP of 8. Pyrolysis of 8 yields *o*-allyltoluene (6) and (*E*)-*o*-(1-propenyl)toluene (9-*E*), two products expected from intramolecular disproportionation of diradical 27, along with all of the remaining products observed in the FVP of 6.

Further evidence for the formation of diradicals by intramolecular hydrogen-atom transfer was obtained from the FVP of *o*-(1-methylallyl)toluene (10). At lower temperatures 11 and 20, the products expected from intramolecular coupling and disproportionation of diradical 30, are obtained. Other products can be derived from diradical 30 by a series of



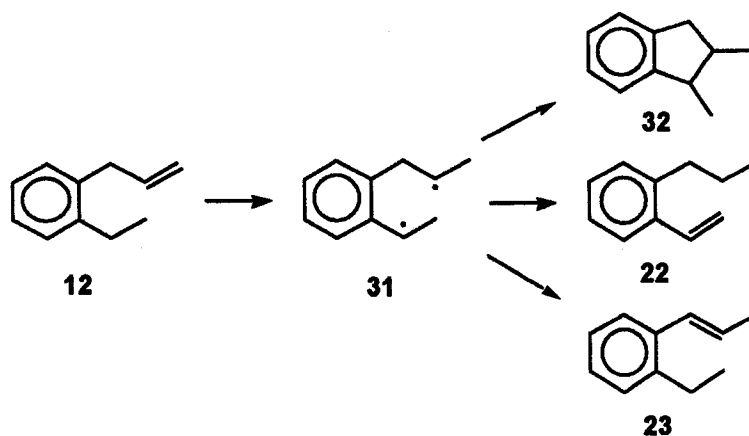
1,2-hydrogen-atom shifts and β -fragmentations, including the major products at higher temperatures, naphthalene (**5**) and indene (**7**). Several reasonable pathways from **30** to **5** and **30** to **7** can be written (Scheme 2).

Scheme 2



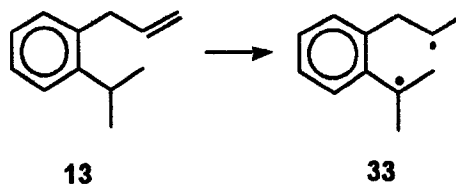
The conversion of **10** to **11** via diradical **30** also appears to be reversible. Pyrolysis of **11** yields **10** and **20**, the intramolecular disproportionation products from diradical **30**, along with the other products obtained from the FVP of **10**.

The FVP of *o*-allylethylbenzene (**12**) was explored with the expectation that the methyl group would stabilize the benzylic radical site of the predicted diradical intermediate **31**, thus favoring the reaction at lower temperatures. Once formed by hydrogen-atom transfer, **31** could undergo a number of reactions affording distinct products: intramolecular coupling to give *cis*- and *trans*-2,3-dimethylindans (**32**) or intramolecular disproportionation reactions to give either **12**, *o*-propylstyrene (**22**), or (*E*)-(*o*-propenyl)ethylbenzene (**23**). FVP of **12** produces compounds **22** and **23**,¹⁷ products consistent with the generation of diradical **31**, but the presence of dimethylindans (**32**) could not be firmly established, although some minor isomeric products of **12** are detected by GC-MS (see Table A-6, Appendix A). Unfortunately,



these minor products are formed in such small amounts that they could not be clearly identified by GC or ^1H NMR spectroscopy. The generation of indene (**7**), naphthalene (**5**), and other products can be explained by mechanisms similar to those presented above to account for the products from **6** and **10**.

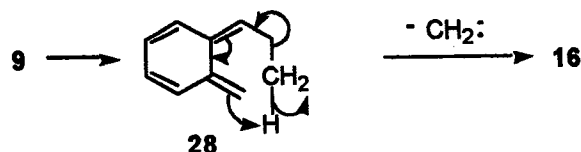
The FVP of *o*-allylcumene (**13**) (Table 3.7) was explored in anticipation that the predicted diradical intermediate (**33**) would be sufficiently stabilized to allow reaction at even



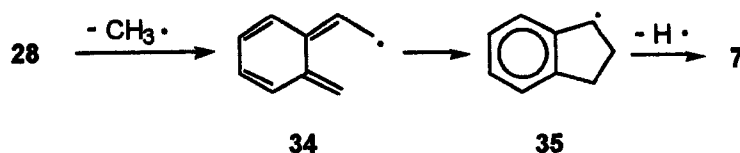
lower temperatures than **12**. Both naphthalene (**5**) and indene (**7**) are major products formed in the FVP of **13** and can be explained by routes similar to those presented above for the other systems. No product resulting from the intramolecular coupling of diradical **33** was identified and there were many lower molecular-weight products resulting from methyl group fragmentations.

The effect of chain lengths on the generation of diradicals by intramolecular hydrogen-atom transfer was studied. Two compounds with a shorter chain, (**9-E/Z**) and **16**, were investigated. FVP of (**9-E/Z**) produces **7** as the major product and significant amounts of *o*-methylstyrene (**16**) (5-10%) which can be explained by a mechanism involving a

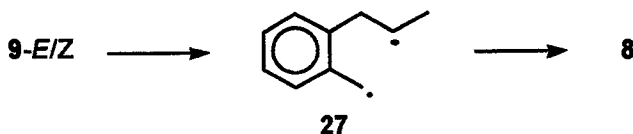
1,5-hydrogen atom shift to form *o*-xylylene intermediate **28** followed by loss of methylene to yield **16**. Formation of intermediate **28** may also account for the relatively large amount of **7**



compared to **6**. Loss of a methyl radical from **28** would yield the resonance stabilized radical **34** and closure of **34** would generate the indanyl radical **35** which could readily lose a hydrogen atom to yield **7**.



Small amounts of 2-methylindan (**8**) are produced in the FVP of (9-*E/Z*) and this is readily explained by formation of diradical **27** by an intramolecular hydrogen-atom transfer.



The FVP products of *o*-methylstyrene (**16**) are similar to those of (9-*E/Z*). Indene (**7**) can be explained by the 1,5-hydrogen shift route with loss of a hydrogen atom instead of a methyl group. Indan (**17**) is readily explained by formation of a diradical by a hydrogen-atom transfer, followed by coupling of the diradical.

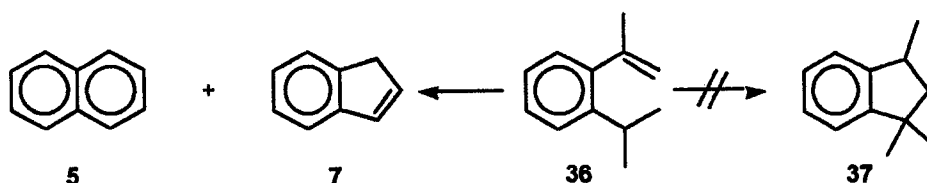
The reversibility of the conversion **16** to **17** is supported by the products of the FVP of **17** under similar conditions. Pyrolysis of **17** produces **16**, the product expected from intramolecular disproportionation of the diradical resulting from ring opening, and **7**. A 1,4 loss of hydrogen,¹⁸ followed by a 1,5-hydrogen shift can, explain the generation of **7** directly from **17**. The 0.9 to 1 ratio of **7** to **17** in this product mixture is lower than the 1.9 to 1 ratio

of these products in the pyrolysis of **16**, indicating that for the pyrolysis of **16**, **17** is probably not the sole source of **7**.

Two compounds with a larger chain length were also studied: *o*-(3-butenyl)toluene (**14**) and *o*-(4-pentenyl)toluene (**15**). In the FVP of **14**, the main reaction is homolytic cleavage of the weak benzylic-allylic carbon-carbon bond (Table 3.8). The dimerization of *o*-methylbenzyl radicals produced from this bond cleavage results in the formation of 1,2-di(*o*-tolyl)ethane (**24**). The allyl radicals should dimerize to form 1,5-hexadiene. However, this product was not detected due to its high volatility. At 900 °C, the major products are *o*-xylene (**25**), benzocyclobutene (**2**), *o*-ethyltoluene (**26**), and styrene (**3**). Products **25**, **2**, and **3** appear to be formed from *o*-methylbenzyl radicals. The route to **26** is unclear.

The main product from the pyrolysis of *o*-(4-pentenyl)toluene (**15**) (Table 3.9) is *o*-methylstyrene (**16**) formed by a retro-ene reaction. Numerous minor side products are formed at higher temperature (800-900 °C).

Brown and coworkers have pyrolyzed *o*-isopropyl- α -methylstyrene (**36**) under similar conditions (800 °C, 0.01 torr), also observing **7** as a major product.¹⁹ In disagreement with the current study where (**9-E/Z**) and **16** give primarily indene (**7**) or the corresponding indan, **5** is the main product and none of the 1,1,3-trimethylindan (**37**), as would be expected by the



intramolecular hydrogen-atom transfer mechanism, is observed. This difference may be a result of the extensive methyl substitution on **36** when compared to **16**. Brown offers no clear mechanistic explanation for the generation of **7** from **36**.

In addition to FVP studies, we investigated the liquid-phase reactions of *o*-(1-methylallyl)toluene (**10**). It is clear that the liquid-phase chemistry of **10** at 400 °C (See Table 3.8) differs markedly from its gas-phase reactions. At a starting concentration of **10** of

0.0724 mol L⁻¹, the major product is double-bond isomer 1-methyl-2-(*o*-tolyl)propene (**20**). Some cyclized products, 2,2-dimethylindan (**11**) as well as 2-methyl-1*H*-indene (**19**) and 3-methyl-1*H*-indene (**18**), were also formed. At a starting concentration of **10** of 0.0142 mol L⁻¹, the yield of **20** is considerably lower, and the yield of **11** is slightly higher. The dependence of the formation of **20** on the concentration of **10** shows that the reaction is not unimolecular. We propose that a radical chain mechanism is responsible for the isomerization to **20**.

Conclusion

Flash vacuum pyrolyses of *o*-allyltoluene (**6**), *o*-(1-methylallyl)toluene (**10**), *o*-allylethylbenzene (**12**), and *o*-allylcumene (**13**) give products whose formation is consistent with the existence of diradical intermediates produced by intramolecular hydrogen-atom transfer. The conversion of **6** and **10** to the corresponding indans via a diradical appears to be reversible based on the products resulting from the FVP of 2-methylindan (**8**) and 2,2-dimethylindan (**11**). ΔH^\ddagger values for the diradical intermediates are estimated to be *ca.* 45 kcal mol⁻¹, easily accessible at 700 to 900 °C.

The role of chain length in these cyclizations is critical. FVP of (*E/Z*)-*o*-(1-propenyl)toluene (**9-E/Z**) and *o*-methylstyrene (**16**) provides evidence for a competing 1,5-hydrogen-atom shift mechanism. On the other hand, the FVP of *o*-(3-butenyl)toluene (**14**) affords products resulting from cleavage of the weak C_α-C_β bond, and FVP of *o*-(4-pentenyl)toluene (**15**) appears to result in a retro-ene reaction rather than a hydrogen-atom transfer.

In the liquid phase, **10** undergoes rearrangement to 1-methyl-2-(*o*-tolyl)propene (**20**), instead of cyclization. A radical chain mechanism is proposed for the rearrangement.

Experimental

Methods and Materials. Some general methods²⁰ have been described previously. Chemical shifts for ^1H and ^{13}C NMR spectroscopy are relative to tetramethylsilane or the accepted chemical shift of the solvent. In the case of the pyrolysis of *o*-allyltoluene- α,α,α - d_3 (**6-d₃**), the ^2H chemical shifts are relative to the methyl signal of **6** and are set at 2.29 ppm and the ^1H chemical shifts are relative to the methylene signal of **6** and are set at 3.42 ppm. GC analyses were performed with a 30m (0.25- μm thickness) DB-1701 capillary column and a flame ionization detector. GCMS was performed at 70-eV EI after separation on DB-1701 or DB-5 capillary columns. All reagents or compounds not explicitly referenced were obtained from commercial sources.

***o*-Allyltoluene (6)** was prepared by a previously published procedure.⁴ ^1H NMR spectroscopy and GCMS data matched those reported.^{2b}

***o*-Allyltoluene- α,α,α - d_3 (**6-d₃**).** *o*-Bromotoluene- α,α,α - d_3 was prepared by a previously published procedure.²¹ ^1H NMR spectroscopy (300-MHz, CD_2Cl_2) δ 7.52 (dd, $J_d = 7.8$ Hz, $J_a = 0.6$ Hz, 1 H), 7.27-7.19 (m, 2 H) 7.08-7.03 (m, 1 H). *o*-Allyltoluene- α,α,α - d_3 (**6-d₃**) was prepared from *o*-bromotoluene- α,α,α - d_3 based on the previously published procedure for the synthesis of *o*-allyltoluene.⁴ ^1H NMR spectroscopy (300 MHz, CCl_4) δ 7.13 (s, 4 H), 6.06-5.93 (m, 1 H), 5.12 (dq, $J_d = 10.2$ Hz, $J_q = 1.5$ Hz, 1 H), 5.02 (dq, $J_d = 17.1$ Hz, $J_q = 1.8$ Hz, 1 H), 3.43 (d, $J = 6.0$ Hz, 2 H); ^2H NMR spectroscopy (400 MHz, CCl_4) δ 2.29 (s, 3 D); GCMS m/z (% base peak) 135 (100), 134 (66.2), 118 (30.6), 117 (86.4), 115 (30.2).

2-Methylindan (8) was prepared by a previously published procedure.²² ^1H NMR spectroscopy data matched those reported.²²

(*E/Z*)-*o*-(1-Propenyl)toluene (9) was prepared in a 1:1.05 cis:trans ratio by a previously published procedure.²³ ^1H NMR spectroscopy (300 MHz, CDCl_3) δ 7.45-7.05 (aromatic region belonging to both isomers). **9-(*E*)**: δ 6.63 (dq, $J_d = 15.6$ Hz, $J_q = 1.8$ Hz, 1

H), δ 6.10 (dq, $J_d = 15.6$ Hz, $J_q = 6.6$ Hz, 1 H), δ 2.32 (s, 3H), δ 1.90 (dd, $J = 6.6, 1.8$ Hz, 3 H). **9-(Z)**: δ 6.43 (dq, $J_d = 11.4$ Hz, $J_q = 1.8$ Hz, 1 H), δ 5.79 (dq, $J_d = 11.4$ Hz, $J_q = 6.9$ Hz, 1 H), δ 2.24 (s, 3H), δ 1.73 (dd, $J = 6.9, 1.8$ Hz, 3 H). [lit.²³ ^1H NMR spectroscopy (100 MHz, CCl_4) **9-E**: δ 7.35-6.90 (m, 4 H), δ 6.51 (d, $J = 15.6$ Hz 1 H), δ 5.97 (dq, $J_d = 15.5$ Hz, $J_q = 6.5$ Hz, 1 H), δ 2.27 (s, 3H), δ 1.87 (dd, $J = 6.5$ and 1.5 Hz, 3 H). **9-(Z)**: δ 7.04 (m, 4 H), δ 6.41 (d, $J = 11.5$ Hz, 1 H), δ 5.74 (dq, $J_d = 11.5$ Hz, $J_q = 7.0$ Hz, 1 H), δ 2.21 (s, 3H), δ 1.74 (dd, $J = 7.0$ and 1.8 Hz, 3 H).

***o*-(1-Methylallyl)toluene (10)** was prepared in 26% yield from *o*-tolylmagnesium bromide and methylallyl chloride by a method patterned after Hurd's procedure.⁴ ^1H NMR spectroscopy (300 MHz, CD_2Cl_2) δ 7.18-7.10 (m, 4 H), 4.84-4.80 (m, 1 H), 4.52-4.50 (m, 1 H), 3.32 (s, 2 H), 2.27 (s, 3 H), 1.74 (s, 3 H); ^{13}C NMR spectroscopy (75.5 MHz, CD_2Cl_2) δ 144.9, 138.3, 137.3, 130.4, 130.1, 126.6, 126.1, 111.5, 42.0, 22.8, 19.5; IR (thin film) ν 3075, 3019, 2970, 2916, 1650, 1494, 1446, 1375, 891 cm^{-1} ; GCMS (70 eV) m/z (% base peak) 146 (57.6), 131 (100), 129 (16.1), 128 (17.3), 116 (14.5), 115 (24.0), 105 (11.4), 91 (35.0), 77 (10.4); HRMS m/z for $\text{C}_{11}\text{H}_{14}(\text{M}^+)$ calcd 146.10955, found 146.10932.

2,2-Dimethylindan (11). 2,2-Dimethylindan-1-one was prepared by a previously published procedure.²⁴ ^1H NMR spectroscopy (300 MHz, acetone- d_6) δ 7.69-7.60 (m, 2 H), 7.54-7.47 (m, 1 H), 7.45-7.36 (1 H, m), 3.02 (s, 2 H), 1.17 (s, 6 H). 2,2-Dimethylindan (11) was prepared from 2,2-dimethylindan-1-one as described previously.²⁵ ^1H NMR spectroscopy (300 MHz, acetone- d_6) δ 7.16-7.02 (m, 4 H), 2.69 (s, 4 H), 1.12 (s, 6 H); GCMS (70 eV) m/z (% base peak) 146 (43.1), 131 (100), 115 (15.2), 91 (26.3).

***o*-Allylethylbenzene (12)** was prepared in 31% yield by a method patterned after Hurd's procedure.⁴ ^1H NMR spectroscopy (300 MHz, acetone- d_6) δ 7.19-7.09 (m, 4 H), 5.97 (ddt, $J_d = 16.9$ Hz, $J_d = 10.3$ Hz, $J_t = 6.5$ Hz, 1 H), 5.03-4.91 (m, 2 H), 3.41 (dt, $J_d = 7.31$ Hz, $J_t = 1.5$ Hz, 2 H), 2.65 (q, $J = 7.5$ Hz, 2 H), 1.18 (t, $J = 7.5$ Hz, 3 H); ^{13}C NMR spectroscopy (75.5 MHz, CD_2Cl_2) δ 142.7, 138.0, 137.9, 129.8, 128.7, 126.8, 126.2, 115.6, 37.3, 25.9,

15.4; IR (thin film) ν 3060, 3014, 2965, 2930, 2870, 1640, 1600, 1485, 1450, 1430, 990, 912 cm^{-1} ; GCMS (70 eV) m/z (% base peak) 146 (24.1), 145 (16.1), 131 (100), 129 (15.0), 128 (12.1), 117 (41.7), 116 (21.5), 115 (35.0), 91 (5.4), 89 (5.2); HRMS m/z for $\text{C}_{11}\text{H}_{14}$ (M^+) calcd 146.10955, found 146.10926.

***o*-Propylstyrene (22).** 1-(*o*-Propylphenyl)ethanol was prepared by a method patterned after Seebach's procedure,²⁶ employing propyl bromide as the electrophile. 1-(*o*-Propylphenyl)ethanol was obtained in 3% yield as a clear oil: ^1H NMR spectroscopy (300 MHz, acetone- d_6) δ 7.55-7.47 (m, 1 H), 7.19-7.07 (m, 3 H), 5.16-5.05 (m, 1 H), 3.974 (d, J = 3.9 Hz, 1 H), 2.65-2.56 (m, 2 H), 1.73-1.53 (m, 2 H), 1.37 (d, J = 6.4 Hz, 3 H), 0.96 (t, J = 7.3 Hz, 3 H). Treatment of 1-(*o*-propylphenyl)ethanol with acetyl chloride in ether and triethylamine gave 1-(*o*-propylphenyl)ethyl acetate as a clear oil in 55% yield. ^1H NMR spectroscopy (300 MHz, acetone- d_6) δ 7.44-7.36 (m, 1 H), 7.22-7.11 (m, 3 H), 6.09 (q, J = 6.5 Hz, 1 H), 2.75-2.55 (m, 2 H), 1.99 (s, 3 H), 1.73-1.53 (m, 2 H), 1.67 (d, J = 6.6 Hz, 3 H), 0.97 (t, J = 7.3 Hz, 3 H). 1-(*o*-Propylphenyl)ethyl acetate was pyrolyzed at 600° C and 0.1 torr. The pyrolysate was dissolved in acetone- d_6 and neutralized. ^1H NMR spectroscopy showed peaks that were consistent with formation of *o*-propylstyrene (22) and (*E*)-*o*-(propenyl)toluene (23) in a ratio of about 4 : 1. Comparison of the GC retention times and GCMS fragmentation patterns of 23 and 22 clearly established that both are produced during the FVP of 12. Compound 22 was also identified by comparison of ^1H NMR spectra:²⁷ (23): ^1H NMR spectroscopy (300 MHz, acetone- d_6) δ (aryl protons and methylene protons are obscured due to overlap) 6.68 (dt, J_d = 15.5 Hz, J_t = 1.5 Hz, 1 H), 6.13 (qd, J_d = 15.5 Hz, J_q = 7.6 Hz, 1 H), 1.87 (dd, J_d = 7.6 Hz, J_d = 1.7 Hz, 3 H), 0.93 (t, J = 7.6 Hz, 3 H); (22): ^1H NMR spectroscopy (300 MHz, acetone- d_6) δ (aryl protons of 22 and 23 overlap) 7.34 (dd, J_d = 17.0 Hz, J_d = 11.0 Hz, 1 H), 5.57 (dd, J_d = 17.0 Hz, J_d = 1.5 Hz, 1 H), 5.26 (dd, J_d = 11.0 Hz, J_d = 1.5 Hz, 1 H), 2.66 (t, J = 7.7 Hz, 2 H), 1.58 (m, 2 H), 0.93 (t, J = 7.3 Hz, 3 H); [lit.²⁷ ^1H NMR spectroscopy (100 MHz, CDCl_3) δ 7.2 (m, 4 H), 7.06 (dd, J_d = 17 Hz, J_d = 12

Hz, 1 H), 5.66 (d, $J = 17$ Hz, 1 H), 5.30 (d, $J = 12$ Hz, 1 H), 2.67 (t, 2 H), 1.60 (m, 2 H), 1.14 (t, $J = 8$ Hz, 3 H)].

***o*-Allylcumene (13)** was formed in 31% yield by the addition of allyl bromide to *o*-cumylmagnesium bromide by a method patterned after Hurd's procedure:⁴ ¹H NMR spectroscopy (300 MHz, CD₂Cl₂) δ 7.31-7.24 (m, 1 H), 7.22-7.15 (m, 1 H), 7.13-7.07 (m, 2 H), 6.00 (ddt, $J = 16.9, 10.3, 6.2$ Hz, 1 H), 5.03-4.90 (m, 2 H), 3.43 (dt, $J = 5.5, 1.5$ Hz, 2 H), 3.19 (septet, $J = 6.9$ Hz, 1 H), 1.20 (s, $J = 7.1$ Hz, 6 H); ¹³C NMR spectroscopy (75.5 MHz, CD₂Cl₂) δ 147.4, 138.3, 137.1, 130.0, 127.0, 126.0, 125.6, 115.5, 37.1, 29.1, 24.0; IR (thin film) ν 3066, 3018, 2962, 2926, 2867, 1636, 1600, 1488, 1449, 1430, 1033, 993, 913 cm⁻¹; HRMS m/z for C₁₂H₁₆ (M⁺) calcd 160.12520, found 160.12530.

***o*-(3-Butenyl)toluene (14)** was prepared by the following modified literature procedure.²⁸ Allylmagnesium bromide (25 mL, 1.0 M solution in ether, 0.025 mol) was added drop wise to a solution of α -chloro-*o*-xylene (3.5 g, 0.025 mol, *ca.* 3.3 mL) in ether (15 mL) at 0 °C. The reaction mixture was stirred at room temperature for 1 h, quenched with H₂O (50 mL), and the phases separated. The aqueous phase was extracted with ether (3 x 50 mL). The organic phases were combined and washed with H₂O (2 x 50 mL) and saturated NaCl (50 mL), and dried (MgSO₄), and the solvent removed *in vacuo*. HPLC purification¹ yielded *o*-(3-butenyl)toluene (1.9 g, 0.013 mol, 64% yield). ¹H NMR spectroscopy (300 MHz, CDCl₃) δ 7.17-7.07 (m, 4 H), 5.84 (qt, $J_q = 10.2$ Hz, $J_t = 6.6$ Hz, 1 H), 5.04 (dq, $J_d = 17.1$ Hz, $J_q = 1.5$ Hz, 1 H), 4.98 (ddt, $J_d = 10.2$ Hz, $J_d = 1.8$ Hz, $J_t = 1.2$ Hz, 1 H), 2.73-2.65 (m, 2 H), 2.37-2.27 (m, $J = 7$ Hz, 2 H), 2.31 (s, 3 H); [lit.²⁹ ¹H NMR spectroscopy (CDCl₃) δ 7.08 (4 H, broad), 6.2-4.8 (4 H, broad), 2.25 (3 H, s)]; GCMS (70 eV) m/z (% base peak) 146 (15.4), 105 (100), 91 (3.1), 77 (10.9) [lit.²⁹ MS 146, 105 (base peak), 91].

***o*-(4-Pentenyl)toluene (15)** was prepared by the following modified literature procedure.³⁰ Crushed Mg turnings (0.36 g, 0.015 mol) were added to THF (55 mL) under Ar atmosphere. 2-Bromotoluene (2.3 g, 0.013 mol, *ca.* 1.6 mL) and CuBr (0.096 g, 0.067

mmol) in HMPA (5 mL) were heated to 50-60 °C for 0.5 h. The Grignard reagent was transferred to an addition funnel and added drop wise to the warm HMPA solution. After the addition was complete, the reaction mixture was refluxed for 2 h, added to a mixture of ice and 1 M HCl in a beaker, and extracted with ether (3 x 50 mL). The ether fractions were combined and washed with H₂O (50 mL) and saturated NaCl (50 mL), and dried (MgSO₄), and the solvent removed *in vacuo*. Flash column chromatography on a silica gel column (30 x 100 mm) with hexanes yielded *o*-(4-pentenyl)toluene (**15**) (0.87 g, 5.4 mmol, 40% yield). ¹H NMR spectroscopy (300 MHz, CDCl₃) δ 7.15-7.05 (m, 4 H), 5.85 (qt, *J*_q = 10.2 Hz, *J*_t = 6.7 Hz, 1 H), 5.04 (dq, *J*_d = 17.1 Hz, *J*_q = 1.7 Hz, 1 H), 4.98 (ddt, *J*_d = 10.2 Hz, *J*_d = 2.2 Hz, *J*_t = 1.2 Hz, 1 H), 2.64-2.55 (m, 2 H), 2.30 (s, 3 H), 2.19-2.11 (m, 2 H), 1.71-1.65 (m, 2 H) [lit.³¹ ¹H NMR spectroscopy (CDCl₃) δ 7.08 (4 H), 5.88 (1 H), 5.05 (2 H), 2.60 (2 H), 2.28 (3 H), 2.6-1.3 (4 H)]; GCMS (70 eV) *m/z* (% base peak) 160 (16.4), 118 (78.4), 106 (33.8), 105 (100), 91 (40.7), 77 (26.7).

o-Methylstyrene (**16**) (99.0%) was quantified by ¹H NMR spectroscopy against triphenylmethane.

Flash vacuum pyrolysis. Flash vacuum pyrolysis (FVP) was performed as previously described.²⁰

Product analysis. FVP reaction mixtures were analyzed by capillary gas chromatography¹ except for the FVP reaction mixtures of *o*-methylstyrene (**16**) and *o*-allyltoluene-*α,α,α*-*d*₃ (6-*d*₃), which were analyzed by ¹H NMR spectroscopy.

GC analysis was performed by injecting 1 μL of the pyrolysate/biphenyl solution. Triplicate pyrolyses were performed, with the exception of FVP of **20** at 700 °C, for which duplicate analysis was performed, and with the exception of FVP of **8**, for which only a single analysis per temperature range was performed. Peaks not appearing in all GC traces for a series of pyrolysis runs at a given temperature were discarded. For most major compounds, FID response factors were determined (**1-7**, **9-11**, **16**, **25-26**, toluene, ethylbenzene,

m/p-xylenes, 1-methylnaphthalene, and 2-methylnaphthalene). Other compounds were assigned a response factor equal to biphenyl. Except where noted, percentages are for moles of product relative to total moles of recovered material. Identification of products was based on GC retention time of authentic samples or those samples whose identity could be clearly established by NMR spectroscopy or GCMS. GCMS was used to determine the molecular weights of minor products where possible.

The ^1H NMR spectroscopy analysis was performed by diluting the pyrolysate/triphenylmethane solution with chloroform-*d* to yield a 3:2 (v/v) ratio of $\text{CCl}_4/\text{CDCl}_3$. The spectra were obtained employing a 10-second delay between scans to ensure complete relaxation of all protons. The relative integrals of the product proton signals were quantified against the methine signal of the triphenylmethane standard. The signals for indene (7) and indan (17) were compared to those of authentic samples.

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Supporting Information: ^1H NMR spectroscopy data for compounds 6, 6-*d*₃, 8, (9-*E/Z*), and 10-17; ^1H NMR spectroscopy data for the pyrolysate mixtures of compounds 6, 6-*d*₃, (9-*E/Z*), 10, 12, 13, and 15-17; ^2H NMR spectroscopy data for compound 6-*d*₃ and the pyrolysate mixture of compound 6-*d*₃; ^{13}C NMR spectroscopy data for compounds 10, 12, and 13; MS data for compound 16 in the pyrolysate of 8; and detailed product analysis of FVP mixtures are available in Appendix A.

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CHAPTER 4. Flash Vacuum Pyrolysis of *o*-Allylphenol and *o*-Allylaniline. Generation of Heterocyclic Compounds

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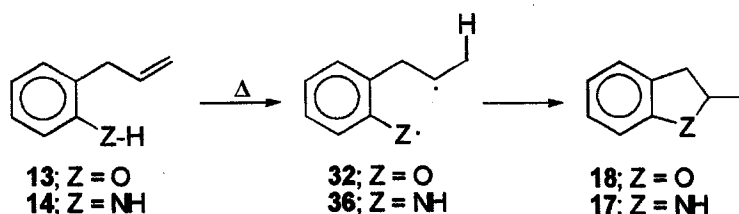
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Abstract

The flash vacuum pyrolysis (FVP) of *o*-allylphenol (**13**) and *o*-allylaniline (**14**) at 600 and 700 °C gives 2,3-dihydro-2-methylbenzofuran (**18**) and 2-methylindoline (**17**), respectively. At the higher temperature of 800 °C, **13** is converted to benzofuran (**19**) as the major product along with several minor products, including **18**. Likewise, at 800-900 °C **14** is converted to indole (**25**) as the major product along with several minor products, including **17**. It is proposed that **13** and **14** are converted to their respective cyclic isomers by a two-step mechanism involving diradicals **32** and **36**, respectively, formed by a reversible intramolecular hydrogen-atom transfer. Production of benzofuran (**19**) and indole (**25**) is explained by con-

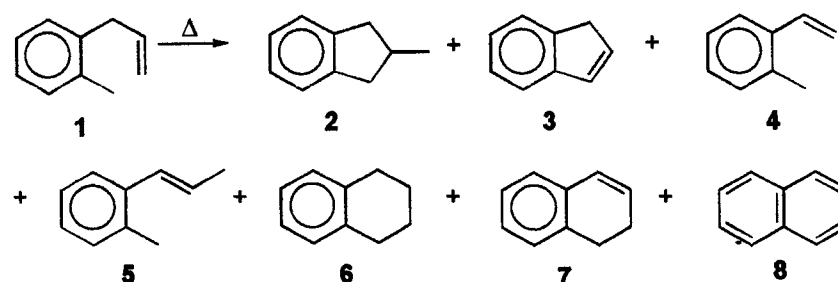


version from **32** and **36** by a series of reactions involving the loss of a methyl group and a hy-

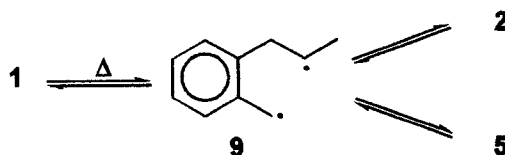
drogen atom. The FVP's of several related molecules, *o*-(ethenyloxy)toluene (15), *o*-(1-methylallyl)phenol (16), and 2-methylindoline (17) were also studied.

Introduction

We recently reported that the flash vacuum pyrolysis (FVP) of *o*-allyltoluene (1) results in the production of 2-methylindan (2) as a major product.¹ Other products include indene (3) as well as smaller amounts of *o*-methylstyrene (4), *E*-*o*-(1-propenyl)toluene (5), tetralin (6), 1,2-dihydronaphthalene (7), and naphthalene (8).

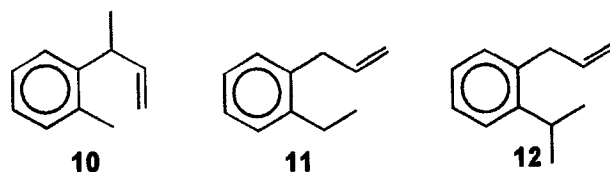


Most of these products can be explained by mechanisms involving diradical 9 formed by thermally-induced reversible intramolecular hydrogen-atom transfer. Intramolecular coupling and intramolecular disproportionation of 9, which are reversible, explain the formation of 2 and 5, respectively. More complicated paths involving 1,2-hydrogen shifts and

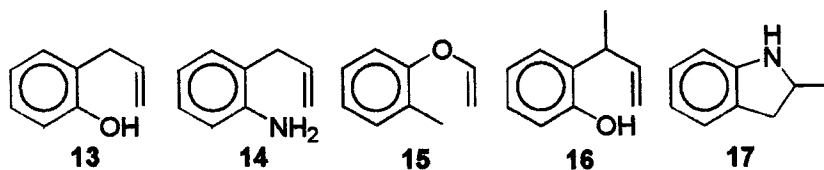


β -fragmentations account for most of the remaining products.¹ Although there are examples of the formation of diradicals by transfer of a hydrogen atom in intramolecular photochemical reactions² and examples of the formation of radical pairs in a few intermolecular thermal reactions,^{3,4,5} we are aware of only one report which proposes the formation of a diradical by thermally-induced intramolecular transfer of a hydrogen atom, and that report is for the cyclization of an organosilicon compound.⁶

We have also previously reported that the FVP's of several related molecules, *o*-(1-methylallyl)toluene (**10**), *o*-allylethylbenzene (**11**), *o*-allylcumene (**12**), (*E/Z*)-*o*-(1-propenyl)toluene (*E/Z*-**5**), and *o*-methylstyrene (**4**) result in products consistent with the generation of diradical intermediates by intramolecular hydrogen-atom transfer.¹



To further test the scope of thermally-induced intramolecular hydrogen-atom transfer we studied the FVP of the phenol and aniline analogs of **1**. The present paper documents the results of FVP studies on *o*-allylphenol (**13**) and *o*-allylaniline (**14**). The FVP's of several related molecules, *o*-(ethenyloxy)toluene (**15**), *o*-(1-methylallyl)phenol (**16**), and 2-methylindoline (**17**) were also studied.



Results

The major products resulting from the FVP of *o*-allylphenol (**13**) are 2,3-dihydro-2-methyl-benzofuran (**18**) and benzofuran (**19**) (see Table 4.1). Small amounts of 2-methylbenzofuran (**20**) and *o*-cresol (**21**) are also produced and there is ¹H NMR spectroscopy evidence for the formation of *E/Z-o*-(1-propenyl)phenol (**22**). Under similar pyrolysis conditions *o*-(ethenyloxy)toluene (**15**), the ether isomer of **13**, yields the same product mixture along with small amounts of **13** (see Table 4.2).

The FVP of *o*-(1-methylallyl)phenol (**16**), the methyl homolog of **13**, yields comparable cyclic products (see Table 4.3). The main products are *cis*- and *trans*-2,3-dimethyl-2,3-dihydrobenzofuran (**23**), **20**, and **19**. Low yields of 2,3-dimethylbenzofuran (**24**) are also observed along with small amounts of several non-characterized C₁₀H₁₂O isomers.

The FVP of the nitrogen analog of **13**, *o*-allylaniline (**14**), yields cyclic amines corresponding to the heterocyclic products observed with the oxygen systems (see Table 4.4). The main products are 2-methylindoline (**17**) and indole (**25**). Low yields of aniline (**26**), *o*-toluidine (**27**), quinoline (**28**) and 1,2,3,4-tetrahydroquinoline (**29**) are also produced. There is ¹H NMR spectroscopy and GC-MS evidence for the generation of significant amounts of *E/Z-o*-(1-propenyl)aniline (**30**) and small amounts of *o*-aminostyrene (**31**). When **17** itself was pyrolyzed under similar conditions the same product mixture was observed including small amounts of **14** (see Table 4.5). The products resulting from the liquid phase thermolysis of **14** (300 °C, 10–48 h) in phenyl ether are the same as those observed with FVP (see Table 4.6), but they are formed in different ratios.

Table 4.1. Products and Recovered Starting Material from the FVP of *o*-Allylphenol (13) at Various Temperatures ^{a,b}

entry	yield, % ^c		
	600 °C	700 °C	800 °C
benzofuran (19)	10	21	48
2-methylbenzofuran (20) ^d	1.4	4.1	7.2
2,3-dihydro-2-methylbenzofuran (18)	27	37	11
<i>o</i> -cresol (21)	5.2	3.6	1.9
<i>Z</i> - <i>o</i> -(1-propenyl)phenol (<i>Z</i> -22) ^d	1.3	2.5	4.0
<i>o</i> -allylphenol (13) ^e	49	18	6.1
<i>E</i> - <i>o</i> -(1-propenyl)phenol (<i>E</i> -22) ^d	3.7	6.9	10
other products	2.2 ^f	6.8 ^f	11 ^f
recovery ^g	94	81	59
conversion ^h	51	82	94

^a FVP conditions: system pressure = 0.10 torr, sample temperature = 0 °C. ^b Amounts determined by GC with a known quantity of biphenyl added as standard with an average standard deviation of 0.9%. Products identified by comparison with authentic samples by retention time or by ¹H NMR spectroscopy/GC-MS are indicated by name. ^c Moles of product divided by total moles of recovered material X100. ^d These products identified by ¹H NMR spectroscopy and/or GC-MS. ^e Starting material purity as determined by FVP at RT is 96% with 3.6% 18. ^f See Table B-1 in Appendix B for a more detailed analysis. ^g Total moles of recovered material divided by moles of starting material X 100. ^h Total moles of recovered material minus moles of recovered starting material divided by total moles of recovered material X 100.

Table 4.2. Products and Recovered Starting Material from the FVP of *o*-(Ethenyloxy)toluene (15) at 800 °C ^{a,b}

entry	yield, % ^c
	800 °C
<i>o</i> -(ethenyloxy)toluene (15) ^d	27
benzofuran (19)	15
2-methylbenzofuran (20) ^e	1.2
2,3-dihydro-2-methylbenzofuran (18)	6.7
<i>o</i> -cresol (21)	18
<i>Z</i> - <i>o</i> -(1-propenyl)phenol (<i>Z</i> -22) ^e	6.4
<i>o</i> -allylphenol (13)	0.7
<i>E</i> - <i>o</i> -(1-propenyl)phenol (<i>E</i> -22) ^e	7.6
other products	18 ^f
recovery ^g	56
conversion ^h	73

^a FVP conditions: system pressure = 0.01 torr, sample temperature = 0 °C. ^b See Table 4.1, note b. ^c See Table 4.1, note c. ^d Starting material purity as determined by FVP at RT is 92% with 5.0% *o*-cresol (21). ^e See Table 4.1, note d. ^f See Table A-2 in Appendix B for a more detailed analysis. ^g See Table 4.1, note g. ^h See Table 4.1, note h.

Table 4.3. Products and Recovered Starting Material from the FVP of *o*-(1-Methylallyl)phenol (16) at Various Temperatures ^{a,b}

entry	yield, % ^c		
	600 °C	700 °C	800 °C
benzofuran (19)	3.0	26	71
2-methylbenzofuran (20) ^d	9.4	21	14
<i>trans</i> -2,3-dihydro-2,3-dimethylbenzofuran (<i>trans</i> -23) ^e	41	26	1.7
<i>cis</i> -2,3-dihydro-2,3-dimethylbenzofuran (<i>cis</i> -23) ^e	18	9.1	1.0
2,3-dimethylbenzofuran (24) ^d	3.1	4.8	2.9
<i>o</i> -(1-methylallyl)phenol (16) ^f	14	—	—
other products	12 ^g	13 ^g	8.8 ^g
recovery ^h	73	65	65
conversion ⁱ	86	100.0	100.0

^a See Table 4.1, note a. ^b See Table 4.2, note b. ^c See Table 4.1, note c. ^d See Table 4.1, note d. ^e See note d, including comparison to ¹H NMR spectroscopy reported in the literature.⁷ ^f Starting material purity as determined by FVP at RT is 100%. ^g See Table A-3 in Appendix B for a more detailed analysis. ^h See Table 4.1, note g. ⁱ See Table 4.1, note h.

Table 4.4. Products and Recovered Starting Material from the FVP of *o*-Allylaniline (14) at Various Temperatures ^{a,b}

entry	yield, % ^c			
	625 °C	700 °C	800 °C	920 °C
aniline (26)	—	—	2.0	4.6
<i>o</i> -toluidine (27)	0.2	2.8	11	4.2
<i>o</i> -aminostyrene (31) ^d	—	0.9	3.9	2.5
<i>o</i> -allylaniline (14) ^e	87	63	11	0.9
2-methylindoline (17)	8.2	16	13	1.5
<i>E</i> - <i>o</i> -(1-propenyl)aniline (<i>E</i> -30) ^d	0.8	4.2	6.6	1.9
quinoline (28)	0.6	1.0	2.4	3.2
indole (25)	3.4	3.3	32	72
<i>Z</i> - <i>o</i> -(1-propenyl)aniline (<i>Z</i> -30) ^d	—	8.2	14	—
1,2,3,4-tetrahydroquinoline (29)	—	—	0.8	—
other products	—	0.8 ^f	4.1 ^f	9.0 ^f
recovery ^g	87	86	60	47
conversion ^h	13	37	89	99

^a FVP conditions: system pressure = 0.15 torr, sample temperature = RT-55 °C. ^b See Table 4.2, note b. ^c See Table 4.1, note c. ^d See Table 4.1, note d, including comparison to ¹H NMR spectroscopy reported in the literature.⁸ ^e Starting material purity as determined by ¹H NMR spectroscopy quantification against durene: 625 °C experiments, 93% with 4.5% 17; 700 °C experiment, 85% with 4.5% 17; 800-900 °C experiments, 96% with 2.9% 17. ^f See Table A-4 in Appendix B for a more detailed analysis. ^g See Table 4.1, note g. ^h See Table 4.1, note h.

Table 4.5. Products and Recovered Starting Material from the FVP of 2-Methylindoline (17) at 800 °C ^{a,b}

entry	yield, % ^c	
	800 °C	820 °C
aniline (26)	0.9	1.5
<i>o</i> -toluidine (27)	18	17
<i>o</i> -aminostyrene (31) ^d	0.7	1.5
<i>o</i> -allylaniline (14)	5.2	5.8
2-methylindoline (17) ^e	26	18
<i>E</i> - <i>o</i> -(1-propenyl)aniline (<i>E</i> -30) ^d	—	3.2
quinoline (28)	1.0	1.3
indole (25)	38	41
<i>Z</i> - <i>o</i> -(1-propenyl)aniline (<i>Z</i> -30) ^d	9.3	9.2
other products	1.7 ^f	1.0 ^f
recovery ^g	44	55
conversion ^h	75	82

^a FVP conditions: system pressure = 0.20 torr, sample temperature = 35 °C. ^b See Table 4.2, note b. ^c See Table 4.1, note c. ^d See Table 4.4, note d. ^e Starting material 99% pure as determined by GC assay. ^f See Table A-5 in Appendix B for a more detailed analysis. ^g See Table 4.1, note g. ^h See Table 4.1, note h.

Table 4.6. Products and Recovered Starting Material from the Liquid-Phase Thermolysis of *o*-Allylaniline (14) in Phenyl Ether (300 °C) for various lengths of time.

entry	yield, % ^c		
	10.5 h	24 h	48 h
aniline (26)	trace	9.6	24.9
<i>o</i> -allylaniline (14) ^d	88	4.3	2.2
2-methylindoline (17)	9.6	40	31
<i>E</i> - <i>o</i> -(1-propenyl)aniline (<i>E</i> -30) ^e	—	7.1	6.6
quinoline (28)	0.1	4.4	8.1
indole (25)	1.9	34	27
1,2,3,4-tetrahydroquinoline (29)	—	0.5	—
other products	<i>f</i>	<i>g</i>	<i>h</i>
recovery ⁱ	84	72	55
conversion ^j	12	96	98

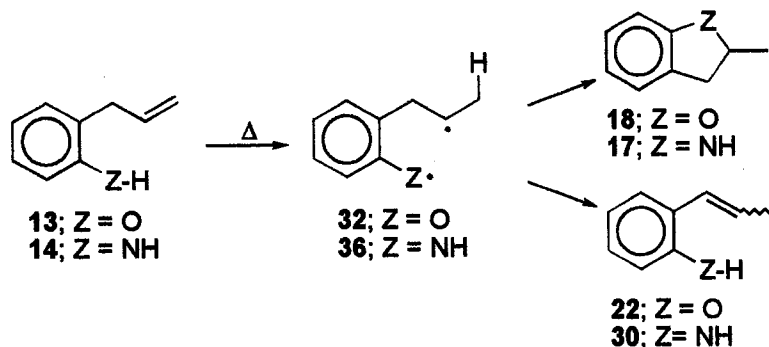
^a Thermolysis conditions: concentration of 10.5 h run = 0.24 M, concentration of 24 h and 48 h runs = 0.15 M. ^b See Table 4.2, note b. ^c See Table 4.1, note c. ^d Starting material purity as determined by ¹H NMR spectroscopy quantification against durene. ^e See Table 4.4, note d. ^f Unidentified products constitute 0.3% total area by GC. ^g Unidentified products constitute 8.9% total area by GC. ^h Unidentified products constitute 19% total area by GC. ⁱ See Table 4.1, note g. ^j See Table 4.1, note h.

Discussion

We have observed that both the oxygen and nitrogen analogs of *o*-allyltoluene (**1**) yield FVP products similar to those observed in the FVP of the parent compound. In both cases isomerization of the starting material to a five-membered heterocyclic ring appears to be the major route of conversion at lower pyrolysis temperatures. *o*-Allylphenol (**13**) converts to 2,3-dihydro-2-methylbenzofuran (**18**) in 11-27% yield while *o*-allylaniline (**14**) converts to 2-methylindoline (**17**) in 2-16% yield. Other isomerization products result from repositioning of the double bond. In the FVP of **13**, both *E* and *Z*-*o*-(1-propenyl)phenol (**22**) are observed in a combined 5-14% yield. Similarly, both *E* and *Z*-*o*-(1-propenyl)aniline (**30**) are observed in a combined 1-20% yield in the FVP of **14**. In the latter system however a small amount of the six-membered heterocyclic ring product 1,2,3,4-tetrahydroquinoline (**29**) is observed at 800 °C. In addition to these isomers, many of the non-isomeric products observed in the FVP of **13** and **14** are also analogous to non-isomeric products observed in the FVP of **1**. As pyrolysis temperature increases, products resulting from isomerization decrease and the main product becomes benzofuran (**19**) in the phenol system and indole (**25**) in the aniline system.

These isomerizations may be rationalized by a mechanism similar to the diradical mechanism we have previously proposed to explain the FVP products of the parent compound.¹ A thermally-induced intramolecular 1,6-hydrogen-atom transfer would result in the formation of 1,5-diradicals **32** and **36**, respectively (Scheme 1). Accordingly, cyclic products **17** and **18** would result from intramolecular coupling while repositioning of the double bond in **22** and **30** would result from intramolecular disproportionation. In the aniline system heterocyclic product **29** can be explained in a similar manner by a 1,5-hydrogen-atom transfer. A 1,6-diradical would result which, upon intramolecular coupling, could cyclize to the six-membered ring. Furthermore, Benson-type calculations demonstrate that the energy required for formation of these diradicals is attainable at the temperatures employed in these

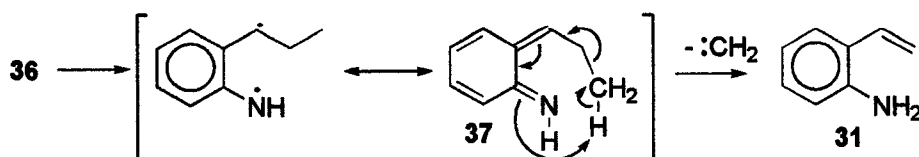
Scheme 1



experiments.⁹ It should be noted that **32** and **36** have previously been proposed as intermediates in the photolytic cyclizations of **13** and **14**, respectively.¹⁰ However, in reference to the photolytic conversion of **13** to **18** most sources do not promote a diradical mechanism but instead propose an excited-state proton transfer mechanism.¹¹

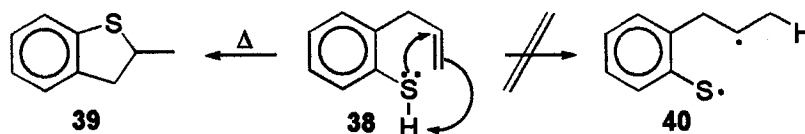
Besides the photolytic conversions mentioned above other non-pyrolytic conditions which afford these conversions include the acid-catalyzed conversion of **13** to **18**,¹² the aqueous phase thermolysis of **13**,¹³ and the organolanthanide-catalyzed intramolecular hydroamination/cyclization of **14** to **17**.¹⁴

The remaining products from the FVP's of **13** and **14** are not as easily rationalized by a diradical mechanism; however, a series of 1,2-hydrogen shifts and β -fragmentations, following from diradicals **32** and **36**, may explain the presence of compounds **19**, **20**, **25**, and **28**.¹⁵ In the aniline system, formation of *o*-aminostyrene (**31**) might be explained by the loss of a methylene group from imine intermediate **37** (*note, there is some ¹H NMR spectroscopy evidence for the formation of analogous o-vinylphenol in the FVP of o-allylphenol*). We do not have a good explanation for the formation of aniline (**26**) or *o*-toluidine (**27**) in the FVP of **14**,



nor for the formation of *o*-cresol (**21**) in the FVP of **13**. It is possible that these products result from fragmentation and bimolecular reactions, particularly at higher temperatures.

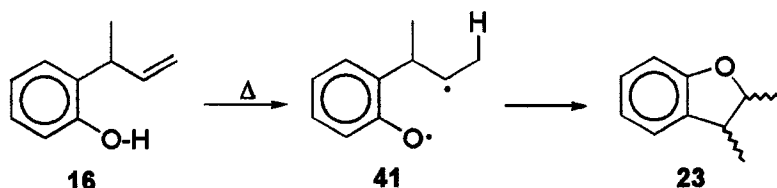
Work by previous researchers demonstrates the possibility of a polar mechanism in these thermally-induced cyclizations. Kwart and coworkers have observed the complete and exclusive thermal rearrangement of *o*-allylthiophenol (**38**) to thiacoumaran (**39**), the sulfur analog of **17** and **18**.¹⁷ The rearrangement reportedly occurs under comparatively mild conditions (76-80 °C at 3 torr). They propose a concerted mechanism involving intramolecular protonation of the double bond with concurrent cyclization.^{17a} The estimated ΔH° value (Benson's method)⁹ for the conversion of **38** to diradical **40** is 3-3.5 kcal/mol lower than those calculated for the conversions of **13** and **14** to their respective diradicals. The relatively lower barrier calculated for hydrogen-atom transfer in the thiol system is not small enough to explain the relative ease of the overall conversion of **38** to **39**. It therefore appears as if diradical **40** does not play an important role in the cyclization of the sulfur analog.



Unlike Kwart's observations with **38** we do not observe complete or easy conversions of the oxygen and nitrogen analogs to their respective five-membered ring isomers. This fact does not preclude the presence of Kwart's concerted mechanism in the FVP's of **13** and **14** and consequently a polar mechanism cannot be ruled out under the scope of this study.

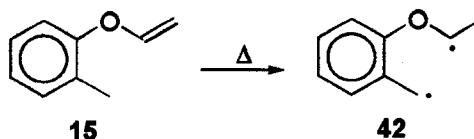
The reversibility of the **14** to **17** conversion under FVP conditions is established by the FVP of **17** which yields *o*-allylaniline (**14**) and *E*- and *Z*-*o*-(1-propenyl)aniline (**30**). Additionally, most of the remaining products observed in the FVP of **14** are also present. The three aniline products, **14** and *E*- and *Z*-**30**, are readily rationalized by ring opening of **17** to diradical **36** followed by intramolecular disproportionation. As in the pyrolysis of **14** we cannot rule out the presence of a polar mechanism.

Attaching a methyl group to the allylic substituent of **13** does not appear to alter the rearrangement significantly as *o*-(1-methallyl)phenol (**16**) yields *cis*- and *trans*-2,3-dimethyl-2,3-dihydrobenzofuran (**23**) as major products under FVP conditions at 600 °C. These products are consistent with generation and intramolecular closure of diradical **41**. At higher



temperatures (700-800 °C) benzofuran (**19**) and 2-methylbenzofuran (**20**) become the major products along with small amounts of 2,3-dimethylbenzofuran (**24**). Formation of **19**, **20**, and **24** can be rationalized by β -fragmentation and succeeding cyclizations.¹⁵ In a related study by van Meurs and coworkers it was demonstrated that under flow pyrolysis conditions at 700 °C **19** and **20** are formed from a mixture of *cis*- and *trans*-**23**.¹⁸ Generation of diradical **41** through ring opening of **23** was invoked to explain these products.

The FVP of *o*-(ethenyloxy)toluene (**15**), a non-phenolic isomer of *o*-allylphenol (**13**), yields precisely the same product mixture observed in the FVP of **13**. The absence of a phenolic hydrogen results in a compound that more closely matches the parent *o*-allyltoluene (**1**). Consequently, the lack of a phenolic hydrogen makes it somewhat difficult to imagine a polar mechanism in its thermal isomerization. Formation of **18** can be accounted for by the conversion of **15** to diradical **42** which could readily cyclize by intramolecular coupling. Ring



opening of **18** at the C-O bond would yield diradical **32** (Scheme 1) from which intramolecular disproportionation would produce **13** and **22**. As with the FVP of **13** however, we do not have a good explanation for the relatively large amount of **21** observed.

Finally, in addition to FVP, the liquid-phase thermolysis of *o*-allylaniline (**14**) was studied. Thermolysis of **14** in phenyl ether under sealed-tube conditions yields products similar to those observed during FVP. 2-Methylindoline (**17**) is produced in greater relative yield while *o*-aminostyrene (**31**), *o*-toluidine (**27**), and the C₉H₁₁N isomer attributed to *Z*-*o*-(1-propenyl)aniline (**Z-30**) are absent. The lack of **31** and the drop in the yield of indole (**25**) under extended thermolysis run time is readily explained by polymerization. The absence of **Z-30** can be explained by isomerization to the more stable *E*-isomer. Large amounts of aniline (**26**) and significant amounts of uncharacterized products most likely result from fragmentations and bimolecular reactions.

Conclusions

The FVP's of *o*-allylphenol (**13**) and *o*-allylaniline (**14**) result in product mixtures analogous to that observed in the FVP of the parent system, *o*-allyltoluene (**1**). As with **1** we have invoked a thermally induced diradical mechanism to explain the formation of the isomeric products as well as the numerous fragmentation products. Although the diradical mechanism is certainly plausible our results do not rule out a polar mechanism as invoked by others in the thermally induced transformation of *o*-allylthiophenol (**38**) to thiocoumaran (**39**).¹⁷ The results from the FVP of 2-methylindoline (**17**) firmly establish the reversibility of the **14** to **17** conversion while the results from the FVP's of *o*-(ethenyloxy)toluene (**15**) and *o*-(1-methylallyl)phenol (**16**) provide additional evidence for the generality of the isomerization/decomposition of ortho substituted allyl benzenes.

Experimental Section

Methods and materials.

Some general methods¹⁹ have been described previously. All reagents or compounds not explicitly referenced were obtained from commercial sources. *o*-Allylphenol (**13**) and 2-methylindoline (**17**) were obtained from Aldrich and purified by column chromatography and vacuum distillation, respectively, prior to use.

***o*-(Ethenyloxy)toluene (15).** *o*-(2-Bromoethoxy)toluene was prepared by a previously published procedure.²⁰ *o*-(Ethenyloxy)toluene (**15**) was prepared from *o*-(2-bromoethoxy)toluene by a modification of Kirmse's method.²¹ A solution of potassium *tert*-butoxide (1.62 g, 14 mmol) in DMSO (6.8 g) was added to a solution of *o*-(2-bromoethoxy)toluene (2.5 g, 12.0 mmol) in DMSO (8.3 mL) cooled in an ice bath which (< 15 °C). After addition of the base, the mixture was stirred for 20 min. at room temperature and then poured into ice water (30 mL), neutralized with H₂SO₄, and extracted with ether (4 x 15 mL). The combined ether layers was washed with sat'd. NaHCO₃ (30 mL) and H₂O (30 mL), dried over NaSO₄, filtered, concentrated under reduced pressure, and distilled to afford 0.99 g (65%) yield of **15**. ¹H NMR spectroscopy data of **15** matched those reported.²¹

***o*-(1-Methylallyl)phenol (16).** *o*-(1-methylallyl)phenol (**16**) was prepared from phenyl crotyl ether by Claisen's method.^{9a} ¹H NMR spectroscopy data of **16** matched those reported.²²

***o*-Allylaniline (14).** *o*-Allylaniline (**14**) was prepared from *N*-allylaniline by a modification of Hansen's method.²³ A solution of *N*-allylaniline (0.30 mL, 2.3 mmol) in 0.09 M H₂SO₄ (15.0 mL) was placed into a 25 mL ampoule and freeze-thaw deoxygenated using a dry ice/isopropanol bath, Ar, and a vacuum of *ca.* 0.03 torr. The ampoule was sealed under vacuum and then heated to *ca.* 165 °C in a pyrolysis oven for 2 h. After cooling, the ampoule was opened and the contents neutralized with 30 mL of saturated NaHCO₃ solution. The re-

sulting cloudy-white mixture was extracted with ether (2 x 30 mL) and the combined ether layers were dried over MgSO₄ and filtered. The product was purified by flash column chromatography (2:1 hexanes/ethyl acetate) and isolated under reduced pressure yielding a clear, slightly yellow oil (0.16 g, 55% yield). ¹H NMR spectroscopy data of **14** matched those reported.²⁴

Flash Vacuum pyrolysis. Flash vacuum pyrolysis (FVP) was performed as previously described.²⁵

Sealed-Tube Thermolysis. A weighed sample (*ca.* 35 mg) of *o*-allylaniline (**14**) was dissolved in 1-1.5 mL of freshly distilled phenyl ether and placed into a 25 mL ampoule. The solution was then freeze-thaw de-oxygenated and sealed as described above. Upon completion of pyrolysis the ampoule was opened and the contents diluted with *ca.* 2.5 mL of cyclohexane. A known amount of biphenyl in cyclohexane was then added as a standard for GC analysis.

Product analysis. FVP and sealed-tube reaction mixtures were analyzed by capillary gas chromatography as previously described.¹ Triplicate pyrolyses were performed only in the FVP of **13** and **16**. FID response factors were calculated for compounds **13**, **18**, **19**, **14**, **17**, **25**, and **29**. Other compounds were assigned a response factor equal to biphenyl except for compounds **16** and *E*-**22**, which were assigned a response factor equal to **13**, compound **23**, which was assigned a response factor equal to **18**, and compounds **20** and **24**, which were assigned a response factor equal to **19**.

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Supporting Information: ¹H NMR spectroscopy data for compounds **14**, **15**, and **16**; ¹H NMR spectroscopy data for the pyrolysate mixtures of compounds **13**, **14**, **15**, **16**, and **17**;

MS data for compound **20** in the pyrolysate of **13**, compound **21** in the pyrolysate of **15**, compound **23** in the pyrolysate of **16**, and compounds **30** and **31** in the pyrolysate of **14**; and detailed product analysis of FVP mixtures are available in Appendix B.

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CHAPTER 5. Evidence that Aryl Substitution in the 3 Position of Mono-substituted Terminal Epoxides Promotes Selective Isomerization to the Corresponding Aldehydes Under FVP Conditions

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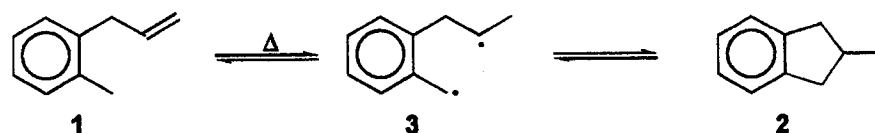
Abstract

In the process of studying intramolecular hydrogen atom transfers in ortho substituted toluenes, we pyrolyzed 3-(*o*-tolyl)propene oxide (**6**) under flash vacuum conditions. At 300 °C, flash vacuum pyrolysis (FVP) results in the surprisingly exclusive, and virtually complete, rearrangement of **6** to 3-(*o*-tolyl)propionaldehyde (**12**). Under similar conditions, 3-(*p*-tolyl)propene oxide (**7**) also yields exclusive rearrangement to its isomeric aldehyde, 3-(*p*-tolyl)propionaldehyde (**14**). The similarity of these two rearrangements argues against an intramolecular hydrogen atom transfer from the methyl to the oxygen of the epoxy ring. To test the generality of the epoxide to aldehyde rearrangement, several other related monosubstituted terminal epoxides, including 1-octene oxide (**8**), propene oxide (**9**), 4-phenyl-1-butene oxide (**10**), and 3-cyclohexylpropene oxide (**11**), were pyrolyzed under similar conditions.

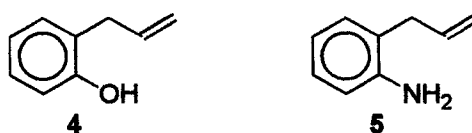
Introduction

We recently proposed a thermally-induced reversible intramolecular hydrogen-atom transfer to explain the products formed in the flash vacuum pyrolysis (FVP) of *o*-allyltoluene (**1**).¹ A major product observed in the FVP of **1** is 2-methylindan (**2**), explained by the gen-

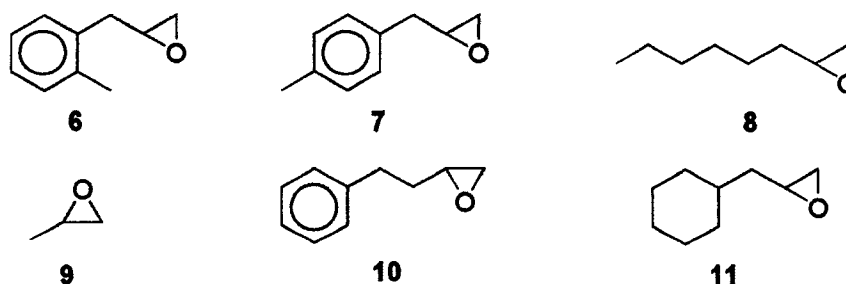
eration and intramolecular coupling of diradical **3**. We have also recently reported that under similar conditions *o*-allylphenol (**4**) and *o*-allylaniline (**5**) yield products analogous to those



observed in the FVP of **1**, providing tentative evidence for intramolecular hydrogen-atom transfer in the FVP of oxygen and nitrogen analogs of **1**.²



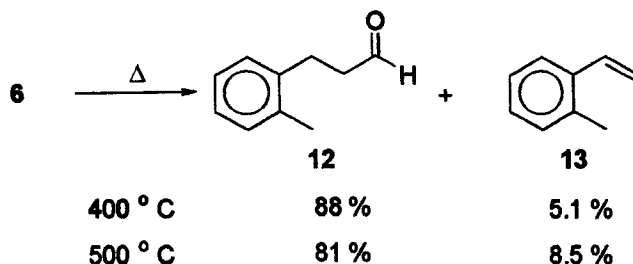
It occurred to us that a diradical might be generated by an intramolecular hydrogen-atom transfer to an atom on a small ring with concurrent ring opening. We proposed that ring strain release might provide the driving force for the reaction. Evidence for a diradical thus generated would take the form of products consistent with intramolecular coupling and disproportionation. We now present our study of the FVP's of 3-(*o*-tolyl)propene oxide (**6**) and several other related monosubstituted terminal epoxides including 3-(*p*-tolyl)propene oxide (**7**), 1-octene oxide (**8**), propene oxide (**9**), 4-phenyl-1-butene oxide (**10**), and 3-cyclohexylpropene oxide (**11**).



Results

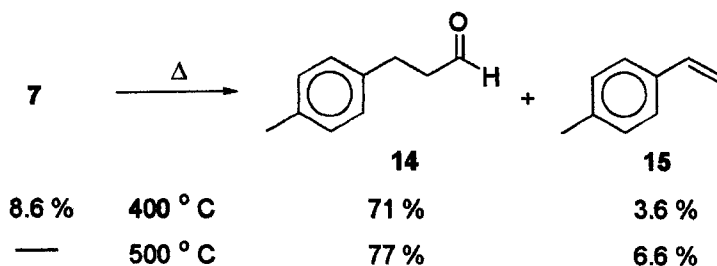
The FVP of 3-(*o*-tolyl)propene oxide (**6**) at 0.10 torr (400-500 °C, sample head at ambient temperature) yields 3-(*o*-tolyl)propionaldehyde (**12**) along with small amounts of

o-methylstyrene (**13**), and minor amounts of several C₁₀H₁₀ isomers which we have not identified.³ FVP of **6** at 250 °C results in a product mixture composed primarily of **6** and **12** in a

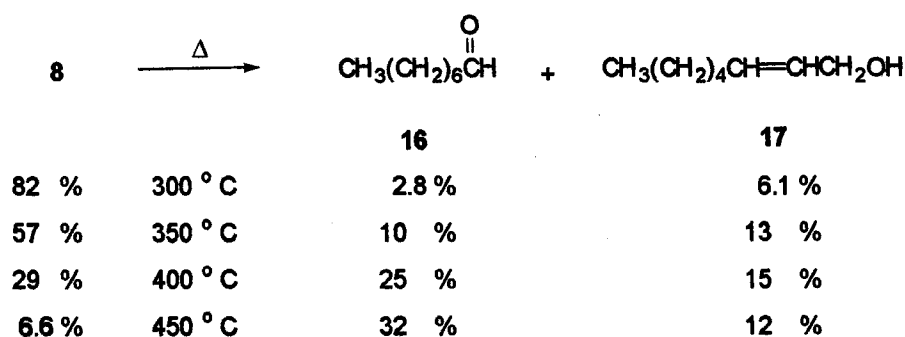


1:1.2 ratio.⁴ Almost complete conversion of **6** to **12** is observed at 300 °C with the detection of only trace amounts of **6** and **13**.

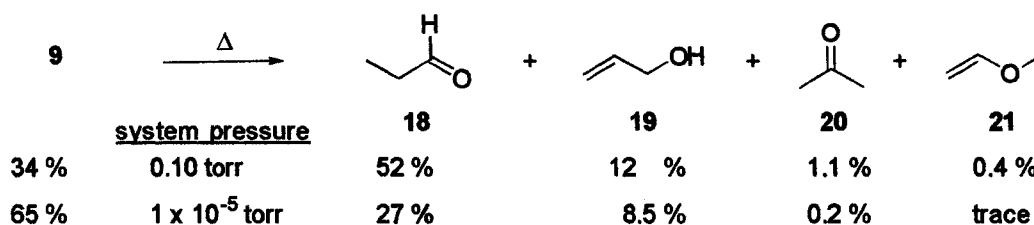
The FVP of 3-(*p*-tolyl)propene oxide (**7**), under similar conditions, yields 3-(*p*-tolyl)propionaldehyde (**14**) as the main product along with small amounts of *p*-methylstyrene (**15**) and a minor amount of an unidentified C₁₀H₁₀ product.³ FVP of **7** at 250 °C results in a product mixture composed primarily of **7** and **14** in a 2:1 ratio.⁴ Absolute yields for the major components in the product mixtures of the 400 °C and 500 °C runs were determined and are listed below.⁵



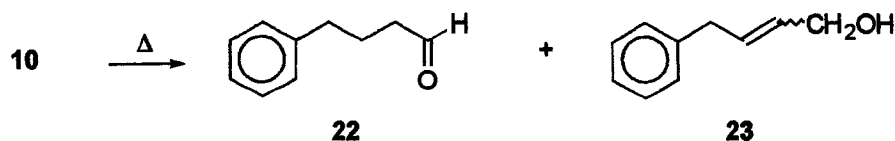
The FVP of 1-octene oxide (**8**) at 0.10 torr (300–450 °C, sample head at ca. -35 °C) yields octanal (**16**) and *cis/trans*-2-octenol (**17**) as major products. Absolute yields of **16**, **17** and recovered **8** are listed below.⁵ Evidence for several olefinic products is observed by both ¹H NMR spectroscopy and GCMS.



The high volatility of propene oxide (9) requires that FVP be performed at low sample head temperatures (-115 to -90°C) and high oven temperatures for appreciable conversion. FVP of 9 at 800 °C (1×10^{-5} to 0.10 torr) yields propanal (18) and allyl alcohol (19) as major products along with small amounts of acetone (20) and minor amounts of methyl vinyl ether (21). Relative yields based on ^1H NMR spectroscopy are listed below.⁴

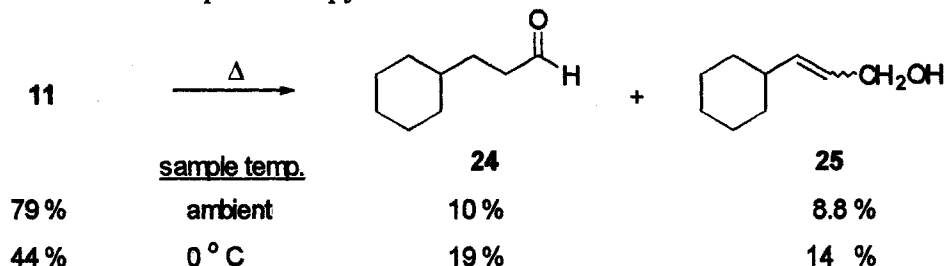


The FVP of 4-phenyl-1-butene oxide (10) at 0.10 torr (400 °C, sample head at ca. -10 °C) yields 4-phenylbutyraldehyde (22) (8.4%).⁵ There is IR and ^{13}C NMR spectroscopy evidence for an allyl alcohol in the product mixture but the presence of 4-phenyl-2-butenol (23) could not be firmly established by ^1H NMR spectroscopy. As with the FVP of 8, evidence for several olefinic products is observed by both ^1H NMR spectroscopy and GCMS.



The FVP of 3-cyclohexylpropene oxide (11) at 0.10 torr (300 °C, sample head at ambient temperature and at ca. 0 °C) yields 3-cyclohexylpropionaldehyde (24) and *cis/trans*-3-cyclohexyl-2-octenol (25) as major products. Quantification results for 24, 25,

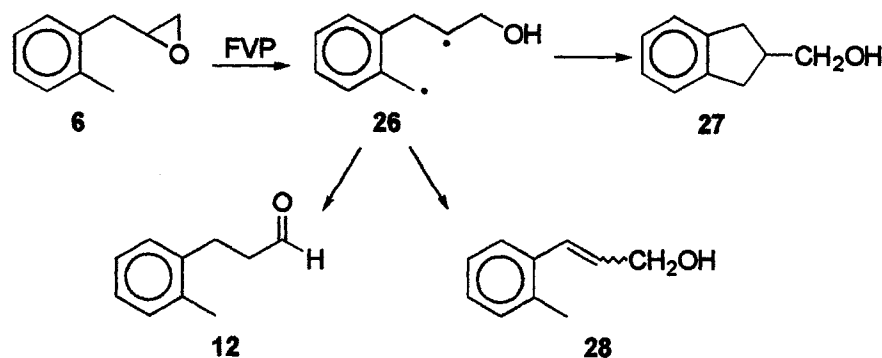
and unconverted 11 are listed below.⁵ Again, evidence for several olefinic products are observed by both ¹H NMR spectroscopy and GCMS.



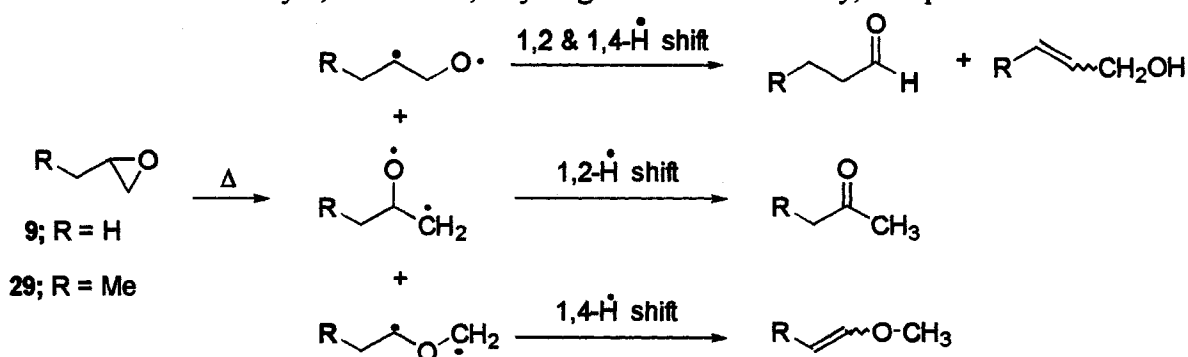
Discussion

We fully expected the presence of 3-(*o*-tolyl)propionaldehyde (12) in the FVP of 3-(*o*-tolyl)propene oxide (6), having predicted the generation of diradical intermediate 26 by a thermally induced intramolecular hydrogen-atom transfer (Scheme 1). However, the absence of the intramolecular coupling product 27 and intramolecular disproportionation product 28 argues against the presence of diradical 26 in the mechanism. More importantly, the FVP of the para isomer, 3-(*p*-tolyl)propene oxide (7), yields a parallel product mixture, indicating that the position of the methyl group, critical for intramolecular hydrogen atom transfer, does not greatly affect the selective rearrangement of the benzylic epoxide to the aldehyde. The slightly higher yield of isomerization of 6 over 7 at 250 °C may simply be due to the steric effect of the ortho substituent.

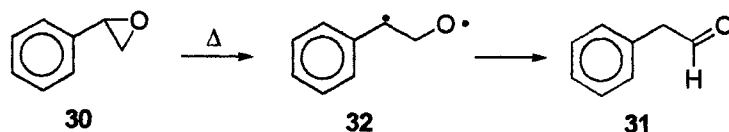
Scheme 1



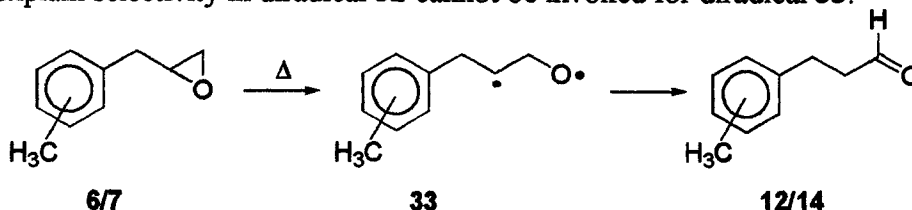
Although several efficient catalytic methods for selectively converting terminal epoxides to aldehydes have been reported,⁶ the gas-phase regioselective thermal isomerizations of **6** and **7** to their respective aldehydes are surprising. In the few gas-phase pyrolyses previously reported for monosubstituted terminal epoxides, mixtures of aldehyde and ketone isomers, along with smaller amounts of allylic alcohol and methyl vinyl ether isomers, are observed.⁷ In the static and shock tube pyrolyses of propene oxide (**9**) and 1,2-butene oxide (**29**) three parallel two-step mechanisms have been proposed in which ring scission to one of three possible diradicals is followed by 1,2- and/or 1,4-hydrogen shifts. Selectivity, comparable to that



which we have observed with **6** and **7**, has been reported previously only in the liquid-phase thermal isomerization of 1,2-epoxyethylbenzene (**30**) to phenylethanal (**31**).⁸ The authors of that study propose benzylic stabilization of diradical **32**, resulting from epoxide ring opening, to explain the absence of acetophenone. A 1,2-hydrogen shift in **32**, as evidenced by isotopic labeling studies, explains the formation of **31**.^{8b} While we may also propose epoxide ring



opening as a possible path for FVP isomerizations of **6** and **7**, the benzylic stabilization invoked to explain selectivity in diradical **32** cannot be invoked for diradical **33**.

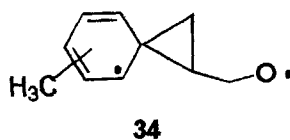


The fact that quartz (SiO_2) tubes were employed in the pyrolyses of the epoxides in our study forces us to consider the possibility of surface catalyzed ring-opening. While unlikely, we cannot rule out the potential for acidic O-H groups on the tube surface to catalyze the opening of the epoxide ring.^{6h}

To test if aromatic substitution on the third carbon of monosubstituted terminal epoxides is necessary for regioselective isomerization under FVP conditions the FVP's of 1-octene oxide (**8**), propene oxide (**9**), 4-phenyl-1-butene oxide (**10**) and 3-cyclohexylpropene oxide (**11**) were studied under similar conditions. Straight chain aliphatic substitution is represented by **8** while **9** represents the most fundamental monosubstituted terminal epoxide. Epoxide **10** tests the effect of moving the aryl substitution to the 4 position and **11** tests for the effect of a large group, other than phenyl, on the 3 position.

In contrast to the FVP's of **6** and **7**, the three non-aromatic cases, **8**, **9**, and **11**, yield very strong evidence for the formation of the allylic alcohol isomer as a major product in addition to the formation of the aldehyde isomer. Though not clearly shown by ^1H NMR spectroscopy, ^{13}C NMR spectroscopy and IR analyses established the presence of the allylic alcohol isomer of **10**. Also, in contrast to previously reported static and shock tube pyrolyses of monosubstituted terminal epoxides, the FVP's of **8**, **10**, and **11** yield little or no evidence for the formation of ketone or vinyl ether product. FVP of **9** yields only a small amount of acetone and a trace amount of methyl vinyl ether. The cause of the difference in products between FVP and static/shock tube pyrolyses is unclear.

The absence of allylic alcohol products in the flash vacuum pyrolyses of **6** and **7** is puzzling.⁹ A simple steric explanation can be excluded due to lack of selectivity in the FVP of **11**. Perhaps a phenyl-bridged resonance-stabilized diradical, **34**, is formed directly from **6** and **7**, precluding the 1,4-hydrogen shift necessary for the allylic alcohol product. This situation is



similar to bridging proposed in neophyl-like migrations of aryl groups.¹⁰ However, phenyl bridging does not explain the lack of vinyl ether products. Perhaps this may be explained by a polar transition state favoring C-O cleavage over C-C.

In summary, the FVP induced isomerization of 3-(*o*-tolyl)propene oxide (6) and 3-(*p*-tolyl)propene oxide (7) to high yields of 3-(*o*-tolyl)propionaldehyde (12) and 3-*p*-tolylpropionaldehyde (14), respectively, has been observed. The selectivity of these isomerizations is unexpected considering that 1-octene oxide (8), propene oxide (9), 4-phenyl-1-butene oxide (10), and 3-cyclohexylpropene oxide (11) yield significant amounts of allylic alcohol isomer in addition to the expected aldehyde isomer under similar conditions. Although we do not fully understand the effect of aryl substitution on the isomerization mechanism we conclude that aryl substitution in the 3 position of monosubstituted terminal epoxides promotes selective isomerization to the corresponding aldehydes under FVP conditions. The FVP of 11 demonstrates that a simple steric effect does not explain the selectivity. We propose that a phenyl-bridged resonance-stabilized diradicals formed directly from epoxides 6 and 7 may explain this selectivity.

Experimental Section

Methods and materials.

Some general methods¹¹ have been described previously. All reagents or compounds not explicitly referenced were obtained from commercial sources. The syntheses of epoxides **6**, **7**, **10**, and **11** were accomplished by Paquette's procedure.¹² The resulting crude epoxides were purified by vacuum distillation and quantified against durene standard by ¹H NMR spectroscopy.

3-(*o*-Tolyl)propene oxide (6). *o*-Allyltoluene was prepared by a previously described procedure.¹³ 3-(*o*-Tolyl)propene oxide (**6**) (95.4% purity) was prepared from *o*-allyltoluene in 60% yield.¹⁴ ¹H NMR spectroscopy (300 MHz, CCl₄:CD₂Cl₂, 4:1 (v/v)) δ 7.15-7.06 (m, 4 H), 3.09-3.03 (m, 1 H), 2.84 (ABX, *J*_{AB} = 14.7 Hz, *J*_{AX} = 5.4 Hz, *J*_{BX} = 5.1 Hz, Δ*v* = 28.8 Hz, 2 H), 2.70 (dd, *J* = 5.1, 3.9 Hz, 1 H), 2.42 (dd, *J* = 5.1, 2.7 Hz, 1 H), 2.32 (s, 3 H).

3-(*p*-Tolyl)propene oxide (7). *p*-Allyltoluene was prepared by the same procedure used above for *o*-allyltoluene.¹⁵ 3-(*p*-Tolyl)propene oxide (**7**) (98% purity) was prepared from *p*-allyltoluene in 66% yield. ¹H NMR spectroscopy (300 MHz, CCl₄/CD₂Cl₂, 3:1 (v/v)) δ 7.06 (s, 4 H), 3.05-2.97 (m, 1 H), 2.84 (ABX, *J*_{AB} = 14.4 Hz, *J*_{AX} = 5.4 Hz, *J*_{BX} = 5.4 Hz, Δ*v* = 26.4 Hz, 2 H), 2.68 (dd, *J* = 5.1, 3.9 Hz, 1 H), 2.43 (dd, *J* = 5.1, 2.4 Hz, 1 H), 2.32 (s, 3 H); [lit.¹⁴ ¹H NMR spectroscopy (60 MHz, CCl₄) δ 6.60 (s, 1 H), 2.80 (d, 1 H), 2.70 (d, 1 H), 2.35 (d, 1 H), 2.65 (d, 2 H), 2.20 (s, 3 H)].

4-Phenyl-1-butene oxide(10). 4-Phenyl-1-butene oxide (**10**) (94% purity) was prepared from 4-phenyl-1-butene in 72% yield. ¹H NMR spectroscopy (300 MHz, CCl₄:CD₂Cl₂, 3:1 (v/v)) δ 7.30-7.14 (m, 5 H), 2.92-2.68 (m, 4 H), 2.41 (dd, *J* = 2.7, 5.4 Hz, 1 H), 1.95-1.74 (m, 2 H); [lit.¹⁶ (CCl₄) δ 7.2-7.0 (m, 5 H), 2.9-2.5 (m, 3 H), 2.4-2.2 (m, 1 H), 1.9-1.5 (m, 2 H)].

3-Cyclohexylpropene oxide (11). Allylcyclohexane was prepared by a previously published procedure.¹⁷ 3-Cyclohexylpropene oxide (**11**) (81% purity) was prepared from al-

allylcyclohexane in 66% yield. ^1H NMR spectroscopy (300 MHz, $\text{CCl}_4/\text{CD}_2\text{Cl}_2$, 3:1 (v/v)) δ 2.90-2.84 (m, 1 H), 2.69-2.66 (dd, $J = 5.4$, 3.9 Hz, 1 H), 2.37-2.34 (dd, $J = 5.4$, 2.4 Hz, 1 H), 1.9-0.9 (m, 13 H) [lit. 18 ^1H NMR spectroscopy (250 MHz, CDCl_3) δ 3.1-2.1 (m, 3 H), 2.1-0.4 (m, 13 H)].

Flash vacuum pyrolysis. Flash vacuum pyrolysis (FVP) was performed as previously described,¹⁹ with the exception that the pyrolysis tube was not packed with quartz chips.

Product analysis. FVP reaction mixtures were quantified by ^1H NMR spectroscopy against durene standard in a $\text{CCl}_4:\text{CD}_2\text{Cl}_2$, 3:1 (v/v) solution. The spectra were obtained on a Varian VXR-300 NMR spectroscopy employing an extra 10 second delay between scans to ensure complete relaxation of all protons. The NMR spectroscopy signals for 3-(*o*-tolyl)propionaldehyde (**12**),²⁰ *p*-methylstyrene (**15**),²¹ *cis/trans*-2-octenol (**17**),²² methyl vinyl ether (**21**),²³ 4-phenylbutyr-aldehyde (**22**),²⁴ 4-phenyl-2-butenol (**23**),²⁵ and *cis/trans*-3-cyclohexyl-2-octenol (**25**)²⁶ were compared to literature values. The NMR spectroscopy signals for *o*-methylstyrene (**13**), octanal (**16**), 2-octanone, propanal (**18**), allyl alcohol (**19**), and acetone (**20**) were compared to those of authentic samples. The ^1H NMR spectroscopy signals for 3-*p*-tolylpropionaldehyde (**14**) were compared with those of **12** and the ^1H NMR spectroscopy signals for 3-cyclohexylpropionaldehyde (**24**) were compared to those of **16**.

Acknowledgment. This work was supported by the U. S. Department of Energy, Office of Chemical Sciences, under Contract W-7405-ENG-82.

Supporting Information Available: ^1H NMR spectra for compounds **6-11** and allylcyclohexane; ^{13}C NMR spectra for FVP mixtures of compounds **7** and **10**; and IR data for the FVP mixtures of compounds **8**, **10**, and **11** are available in Appendix C.

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CHAPTER 6. Is There Evidence for Formation of a Diradical by Intramolecular Hydrogen Atom Transfer in the Flash Vacuum Pyrolysis of *o*-Cyclopropylmethyltoluene?

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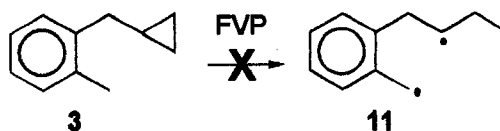
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Abstract

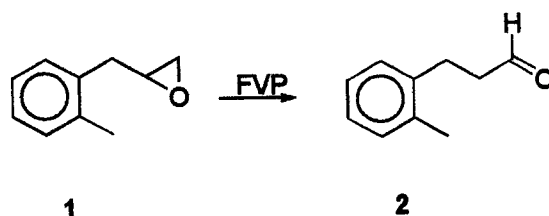
In an effort to determine the range of systems in which diradicals are generated by thermally-induced intramolecular hydrogen atom transfer, the flash vacuum pyrolysis (FVP) of *o*-cyclopropylmethyltoluene (**3**) was studied. However, the absence of key intramolecular coupling and disproportionation products is inconsistent with the formation of 1,5-diradical intermediate **11** in the FVP of **3**. In addition, the FVP of *p*-cyclopropylmethyltoluene (**4**)



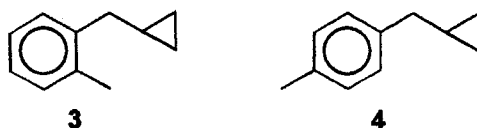
yields parallel products to those of the ortho system; indicating that an intramolecular hydrogen atom transfer from the *o*-methyl group to an atom in the cyclopropyl ring in **3** is apparently not occurring.

Introduction

As part of our efforts to determine the range of systems where diradicals are generated by intramolecular hydrogen atom transfer, we have sought to utilize the inherent strain energy of small ring systems. To this end, we have recently studied flash vacuum pyrolysis (FVP) on 3-(*o*-tolyl)propene oxide (**1**), observing the gas-phase thermal isomerization of **1** to aldehyde **2**.¹ We did not, however, find evidence for intramolecular hydrogen atom transfer.



We now report that the hydrocarbon analog of **1**, *o*-cyclopropylmethyltoluene (**3**), was also studied under similar conditions. As with epoxides **1** and **2** it occurred to us that a diradical might be generated by an intramolecular hydrogen-atom transfer from the ortho methyl group to one of the carbon atoms of the cyclopropyl ring with concurrent ring opening. We proposed that ring strain release might provide the driving force for the reaction. As a comparison we also studied *p*-cyclopropylmethyltoluene (**4**).



Results

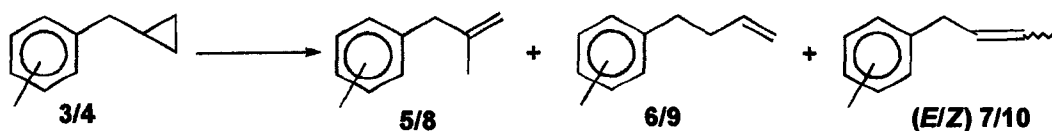
The FVP's of **3** and **4** at 700 °C (pressure = 0.08 torr, sample temperature = 0 °C) yield parallel product mixtures and conversions. Evidence for four rearrangement products was found in both pyrolysate mixtures by GCMS analysis (Table 6.1). Both ¹H NMR spectroscopy and MS results show that the isomers are aromatic olefins and allow for tentative product assignments.² The FVP of **3** yields evidence for *o*-(2-methyl-2-propenyl)toluene (**5**), *o*-(3-buten-yl)toluene (**6**), and (*E/Z*)-*o*-(2-butenyl)toluene (**7**). Evidence for a parallel product

Table 6.1. Products and Recovered Starting Material from the FVP's of *o*-Cyclopropylmethyltoluene (3) and *p*-Cyclopropylmethyltoluene (4) at 700 °C.

<i>o</i> -Cyclopropylmethyltoluene			<i>p</i> -Cyclopropylmethyltoluene		
compound	GC retention time ^a	yield, % ^b	compound	GC retention time ^a	yield, % ^b
5	0.796	3.8	8	0.814	4.6
6	0.861	8.0	9	0.870	6.3
<i>E</i> or <i>Z</i> 7	0.916	15	<i>E</i> or <i>Z</i> 10	0.943	13
<i>E</i> or <i>Z</i> 7	0.961	17	<i>E</i> or <i>Z</i> 10	0.976	15
3	1.000	30	4	1.000	33
recovery ^c		74	recovery ^c		72

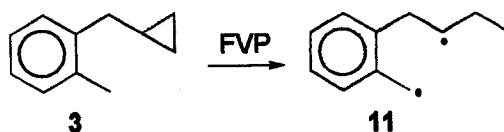
^a Relative to starting material retention time. ^b Mass of product divided by initial mass of starting material X 100. ^c Mass of four isomers and recovered starting material divided by initial mass of starting material X 100.

mixture of *p*-(2-methyl-2-propenyl)toluene (**8**), *p*-(3-butenyl)toluene (**9**), and (*E/Z*)-*p*-(2-butenyl)toluene (**10**) is observed in the FVP of **4**. Both systems experience almost 70 % conversion and the relative ratios of olefinic products to remaining starting material are also very similar.



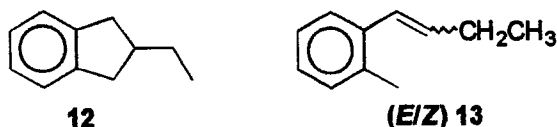
Discussion

As with epoxide **1** we proposed that ring strain in **3** might provide the driving force for an intramolecular transfer of a hydrogen atom from the ortho methyl group to one of the atoms of the cyclopropyl ring. We expected that evidence for the formation of diradical **11** would be provided by the formation of products consistent with intramolecular coupling and



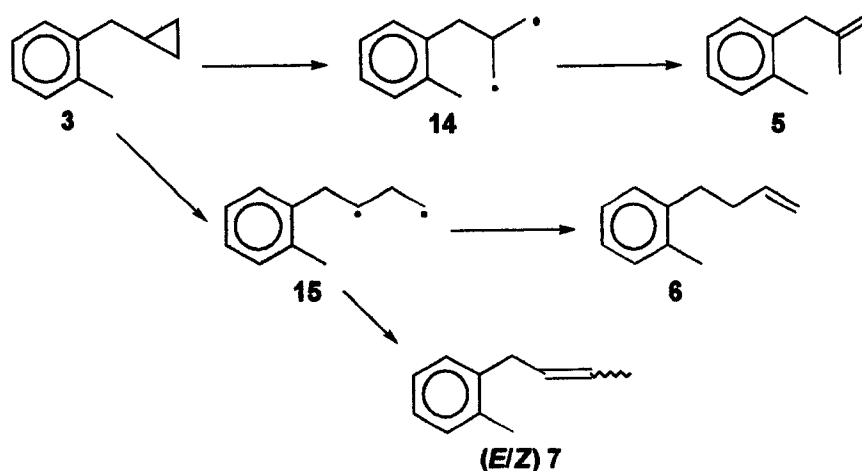
disproportionation. The results, however, tend to refute the presence of **11**. Furthermore, the mixture of rearrangement products observed contrasts the virtually selective rearrangement observed with the epoxide analog.

The most significant evidence *against* intramolecular hydrogen atom transfer is the fact that a parallel product mixture is observed in the FVP of *p*-cyclopropylmethyltoluene (**4**). Clearly, the presence of a methyl ortho to the cyclopropylcarbinyl group is unnecessary for the cyclopropyl rearrangement under these conditions. Furthermore, although the isomeric olefin products (*E/Z*) **7** can be explained by invoking intramolecular disproportionation from diradical **11**, ¹H NMR spectroscopy and MS evidence is lacking for either the intramolecular coupling product 2-ethylindane (**12**) or the intramolecular disproportionation products (*E/Z*)-*o*-(1-butenyl)toluene (**13**).³



The four olefinic isomers observed in the FVP's of both **3** and **4** can be conveniently explained by a cyclopropyl ring opening mechanism. Cleavage at the C2-C3 bond of the cyclopropyl ring would yield diradical intermediate **14**. A subsequent 1,2-hydrogen atom shift would then produce **5**. Conversely, cleavage at the C1-C2 bond of the cyclopropyl ring

would yield diradical intermediate **15**. Two different 1,2-hydrogen atom shifts resulting in olefins would now be possible. A 1,2-hydrogen atom shift to the internal radical would result in the formation of **6**. Similarly, a 1,2-hydrogen atom shift to the terminal radical would produce the (*E/Z*) mixture **7**.



Several reviews as well as recent studies on both the geometric and structural thermal isomerizations of cyclopropanes are available.^{5,6} 1,3-Diradicals resulting from thermally induced cyclopropyl ring opening are commonly proposed as intermediates. In the absence of other paths these diradicals either couple to regenerate the cyclopropyl ring or undergo 1,2-hydrogen atom shifts to generate olefins.

In conclusion, there is no evidence that a 1,5-diradical, resulting from an intramolecular hydrogen atom transfer, is formed in the FVP of *o*-cyclopropylmethyltoluene (**3**). The four olefinic isomers we observed are, however, consistent with the generation of 1,3-diradicals by cyclopropyl ring fission.

Experimental Section

Methods and materials.

Some general methods⁷ have been described previously. ¹H NMR spectra were obtained on a Varian-VXR-300 instrument employing an extra 10-second delay between scans to ensure complete relaxation of all protons. GC analyses were performed on a Hewlett-Packard HP5890 II PLUS gas chromatograph equipped with a 30m DB-5 capillary column (0.25- μ m thickness) and a flame ionization detector. GCMS was performed on a Finnegan Magnum spectrometer with 70-eV EI after separation on a DB-5 capillary column. All reagents or compounds not explicitly referenced were obtained from commercial sources.

The syntheses of cyclopropanes **3** and **4** from their respective allyltoluenes were based on Friedrich's synthesis of benzylcyclopropane with three significant alterations: The preparations were carried out in microscale, a Hickmann distillation apparatus was employed to purify the resulting crude cyclopropanes, and the zinc-copper couple employed in the Simmons-Smith reaction was purchased from a commercial source.⁸ Purity was determined by ¹H NMR spectroscopy using durene as an internal standard.

***o*-Cyclopropylmethyltoluene (3).** *o*-Allyltoluene (**16**) was prepared by a previously described procedure.⁹ *o*-Cyclopropylmethyltoluene (**3**) (66% purity) was prepared from *o*-allyltoluene in 45% yield. ¹H NMR spectroscopy (300 MHz, CCl₄:CD₂Cl₂, 4:1 (v/v)) δ 7.25-6.95 (m, 4 H), 2.51 (d, J = 6.6, 2 H), 2.28 (s, 3 H), 1.02-0.93 (m, 1 H), 0.55-0.48 (m, 2 H), 0.19-0.14 (m, 2 H). [lit.¹⁰ ¹H NMR spectroscopy (neat, benzene as external reference) δ 7.0 (m, 4 H), 2.6-2.1 (m, 5 H), 1.0-0.2 (m, 5 H)]. The two impurities present in largest amount are unreacted *o*-allyltoluene at 6.0% and diethyl ether at 1.8%.

***p*-Cyclopropylmethyltoluene (4).** *p*-Allyltoluene (**17**) was prepared by the same procedure used above for *o*-allyltoluene. *p*-Cyclopropylmethyltoluene (**4**) (75% purity) was prepared from *p*-allyltoluene in 32% yield. ¹H NMR spectroscopy (300 MHz, CD₂Cl₂) δ 7.16-7.02 (m, 4 H), 2.49 (d, J = 6.9 Hz, 2 H), 2.31 (s, 3 H), 1.04-0.87 (m, 1 H), 0.52-0.46 (m, 2

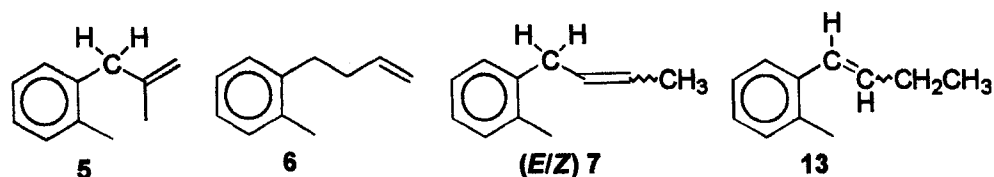
H), 0.21-0.16(m, 2 H). The two impurities present in largest amount are unreacted *o*-allyltoluene at 3.6% and diethyl ether at 4.8%. Although **4** is a known compound, prepared by Collins and coworkers using a different method, its ^1H NMR spectrum is not available in the literature.¹¹

Flash vacuum pyrolysis. Flash vacuum pyrolysis (FVP) was performed as previously described.¹²

Product analysis. The products, as part of the FVP reaction mixtures, were analyzed by ^1H NMR spectroscopy, GC, and GCMS and quantified against durene standard in a $\text{CCl}_4:\text{CD}_2\text{Cl}_2$, 3:1 (v/v) solution. All figures referred to in the following paragraph are located in Appendix D.

FVP isomerization products of *o*-cyclopropylmethyltoluene (**3**) were assigned as follows. First, the presence of four isomerization products was established by GC-MS (see figures D-8 through D-12). Evidence for *o*-(2-methyl-2-propenyl)toluene (**5**) was found by ^1H NMR spectroscopy analysis of the product mixture where a singlet at 3.17 ppm can be assigned to the methylene protons (see figure D-6). The crowded nature of the spectrum precludes the assignment of additional protons. Evidence for *o*-(3-butenyl)toluene (**6**) cannot, at least with any confidence, be found in the ^1H NMR spectrum due to numerous benzylic, allylic, and olefinic signals. However, the mass spectrum of the second $\text{C}_{11}\text{H}_{14}$ isomer to elute by GC displays a prominent peak at m/e 105 consistent with the loss of an allyl radical (see figure D-10). Note, the three other isomers yield virtually identical mass spectra and lack the prominent m/e 105 peak (see figures D-9, -11, and -12). Finally, evidence that the two remaining $\text{C}_{11}\text{H}_{14}$ isomers are *E* and *Z*-*o*-(2-butenyl)toluene (**7**) was found by ^1H NMR spectroscopy analysis of the product mixture. Two sets of doublets, one at 1.678 and 1.658 ppm and the other at 1.735 and 1.715 ppm can be assigned to the allylic methyls (see figure D-7). In addition, two sets of multiplets, one centered at 3.25 ppm and the other centered at 3.33 ppm, can be assigned to the methylene protons (see figure D-6). Conversely, there is no ^1H NMR spec-

troscopy or GC-MS evidence for styrene products (*E/Z*) 13; the area between 6.0 and 6.8 ppm, where olefinic protons geminal to an aromatic ring typically appear, is clear (see figure D-4 and D-5).



The FVP isomerization products of *p*-cyclopropylmethyltoluene (4) were assigned similarly to those of 3. Four isomerization products were established by GC-MS (see figures D-15 through D-19). Evidence for *p*-(2-methyl-2-propenyl)toluene (8) was found by ^1H NMR spectroscopy analysis of the product mixture where a singlet at 2.86 ppm can be assigned to the methylene protons (see figure D-24). The crowded nature of the spectrum precludes the assignment of additional protons. As with 5, the ^1H NMR spectrum of the product mixture is too crowded to yield evidence for *p*-(3-butenyl)toluene (9). However, the mass spectrum of the second $\text{C}_{11}\text{H}_{14}$ isomer to elute by GC displays a prominent peak at m/e 105 consistent with the loss of an allyl radical (see figure D-17). Again, the three other isomers have virtually identical mass spectra and lack the prominent m/e 105 peak (see figures D-16, -18, and -19). Finally, evidence that the two remaining $\text{C}_{11}\text{H}_{14}$ isomers are *E* and *Z*-*p*-(2-butenyl)toluene (10) was found by ^1H NMR spectroscopy analysis of the product mixture. Two sets of multiplets, one centered at 3.36 ppm and the other centered at 3.27 ppm, can be assigned to the methylene protons (see figure D-14).

Acknowledgment. The U. S. Department of Energy, Office of Chemical Sciences, under Contract W-7405-ENG-82 supported this work.

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CHAPTER 7. The Flash Vacuum Pyrolysis of *o*- and *p*-Cyclohexyltoluene: The Importance of the Position of the Methyl Group

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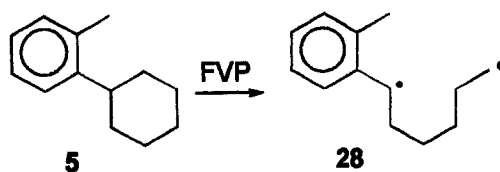
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Abstract

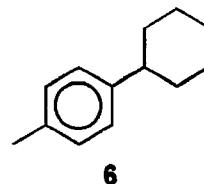
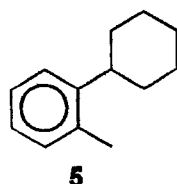
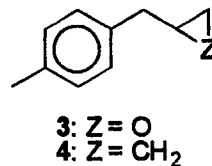
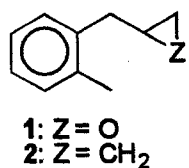
In our efforts to determine the range of systems in which diradicals are generated by thermally-induced intramolecular hydrogen atom transfer, the flash vacuum pyrolysis (FVP) of *o*-cyclohexyltoluene (**5**) was performed. The resulting products, however, are readily explained by homolytic cyclohexyl ring opening to diradical **28**. The FVP of the para isomer (**6**) yields results consistent with the generation of an analogous diradical. However, the methyl is retained in the para case.



Introduction

In our search for systems that generate diradicals by intramolecular hydrogen atom transfer we have studied the Flash Vacuum Pyrolysis (FVP) of 3-(*o*-tolyl)propene oxide (**1**) and *o*-cyclopropylcarbinytoluene (**2**), molecules that have strained rings, and their para isomers **3** and **4**, respectively.^{1,2} For comparison to an analogous system that does not have ring strain we studied the FVP of *o*-cyclohexyltoluene (**5**) and *p*-cyclohexyltoluene (**6**). Each of

the three systems, propene oxide, cyclopropylcarbiny, and cyclohexyl, behaves somewhat differently. We now report the results of the study of the FVP of **5** and **6**.



Results

FVP of *o*-cyclohexyltoluene (**5**) at 800 °C and 850 °C yields indene (**7**) as the main product (see Table 7.1). Minor products include *o*-methylstyrene (**8**), *o*-allyltoluene (**9**), 2-methylindan (**10**), 3-methyl-1-*H*-indene, (**11**) 2-methyl-1-*H*-indene (**12**), 1,2-dihydronaphthalene (**13**), naphthalene (**14**), and 1-(2-methylphenyl)-1-hexene (**15**).

On the other hand, FVP of *p*-cyclohexyltoluene (**6**) at 800 °C and 850 °C yields 6-methylindene (**16**) as the main product, retaining the methyl group (see Table 7.2). The minor products are similar to those observed with **5**, including *p*-methylstyrene (**17**), *p*-allyltoluene (**18**), and 1-(4-methylphenyl)-1-hexene (**19**) as well as a non-characterized C₁₁H₁₂ compound.

Table 7.1. Products and Recovered Starting Material from the FVP of *o*-Cyclohexyltoluene (5) at 800 °C and 850 °C.^{a, b}

compound	Yield, % ^c	
	800 °C	850 °C
<i>o</i> -methylstyrene (8)	1.8	4.1
indene (7)	7.9	21
<i>o</i> -allyltoluene (9)	1.3	1.9
2-methylindan (10)	0.6	1.6
3-methyl-1 <i>H</i> -indene (11)	1.8	3.5
2-methyl-1 <i>H</i> -indene (12)	1.2	2.2
1,2-dihydronaphthalene (13)	1.9	3.6
naphthalene (14)	0.9	4.1
1-(2-methylphenyl)-1-hexene (15)	1.7	1.3
<i>o</i> -cyclohexyltoluene (5) ^d	75	42
other products	5.6 ^e	15 ^e
recovery ^f	89	75
Conversion ^g	24	58

^a FVP conditions: system pressure $\cong 5 \times 10^{-5}$ torr, sample temperature $\cong 0$ °C. ^b Amounts determined by GC with a known quantity of triphenylmethane added as standard with an average standard deviation of 0.9%. ^c Moles of product divided by total moles of recovered material X 100. ^d Starting material purity, as determined by GC, is 98%. ^e See Table E-1 in Appendix E for a more detailed analysis. ^f Total moles of recovered material divided by moles of starting material used X 100. ^g Total moles of recovered material minus moles of recovered starting material divided by total moles of recovered material X 100.

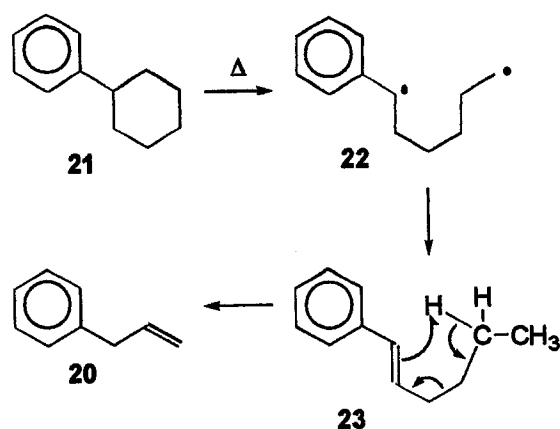
Table 7.2. Products and Recovered Starting Material from the FVP of *p*-Cyclohexyltoluene (6) at 800 °C and 850 °C.^{a, b}

compound	Yield, % ^c	
	800 °C	850 °C
<i>p</i> -methylstyrene (17)	1.1	3.1
<i>p</i> -allyltoluene (18)	0.4	2.7
C ₁₁ H ₁₂	1.2	3.1
6-methylindene (16)	7.2	19.6
1-(4-methylphenyl)-1-hexene (19)	1.3	1.2
C ₁₃ H ₁₈ ^d	3.0	2.0
<i>p</i> -cyclohexyltoluene (6) ^e	83.8	60.7
other products	2.1 ^f	7.7 ^f
recovery ^g	87.2	66.9
conversion ^h	16.6	38.3

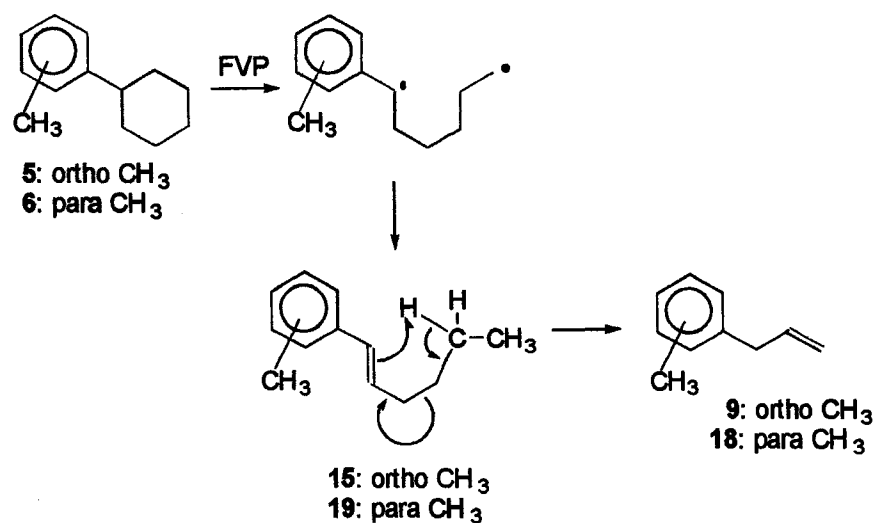
^a See Table 7.1, note a. ^b See Table 7.1, note b. ^c See Table 7.1, note c. ^d Impurity present in starting material at 3.1 % (as determined by GC). ^e Starting material purity as determined by GC is 97 %. ^f See Table E-2 in Appendix E for a more detailed analysis. ^g See Table 7.1, note f. ^h See Table 7.1, note g.

Discussion

Zimmermann et al., in explaining the steam-induced high-temperature formation of allylbenzene (**20**) from cyclohexyl benzene (**21**), have proposed a mechanism that also begins to explain our observations in the FVPs of **5** and **6**.³ They propose that cyclohexyl ring opening generates diradical intermediate **22** followed by intramolecular disproportionation to yield 1-phenylhexene (**23**). They then invoke a retro-ene reaction to explain the formation of **20**.

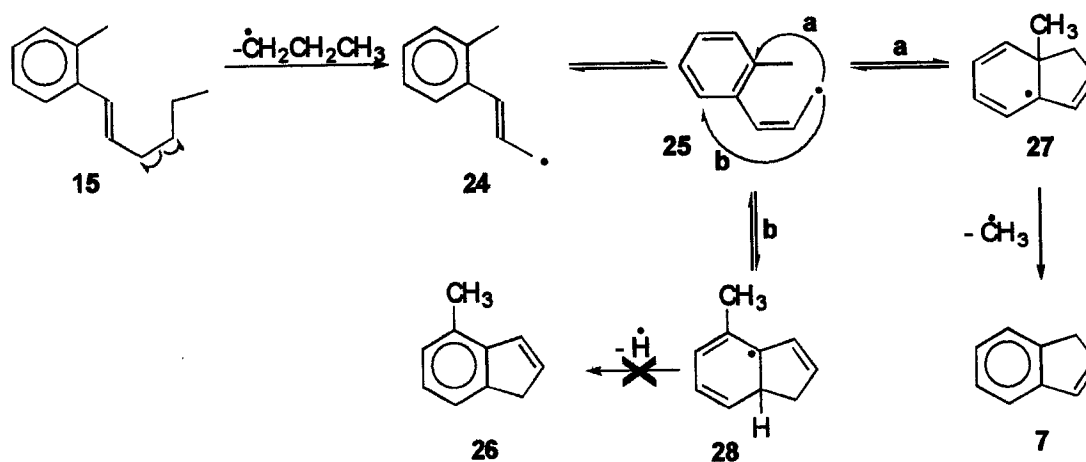


This mechanism, when applied to our results, provides a ready explanation for the formation of the allyltoluene (**9**, **18**) and 1-(methylphenyl)-1-hexene (**15**, **19**), products

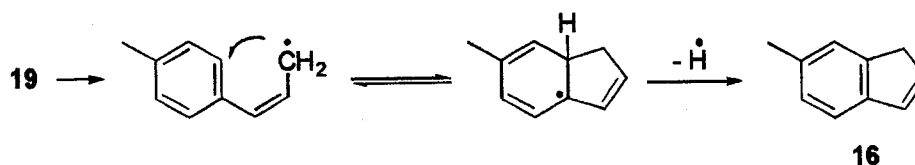


observed in the FVPs of **5** and **6**. However, in order to explain the main products, indene (**7**) from **5** and 6-methylindene (**16**) from **6**, we must extend Zimmermann's mechanism.

In the ortho system, homolytic cleavage between carbons 3 and 4 of the hexene side chain of **15** would yield an *n*-propyl radical and resonance stabilized radical (**24**). Intramolecular addition into the aromatic ring followed by loss of a methyl radical would then result in **7**. It is, however, surprising that there is no evidence for 4-methylindene (**25**) in the product mixture. One would expect that intramolecular addition into the ring at the non-methyl substituted ortho position would occur as readily, if not more readily, than at the methyl substituted position. Reversibility and a favorable equilibrium for radical **26** over radical **27** may explain the selectivity of intramolecular addition in radical **24**. Also, the loss of a methyl radical in the last step should be favored over the loss of a hydrogen atom, favoring the formation of **7** over **25**.⁴



A similar mechanism can be invoked to explain the formation of 6-methylindene (**16**) as the main product in the FVP of *p*-cyclohexyltoluene (**6**). In contrast, the position of the



methyl group para to the cyclohexyl group results in the loss of a hydrogen atom in the final step.

There is one possible, though less likely, alternate explanation for the product mixture from the FVP of **5**. In a previous study we observed many of the same products in the FVP of *o*-allyltoluene (**9**) as we have in the FVP of **5**, though with dissimilar ratios.⁵ In that study we discovered evidence that the rearrangement of **9** occurs through a diradical mechanism initiated by an intramolecular hydrogen atom transfer. It is possible that some of the remaining products from the FVP of **5** may result from the secondary pyrolysis of **9**. However, considering that the para system undergoes conversion at a comparable rate to the ortho system causes us to rule this out as the main mechanism.

In conclusion, the FVPs of *o*-cyclohexyltoluene (**5**) at 800 °C and 850 °C do not appear to proceed by a thermally induced intramolecular hydrogen atom transfer; a characteristic shared by the 3-(*o*-tolyl)propene oxide (**1**) and *o*-cyclopropylmethyltoluene (**2**) analogs. Similar products and conversions obtained in the FVPs of the para isomer, **6**, support this conclusion. While the FVPs of **5** and **6** yield different main products, indene (**7**) and 6-methylindene (**16**), respectively, the same radical mechanism can explain the formation of both products. The position of the methyl group para to the cyclohexyl group in **6** puts it in a position that does not allow it to cleave in the final step.

Experimental Section

Methods and materials.

Some general methods⁶ have been described previously. ¹H NMR spectra were obtained on a Nicolet NT-300, a Varian-VXR-300, or a Bruker DRX-400 instrument. An extra 10-second delay between scans was employed to ensure complete relaxation of all protons. Fully decoupled ¹³C NMR spectra were recorded on a Bruker DRX-400 (100MHz) spectrometer. GC analyses were performed on a Hewlett-Packard HP5890 II PLUS gas

chromatograph equipped with a 30m DB-5 capillary column (0.25- μ m thickness) and a flame ionization detector. GCMS was performed on a Finnegan Magnum spectrometer with 70-eV EI after separation on a DB-5 capillary column. All reagents or compounds not explicitly referenced were obtained from commercial sources.

***o*-Cyclohexyltoluene (5).** 1-*o*-Tolylcyclohexanol (**26**) was prepared in 75 % yield (92 % purity by GC) from *o*-bromotoluene and cyclohexanone by the Grignard procedure outlined by Kumada.⁷ ¹H NMR spectroscopy (300 MHz, CD₂Cl₂) δ 7.44-7.10 (m, 4 H), 3.70-3.66 (m, 1 H), 2.61 (s, 3 H), 2.40-1.47 (m, 10 H). Although **26** is a known compound, prepared most recently by Thurkauf and coworkers using a different method, its ¹H NMR spectrum is not available in the literature.⁸ 1-*o*-Tolylcyclohexene (**27**) was prepared from **26** in 68.7 % yield by a general procedure for dehydrating hindered tertiary alcohols.⁹ To prevent possible polymerization **27** was not purified but was instead immediately hydrogenated. ¹H NMR spectroscopy (300 MHz, CD₂Cl₂) δ 7.26-7.03 (m, 4 H), 5.55-5.52 (m, 1 H), 2.35-1.50 (m, 11 H). [lit.¹⁰ ¹H NMR spectroscopy (CCl₄) δ 7.01 (4 H), 5.59 (1 H), 2.23 (3 H), (1.69 (8 H))]. *o*-Cyclohexyltoluene (**5**) was prepared from **27** by hydrogenation. Into a 500-mL hydrogenation flask 0.5 g of 10% Pd/C were added along with 40 mL of 200 proof ethanol. Following the solvent, 5 g of **27** were added and the flask was attached to a Parr[®] hydrogenator. Following a hydrogen purge the flask was pressurized to 20 psig with hydrogen and shaking initiated. After 2.5 hours the pressure gauge indicated 0 psig and the flask was re-pressurized to 20 psig with hydrogen and allowed to shake on the hydrogenator until no more hydrogen was consumed. The contents of the flask were then filtered through diatomaceous earth and the resulting clear yellow solution was rotoevaporated. A crude yield of 81.9% was obtained. The resulting crude product was vacuum distilled at 2.5 mm Hg and 70 °C to yield 98.4 % pure material (based on GC analysis). ¹H NMR spectroscopy (400 MHz, CD₂Cl₂) δ 7.23-7.05 (m, 4 H), 2.80-2.70 (m, 1 H), 2.35 (s, 3 H), 1.95-1.65 (m, 5 H), 1.55-1.25 (m, 5 H). ¹³C NMR spectroscopy (100 MHz, CD₂Cl₂) δ 146.40, 135.54, 130.46, 126.39,

125.73, 125.66, 40.41, 34.09, 27.74, 26.74, 19.43. [lit.¹¹ ^1H NMR spectroscopy (300 MHz, CDCl_3) δ 7.20-6.90 (m, 4 H), 2.74-2.62 (m, 1 H), 2.32 (s, 3 H), 1.90-1.65 (m, 5 H), 1.45-1.15 (m, 5 H). ^{13}C NMR spectroscopy (75 MHz, CDCl_3) δ 145.86 (s), 135.15 (s), 130.17 (d), 126.07 (d), 125.43 (d), 125.34 (d), 40.16 (d), 33.70 (t), 27.21 (t), 26.38 (t), 19.29 (q).

***p*-Cyclohexyltoluene (6).** Except where noted, 1-*p*-tolylcyclohexanol (**28**), 1-*p*-tolylcyclohexene (**29**), and *p*-cyclohexyltoluene (**6**) were prepared as described above for their ortho analogs. Precursors **28** (78 % yield) and **29** (64 % yield) were not purified. ^1H NMR spectroscopy for **28**: (300 MHz, CD_2Cl_2) δ 7.38 (d, $J = 6.0$ Hz, 2 H), 7.15 (d, $J = 6.0$ Hz, 2 H), 3.71-3.67 (m, 1 H), 2.33 (s, 3 H), 2.00-1.17 (m, 10 H). [lit.¹² ^1H NMR spectroscopy (200 MHz, CDCl_3) δ 7.45-7.35 (m, 2 H), 7.20-7.10 (m, 2 H), 2.33 (s, 3 H), 1.85-1.55 (m, 11 H)]. ^1H NMR spectroscopy for **29**: (300 MHz, CD_2Cl_2) δ 7.28 (d, $J = 6.0$ Hz, 2 H), 7.12 (d, $J = 6.0$ Hz, 2 H), 6.15-6.07 (m, 1 H), 2.45-1.35 (m, 11 H). [lit.¹³ ^1H NMR spectroscopy (60 MHz, CDCl_3) δ 7.10-7.696 (ABq, $J = 8.4$ Hz, 4 H), 5.70-6.10 (m, 1 H), 2.50-1.30 (m, 11 H)]. Compound **29** was hydrogenated and an 81.2 % yield of crude **6** was obtained. Vacuum distillation at 2 mm Hg was employed to purify **6** and the fraction distilling over between 75 °C and 80 °C was collected. GCMS analysis established 96.9 % purity with 3.1 % of an isomeric impurity. ^1H NMR spectroscopy (300 MHz, CD_2Cl_2) δ 7.10 (s, 4 H), 2.52-2.42 (m, 1 H), 2.31 (s, 3 H), 1.90-1.70 (m, 5 H), 1.50-1.20 (m, 5 H). [lit.¹⁴ ^1H NMR spectroscopy (300 MHz, CDCl_3) δ 7.08 (s, 4 H), 2.45 (tt, $J = 3.2$ and 10.8, 1 H), 2.31 (s, 3 H), 1.86-1.81 (m, 4 H), 1.71-1.73 (m, 1H), 1.45-1.31 (m, 4 H), 1.21-1.29 (m, 1H).

Flash vacuum pyrolysis. Flash vacuum pyrolysis (FVP) was performed as previously described.¹⁵

Product analysis. The products, as part of the FVP reaction mixtures, were analyzed by ^1H NMR spectroscopy, GC, and GCMS and quantified against durene standard in a $\text{CCl}_4\text{:CD}_2\text{Cl}_2$, 3:1 (v/v) solution.

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Supporting Information Available: Expanded product lists for FVP mixtures of compounds **5**, and **6**. ^1H NMR spectra for compounds **5**, **6** and precursors **26**, **27**, **28**, and **29**; ^1H NMR spectra for FVP mixtures of compounds **5** and **6**; and GCMS data for the FVP mixtures are located in Appendix E.

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CHAPTER 8. GENERAL CONCLUSIONS

In the first two papers presented in this dissertation (Chapters 3 and 4) we propose diradical intermediates generated by thermally-induced intramolecular hydrogen-atom transfers to explain the products observed in the FVPs of ortho substituted allyl benzenes, such as *o*-allyltoluene, *o*-allylphenol, and *o*-allylaniline. The formation of diradicals in this manner has no precedent in the chemistry of hydrocarbons, alcohols, or amines. The main reaction paths of the diradicals thus generated appear to be either coupling to form the respective five-membered carbocyclic or heterocyclic fused-ring systems or intramolecular disproportionation to form either starting material or the respective ortho substituted 1-propenylbenzene. A possibility for future work may include studying the practical application of this hydrogen-atom transfer/diradical coupling reaction to the synthesis of carbocyclic and heterocyclic fused-ring systems.

In the remaining three papers (Chapters 5, 6, and 7), we applied the conditions of the first two studies to molecules in which the allyl moiety of *o*-allyltoluene was replaced by small to medium sized rings. While no conclusive evidence was observed for the thermally-induced intramolecular hydrogen-atom transfer in the epoxide, cyclopropyl, and cyclohexyl systems studied, some of the results proved very interesting as they showed unexpected selectivity for isomerization products, such as the selective isomerization of epoxides to aldehydes and the importance of the methyl position in the cyclohexyl systems.

In paper three (Chapter 5) we reported the unexpectedly selective isomerizations of ortho and para 3-(tolyl)propene oxide to their respective 3-arylpropionaldehydes under FVP conditions. This selectivity, however, does not appear to extend beyond terminal epoxides substituted in the 3-position with an aryl group. All other thermal isomerizations of

mono-substituted terminal epoxides yield mixtures including aldehyde, ketone, allylic alcohols, and vinyl ether isomers. The selectivity observed in the phenyl-substituted systems may be explained by phenyl-bridged resonance stabilization of the diradical formed from C-O cleavage of the epoxide ring. Selectivity of the cleavage position may result from a polar transition state favoring C-O cleavage over C-C cleavage. Future work regarding these selective, FVP induced, epoxide to aldehyde transformations may include studying their applications to other aromatic systems, such as pyrroles, furans, and polycyclic aromatic hydrocarbons.

In the remaining two papers, Chapters 6 and 7, we report that *o*-cyclopropylmethyltoluene and *o*-cyclohexyltoluene appear to undergo thermally induced ring fission under FVP conditions, resulting in 1,3- and 1,6-diradical intermediates, respectively. In both cases olefinic isomers are observed, resulting from intramolecular disproportionations of the diradical intermediates. Further decomposition of the olefinic products of *o*-cyclohexyltoluene appears to result from retro-ene reactions and radical fragmentations.

APPENDIX A.
RAW DATA TABLES AND FIGURES FOR CHAPTER 2.

Table A-1. Products and recovered starting material, total recovery of material, and conversion from the FVP of *o*-allyltoluene (6) at various temperatures *a*, *b*

entry	yield, % ^c			
	RT ^d	700 °C	800 °C	900 °C
toluene	0.57	—	1.05	3.03
ethylbenzene	—	—	0.55	1.92
<i>m/p</i> -xylene	—	—	0.51	0.18
<i>o</i> -xylene (25)	—	—	0.23	1.92
styrene (3)	—	—	0.75	3.45
benzocyclobutene (2)	—	—	0.35	1.19
allylbenzene	—	—	—	0.26
propylbenzene	—	—	—	0.12
<i>o</i> -ethyltoluene (26)	—	—	1.46	0.94
AA-118 [C ₉ H ₁₀]	—	—	—	0.09
<i>o</i> -methylstyrene (16)	—	1.06	3.32	5.75
AB-118 [C ₉ H ₁₀]	—	—	—	0.29
benzaldehyde	—	—	—	0.17
indan	—	—	—	0.68
<i>trans</i> -β-methylstyrene	—	—	—	0.11
<i>m/p</i> -allyltoluene	1.94	1.97	1.76	0.79
<i>o</i> -allyltoluene (6)	96.47	90.90	45.36	6.56
indene (7)	—	0.83	6.86	31.96
2-methylindan (8)	—	4.09	25.34	14.08
1-methylindan	—	—	1.43	0.60
TD-130 [C ₁₀ H ₁₀]	—	—	0.14	0.92
TE-130 [C ₁₀ H ₁₀]	—	—	—	0.11
<i>o</i> -methylbenzaldehyde	—	—	0.28	0.15
<i>E</i> - <i>o</i> -(1-propenyl)toluene (9- <i>E</i>)	—	—	2.90	3.50
TH-130 [C ₁₀ H ₁₀]	—	—	—	0.18
3-methyl-1H-indene (18)	—	—	0.72	3.47
tetralin (1)	—	0.32	2.74	3.28
2-methyl-1H-indene (19)	—	—	0.42	0.73

entry	yield, % ^c			
	RT ^d	700 °C	800 °C	900 °C
TK-130 [C ₁₀ H ₁₀]	—	—	1.20	2.43
1,2-dihydronaphthalene (4)	—	0.55	1.42	1.10
TL-128 [C ₁₀ H ₈]	0.40	—	—	0.98
naphthalene (5)	0.39	—	0.96	8.09
TN	—	—	—	^e
TO-148 [C ₁₁ H ₁₆]	—	—	—	0.10
2-methylnaphthalene	—	—	—	0.17
1-methylnaphthalene	—	—	—	0.24
2,2'-dimethylbiphenyl	0.24	0.27	0.25	0.39
AC-182 [C ₁₄ H ₁₄]	—	—	—	0.10
recovery ^f	94.62	83.31	88.77	72.83
conversion ^g	^d	9.10	54.64	93.44

^a FVP conditions: system pressure = 0.10 torr, sample temperature = 0 °C.

^b Amounts determined by GC with a known quantity of biphenyl added as standard. Data represent the average of triplicate runs. Products identified by comparison with authentic samples by retention time and GCMS are indicated by name. Products that were identified by GCMS only are indicated by code: XY-nnn, where 'X' corresponds to the system where first observed (T = 1 [For a full description of the tetralin (1) pyrolysis products see Table A-II of Malandra, J. L., Ph.D. Dissertation, Iowa State University of Science and Technology, 1993] A = 6, MI = 8, M = 10, E = 11, C = 13, B = 14, P = 15), 'Y' to the individual unknown product (A, B, C, etc.), and 'nnn' to the nominal mass. ^c Moles of product divided by total moles of recovered material. ^d Starting material purity assay. ^e Unidentified product which constitutes < 0.25% total area by GC. ^f Total moles of recovered material divided by moles of starting material used. ^g Total moles of recovered material minus moles of recovered starting material divided by total moles of recovered material.

Table A-2. Products and recovered starting material, total recovery of material, and conversion from the FVP of 2-methylindan (8) at various temperatures *a, b*

entry	yield, % ^c		
	700 °C	750 °C	850 °C
toluene	—	0.04	1.49
ethylbenzene	—	0.09	2.43
<i>o</i> -xylene (25)	—	0.04	0.43
styrene (3)	—	—	0.72
benzocyclobutene (2)	—	0.13	0.42
propylbenzene	—	—	0.09
<i>o</i> -ethyltoluene (26)	—	0.06	0.40
MIA-132 [C ₁₀ H ₁₂] ^d	—	0.04	0.58
<i>o</i> -methylstyrene (16) ^d	—	0.05	0.67
<i>Z</i> - <i>o</i> -(1-propenyl)toluene (9- <i>Z</i>)	—	—	1.25
<i>o</i> -allyltoluene (6)	0.50	1.55	3.58
indene (7)	0.78	2.38	26.41
2-methylindan (8) ^e	97.36	92.12	47.84
1-methylindan	0.23	0.55	1.20
TD-130 [C ₁₀ H ₁₀]	0.18	0.33	0.87
<i>E</i> - <i>o</i> -(1-propenyl)toluene (9- <i>E</i>)	—	0.29	2.19
3-methyl-1H-indene (18)	0.95	1.60	3.37
2-methyl-1H-indene (19)	—	—	0.65
1,2-dihydronaphthalene (4)	—	0.18	0.68
TL-128 [C ₁₀ H ₈]	—	0.26	1.08
naphthalene (5)	—	0.30	3.60
1-methylnaphthalene	—	—	0.06
recovery ^f	84.38	93.51	94.83
conversion ^g	2.46	8.09	52.11

^a See Table 1.1, note *a*. ^b See Table 1.1, note *b*. ^c See Table 1.1, note *c*. ^d MIA-132 [C₁₀H₁₂] and *o*-methylstyrene (**16**) yield a single, unresolved peak by GC analysis. By GC-MS (see Figures S-8 and S-9) it was determined that two compounds were present. For calculation purposes the area of the GC peak was divided in half. ^e Starting material 80.3 mol % pure by ¹H NMR quantification against durene. ^f See Table 1.1, note *f*. ^g See Table 1.1, note *g*.

Table A-3. Products and recovered starting material, total recovery of material, and conversion from the FVP of *E/Z*-*o*-(1-Propenyl)toluene (9-*E/Z*) at various temperatures *a*, *b*

entry	yield, % <i>c</i>	
	900 °C	1000 °C
toluene	3.16	5.61
ethylbenzene	1.64	0.45
<i>o</i> -xylene (25)	1.20	1.46
styrene (3)	2.60	5.39
benzocyclobutene (2)	0.66	0.29
propylbenzene	0.15	—
<i>o</i> -ethyltoluene (26)	0.54	—
<i>o</i> -methylstyrene (16)	9.88	4.34
<i>Z</i> - <i>o</i> -(1-propenyl)toluene (9- <i>Z</i>) <i>d</i>	8.02	0.67
<i>o</i> -allyltoluene (6)	1.11	0.20
indene (7)	36.52	53.31
2-methylindan (8)	4.73	0.77
1-methylindan	0.26	—
TD-130 [C ₁₀ H ₁₀]	0.99	1.65
<i>E</i> - <i>o</i> -(1-propenyl)toluene (9- <i>E</i>) <i>d</i>	16.36	2.25
3-methyl-1H-indene (18)	4.25	5.13
2-methyl-1H-indene (19)	0.77	0.26
1,2-dihydronaphthalene (4)	0.54	—
TL-128 [C ₁₀ H ₈]	0.76	0.93
naphthalene (5)	5.57	16.70
2-methylnaphthalene	0.14	0.28
1-methylnaphthalene	0.16	0.30
recovery <i>e</i>	83.67	54.56

entry	yield, % ^c	
	900 °C	1000 °C
conversion ^f	75.62	97.07

^a See Table 1.1, note *a*. ^b See Table 1.1, note *b*. ^c See Table 1.1, note *c*. ^d Starting material 86.0 % pure by ¹H NMR quantification against triphenyl methane: E/Z = 0.955

^e See Table 1.1, note *f*. ^f See Table 1.1, note *g*.

Table A-4. Products and recovered starting material, total recovery of material, and conversion from the FVP of *o*-methylallyltoluene (10) at various temperatures ^{a,b}

entry	yield, % ^c				
	RT ^d	700°C	800 °C	850 °C	900 °C
toluene	3.28	0.27	0.68	1.93	3.73
ethylbenzene	0.01	—	1.03	2.53	3.18
<i>m/p</i> -xylene	—	—	0.75	0.15	—
<i>o</i> -xylene (25)	—	—	0.41	1.71	4.26
styrene (3)	—	—	—	1.10	4.96
benzocyclobutene (2)	0.03	0.13	0.80	1.13	1.43
propylbenzene	0.07	—	—	0.21	—
<i>o</i> -ethyltoluene (26)	—	0.27	4.24	4.49	2.73
<i>o</i> -methylstyrene (16)	—	0.29	0.92	1.45	1.82
methylallylbenzene	0.03	—	0.41	0.28	—
MA	—	—	<i>e</i>	—	—
1-methylpropenylbenzene	0.23	0.12	0.67	0.64	—
indene (7)	—	—	2.71	5.92	16.64
MB	—	—	<i>e</i>	<i>e</i>	—
MC	—	—	—	<i>e</i>	—
2,2-dimethylindan (11)	—	4.03	31.71	24.08	9.76
MD-130 [C ₁₀ H ₁₀]	—	—	1.02	1.17	1.49
ME-146 [C ₁₁ H ₁₄]	0.24	1.08	0.35	0.62	—
MF	—	<i>e</i>	—	—	—
<i>o</i> -methylallyltoluene (10)	94.54	89.57	30.15	22.22	6.21
MG	—	<i>e</i>	—	—	—
1-(<i>o</i> -tolyl)-2-methylpropene (20)	—	0.70	5.99	6.58	4.68
MH	—	<i>e</i>	<i>e</i>	<i>e</i>	—
3-methyl-1H-indene (18)	—	0.18	3.28	4.50	5.23

entry	yield, % ^c				
	RT ^d	700°C	800 °C	850 °C	900 °C
MI-130 [C ₁₀ H ₁₀]	—	—	0.34	0.77	1.10
MJ	—	—	<i>e</i>	<i>e</i>	—
MK-130 [C ₁₀ H ₁₀]	—	—	—	0.76	3.68
2-methyl-1H-indene (19)	—	0.42	3.47	4.35	4.00
ML-128 [C ₈ H ₁₀]	—	0.16	0.63	0.69	2.12
MM-146 [C ₁₁ H ₁₄]	1.40	0.26	1.02	1.22	—
benzofulvene	—	—	1.30	1.08	—
naphthalene (5)	—	0.08	4.12	6.56	18.80
MN-144 [C ₁₁ H ₁₂]	—	0.20	—	—	—
MO	—	—	<i>e</i>	—	—
MP-144 [C ₁₁ H ₁₂]	—	0.50	0.29	0.23	—
MQ-144 [C ₁₁ H ₁₂]	—	0.34	0.36	0.39	—
MR-144 [C ₁₁ H ₁₂]	—	0.26	0.25	—	—
MS-144 [C ₁₁ H ₁₂]	—	—	—	0.17	—
2-methylnaphthalene	—	—	0.94	1.13	1.61
1-methylnaphthalene	—	0.23	0.35	0.47	0.86
2,2'-dimethylbiphenyl	0.16	0.93	1.79	1.42	1.72
recovery ^f	100.00	89.00	83.81	80.97	67.31
conversion ^g	<i>d</i>	10.43	69.85	77.78	93.78

^a FVP conditions: system pressure = 0.10 torr, sample temperature = 0 °C. ^b See Table 1.1, note *b*. ^c Moles of product divided by total moles of recovered material. ^d Starting material purity assay. ^e Unidentified product which constitutes < 0.43% total area by GC. ^f Total moles of recovered material divided by moles of starting material used. ^g Total moles of recovered material minus moles of recovered starting material divided by total moles of recovered material.

Table A-5. Products and recovered starting material, total recovery of material, and conversion from the FVP of 2,2-dimethylindan (11) at 900 °C *a,b*,

entry	yield,% ^c
toluene	3.12
DA	<i>d</i>
DB	<i>e</i>
DC	<i>d</i>
ethylbenzene	4.08
o-xylene (25)	0.90
benzocyclobutene (2)	0.26
propylbenzene	1.39
o-ethyltoluene (26)	1.22
o-methylstyrene (16)	0.17
DD	<i>d</i>
DE	<i>d</i>
indene (7)	21.67
DF	<i>d</i>
DG	<i>d</i>
2,2-dimethylindan (11) ^f	10.67
DH	<i>e</i>
o-methylallyltoluene (10)	4.78
1-(o-tolyl)-2-methylpropene (20)	5.01
3-methyl-1H-indene (18)	7.41
MI-130 [C ₁₀ H ₁₀]	1.93
MJ-130 [C ₁₀ H ₁₀]	1.55
2-methyl-1H-indene (19)	5.38
benzofulvene	3.11
naphthalene (5)	24.01

entry	yield,% ^c
DI-144 [C ₁₁ H ₁₂]	0.21
MP-144 [C ₁₁ H ₁₂]	0.14
MS-144 [C ₁₁ H ₁₂]	0.13
2-methylnaphthalene	1.81
1-methylnaphthalene	0.98
2,2'-dimethylbiphenyl	0.08
DJ	<i>d</i>
DK	<i>d</i>
recovery ^g	60.35
conversion ^h	88.33

^a See Table A-I, note *a*. ^b See Table A-I, note *b*. ^c See Table A-I, note *c*.

^d Unidentified product which constitutes < 0.35% total area by GC. ^e Unidentified product which constitutes < 1.82% total area by GC. ^f Assay of starting material in relative area percent: 2,2-dimethylindan (11) (97.2%), unidentified impurities, none of which are detected in the product mixtures (2.8%). ^g See Table A-I, note *f*. ^h See Table A-I, note *g*.

Table A-6. Products and recovered starting material, total recovery of material, and conversion from the FVP of *o*-allylethylbenzene (12) at various temperatures *a,b*

entry	yield, % <i>c</i>			
	RT <i>d</i>	700 °C	750 °C	800 °C
ethylbenzene	0.84	0.78	1.31	2.02
<i>o</i> -xylene (25)	—	—	—	0.70
styrene (3)	—	0.60	1.73	3.64
allylbenzene	—	0.28	0.52	0.42
<i>o</i> -ethylstyrene (21)	—	2.62	5.24	5.47
EA	—	—	—	<i>e</i>
indene (7)	—	1.90	6.91	22.84
2-methylindan (8)	—	4.16	6.21	4.02
MD-130 [C ₁₀ H ₁₀]	—	0.37	0.78	0.34
EB-146 [C ₁₁ H ₁₄]	—	1.14	0.33	1.03
<i>o</i> -bromoethylbenzene	0.35	0.44	0.98	0.70
<i>o</i> -allylethylbenzene (12)	95.84	74.17	48.49	14.62
EC-146 [C ₁₁ H ₁₄]	—	0.21	0.29	—
ED-146 [C ₁₁ H ₁₄]	—	3.91	3.58	2.56
EE-146 [C ₁₁ H ₁₄]	—	0.66	—	—
3-methyl-1H-indene (18)	—	1.83	4.70	6.72
EF-146 [C ₁₁ H ₁₄]	—	—	—	0.58
<i>o</i> -propylstyrene (22)	—	—	1.70	3.55
2-methyl-1H-indene (19)	—	1.76	4.56	6.37
ML-128 [C ₁₀ H ₈]	—	—	0.27	—
<i>E</i> -(<i>o</i> -propenyl)ethylbenzene (23)	—	1.36	2.22	2.10
EG	—	—	<i>e</i>	—
EH	0.47	—	—	—
naphthalene (5)	—	1.57	5.72	19.28

entry	yield, % ^c			
	RT ^d	700 °C	750 °C	800 °C
EI-146 [C ₁₁ H ₁₄]	—	1.43	2.01	1.01
EJ-144 [C ₁₁ H ₁₂]	—	0.37	0.19	—
MP-144 [C ₁₁ H ₁₂]	—	—	0.25	—
EK	1.33	—	—	—
MQ-144 [C ₁₁ H ₁₂]	—	—	0.23	—
EL-144 [C ₁₁ H ₁₂]	—	—	0.76	0.59
2-methylnaphthalene	—	—	0.39	0.62
1-methylnaphthalene	—	—	0.60	0.81
2,2'-diethylbiphenyl	1.17	0.31	—	—
recovery ^f	100.00	78.45	78.67	70.68
conversion ^g		41.81	61.85	89.67

^a See Table 1.1, note *a*. ^b See Table 1.1, note *b*. ^c See Table 1.1, note *c*. ^d Assay of starting material. Percentages given are of relative area by GC. ^e Unidentified product which constitutes < 0.22% total area by GC. ^f See Table 1.1, note *f*. ^g See Table 1.1, note *g*.

Table A-7. Products and recovered starting material, total recovery of material, and conversion from the FVP of *o*-allylcumene (13) at various temperatures *a,b*

entry	yield, % <i>c</i>		
	RT <i>d</i>	700 °C <i>e</i>	750 °C
ethylbenzene	—	—	0.96
<i>o</i> -xylene (25)	—	—	0.75
styrene (3)	—	0.67	2.36
cumene	0.74	1.21	1.11
allylbenzene	—	0.41	0.57
<i>o</i> -ethyltoluene (26)	—	2.21	3.29
<i>o</i> -ethylstyrene (21)	—	2.81	3.67
indene (7)	—	1.74	6.60
CA-146 [C ₁₁ H ₁₄]	—	2.79	3.41
MD-130 [C ₁₀ H ₁₀]	—	0.66	1.45
CB-146 [C ₁₁ H ₁₄]	—	1.19	1.18
CC-160 [C ₁₂ H ₁₆]	—	4.35	3.37
CD	—	<i>f</i>	—
3-methyl-1H-indene (18)	—	3.56	8.19
CE-146 [C ₁₁ H ₁₄]	—	1.02	0.81
<i>o</i> -allylcumene (13)	91.84	53.51	19.88
CF-160 [C ₁₂ H ₁₆]	0.52	0.68	2.58
CG-160 [C ₁₂ H ₁₆]	—	2.50	5.10
CH-160 [C ₁₂ H ₁₆]	—	2.28	—
CI-144 [C ₁₁ H ₁₂]	0.15	0.68	0.72
ML-128 [C ₈ H ₁₀]	—	1.95	3.09
CJ	0.59	—	—
CK-146 [C ₁₁ H ₁₄]	—	0.52	0.55
naphthalene (5)	—	5.10	17.69

entry	yield, % ^c		
	RT ^d	700 °C ^e	750 °C
CL-144 [C ₁₁ H ₁₂]	—	0.98	1.07
CM-160 [C ₁₂ H ₁₆]	—	2.10	1.35
CN-160 [C ₁₂ H ₁₆]	0.39	0.83	0.54
CO	0.13	—	—
MP-144 [C ₁₁ H ₁₂]	—	0.47	0.61
CP	1.79	—	—
EL-144 [C ₁₁ H ₁₂]	—	2.15	2.63
MS-144 [C ₁₁ H ₁₂]	—	0.34	—
CQ	—	<i>f</i>	—
CR	0.48	—	—
CS	0.20	—	—
2-methylnaphthalene	—	2.17	3.78
1-methylnaphthalene	—	1.12	2.69
2,2'-diisopropylbiphenyl	3.18	—	—
recovery ^g	100.00	83.43	73.22
conversion ^h	<i>d</i>	46.49	80.04

^a See Table 1.1, note *a*. ^b See Table 1.1, note *b*. ^c See Table 1.1, note *c*. ^d Assay of starting material. Percentages are of relative area by GC. ^e Duplicate runs performed, rather than triplicate runs. ^f Unidentified product which constitutes < 0.52% total area by GC. ^g See Table 1.1, note *f*. ^h See Table 1.1, note *g*.

Table A-8. Products and recovered starting material, total recovery of material, and conversion from the FVP of *o*-(3-butenyl)toluene (14) at various temperatures ^{a,b},

entry	yield, % ^c			
	RT ^d	700 °C	800 °C	900 °C
toluene	—	—	—	2.29
ethylbenzene	—	—	—	1.59
<i>m/p</i> -xylene	—	—	—	0.75
<i>o</i> -xylene (25)	—	0.40	4.70	18.58
styrene (3)	—	—	0.46	6.80
benzocyclobutene (2)	—	0.36	3.51	15.24
allylbenzene	—	—	—	0.23
propylbenzene	—	—	—	0.32
<i>o</i> -ethyltoluene (26)	—	—	2.97	10.37
<i>o</i> -methylstyrene (16)	—	—	0.51	2.14
indan	—	—	—	0.13
<i>m/p</i> -allyltoluene	—	—	0.95	3.83
<i>o</i> -allyltoluene (6)	—	—	0.21	0.40
BA	—	—	<i>e</i>	—
indene (7)	—	—	0.34	1.64
2-methylindan (8)	—	—	—	0.22
<i>o</i> -methylbenzaldehyde	—	0.33	0.39	0.21
<i>o</i> -(1-propenyl)toluene (9)	—	—	—	0.15
BB-146 [C ₁₁ H ₁₄]	—	—	0.16	0.43
BC-146 [C ₁₁ H ₁₄]	—	—	0.16	0.22
<i>o</i> -(3-butenyl)toluene (14)	100.0	64.20	41.73	15.87
BD-146 [C ₁₁ H ₁₄]	—	0.32	0.25	0.12
2-methyl-1H-indene (19)	—	—	0.23	0.10
TK-130 [C ₁₀ H ₁₀]	—	—	—	0.14

entry	yield, % ^c			
	RT ^d	700 °C	800 °C	900 °C
1,2-dihydronaphthalene (4)	—	—	0.30	0.30
TM	—	—	<i>e</i>	<i>e</i>
naphthalene (5)	—	—	0.45	1.38
BE-146 [C ₁₁ H ₁₄]	—	—	0.20	0.12
BF-156 [C ₁₂ H ₁₂]	—	—	—	0.20
2-methylnaphthalene	—	—	—	0.10
1-methylnaphthalene	—	—	—	0.18
BG-182 [C ₁₄ H ₁₄]	—	—	—	0.46
BH-182 [C ₁₄ H ₁₄]	—	—	—	0.47
BI-196 [C ₁₅ H ₁₆]	—	—	—	0.29
BJ-196 [C ₁₅ H ₁₆]	—	—	2.15	4.24
BK-210 [C ₁₆ H ₁₈]	—	—	0.37	0.49
1,2-di(<i>o</i> -tolyl)ethane (24)	—	34.38	39.36	7.59
BL-178 [C ₁₄ H ₁₀]	—	—	0.63	1.46
BM-208 [C ₁₆ H ₁₆]	—	—	—	0.46
BN-192 [C ₁₅ H ₁₂]	—	—	—	0.47
recovery ^f	102.4	97.77	88.72	110.0
conversion ^g	<i>d</i>	35.80	58.27	84.13

^a FVP conditions: system pressure = 0.010 torr, sample temperature = 0 °C.

^b Amounts determined by GC with a known quantity of biphenyl added as standard. Data for 700 °C represent the average of duplicate runs. Data for 750 °C represent the average of triplicate runs. See Table 1.1, note *b* for notation. ^c See Table 1.1, note *c*. ^d See Table 1.1, note *d*. ^e See Table 1.1, note *e*. ^f See Table 1.1, note *f*. ^g See Table 1.1, note *g*.

Table A-9. Products and recovered starting material, total recovery of material, and conversion from the FVP of *o*-(4-pentenyl)toluene (15) at various temperatures *a,b*

entry	yield, % <i>c</i>			
	RT <i>d</i>	600 °C	700 °C	800 °C
toluene	—	—	0.26	3.24
ethylbenzene	—	—	—	1.32
<i>o</i> -xylene (25)	—	—	1.00	5.65
styrene (3)	—	—	—	2.54
benzocyclobutene (2)	—	—	0.92	3.24
<i>o</i> -ethyltoluene (26)	—	—	0.88	3.15
<i>o</i> -methylstyrene (16)	—	1.52	30.62	59.78
benzaldehyde	—	—	0.21	1.33
indan	—	—	—	1.07
<i>m/p</i> -allyltoluene	—	0.31	0.26	0.51
<i>o</i> -allyltoluene (6)	—	—	0.20	—
indene (7)	—	—	0.34	2.29
<i>o</i> -methylbenzaldehyde	—	—	1.67	2.56
PA	—	—	<i>e</i>	—
PB-146 [C ₁₁ H ₁₄]	—	—	0.82	0.98
naphthalene (5)	—	—	0.11	0.52
PC	<i>e</i>	<i>e</i>	<i>e</i>	—
PD	—	—	<i>e</i>	—
<i>o</i> -(4-pentenyl)toluene (15)	92.42	90.40	52.92	2.97
PE-160 [C ₁₂ H ₁₆]	—	—	0.58	0.52
PF	—	—	<i>e</i>	—
PG-160 [C ₁₂ H ₁₆]	—	—	0.97	1.10
2,2'-dimethylbiphenyl	7.58	7.77	8.23	7.22

entry	yield, % ^c			
	RT ^d	600 °C	700 °C	800 °C
recovery ^e	97.85	96.20	86.59	70.36
conversion ^f	<i>d</i>	9.60	47.08	97.03

^a See Table 1.1, note *a*. ^b See Table 1.1, note *b*. ^c See Table 1.1, note *c*. ^d See Table 1.1, note *d*. ^e Unidentified product which constitutes < 0.35% total area by GC. ^f See Table 1.1, note *f*. ^g See Table 1.1, note *g*.

Table A-10. Products and recovered starting material from the solution-phase thermolysis of *o*-methylallyltoluene (10) in phenyl ether (240 min, 400 °C) at various concentrations ^a

entry	yield,% ^b	
	0.0724 M	0.0145 M
ethylbenzene	1.06	1.15
styrene (3)	3.30	0.93
<i>o</i> -methylstyrene (16)	1.45	1.30
2,2-dimethylindan (11)	3.58	3.89
<i>o</i> -methylallyltoluene (10) ^c	14.03	49.97
1-(<i>o</i> -tolyl)-2-methylpropene (20)	57.73	26.67
3-methyl-1H-indene (18)	6.11	7.72
2-methyl-1H-indene (19)	4.50	2.20
napthalene (5)	4.65	1.22
MP-144 [C ₁₁ H ₁₂]	0.56	0.72
MQ-144 [C ₁₁ H ₁₂]	2.21	1.57
1-methylnapthalene	0.83	2.65

^a Thermolysis conditions: 0.5 mL of phenyl ether solution is degassed and sealed in a glass tube, and then is heated to 400 °C for 240 minutes, then allowed to cool to RT. ^b See Table 1.1, note *b*. ^c See Table S-4 for starting material assay.

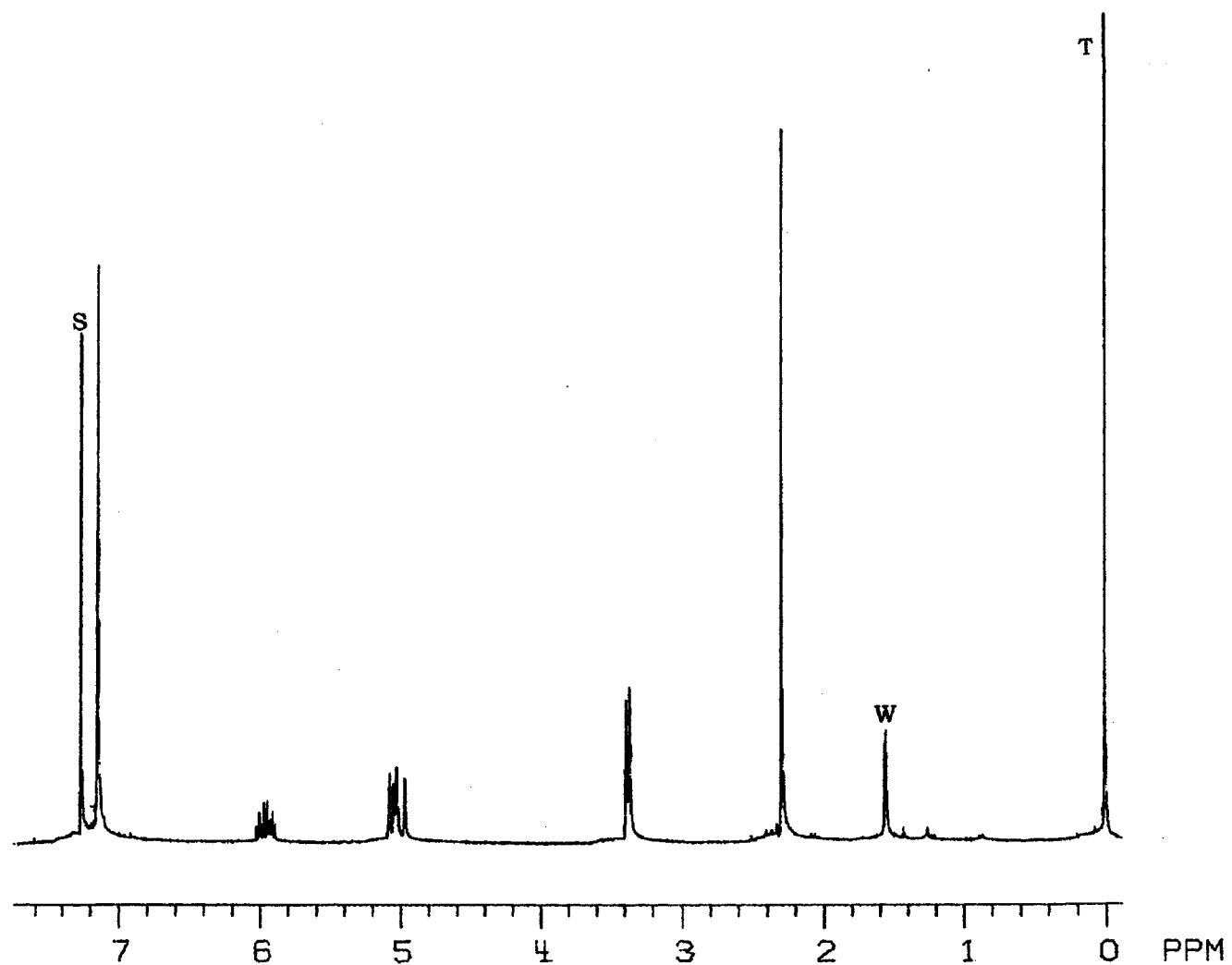


Figure A-1. ^1H NMR Spectrum (300 MHz, CDCl_3) of *o*-allyltoluene (6) (S: Chloroform, T: tetramethylsilane, W: H_2O).

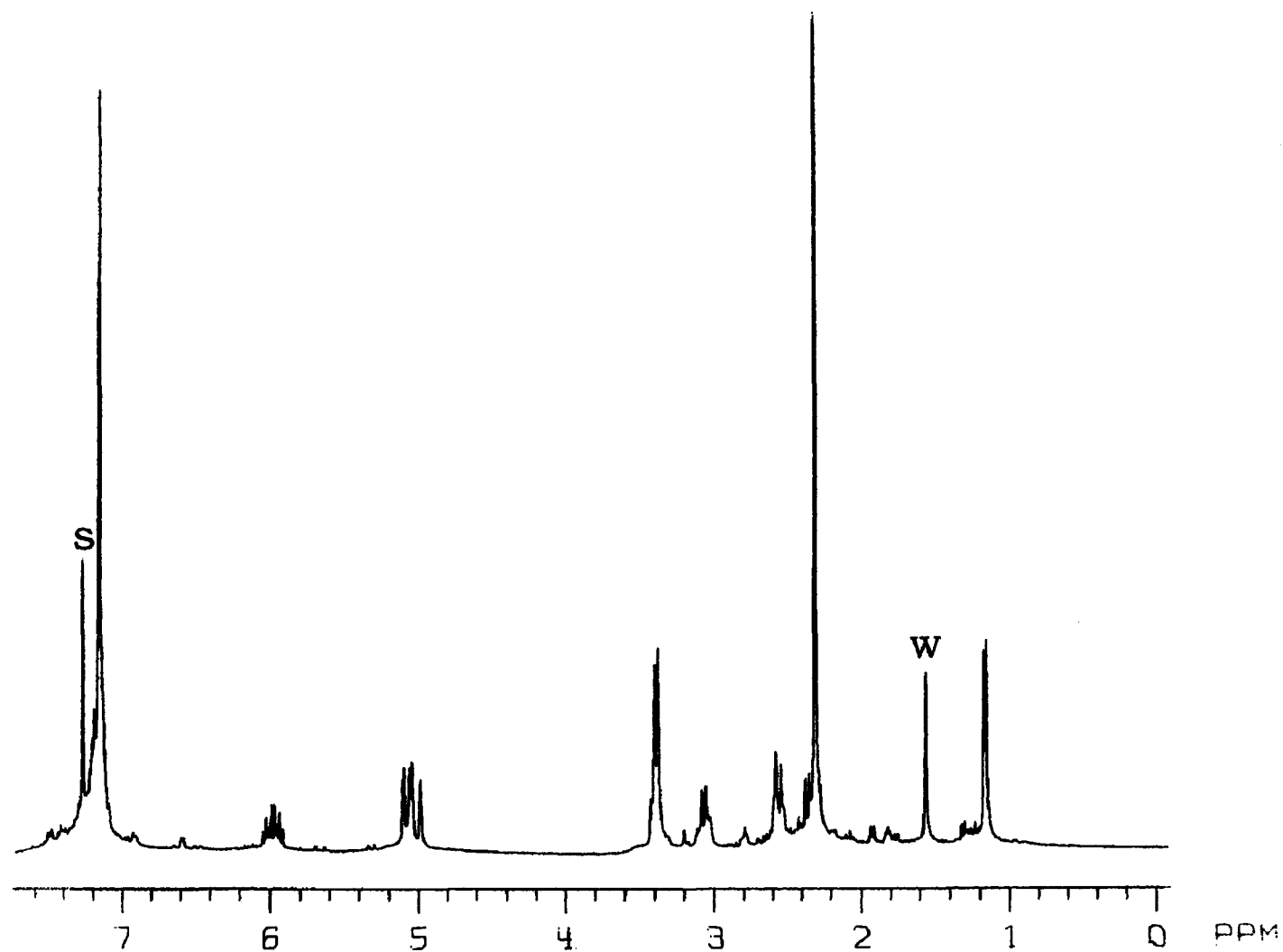


Figure A-2. ^1H NMR spectrum (300 MHz, CDCl_3) of the pyrolysis mixture from the FVP at 800 $^\circ\text{C}$ of *o*-allyltoluene (**6**) (S: chloroform, W: H_2O).

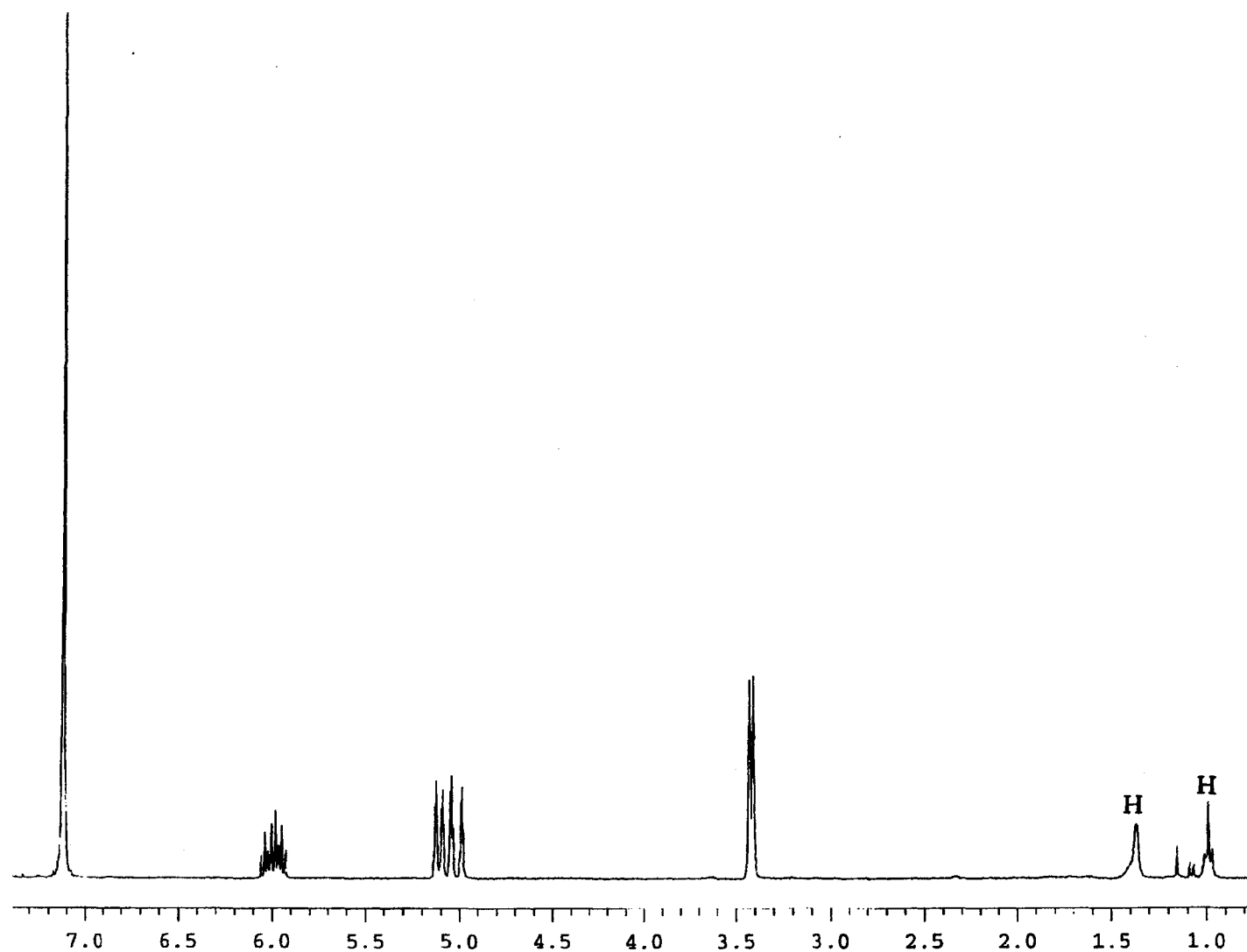


Figure A-3. ^1H NMR spectrum (300 MHz, CCl_4) of *o*-allyltoluene- α,α,α - d_3 ($6\text{-}d_3$) (H: hexane).

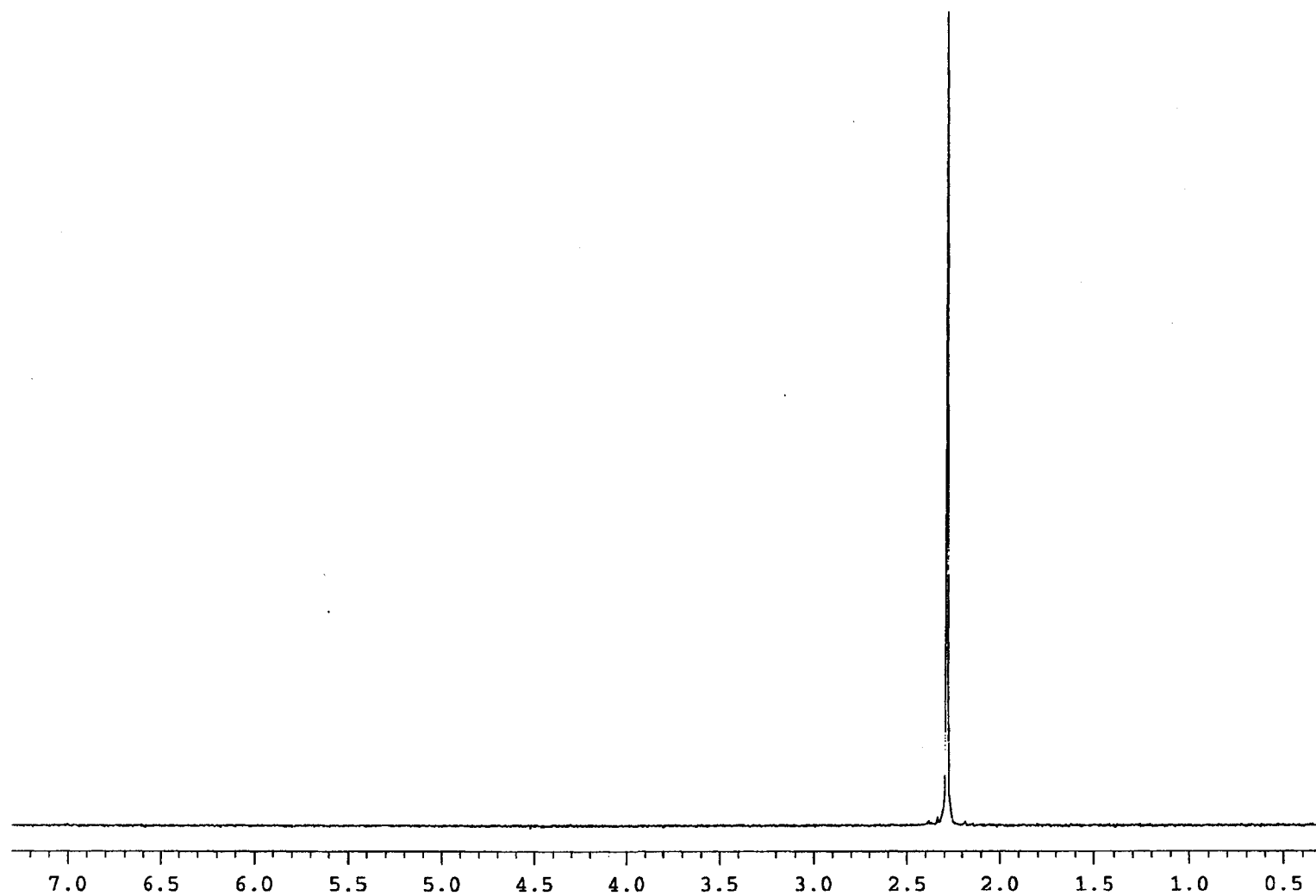


Figure A-4. ^2H NMR spectrum (400 MHz, CCl_4) of *o*-allyltoluene- α,α,α - d_3 ($6\text{-}d_3$).

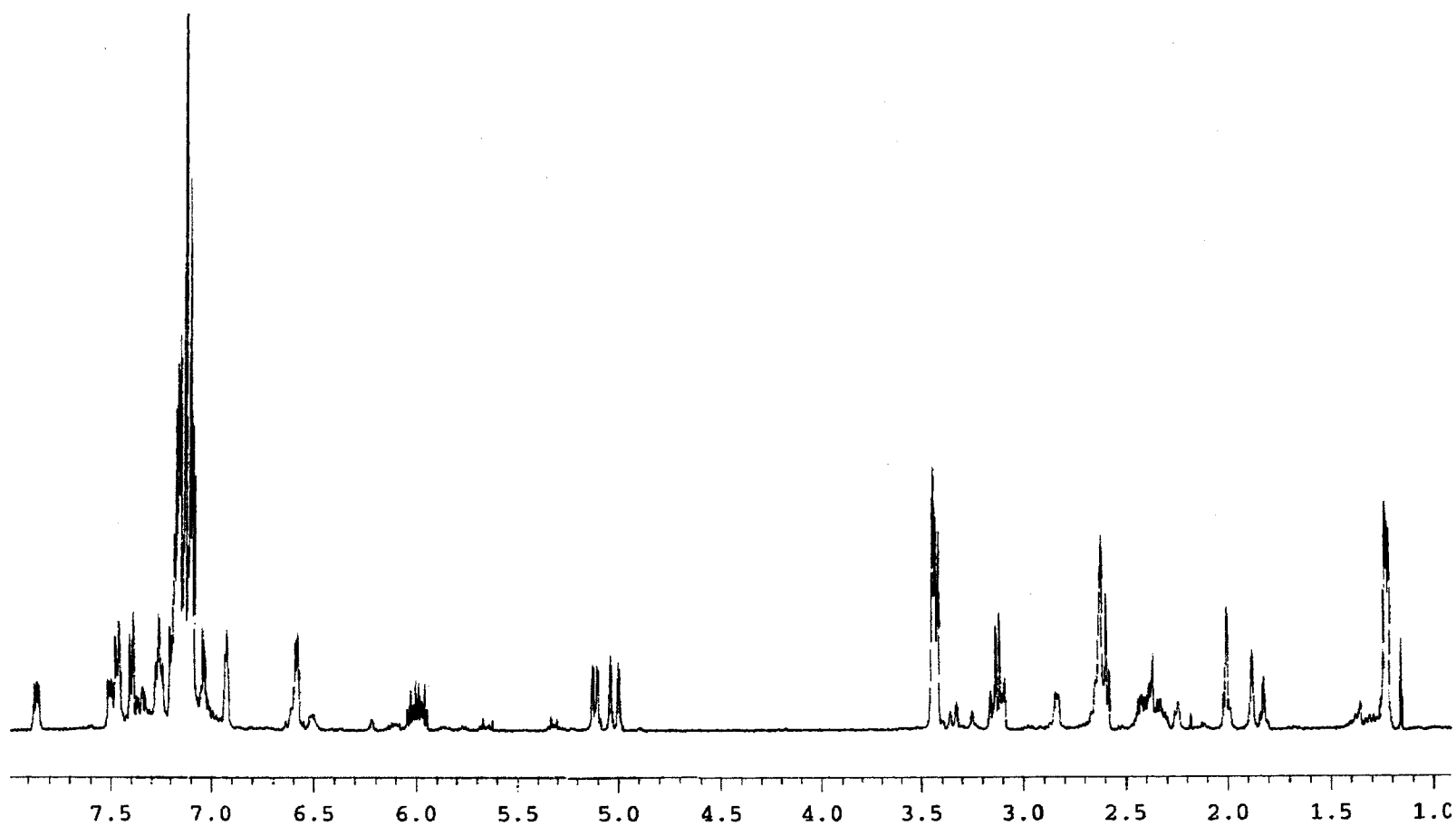


Figure A-5. ^1H NMR spectrum (400 MHz, CCl_4) of the pyrolysis mixture from the FVP at 850 °C of *o*-allyltoluene- a,a,a - d_3 (6 - d_3).

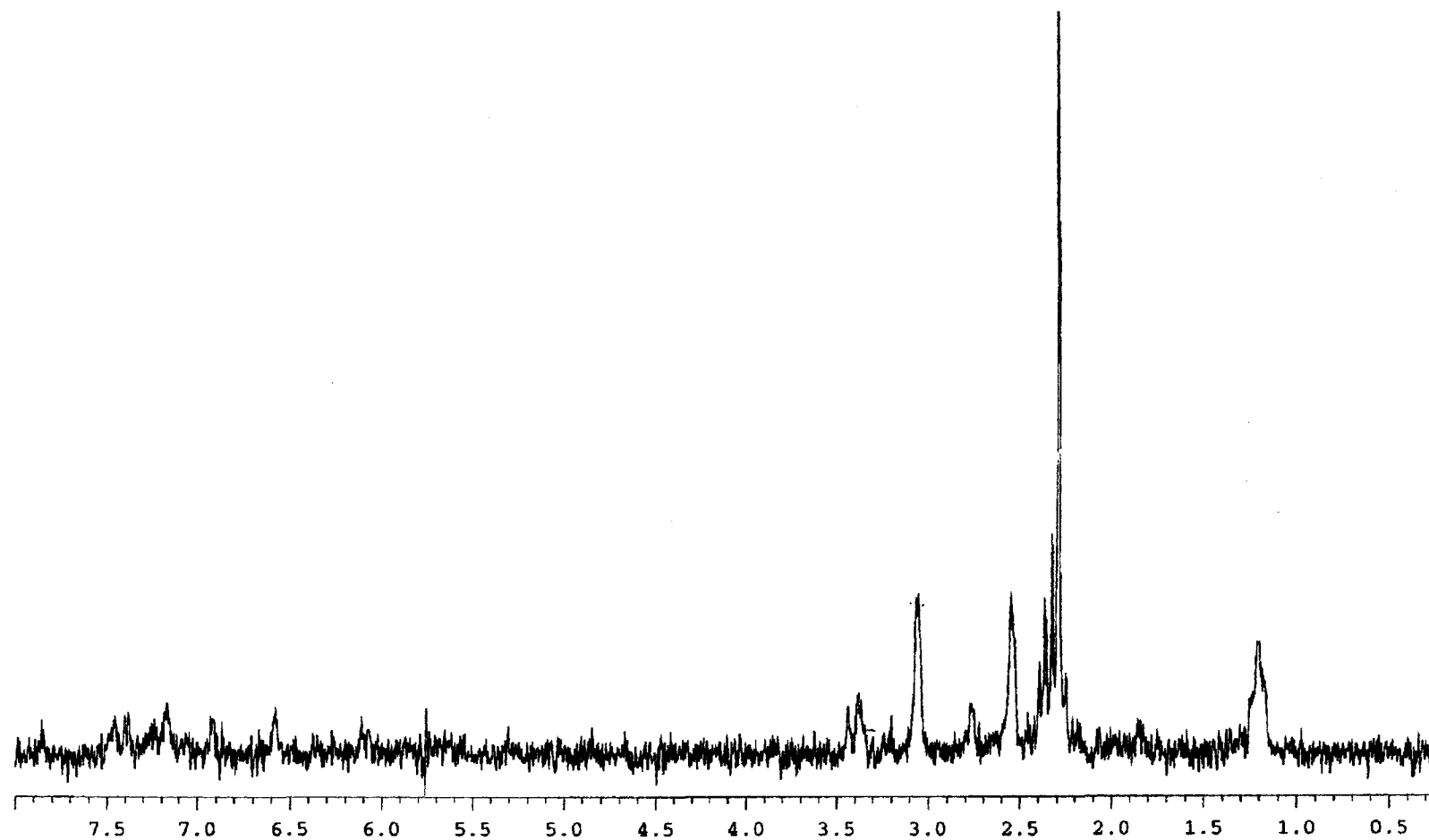


Figure A-6. ^2H NMR spectrum (400 MHz, CCl_4) of the pyrolysis mixture from the FVP at 850 °C of *o*-allyltoluene-*a,a,a*- d_3 (**6- d_3**).

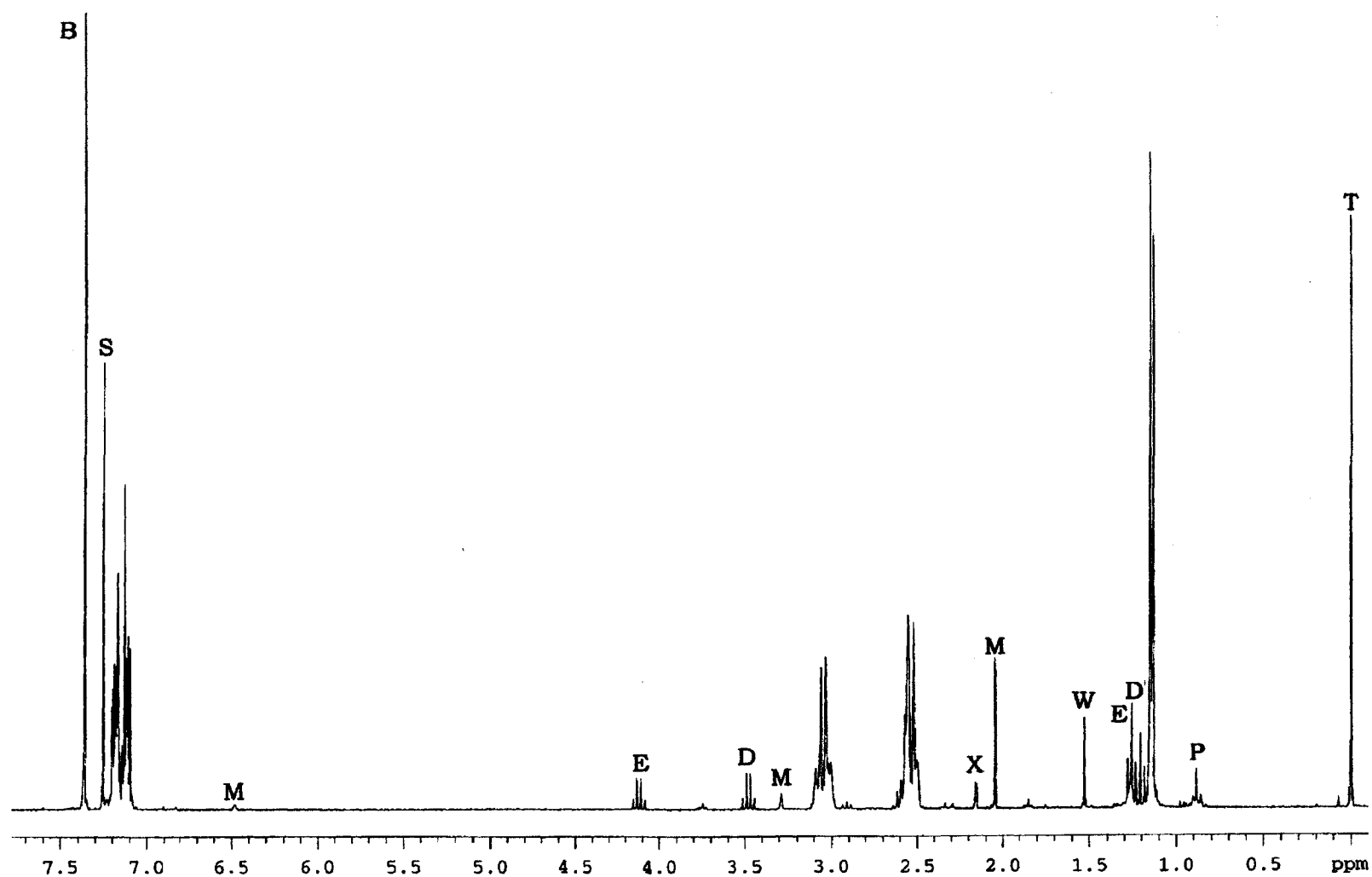


Figure A-7. ^1H NMR spectrum (300 MHz, CDCl_3) of 2-methylindan (**8**) (B: benzene, D: diethyl ether, E: ethanol, M: 2-methyl-1H-indene, P: pentane, S: CHCl_3 , T: tetramethylsilane, W: H_2O , X: unknown impurity).

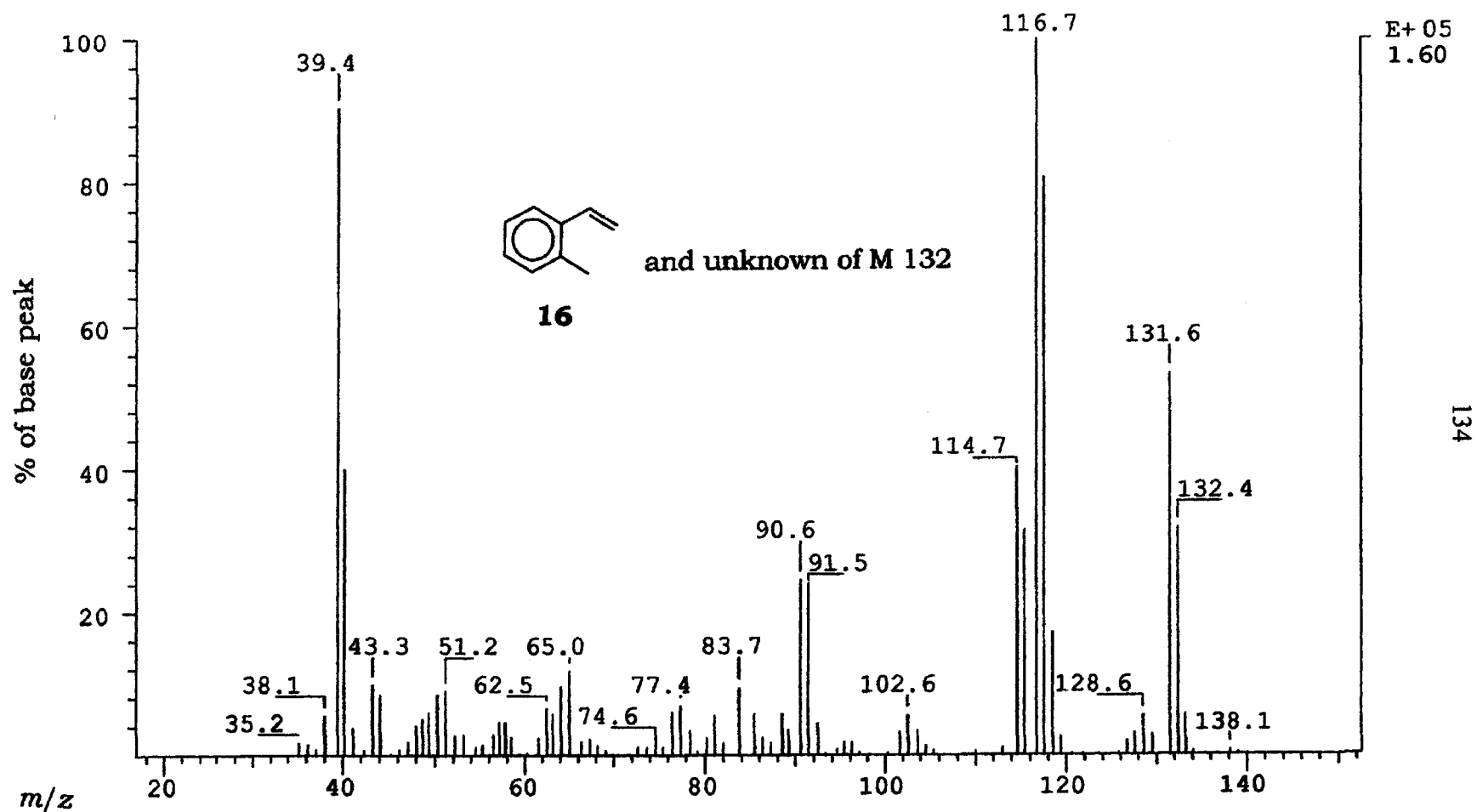


Figure A-8. GC-Mass Spectrum (EI, 70 eV) of the beginning part of the GC peak containing both *o*-methylstyrene (**16**) and an unknown compound of molecular weight 132.

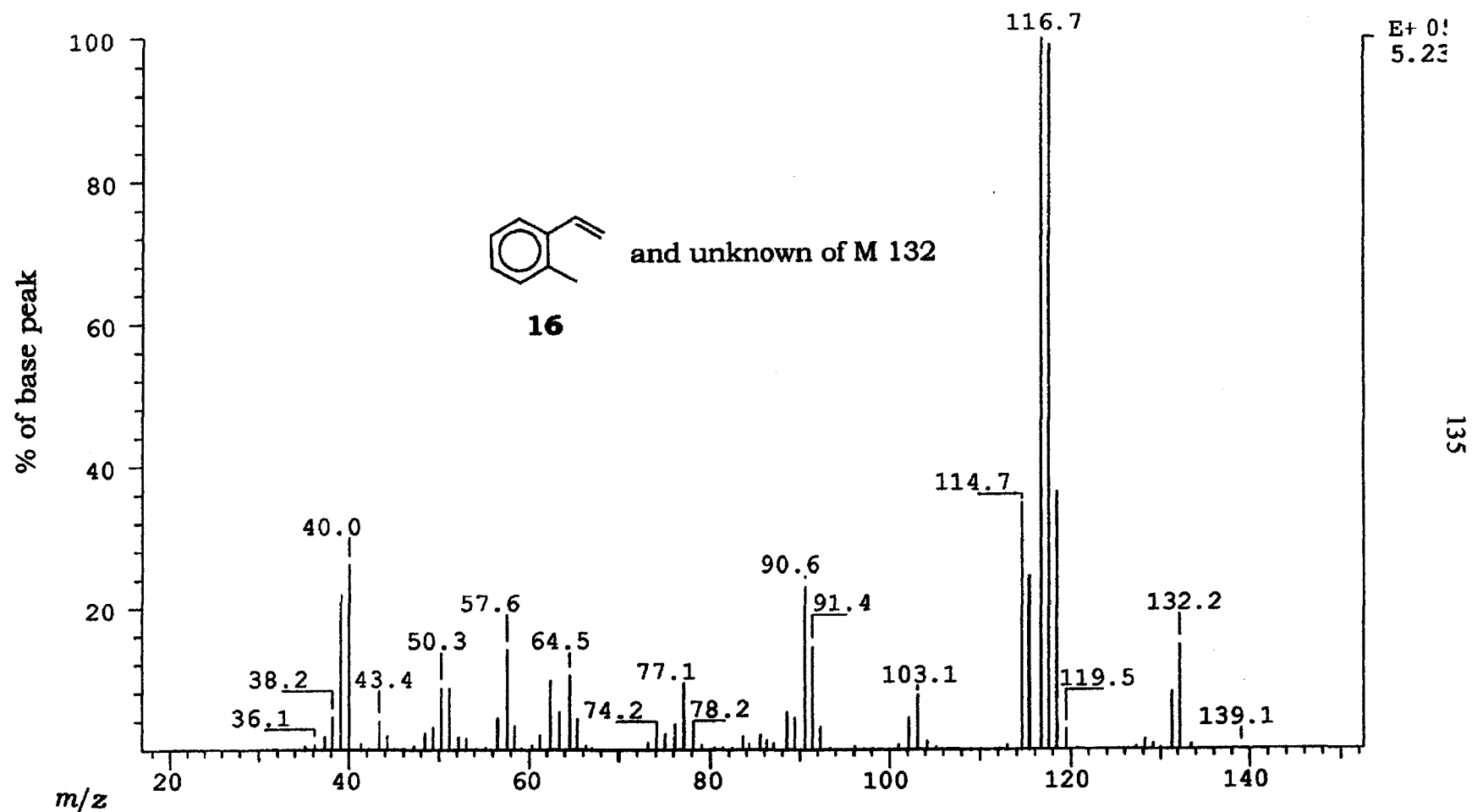


Figure A-9. GC-Mass Spectrum (EI, 70 eV) of the ending part of the GC peak containing both *o*-methylstyrene (**16**) and an unknown compound of molecular weight 132.

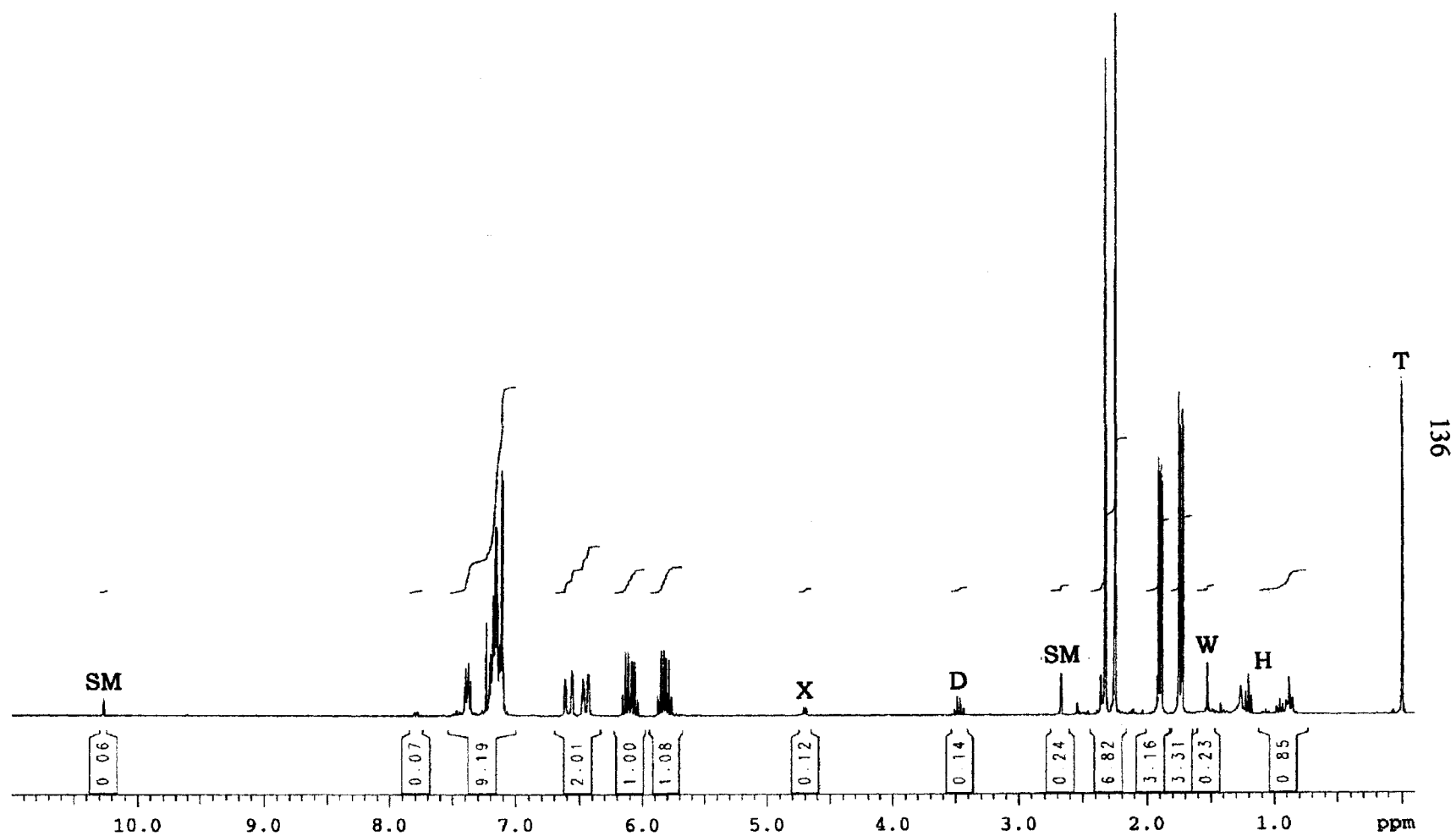


Figure A-10. ^1H NMR spectrum (300 MHz, CDCl_3) of *E/Z*-*o*-(1-propenyl)toluene (**9-E/Z**) (D: diethyl ether, H: high-boiling residue from hexanes, S: CHCl_3 , SM: *o*-tolualdehyde, T: tetramethylsilane, W: H_2O , X: unidentified impurity).

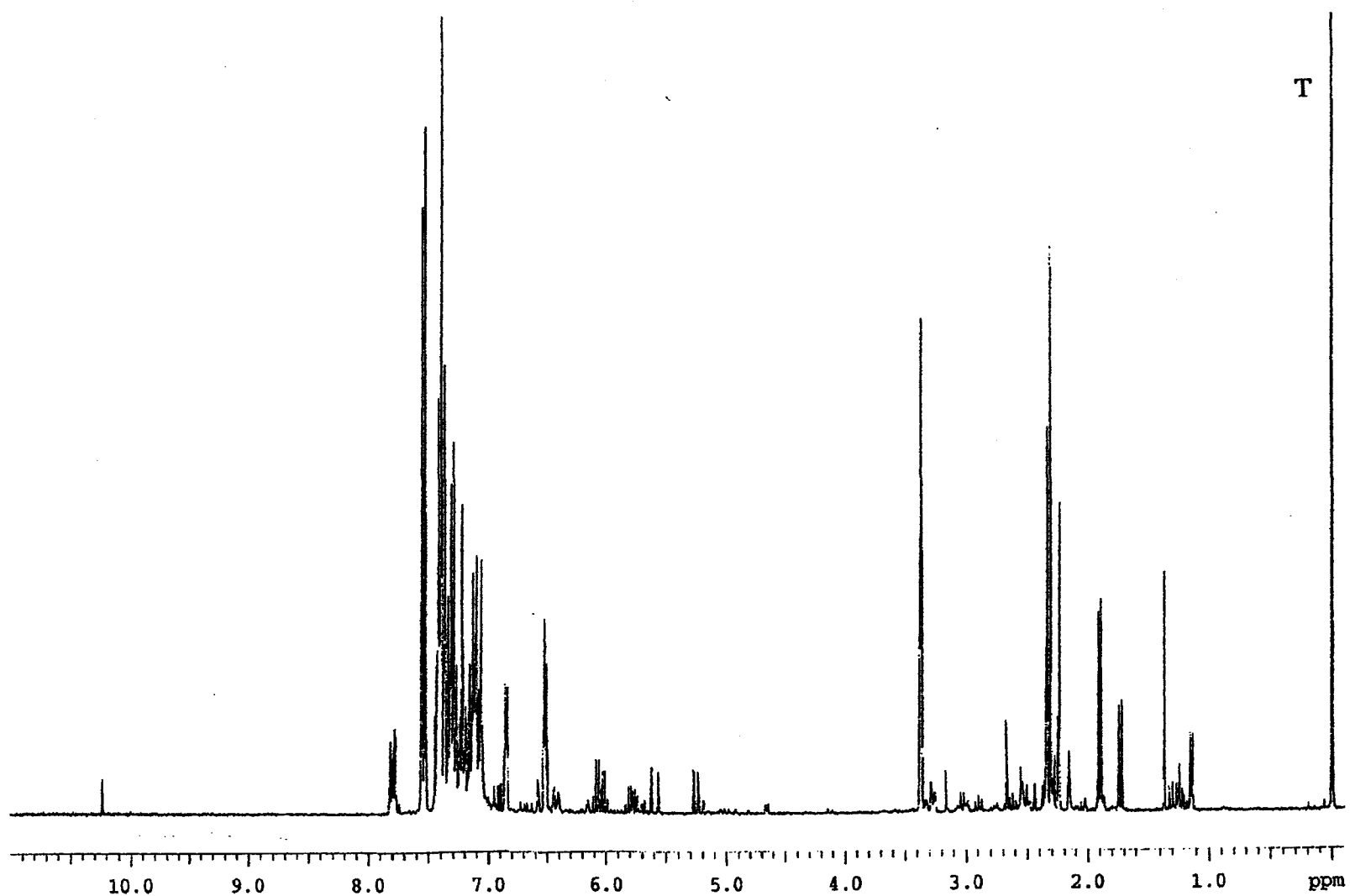


Figure A-11. ^1H NMR spectrum (300 MHz, 3:2 $\text{CCl}_4/\text{CDCl}_3$) of the pyrolysis mixture from the FVP at 900 °C of *E/Z-o*-(1-propenyl)toluene (9-*E/Z*) with biphenyl standard (T: tetramethylsilane).

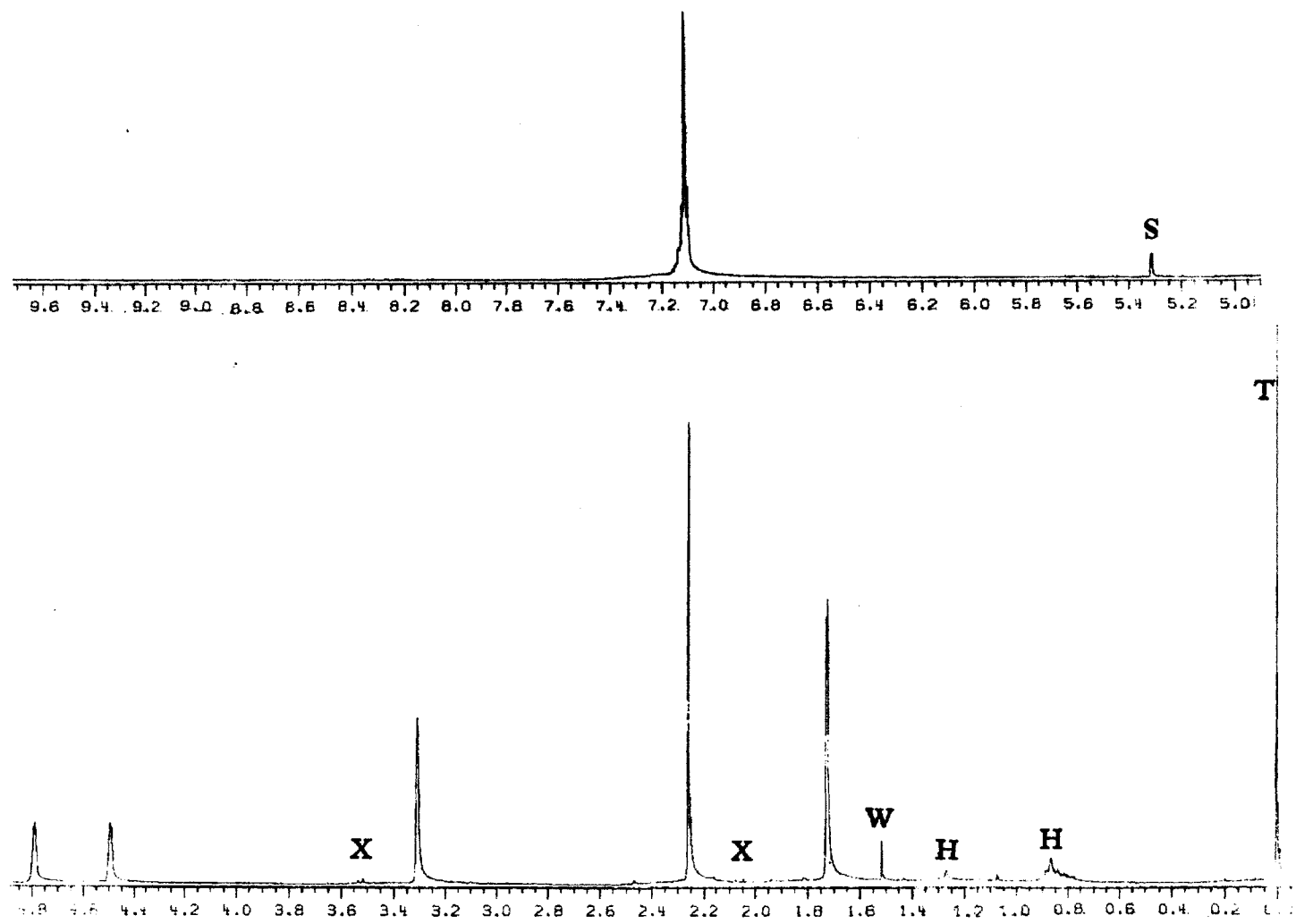


Figure A-12. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of *o*-(1-methylallyl)toluene (**10**) (H: high-boiling residue from hexanes, S: CH_2Cl_2 , T: tetramethylsilane, W: H_2O , X: unidentified impurity).

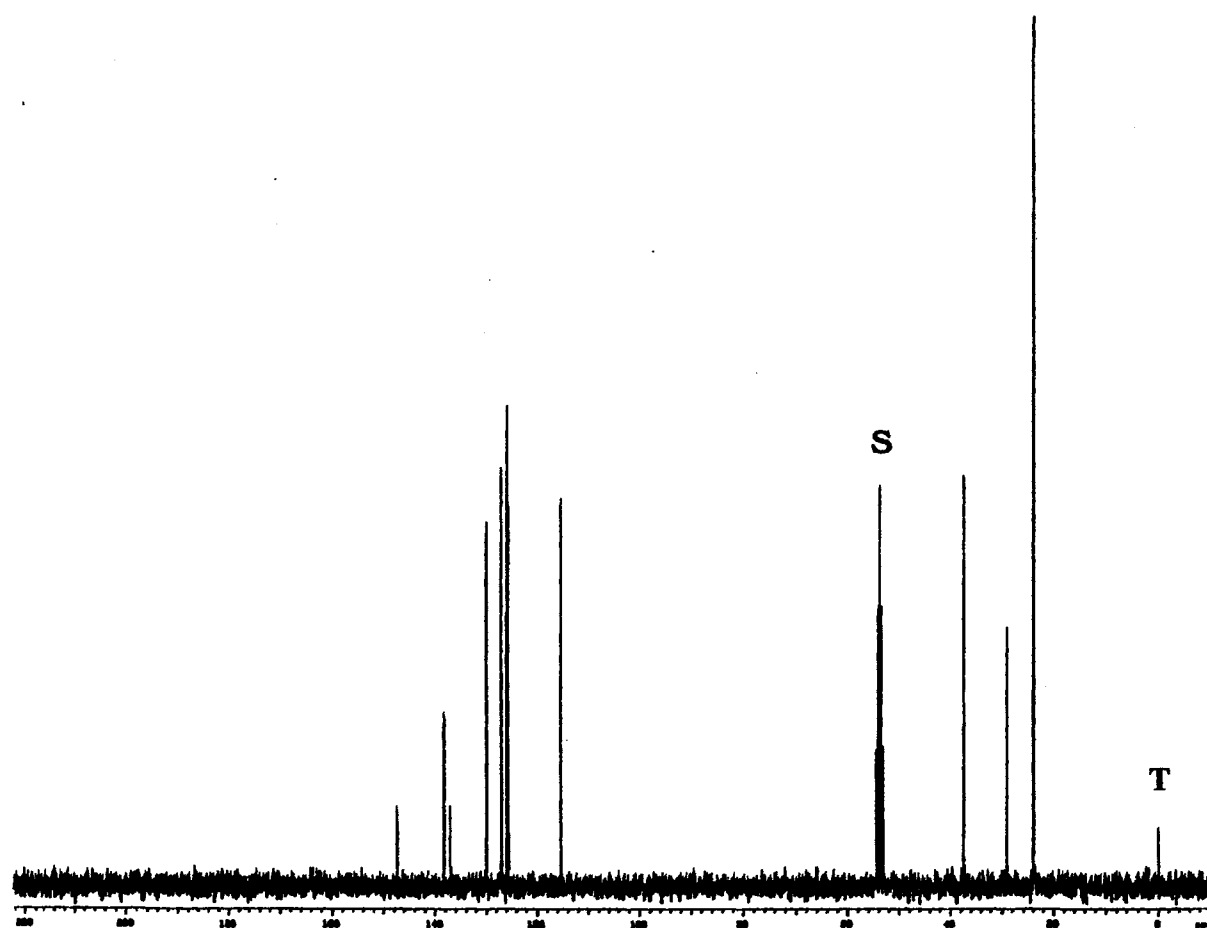


Figure A-13. ^{13}C NMR spectrum (75.5 MHz, CD_2Cl_2) of *o*-(1-methylallyl)toluene (10) (S: CH_2Cl_2 , T: tetramethylsilane).

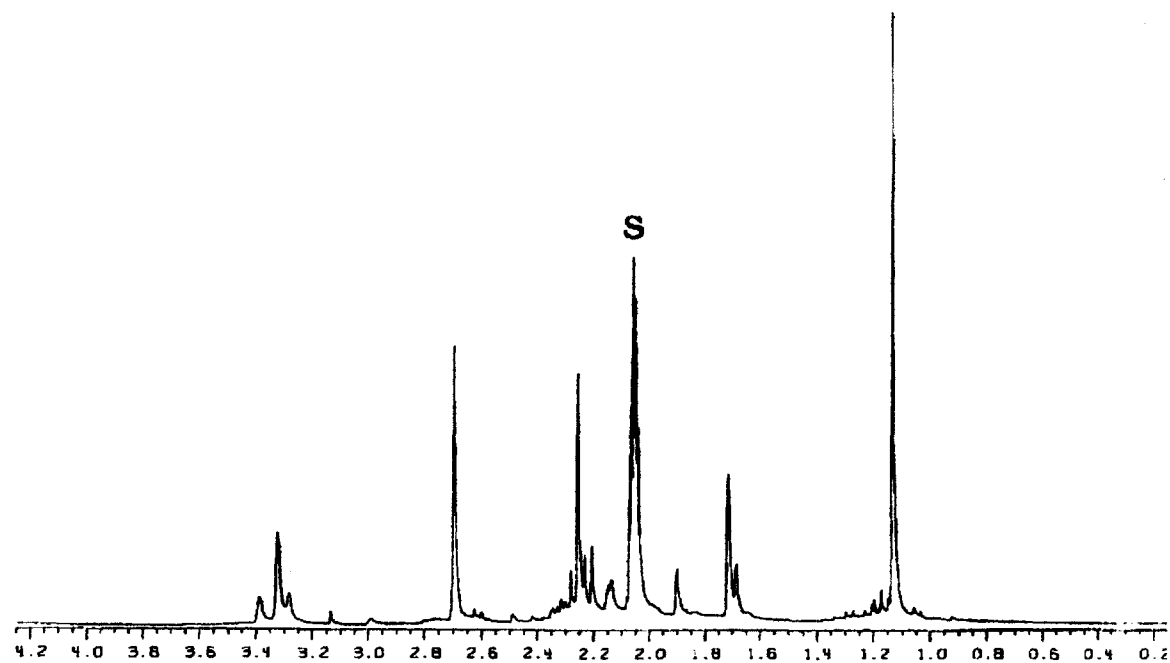
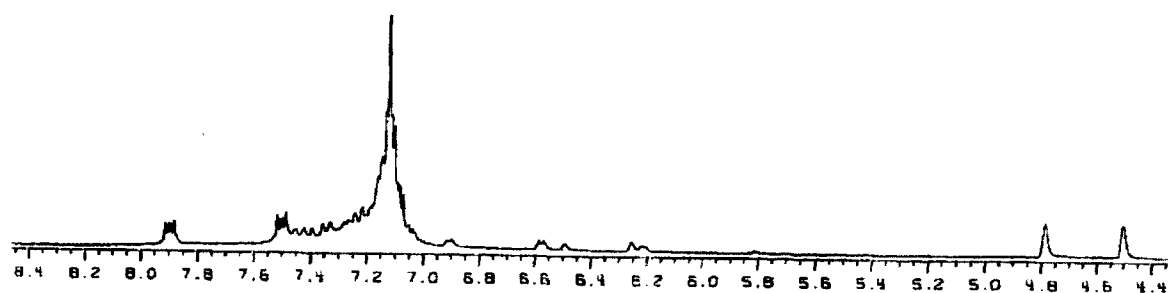


Figure A-14. ^1H NMR spectrum (300 MHz, acetone- d_6) of the pyrolysis mixture from the FVP at 850 $^{\circ}\text{C}$ of *o*-(1-methylallyl)toluene (**10**) (S: acetone- d_6).

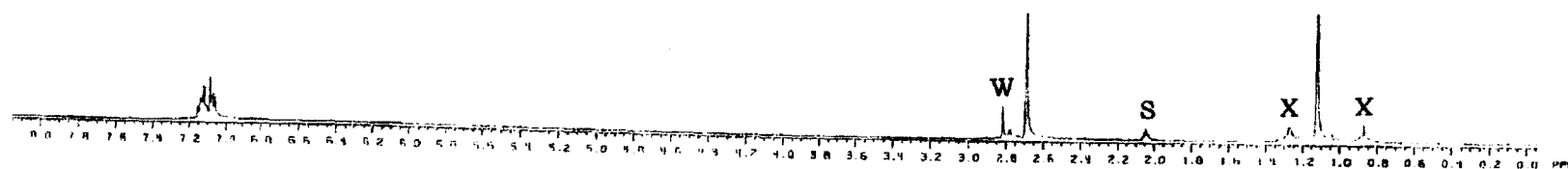


Figure A-15. ^1H NMR spectrum (300 MHz, acetone- d_6) of 2,2-dimethylindan (11) (S: acetone- d_6 , W: H_2O , X: unidentified impurity).

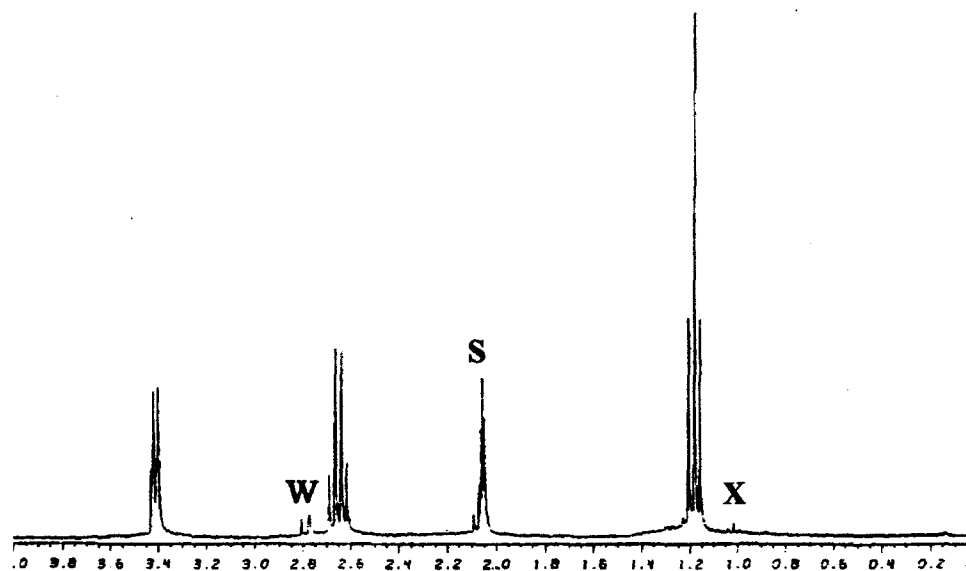
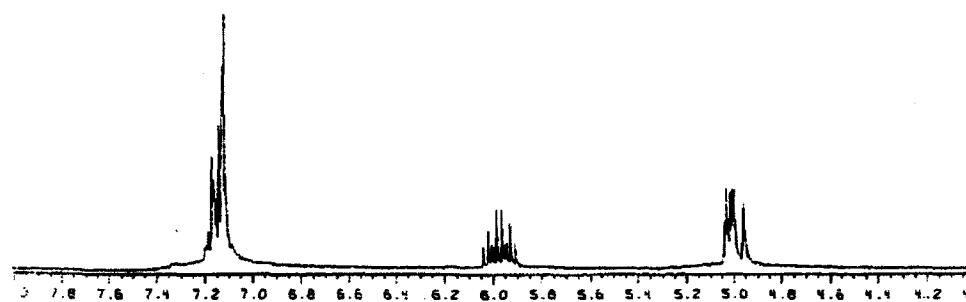


Figure A-16. ^1H NMR spectrum (300 MHz, acetone- d_6) of *o*-allylethylbenzene (12) (S: acetone- d_6 , W: H_2O , X: unidentified impurity).

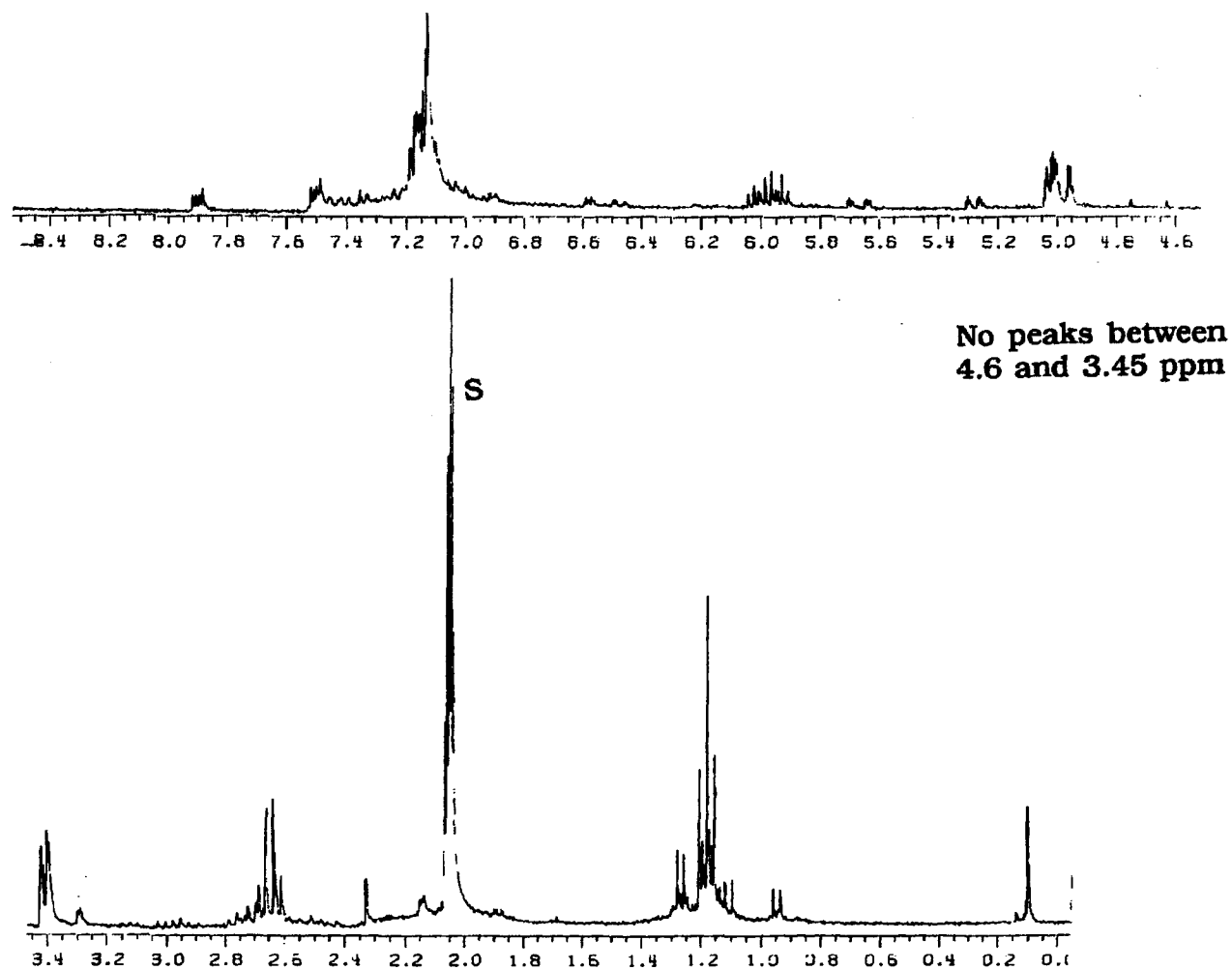


Figure A-18. ^1H NMR spectrum (300 MHz, acetone- d_6) of the pyrolysis mixture from the FVP at 750 °C of *o*-allylethylbenzene (12) (S: acetone- d_5).

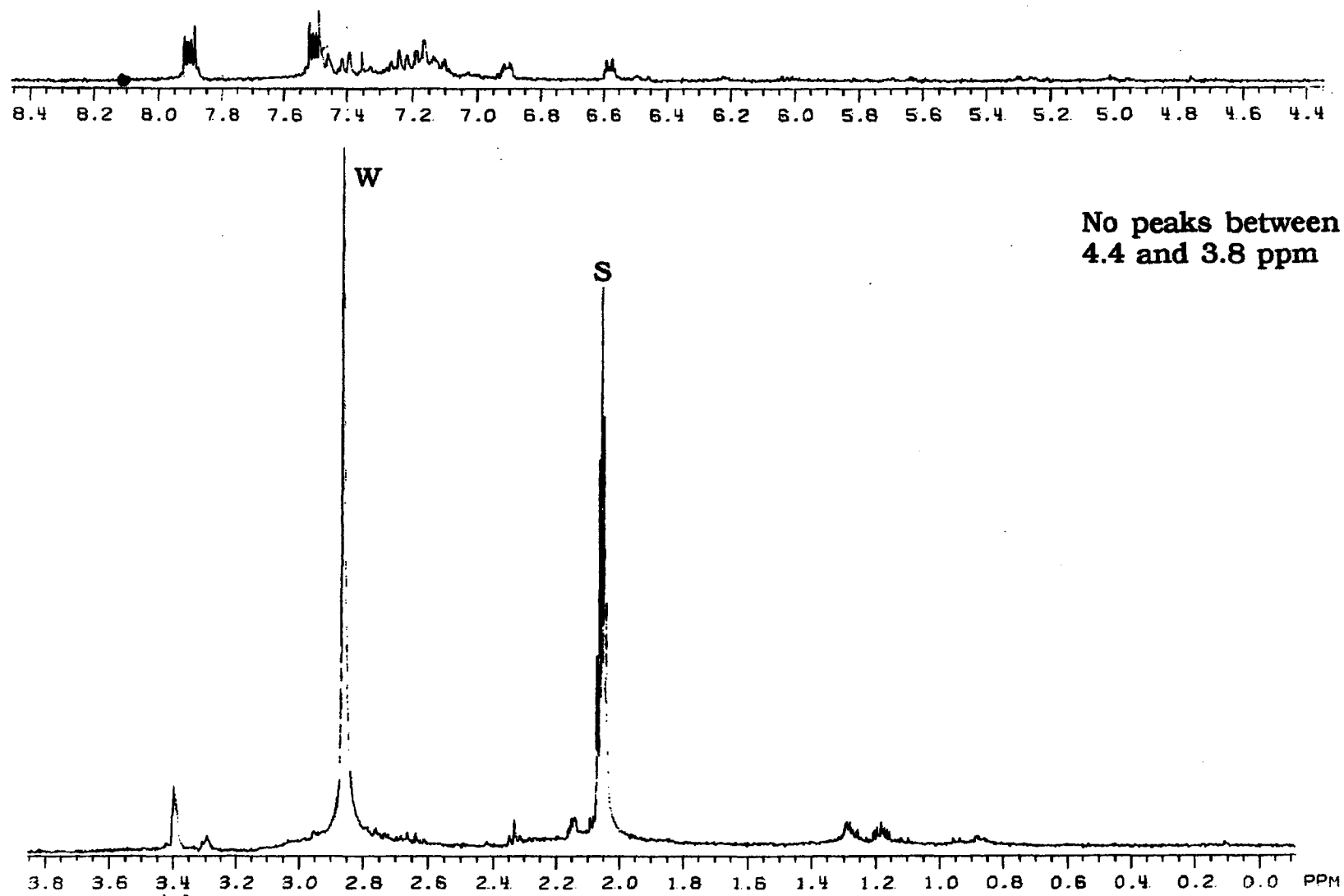


Figure A-19. ^1H NMR spectrum (300 MHz, acetone- d_6) of the pyrolysis mixture from the FVP at 800 °C of *o*-allylethylbenzene (12) (S: acetone- d_5 , W: H_2O).

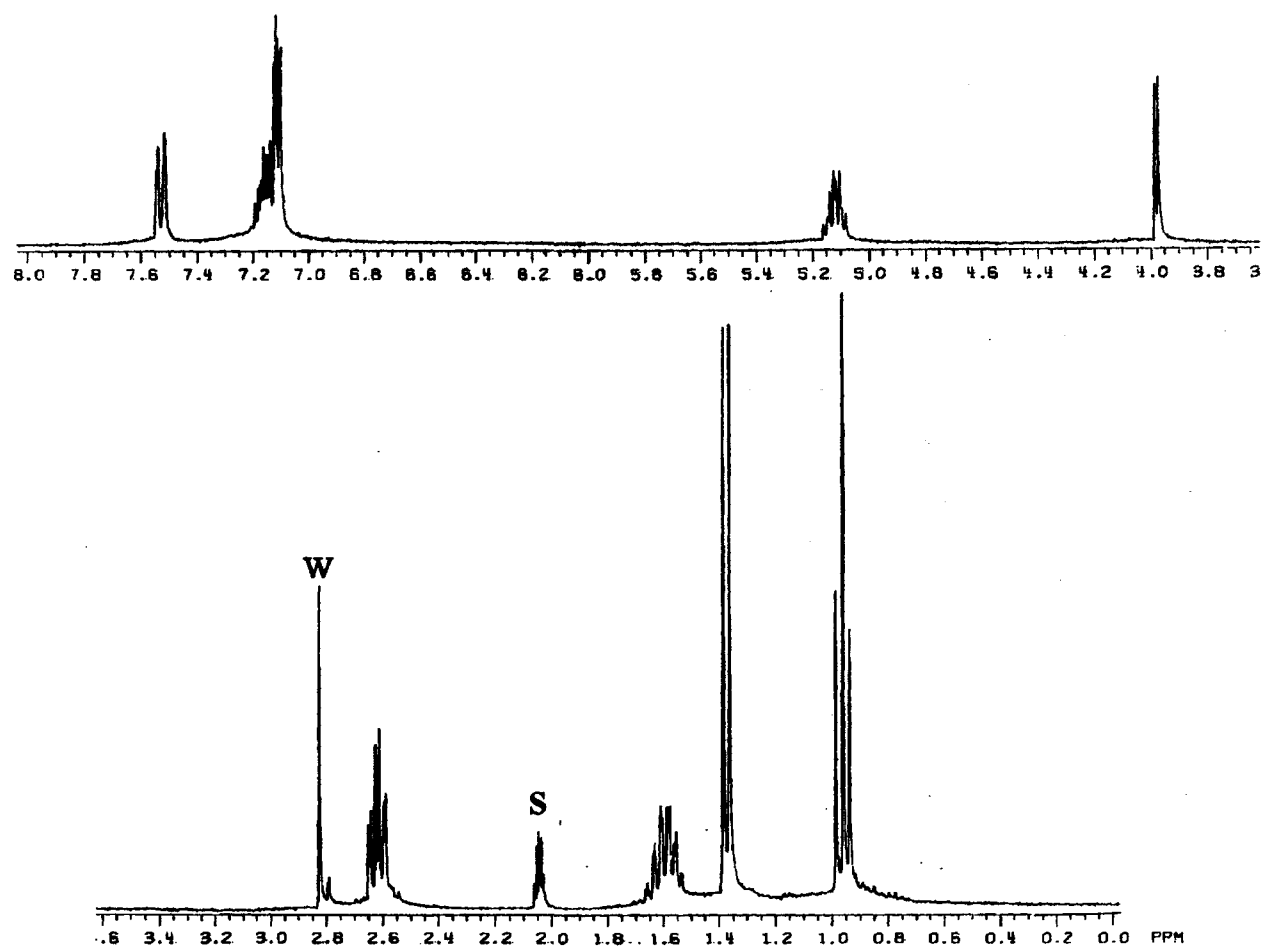


Figure A-20. ^1H NMR spectrum (300 MHz, acetone- d_6) of 1-(*o*-propylphenyl)ethanol (S: acetone- d_6 , W: H_2O).

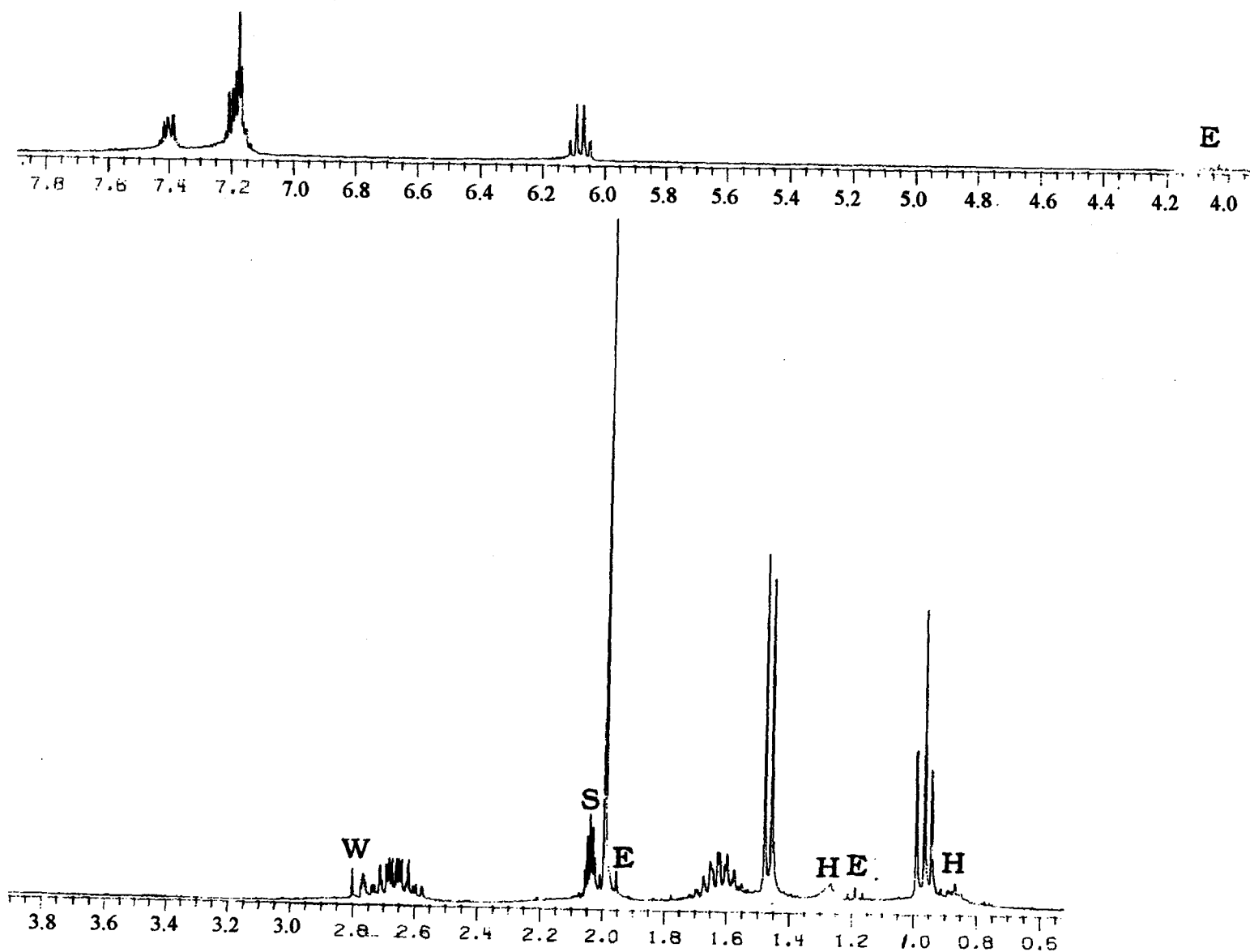


Figure A-21. ^1H NMR spectrum (300 MHz, acetone- d_6) of 1-(*o*-propylphenyl)ethylacetate (S: acetone- d_5 , W: H_2O , H: high-boiling residue from hexanes, E: ethylacetate).

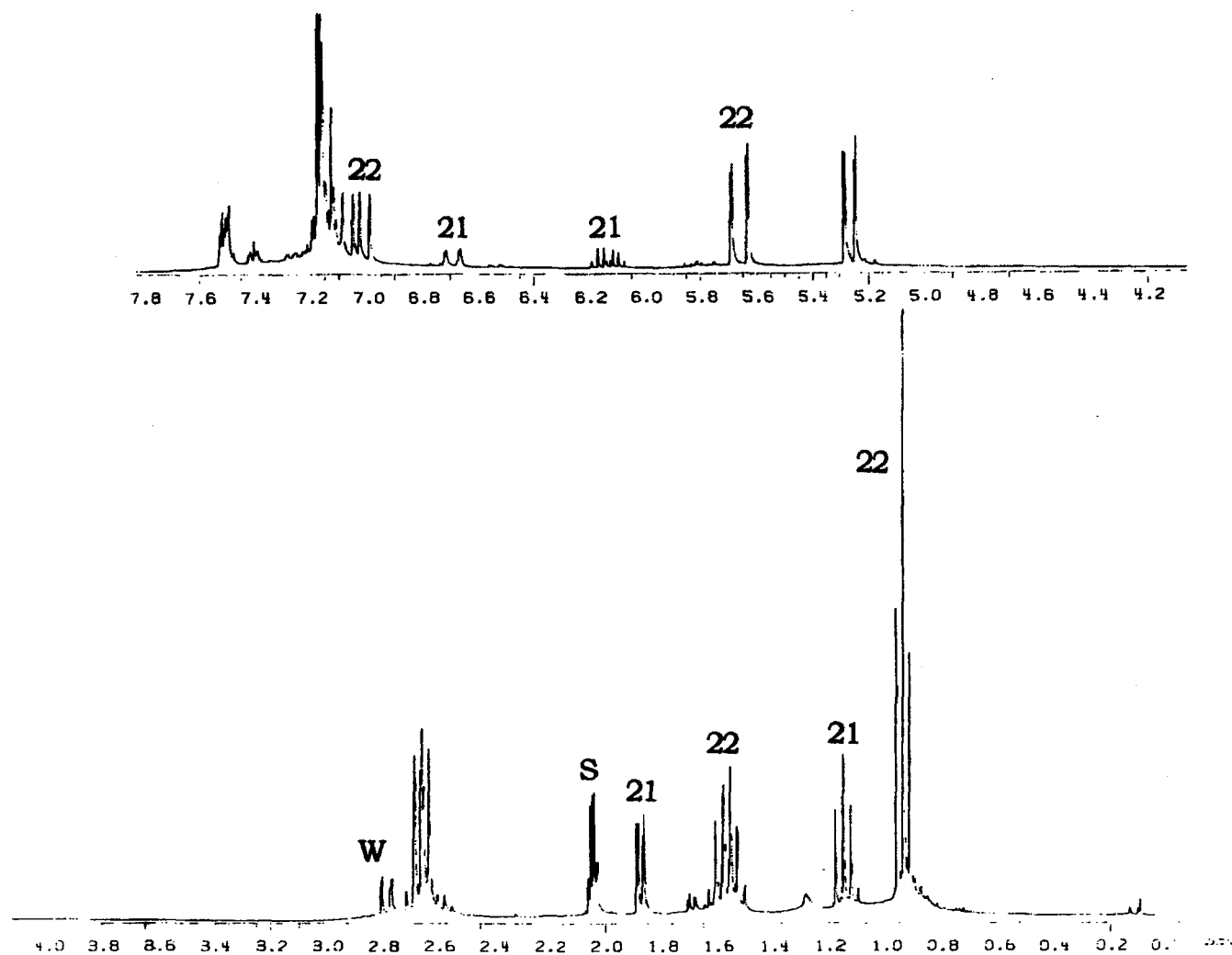


Figure A-22. ^1H NMR spectrum (300 MHz, acetone- d_6) of the pyrolysis mixture from the FVP of 1-(*o*-propylphenyl)ethylacetate, showing *o*-propylstyrene (22), and *E*-(*o*-propenyl)ethylbenzene (23) (22: Compound 22, 23: Compound 23, S: acetone- d_6 , W: H_2O).

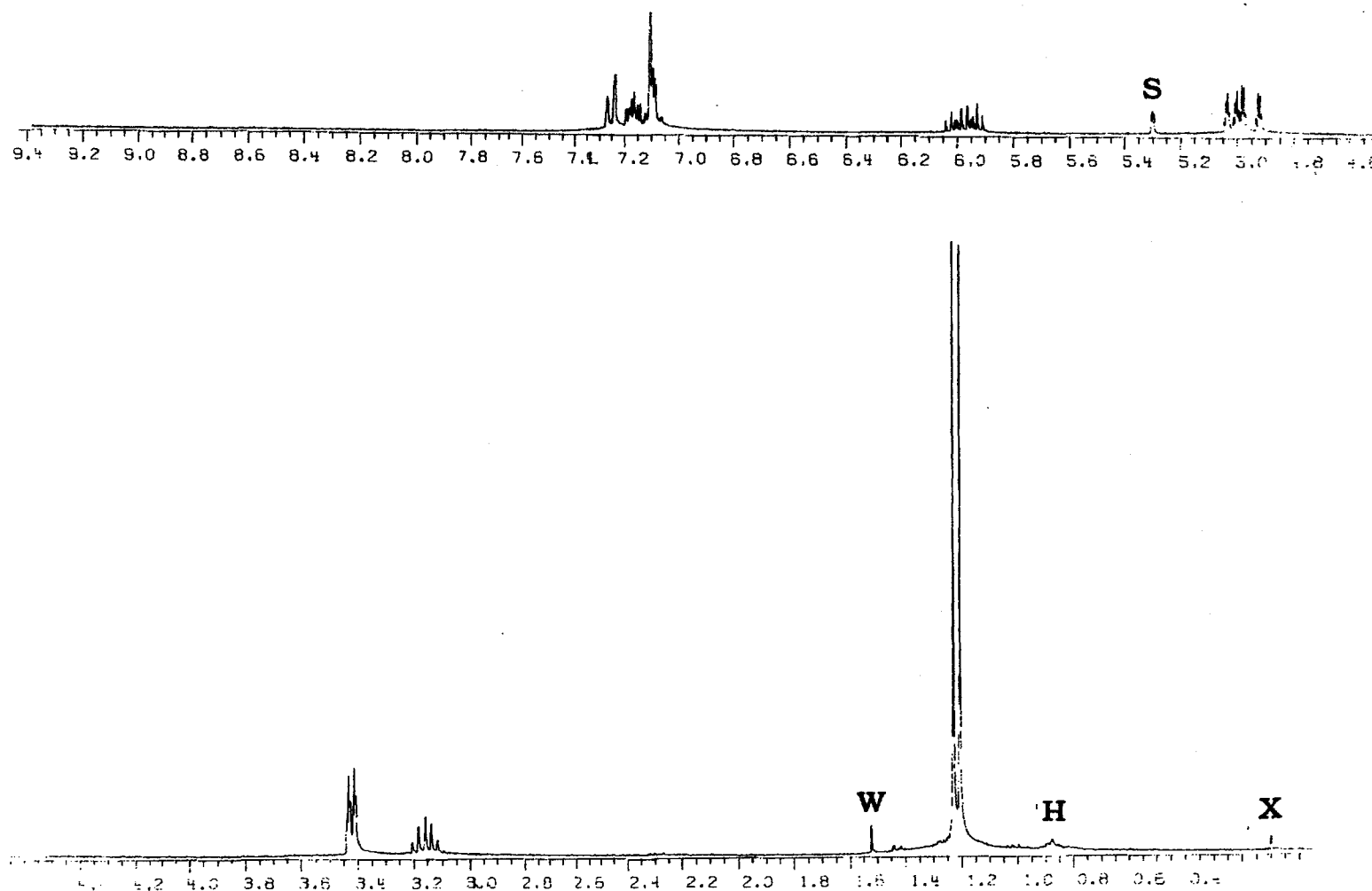


Figure A-23. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of *o*-allylcumene (13) (H: high-boiling residue from hexanes, S: CH_2Cl_2 , W: H_2O , X: unidentified impurity).

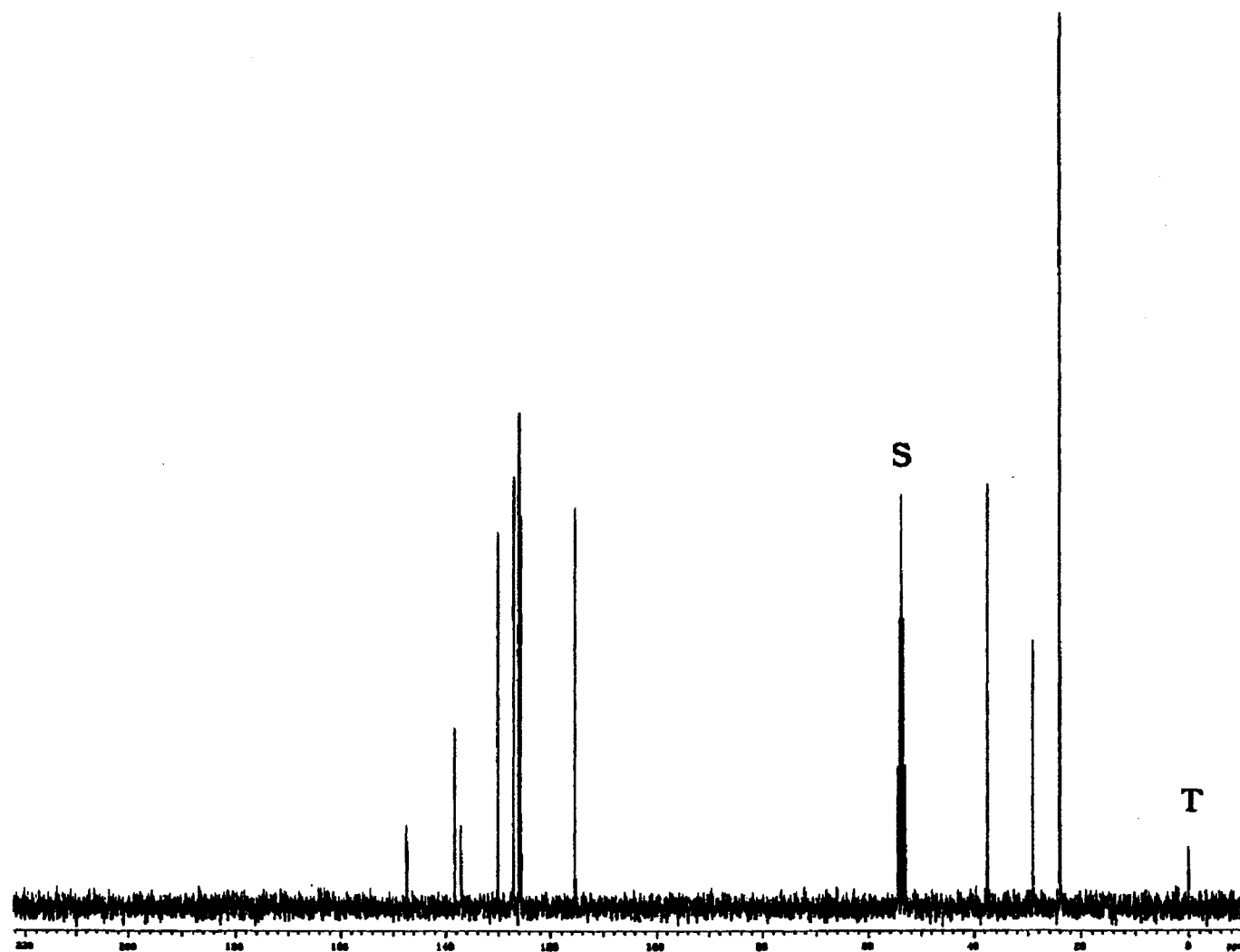


Figure A-24. ^{13}C NMR spectrum (75.5 MHz, CD_2Cl_2) of *o*-allylcumene (13) (S: CH_2Cl_2 , T: tetramethylsilane).

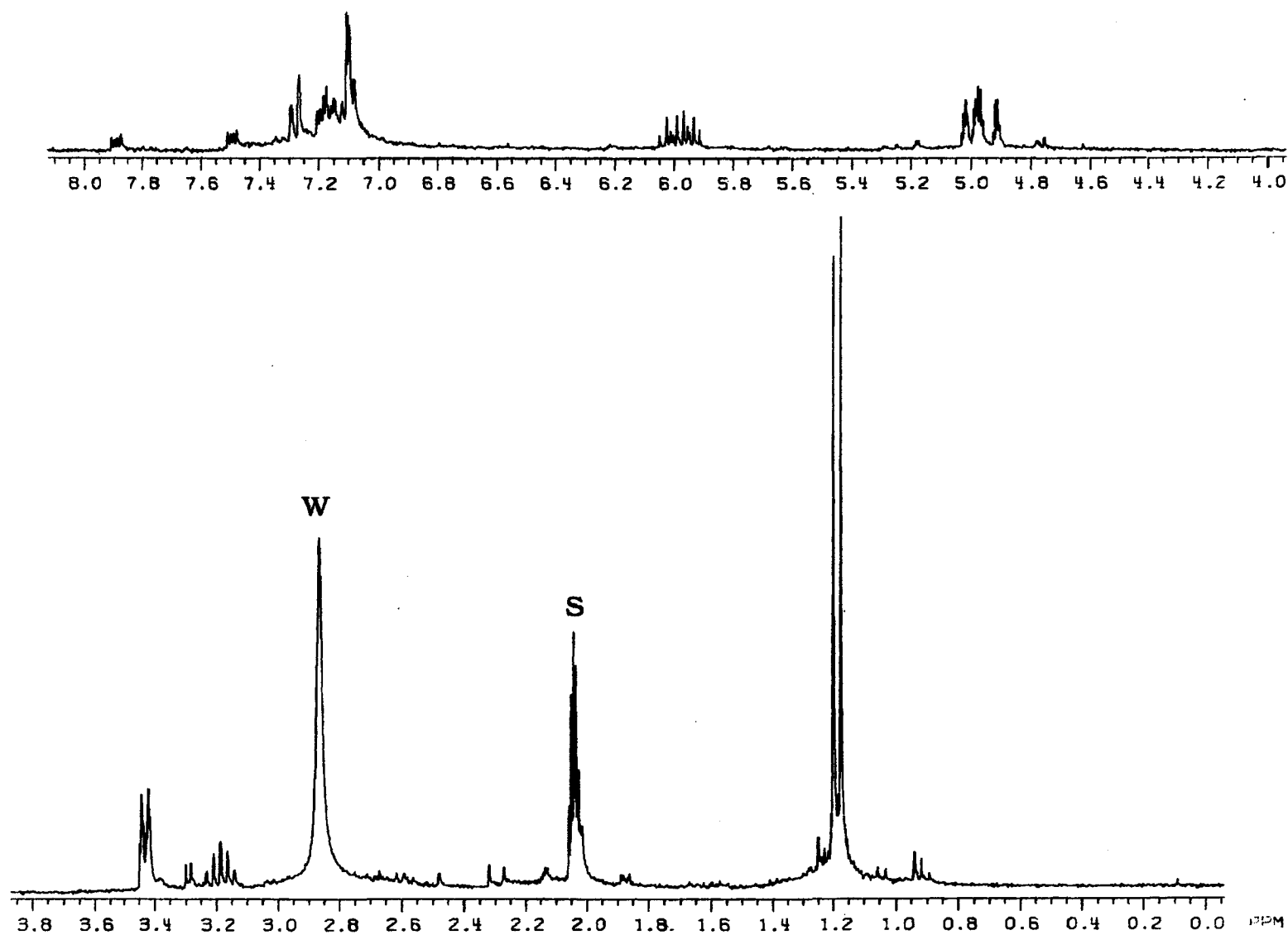


Figure A-25. ^1H NMR spectrum (300 MHz, acetone- d_6) of the pyrolysis mixture from the FVP at 700 $^\circ\text{C}$ of *o*-allylcumene (**13**) (S: acetone- d_5 , W: H_2O).

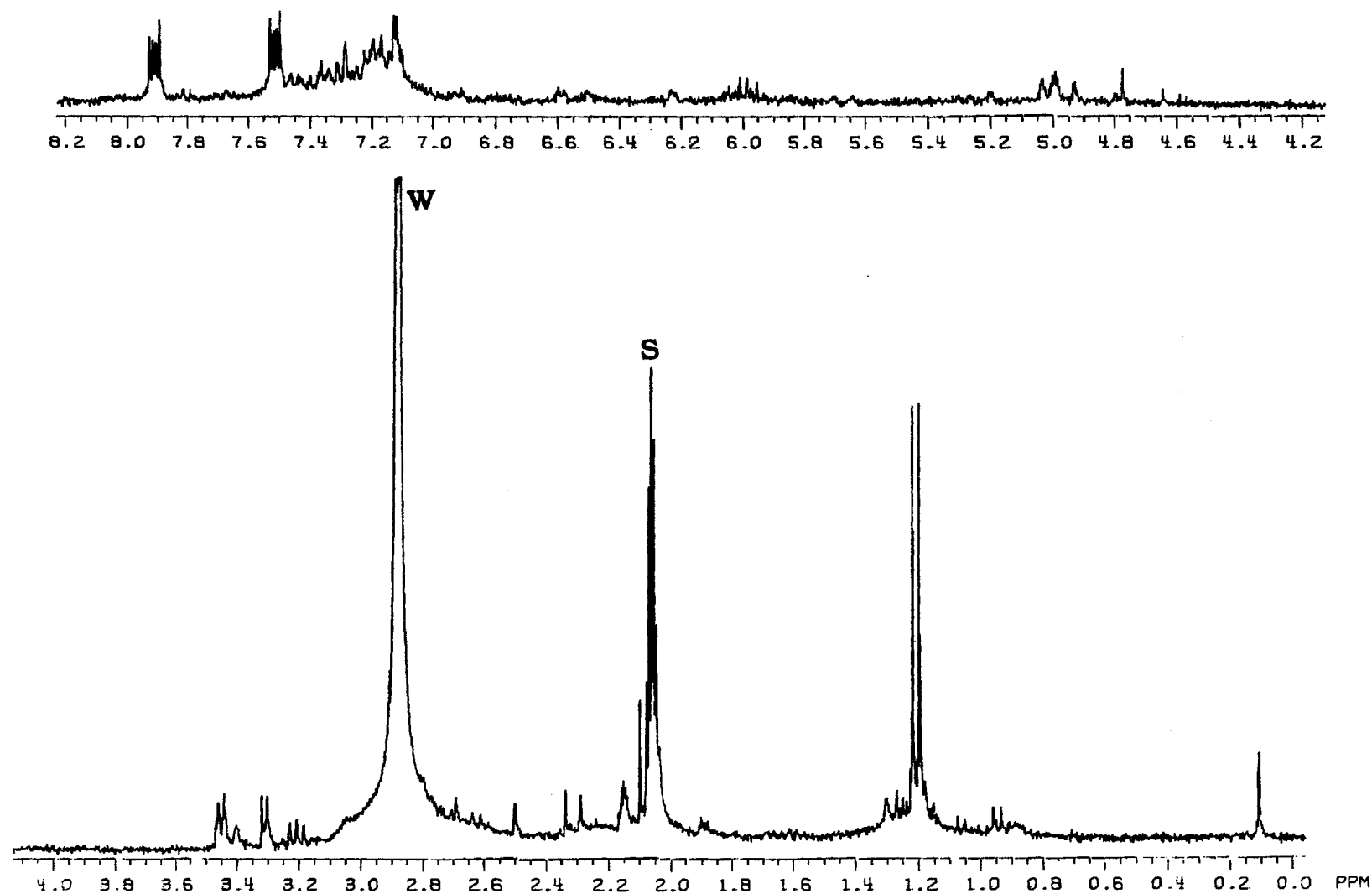


Figure A-26. ^1H NMR spectrum (300 MHz, acetone- d_6) of the pyrolysis mixture from the FVP at 750 °C of *o*-allylcumene (**13**) (S: acetone- d_5 , W: H_2O).

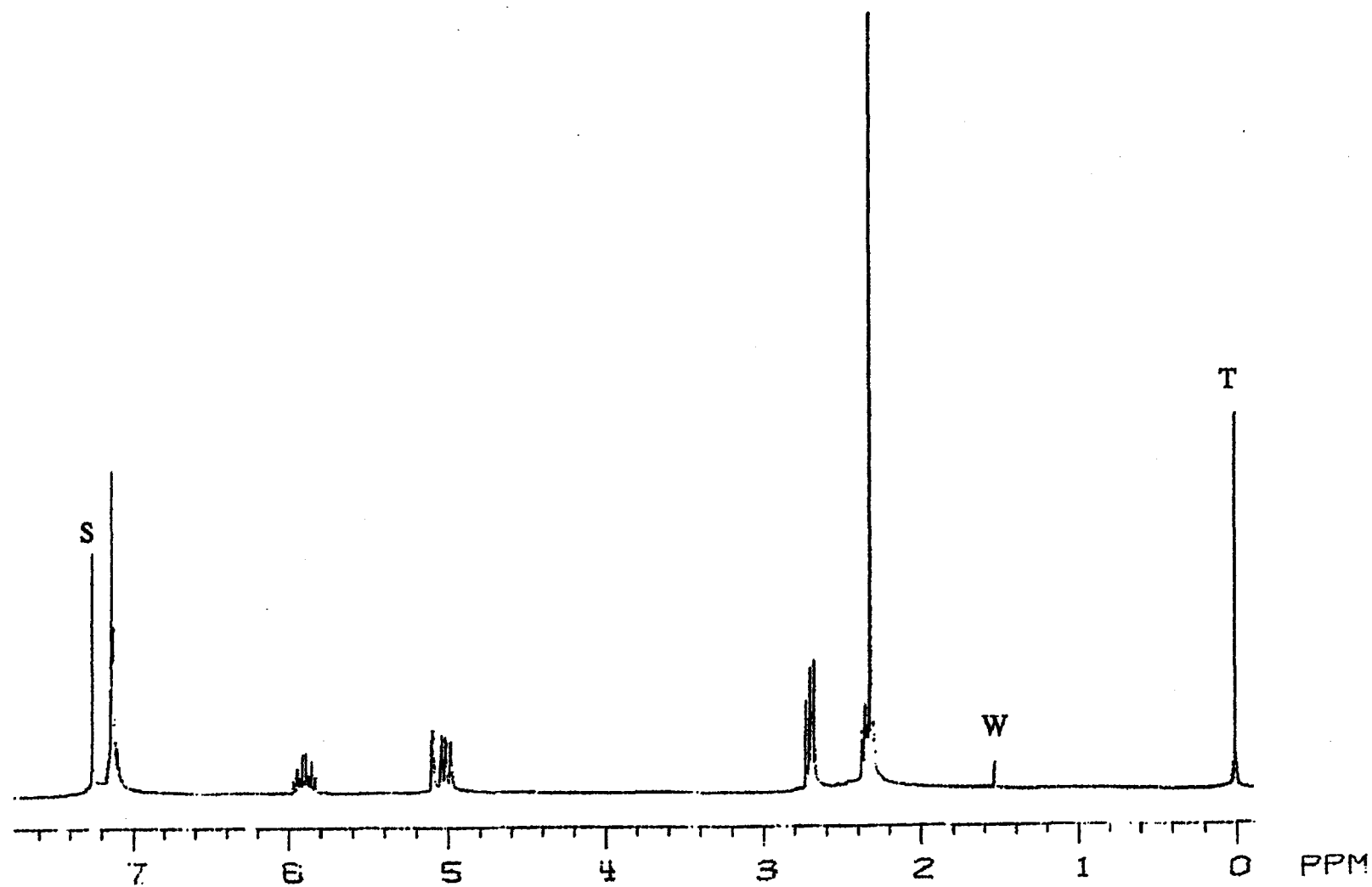
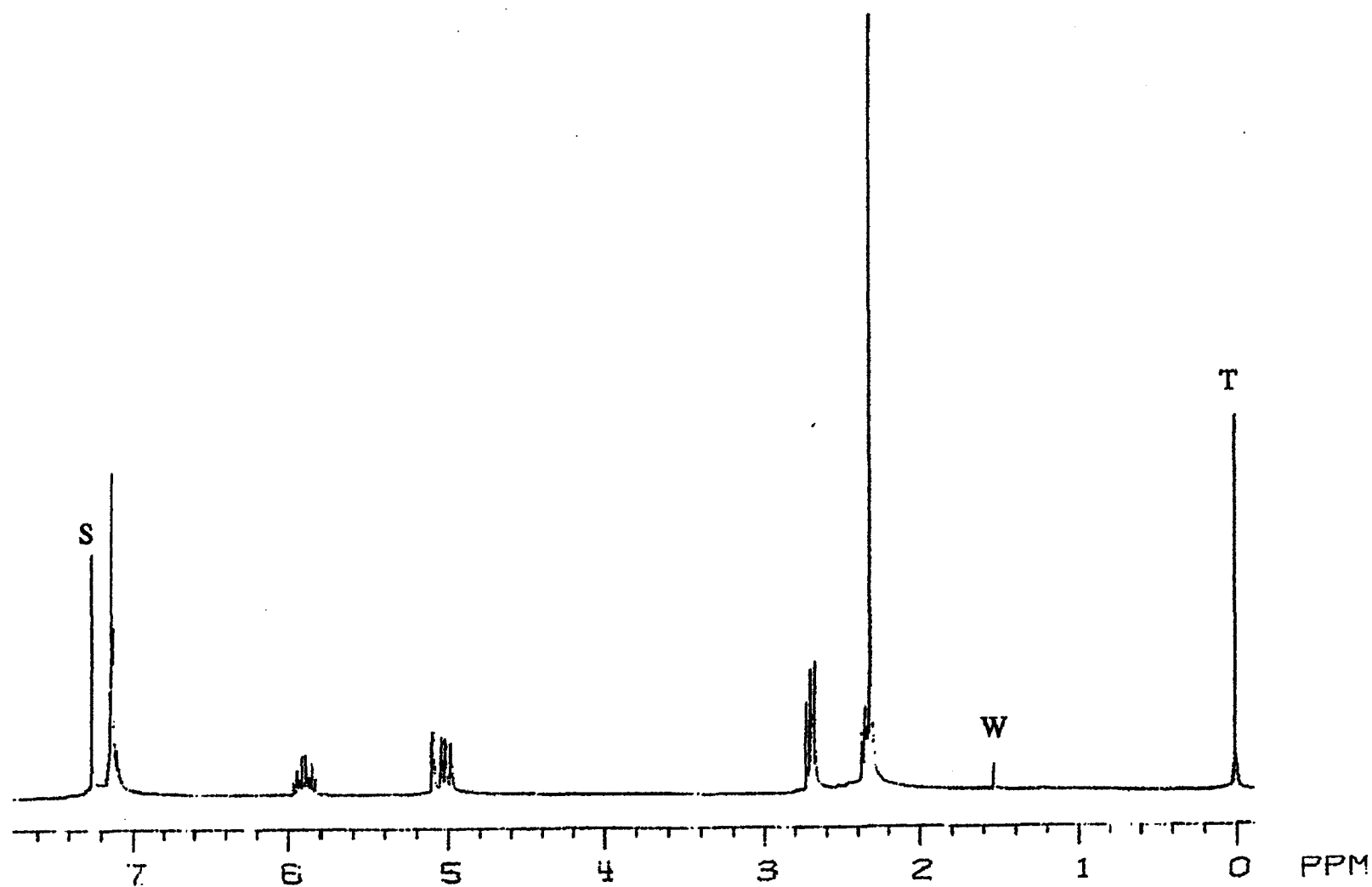


Figure A-27. ^1H NMR spectrum (300 MHz, CDCl_3) of *o*-(3-butenyl)toluene (14) (S: CHCl_3 , T: tetramethylsilane, W: H_2O).



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Figure A-28. ^1H NMR spectrum (300 MHz, CDCl_3) of *o*-(4-pentenyl)toluene (15) (S: CHCl_3 , T: tetramethylsilane, X: unidentified impurity).

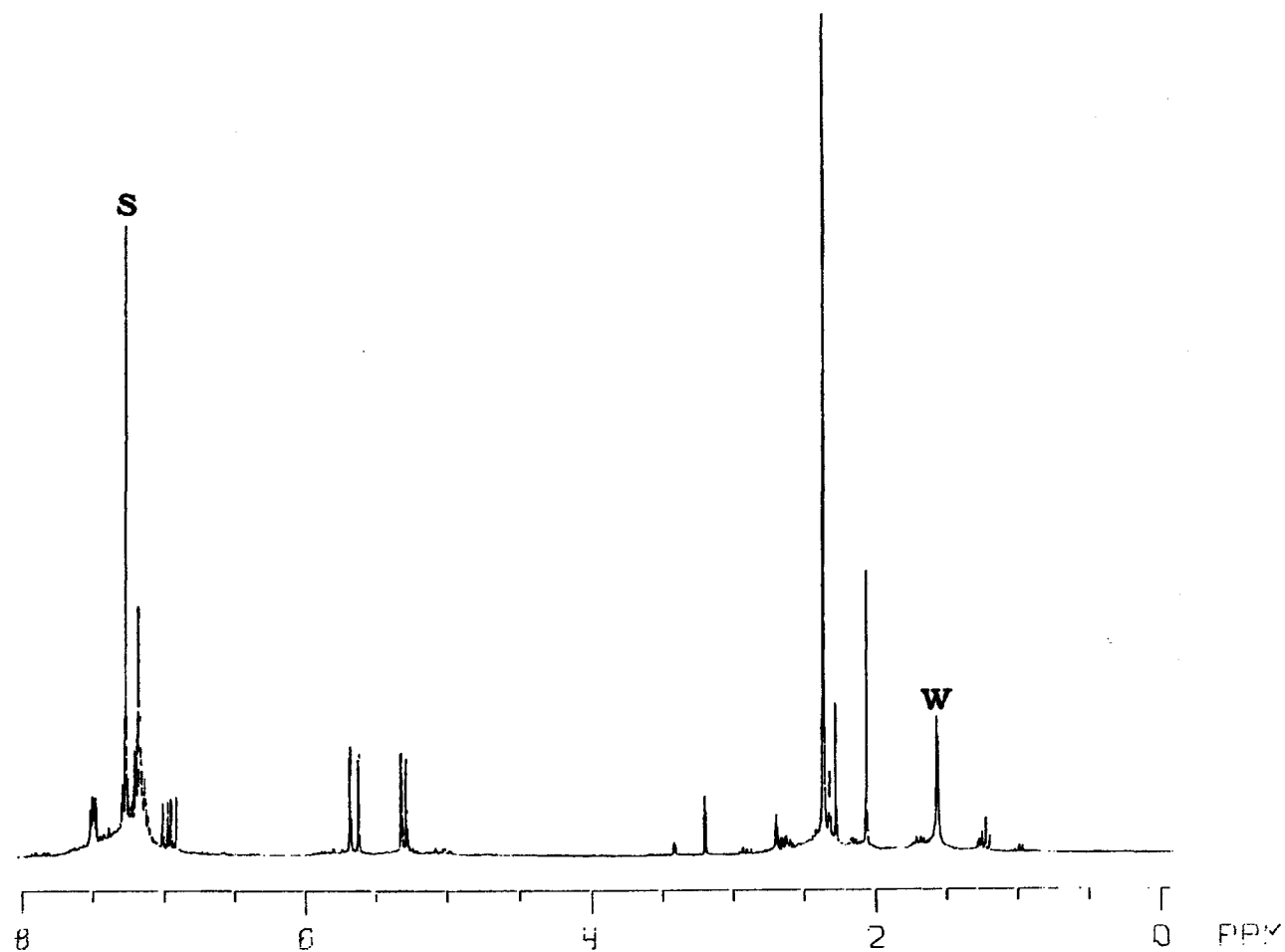


Figure A-29. ^1H NMR spectrum (300 MHz, CDCl_3) of the pyrolysis mixture from the FVP at 800 $^\circ\text{C}$ of *o*-(4-pentenyl)toluene (15) (S: CHCl_3 , W: H_2O).

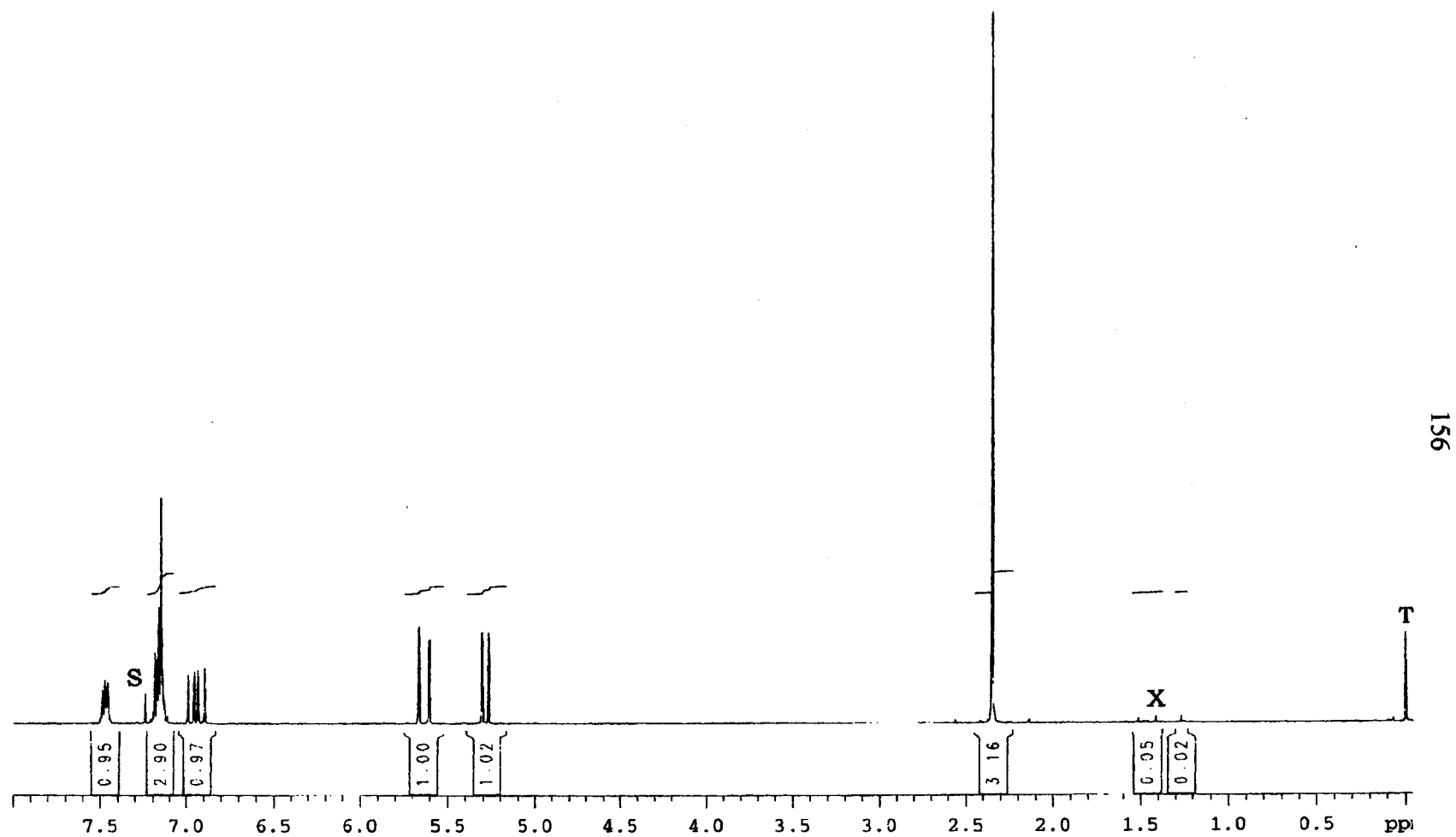


Figure A-30. ^1H NMR spectrum (300 MHz, CDCl_3) of *o*-methylstyrene (16) S: CHCl_3 , T: tetramethylsilane, X: unidentified impurity).

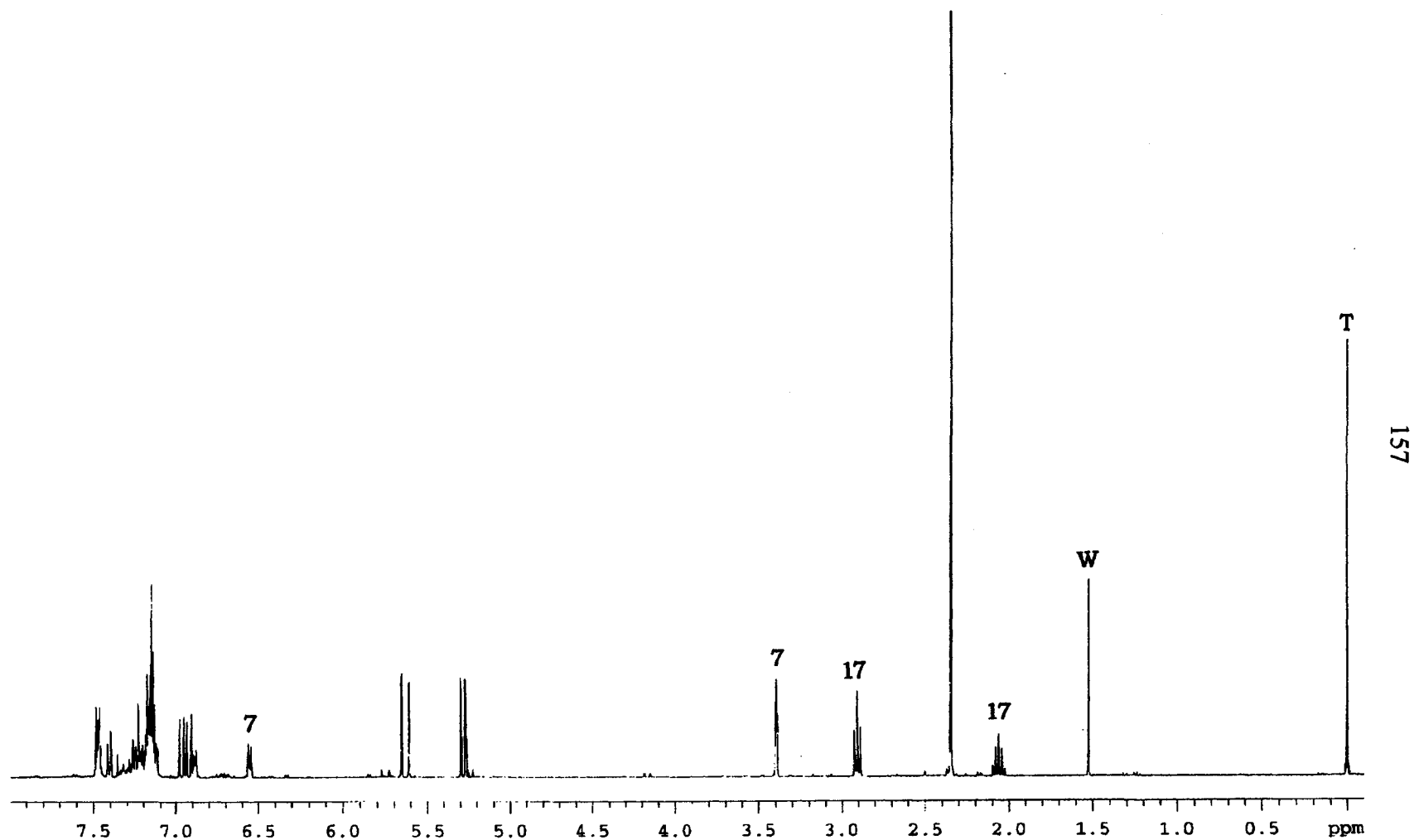


Figure A-31. ^1H NMR spectrum (300 MHz, CDCl_3) of the pyrolysis mixture from the FVP at 950 $^\circ\text{C}$ of *o*-methylstyrene (16) (7: indene (7), 17: indan (17), T: tetramethylsilane, W: H_2O).

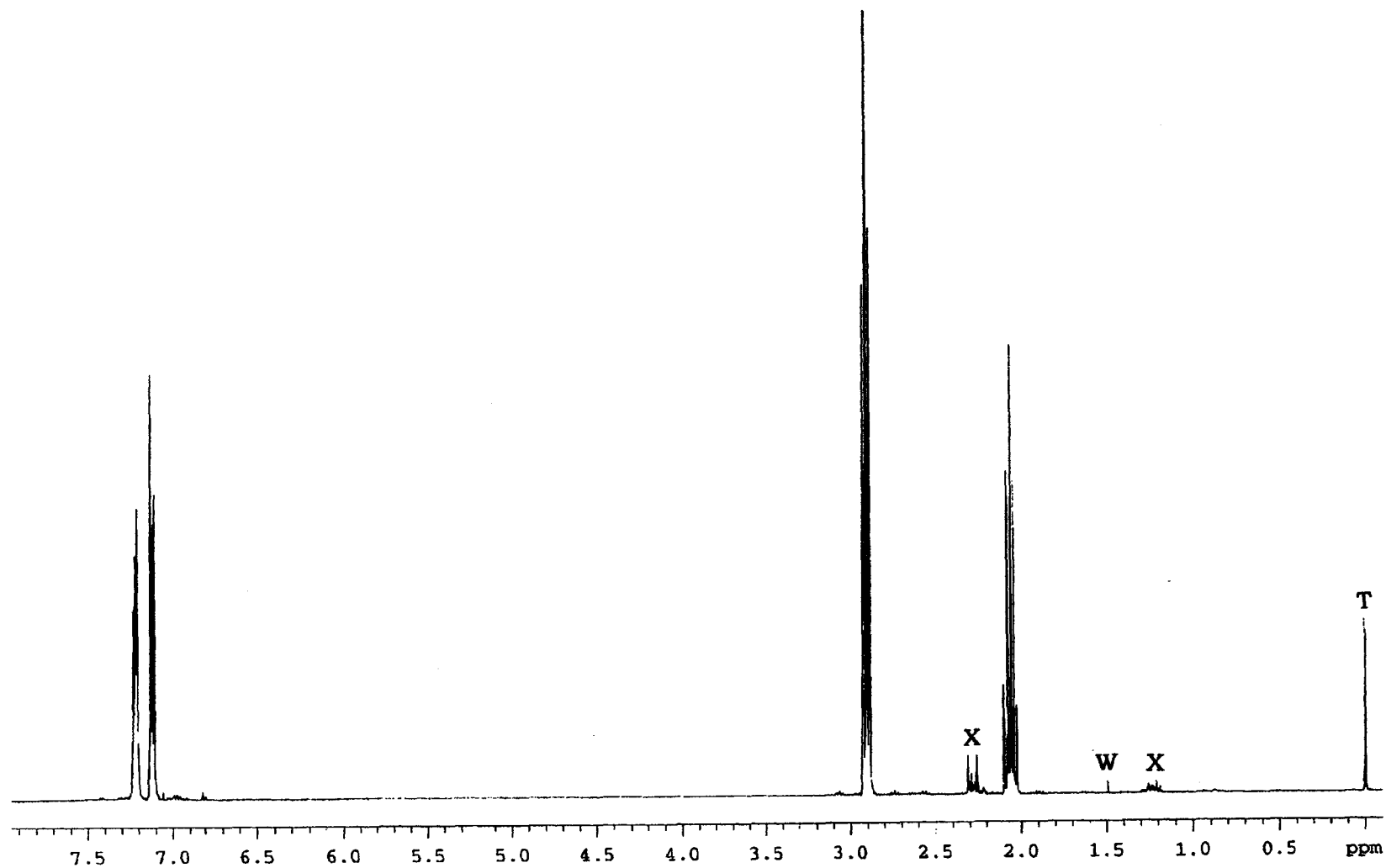


Figure A-32. ^1H NMR spectrum (300 MHz, CDCl_3) of indan (17) (T: tetramethylsilane, W: H_2O , X: unidentified impurity).

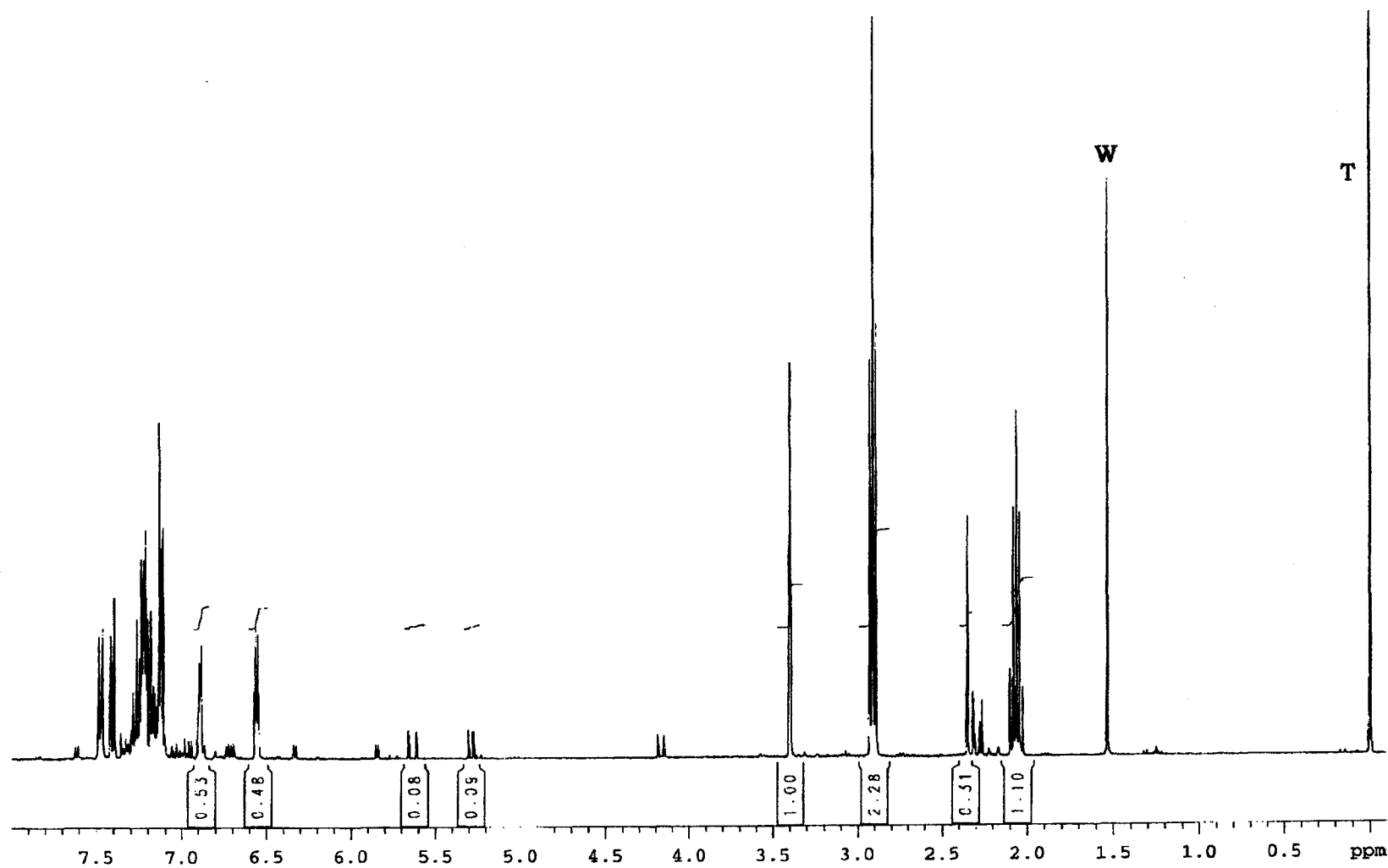


Figure A-33. ^1H NMR spectrum (300 MHz, CDCl_3) of the pyrolysis mixture from the FVP at 950 °C of indan (17) (T: tetramethylsilane, W: H_2O , X: unidentified impurity).

APPENDIX B.
RAW DATA TABLES AND FIGURES FOR CHAPTER 4.

Table B-1. Products and recovered starting material from the FVP of *o*-allylphenol (13) at various temperatures ^{a,b}

entry	yield, % ^c			
	RT ^d	600°C	700 °C	800 °C
ethylbenzene	—	—	—	0.29
<i>m/p</i> -xylene	—	—	—	0.14
phenylacetylene	—	—	0.10	0.35
styrene	—	—	0.18	0.77
benzofuran (19)	—	10.17	20.56	48.39
indene	—	—	0.22	1.12
1-phenylpropyne	—	—	—	0.16
AA-130 [C ₁₀ H ₁₀]	—	—	0.09	0.12
AB-132 [C ₉ H ₈ O]	—	0.05	—	0.26
2-methylbenzofuran (20) ^e	—	1.41	4.08	7.18
AC-134 [C ₉ H ₁₀ O]	—	—	—	1.37
2,3-dihydro-2-methylbenzofuran (18)	3.58	26.99	37.41	11.12
AD-134 [C ₉ H ₁₀ O]	—	0.86	2.84	1.56
AE-132 [C ₉ H ₈ O]	—	—	0.16	0.23
AF-130 [C ₁₀ H ₁₀]	—	0.78	1.88	1.58
AG-132 [C ₉ H ₈ O]	—	0.22	0.50	1.43
<i>o</i> -cresol (21) ^e	—	5.16	3.61	1.88
AH-146 [C ₁₀ H ₁₂ O]	—	0.04	0.13	0.15
<i>Z</i> - <i>o</i> -(1-propenyl)phenol (Z-22) ^e	—	1.30	2.49	4.02
AI-146 [C ₁₀ H ₁₂ O]	—	—	0.30	0.10
AJ-120 [C ₈ H ₈ O]	—	0.28	0.30	0.92
<i>o</i> -allylphenol (13)	96.42	48.98	18.10	6.09
AK-132 [C ₉ H ₈ O]	—	—	—	0.11

entry	yield, % ^c			
	RT ^d	600°C	700 °C	800 °C
AL-132 [C ₉ H ₈ O]	—	0.06	0.39	0.50
<i>E</i> -(<i>o</i> -1-propenyl)phenol (<i>E</i> -22) ^e	—	3.71	6.94	10.12
recovery ^f		93.59	80.98	58.52
conversion ^g	<i>d</i>	51.02	81.90	93.91

^a FVP conditions: system pressure = 0.10 torr, sample temperature = 0 °C. ^b Amounts determined by GC with a known quantity of biphenyl added as standard. Data represent the average of triplicate runs. Products identified by comparison with authentic samples or those that could be identified ¹H NMR/GC-MS are indicated by name. Products that were identified by GCMS only are indicated by code: XY-*nnn*, where 'X' corresponds to the system first observed (A = *o*-allylphenol, E = *o*-(ethenyloxy)toluene, M = *o*-(1-methylallyl)phenol, AA = *o*-allylaniline, and MI = 2-methylindoline) 'Y' to the individual unknown product (A, B, C, etc.), and '*nnn*' to the nominal mass. ^c Moles of product divided by total moles of recovered material. ^d Starting material purity assay. ^e These products identified by ¹H NMR and/or GC-MS. ^f Total moles of recovered material divided by moles of starting material used. ^g Total moles of recovered material minus moles of recovered starting material divided by total moles of recovered material.

**Table B-2. Products and Recovered Starting Material from the FVP of
o-(Ethenyl)oxytoluene (15) at 800 °C ^{a,b}**

entry	yield, % ^c
	800 °C
<i>o</i> -xylene	4.8
phenylacetylene	1.5
<i>o</i> -(ethenyloxy)toluene (15) ^d	27.0
benzofuran (19)	14.7
EA-134 [C ₉ H ₁₀ O]	4.4
2-methylbenzofuran (20) ^e	1.2
2,3-dihydro-2-methylbenzofuran (18)	6.7
EB-134 [C ₉ H ₁₀ O]	0.5
phenol	2.6
EC-134 [C ₉ H ₁₀ O]	0.9
ED-134 [C ₉ H ₁₀ O]	0.8
<i>o</i> -cresol (21)	18.1
EE-134 [C ₉ H ₁₀ O]	2.8
<i>o</i> -ethylphenol	0.5
<i>Z</i> - <i>o</i> -(1-propenyl)phenol (<i>Z</i> -22) ^e	6.4
<i>o</i> -allylphenol (13)	0.7
<i>E</i> - <i>o</i> -(1-propenyl)phenol (<i>E</i> -22) ^e	7.6
recovery ^f	55.5
conversion ^g	73.0

^a FVP conditions: system pressure = 0.01 torr, sample temperature = 0 °C. ^b See Table B-1, note b. ^c See Table B-1, note c. ^d Starting material purity as determined by FVP at RT is 92.1 % with 5.0 % *o*-cresol (21). ^e See Table B-1, note e. ^f See Table B-1, note f. ^g See Table B-1, note g.

Table B-3. Products and recovered starting from the FVP of *o*-(1-methylallyl)phenol (16) at various temperatures *a,b*

entry	yield, % <i>c</i>			
	RT <i>d</i>	600°C	700 °C	800 °C
toluene	—	—	2.58	0.70
phenylacetylene	—	—	0.36	1.33
styrene	—	—	0.43	0.62
MA-148 [C ₁₀ H ₁₂ O]	—	—	—	—
benzofuran (19)	—	3.04	26.33	71.11
indene	—	—	0.15	0.50
MB-132 [C ₉ H ₈ O]	—	—	0.38	—
MC-148 [C ₁₀ H ₁₂ O]	—	—	—	0.11
MD-148 [C ₁₀ H ₁₂ O]	—	—	—	0.11
ME-148 [C ₁₀ H ₁₂ O]	—	—	—	2.32
2-methylbenzofuran (20) <i>e</i>	—	9.35	21.10	14.45
MF-148 [C ₁₀ H ₁₂ O]	—	0.86	—	—
<i>trans</i> -2,3-dimethyl-2,3-dihydrobenzofuran (<i>trans</i> -23) <i>f</i>	—	40.72	25.63	1.72
MG-148 [C ₁₀ H ₁₂ O]	—	—	0.68	0.53
MH-132 [C ₉ H ₈ O]	—	—	0.17	—
MI-136 [C ₉ H ₁₂ O]	—	—	—	0.38
<i>cis</i> -2,3-dimethyl-2,3-dihydrobenzofuran (<i>cis</i> -23) <i>f</i>	—	18.12	9.07	1.03
MJ-148 [C ₁₀ H ₁₂ O]	—	1.00	1.23	0.71
MK-148 [C ₁₀ H ₁₂ O]	—	3.60	0.90	0.48
ML-146 [C ₁₀ H ₁₀ O]	—	0.18	0.97	0.24
MM-146 [C ₁₀ H ₁₀ O]	—	0.38	—	—
MN-146 [C ₁₀ H ₁₀ O]	—	0.46	—	—
2,3-dimethylbenzofuran (24) <i>e</i>	—	3.08	4.79	2.85

entry	yield, % ^c			
	RT ^d	600°C	700 °C	800 °C
MO-148 [C ₁₀ H ₁₂ O]	—	0.82	1.70	0.24
MP-144 [C ₁₀ H ₈ O]	—	1.34	0.40	0.32
MQ-160 [C ₁₁ H ₁₀ O]	—	1.21	0.42	—
MR-146 [C ₁₀ H ₁₀ O]	—	—	0.73	—
MS-148 [C ₁₀ H ₁₂ O]	—	2.18	—	—
<i>o</i> -(1-methylallyl)phenol (16)	100.00	13.67	—	—
MT-136 [C ₉ H ₁₂ O]	—	—	2.35	0.13
recovery ^g	100.00	73.08 ^h	65.35 ⁱ	64.92 ^j
conversion ^k	<i>d</i>	86.33	100.00	100.00

^a FVP conditions: system pressure = 0.10 torr, sample temperature = 0 °C. ^b See Table B-1, note *b*. ^c See Table B-1, note *c*. ^d Assay of starting material by GC in area percentages. ^e See Table B-1, note *e*. ^f See Table B-1, note *e*, including comparison to ¹H NMR reported in the literature.⁷ ^g See Table B-1, note *f*. ^h Unidentified products constitute 0.18 % total area by GC. ⁱ Unidentified products constitute 0.49 % total area by GC. ^j Unidentified products constitute 0.79 % total area by GC. ^k See Table B-1, note *g*.

Table B-4. Products and Recovered Starting Material from the FVP of *o*-Allylaniline (14) at Various Temperatures ^{a,b}

entry	yield, % ^c			
	625 °C	700 °C	800 °C	920 °C
MIA-105 [C ₇ H ₇ N]	—	—	0.6	—
MIB-104 [C ₈ H ₈]	—	—	0.9	1.0
aniline (26)	—	—	2.0	4.6
MIC-103 [C ₇ H ₅ N]	—	—	0.6	3.5
MID117 [C ₈ H ₇ N]	—	—	0.6	3.7
<i>o</i> -toluidine (27)	0.2	2.8	10.9	4.2
MIE-131 [C ₉ H ₉ N]	0.1	0.7	0.8	0.8
MIF-121 [C ₈ H ₁₁ N]	—	—	0.7	—
<i>o</i> -aminostyrene (31) ^d	—	0.9	3.9	2.5
<i>o</i> -allylaniline (14) ^e	86.7	63.2	11.4	0.9
2-methylindoline (17)	8.2	15.6	12.8	1.5
<i>E</i> - <i>o</i> -(1-propenyl)aniline (<i>E</i> -30) ^d	0.8	4.2	6.6	1.9
quinoline (28)	0.6	1.0	2.4	3.2
indole (25)	3.4	3.3	31.6	72.2
<i>Z</i> - <i>o</i> -(1-propenyl)aniline (<i>Z</i> -30) ^d	—	8.2	13.5	—
1,2,3,4-tetrahydroquinoline(29)	—	—	0.8	—
recovery ^f	86.6 ^g	86.1 ^h	60.5 ⁱ	47.0 ^j
conversion ^k	13.3	36.7	88.6	99.1

^a FVP conditions: system pressure = 0.15 torr, sample temperature = RT-55 °C. ^b See Table B-1, note *b*. ^c See Table B-1, note *c*. ^d See Table B-1, note *d*, including comparison to ¹H NMR reported in the literature. ^e Starting material purity as determined by ¹H NMR quantification against durene: 625 °C experiments, 92.9 % with 4.5 % 17; 700 °C experiment, 85.3 % with 4.5 % 17; 800-900 °C experiments, 96.2 % with 2.9 % 17. ^f See Table B-1, note *f*. ^g Unidentified products constitute 1.57 % total area by GC. ^h Unidentified products constitute 2.26 % total area by GC. ⁱ Unidentified products constitute 8.42 % total area by GC. ^j Unidentified products constitute 9.80 % total area by GC ^k see Table B-1, note *g*.

Table B-5. Products and Recovered Starting Material from the FVP 2-Methylindoline (17) at 800 °C *a,b*

entry	yield, % <i>c</i>	
	800 °C	820 °C
aniline (26)	0.9	1.5
MID-117 [C ₈ H ₇ N]	0.7	0.9
<i>o</i> -toluidine (27)	18.0	16.9
MIE-131 [C ₉ H ₉ N]	0.4	—
<i>o</i> -aminostyrene (31) <i>d</i>	0.7	1.5
<i>o</i> -allylaniline (14)	5.2	5.8
2-methylindoline (17) <i>e</i>	26.3	18.5
<i>E</i> - <i>o</i> -(1-propenyl)aniline (<i>E</i> -30) <i>d</i>	—	3.2
quinoline (28)	1.0	1.3
indole (25)	37.9	41.3
<i>Z</i> - <i>o</i> -(1-propenyl)aniline (<i>Z</i> -30) <i>d</i>	9.3	9.2
recovery <i>f</i>	44.1 <i>g</i>	55.3 <i>h</i>
conversion <i>i</i>	74.7	81.6

a FVP conditions: system pressure = 0.20 torr, sample temperature = 35 °C. *b* See Table B-1, note *b*. *c* See Table B-1, note *c*. *d* See Table B-4, note *d*. *e* Starting material 99.4 % pure as determined by GC assay. *f* See Table B-1, note *f*. *g* Unidentified products constitute 6.10 % total area by GC. *h* Unidentified products constitute 12.58 % total area by GC. *i* See Table B-1, note *g*.

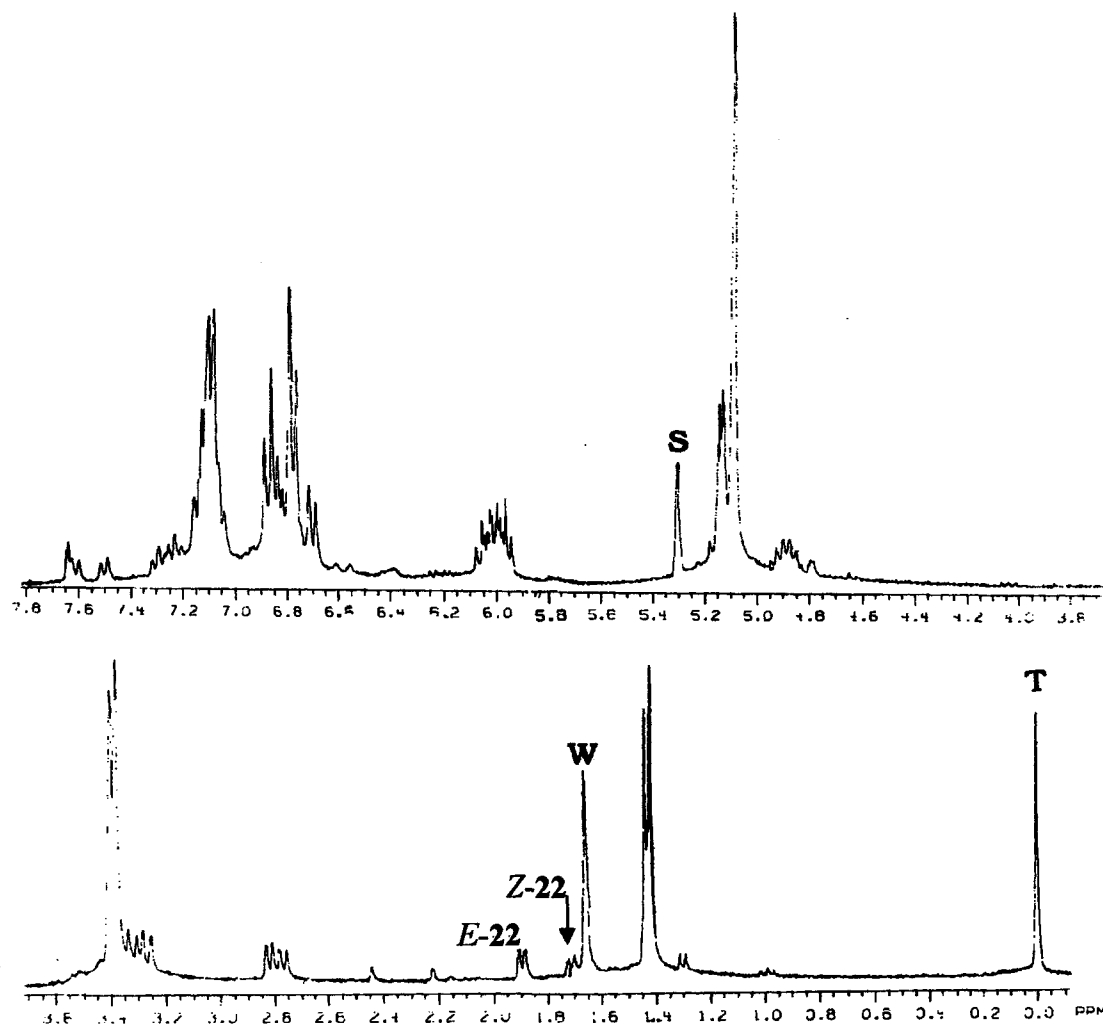


Figure B-1. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of the pyrolysis mixture from the FVP at 700 $^\circ\text{C}$ of *o*-allylphenol (13) (S: CHDCl_2 , T: tetramethylsilane, W: H_2O , E/Z-22: E/Z-*o*-(1-propenyl)phenol).

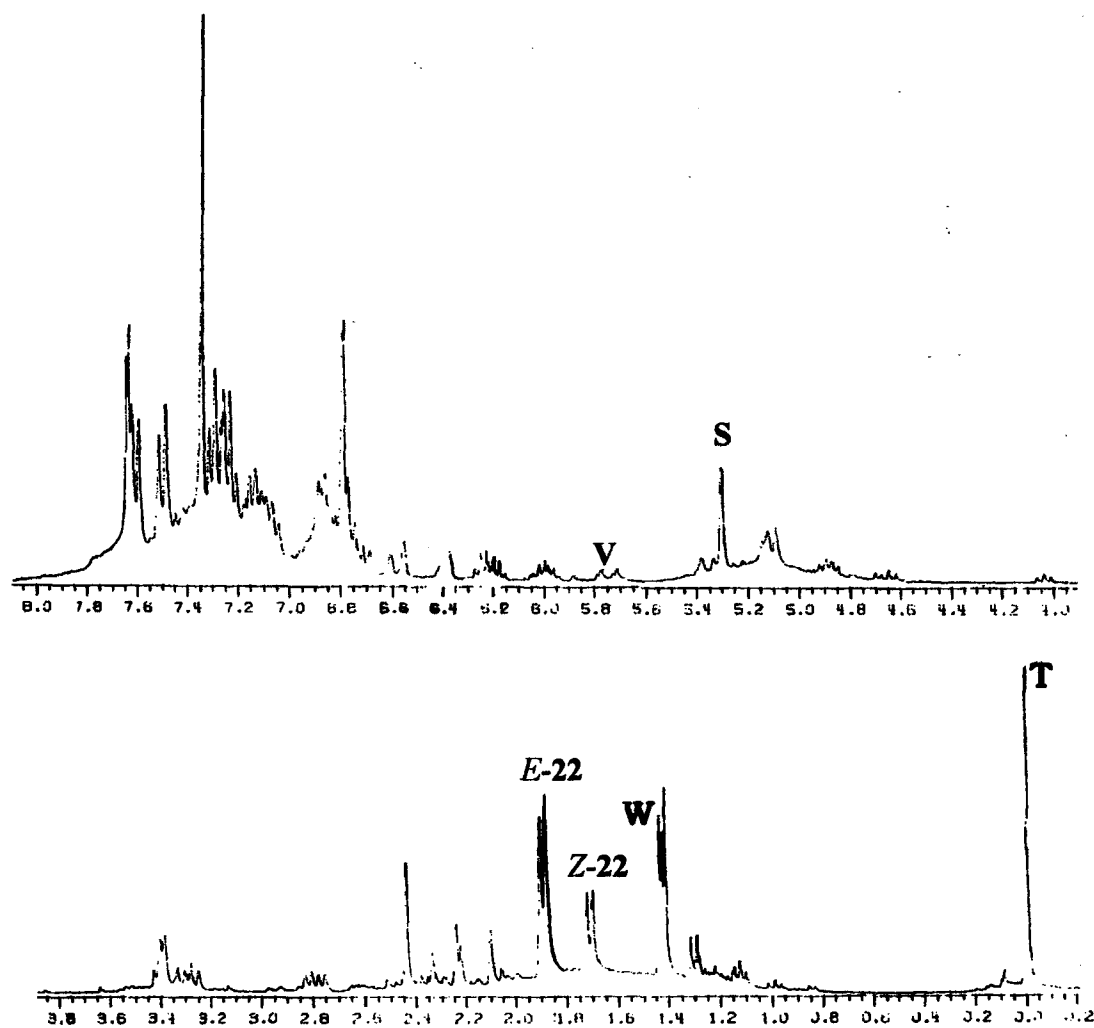


Figure B-2. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of the pyrolysis mixture from the FVP at 800 $^\circ\text{C}$ of *o*-allylphenol (**13**) (S: CHDCl_2 , T: tetramethylsilane, V: *o*-vinylphenol, W: H_2O , E/Z-22: E/Z-*o*-(1-propenyl)phenol).

Run=finn17220 Scan=685 RT=8:34 100%=2580 ADC Mass Range=38-151
18 Feb 93 12:21 Quad scan A2-114-C

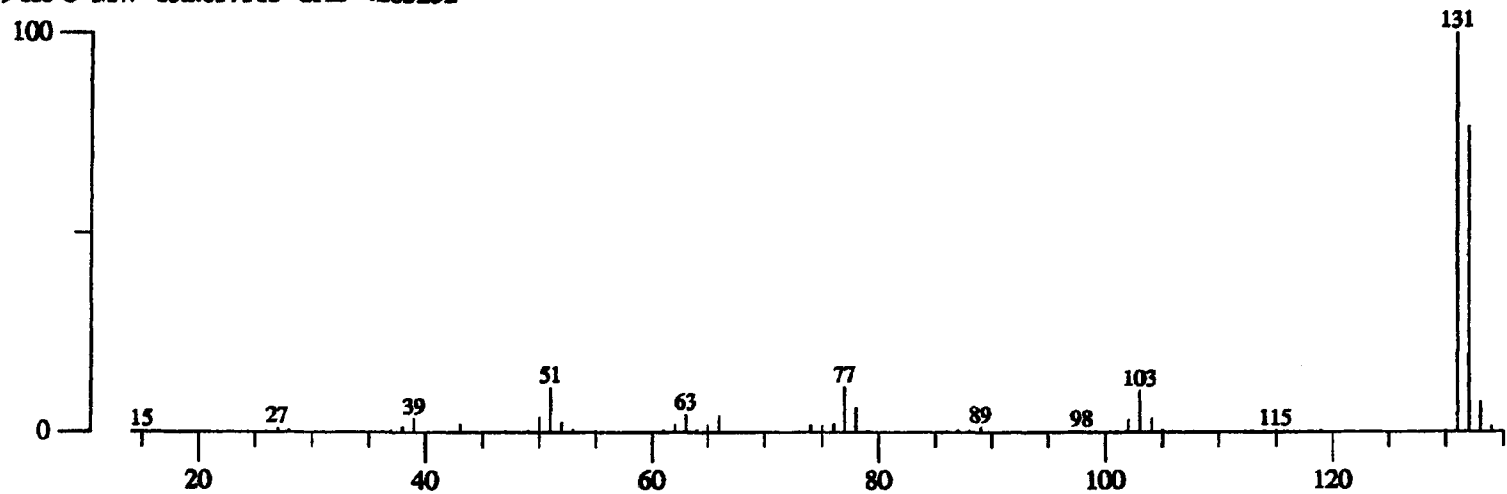
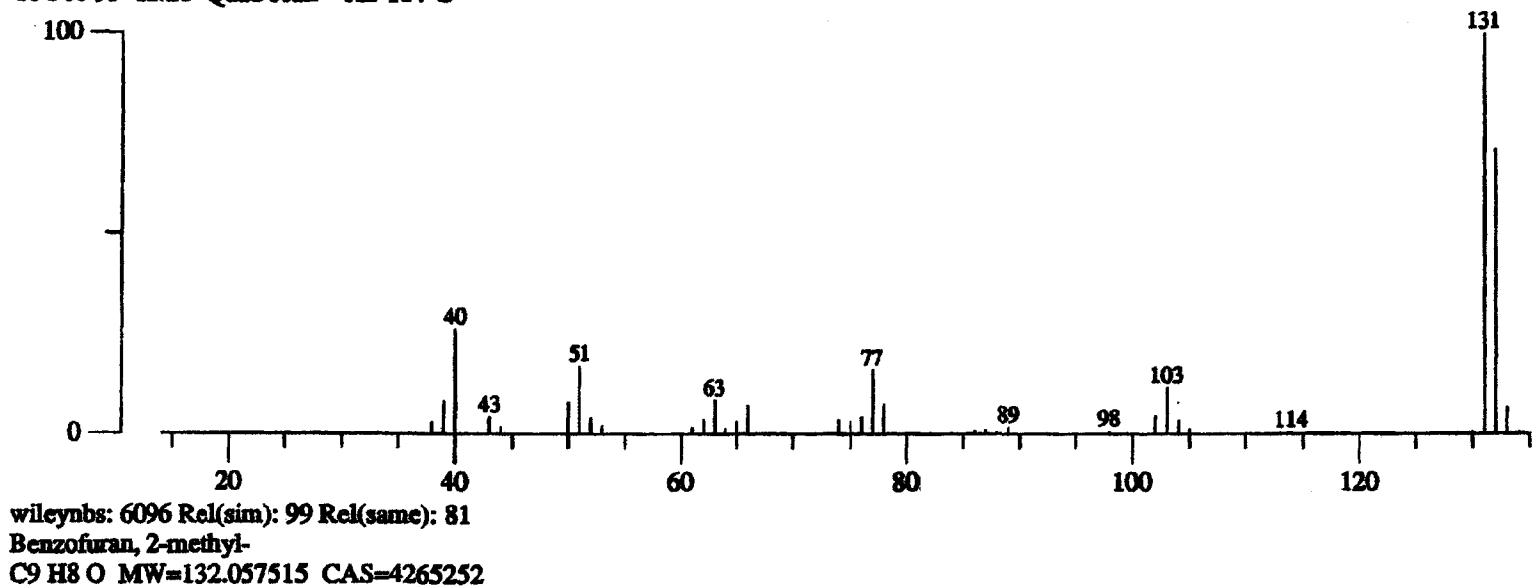


Figure B-3. GC-mass spectrum (EI, 70 eV) of the GC peak assigned to 2-methylbenzofuran (20) in the pyrolysis mixture from the FVP at 800 °C of *o*-allylphenol (13).

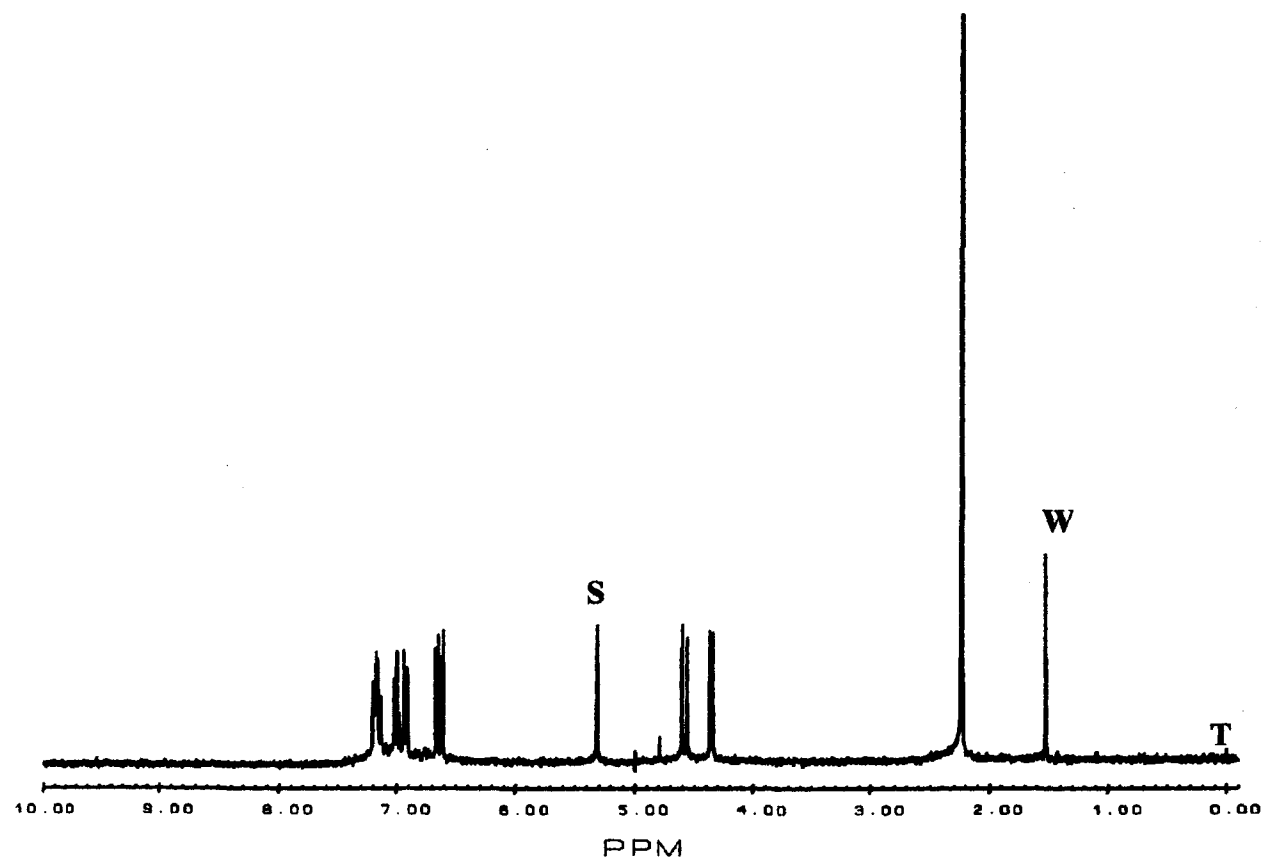


Figure B-4. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of *o*-(ethenyloxy)toluene (**15**) (S: CH_2Cl_2 , T: tetramethylsilane, W: H_2O).

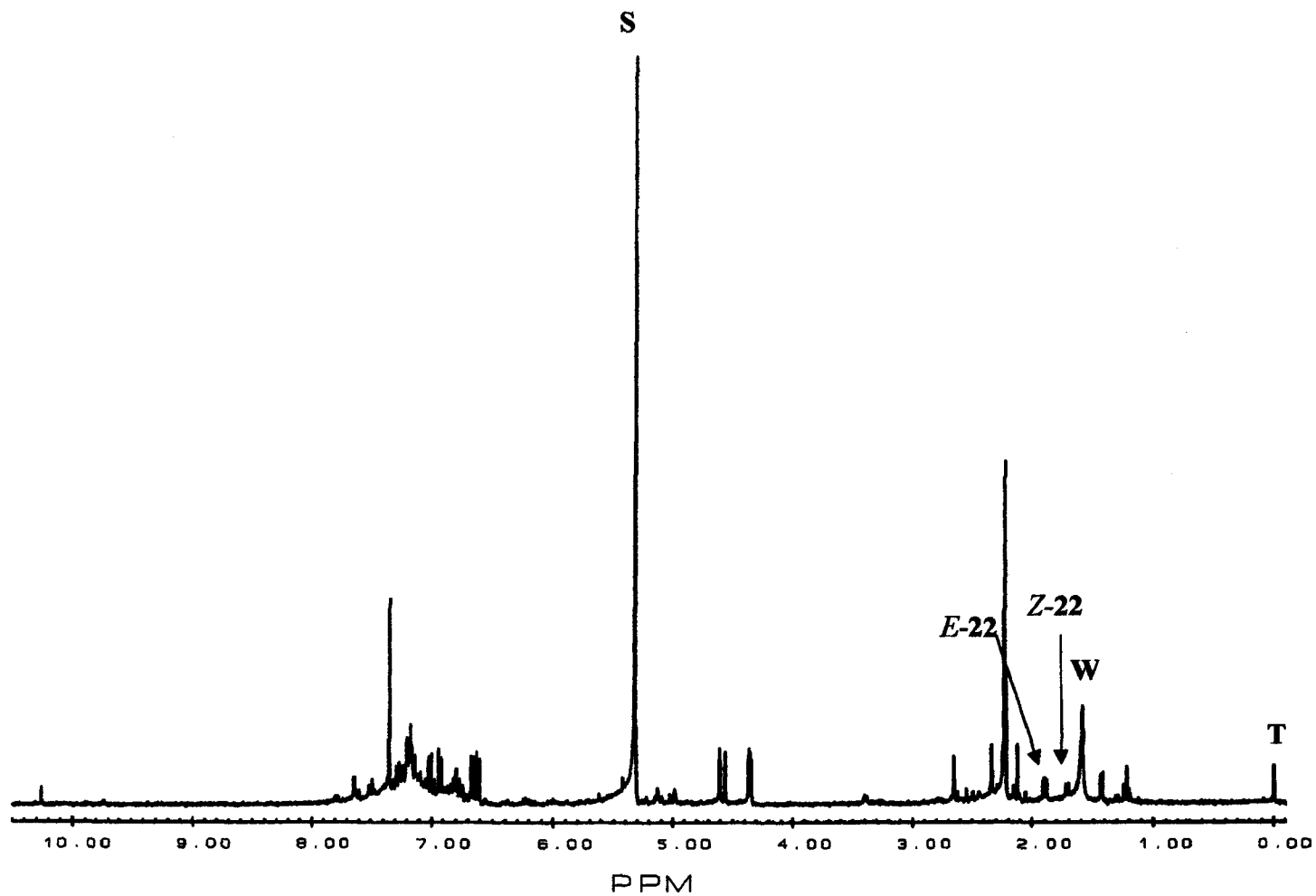


Figure B-5. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of the pyrolysis mixture from the FVP at 800 °C of *o*-(ethenyloxy)toluene (15) (S: CHDCl_2 , T: tetramethylsilane, W: H_2O , E/Z-22: E/Z-*o*-(1-propenyl)phenol).

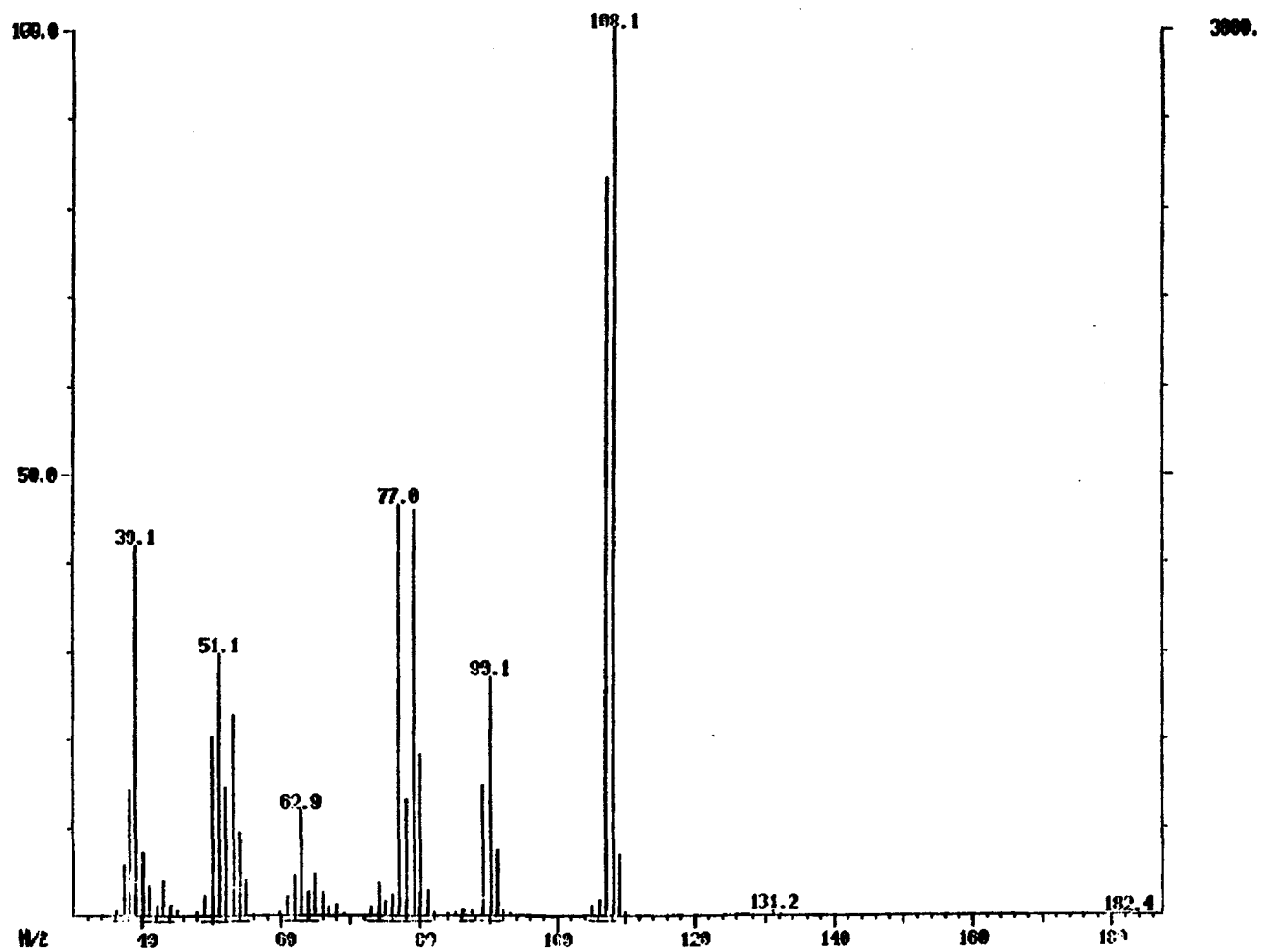


Figure B-6. GC-mass spectrum (EI, 70 eV) of the GC peak assigned to *o*-cresol (21) in the pyrolysis mixture from the FVP at 800 °C of *o*-(ethenyloxy)toluene (15).

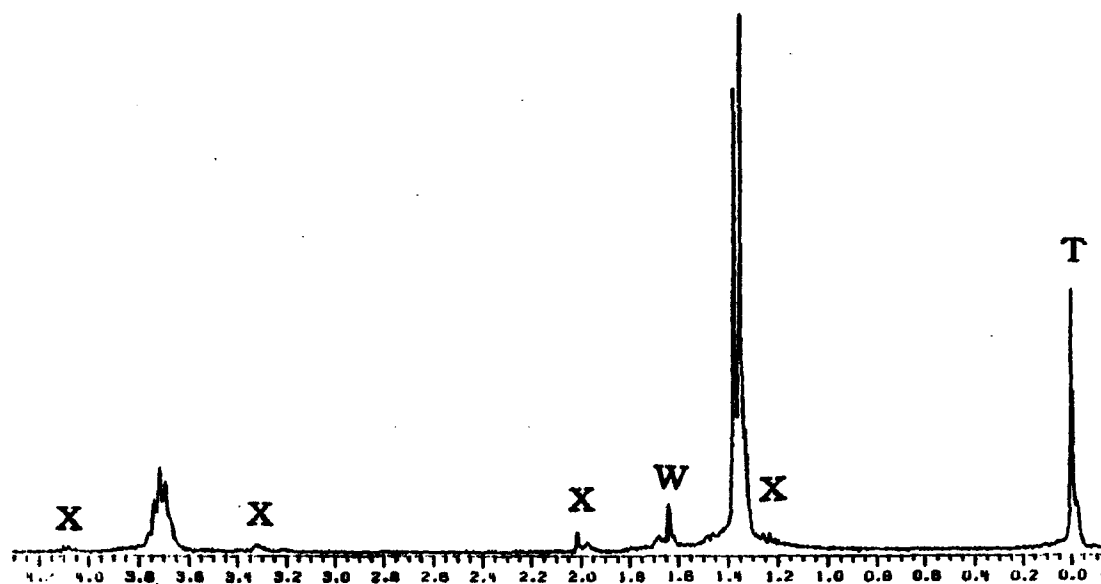
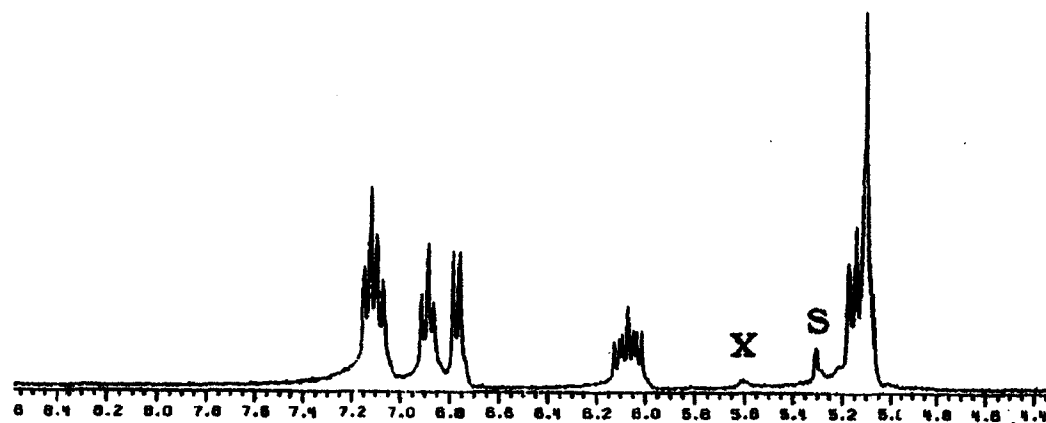


Figure B-7. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of *o*-(1-methylallyl)phenol (**16**) (S: CHDCl_2 , T: tetramethylsilane, W: H_2O , X: unidentified impurity).

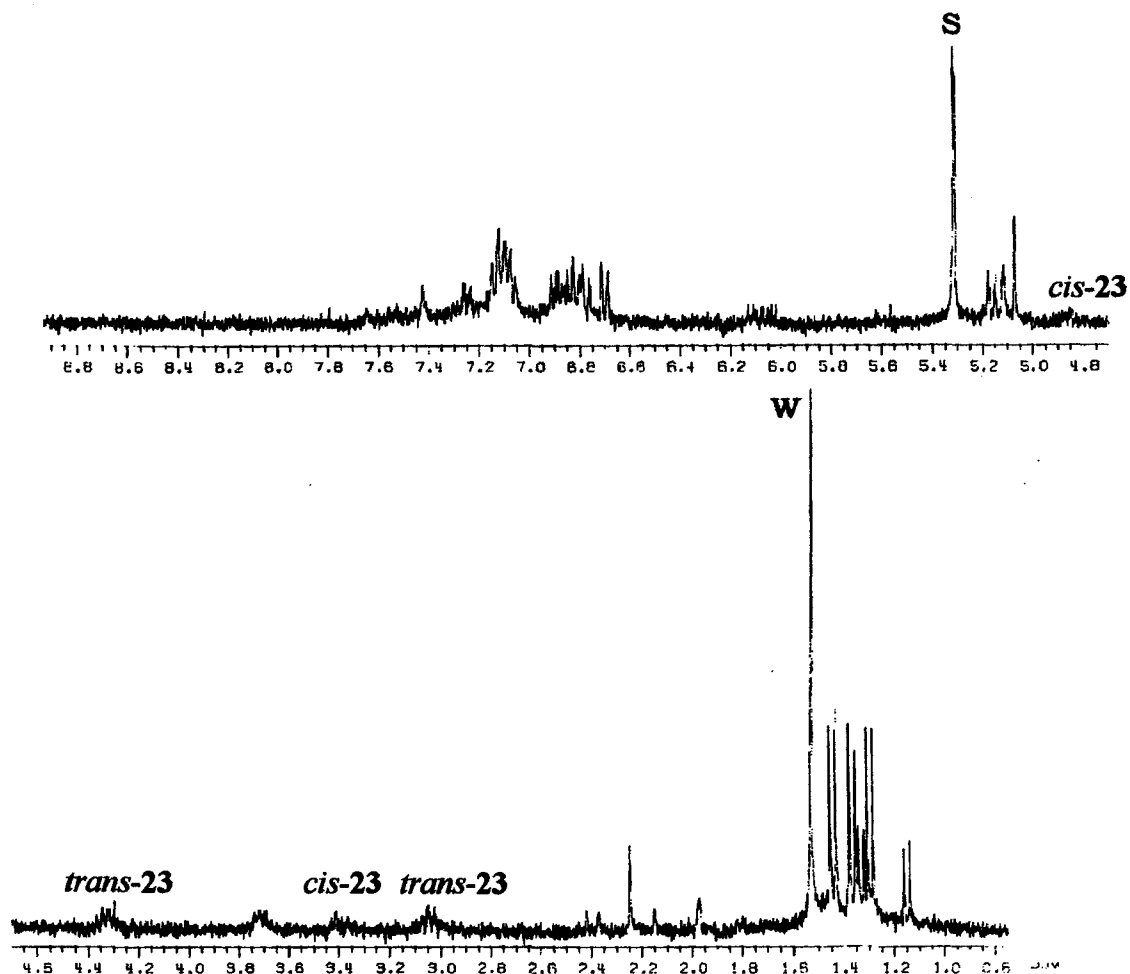


Figure B-8. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of the pyrolysis mixture from the FVP at 800 °C of *o*-(1-methylallyl)phenol (**16**) (S: CHDCl_2 , T: tetramethylsilane, W: H_2O , **23**: *cis*- and *trans*-2,3-dihydro-2,3-dimethylbenzofuran).

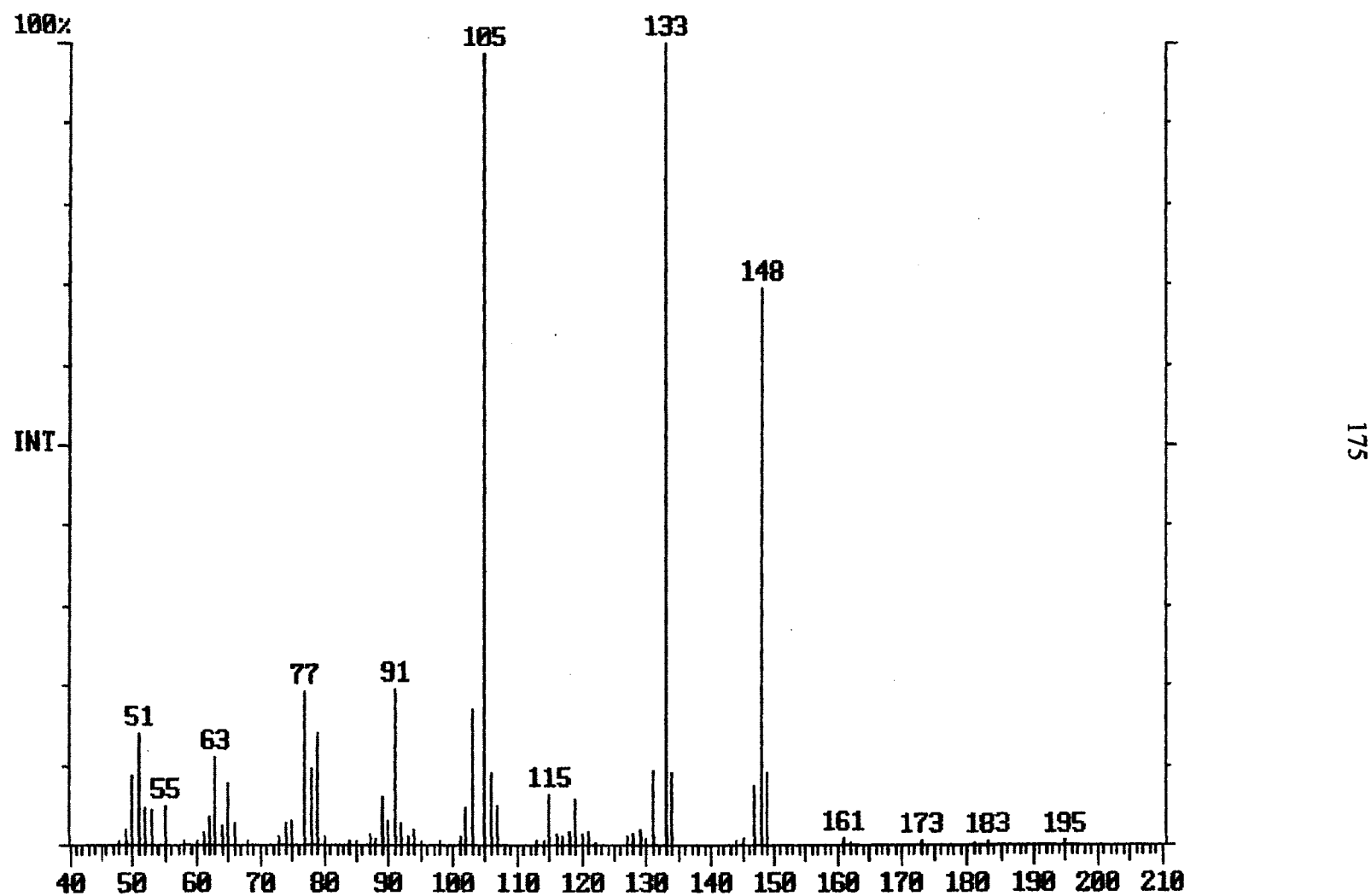


Figure B-9. GC-mass spectrum (EI, 70 eV) of the GC peak assigned to *trans*-2,3-dihydro-2,3-dimethylbenzofuran (23) in the pyrolysis mixture from the FVP at 900 °C of *o*-(1-methylallyl)phenol (16).

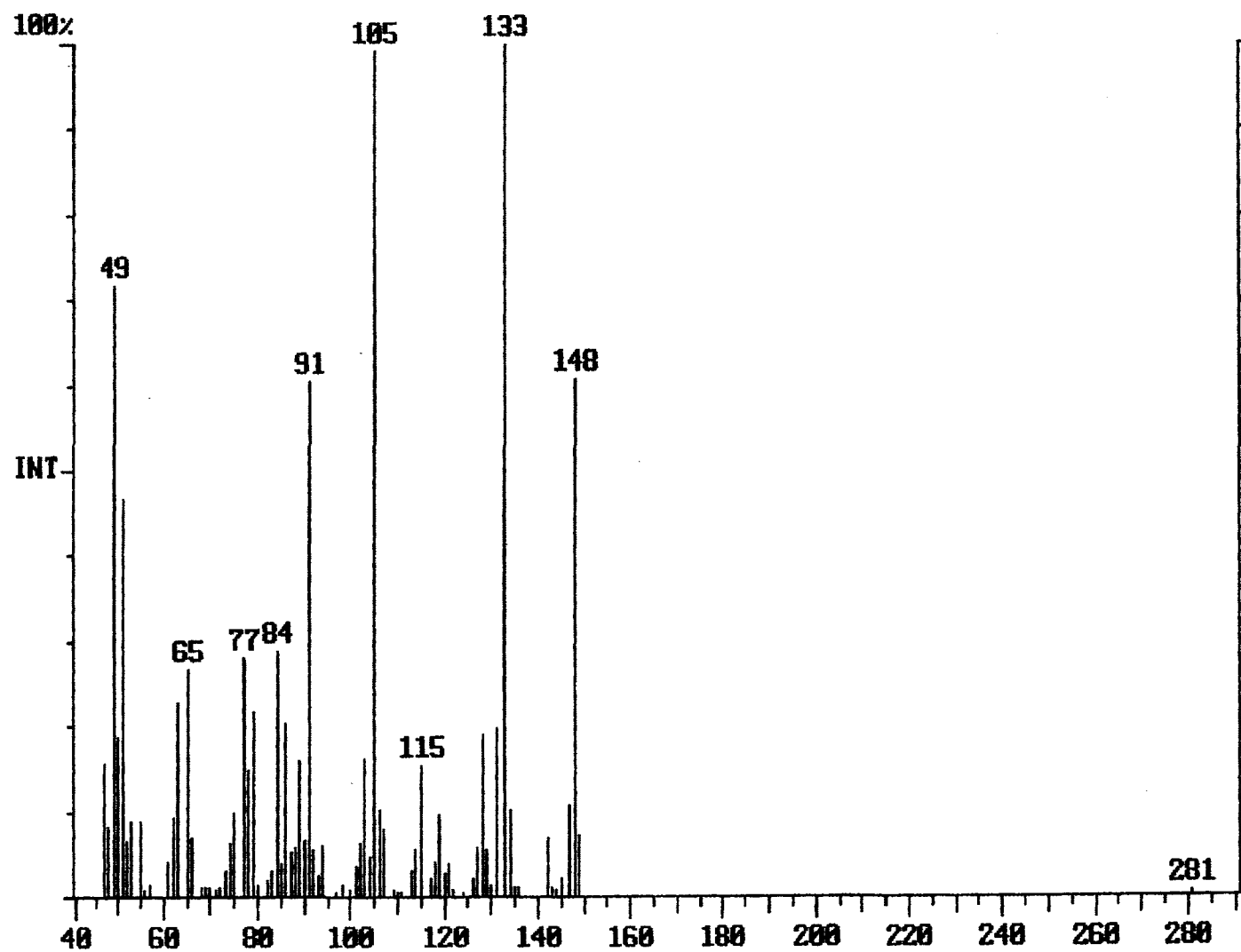


Figure B-10. GC-mass spectrum (EI, 70 eV) of the GC peak assigned to *cis*-2,3-dihydro-2,3-dimethylbenzofuran (23) in the pyrolysis mixture from the FVP at 900 °C of *o*-(1-methylallyl)phenol (16).

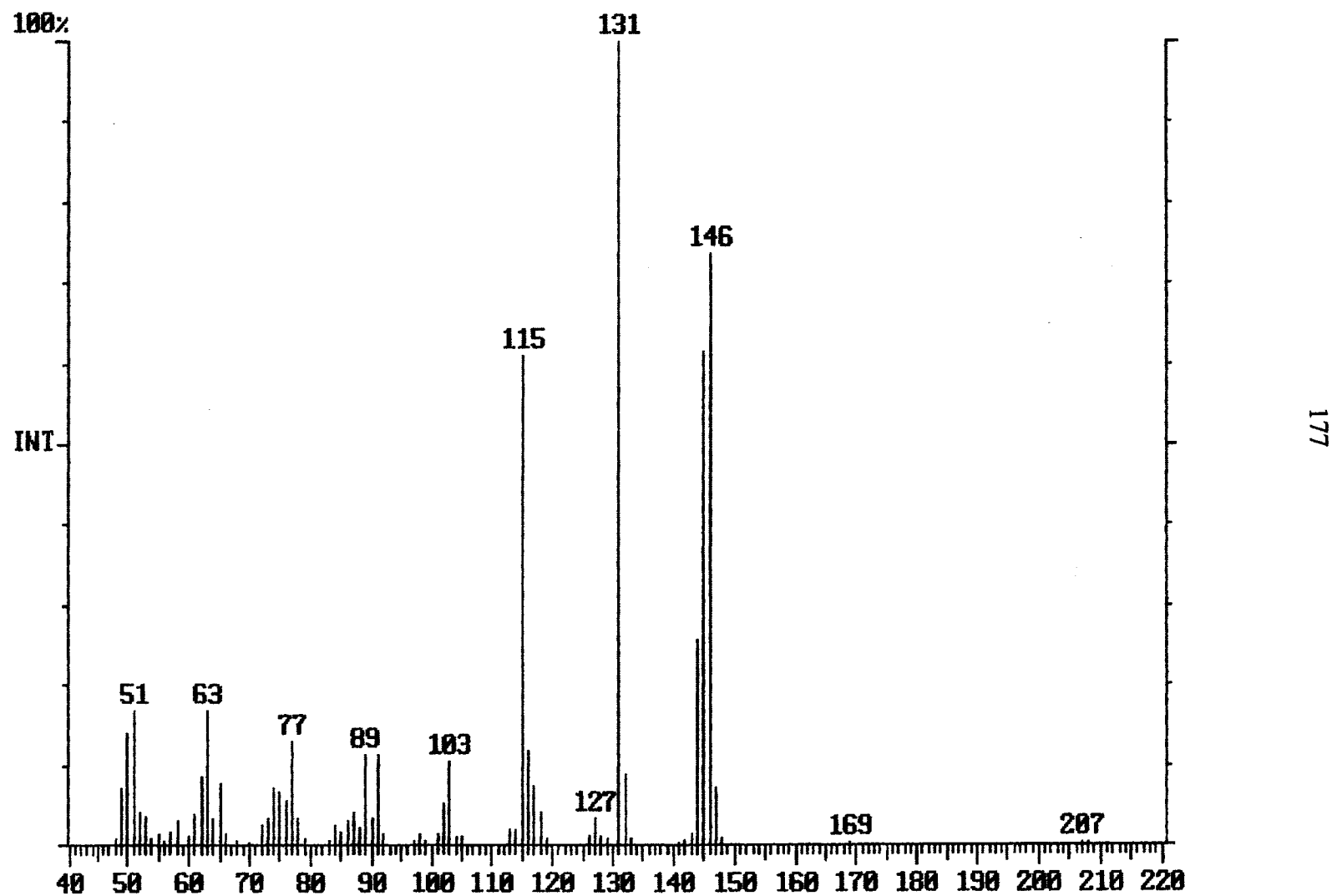


Figure B-11. GC-mass spectrum (EI, 70 eV) of the GC peak assigned to 2,3-dimethylbenzofuran (24) in the pyrolysis mixture from the FVP at 900 °C of *o*-(1-methylallyl)phenol (16).

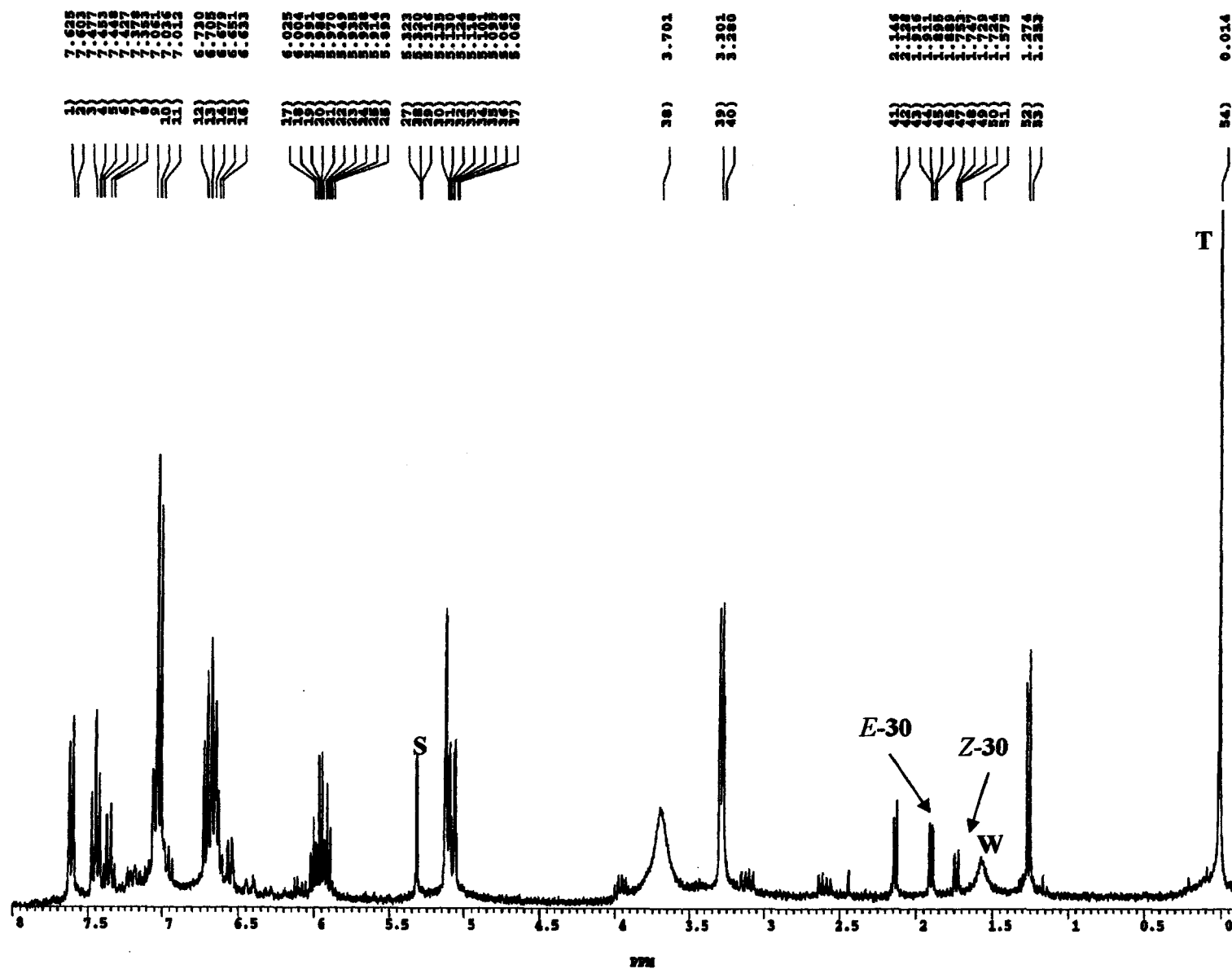


Figure B-13. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of the pyrolysis mixture from the FVP at 700 °C of *o*-allylaniline (14) (S: CH_2Cl_2 , T: tetramethylsilane, W: H_2O , *E/Z*-30 : *E/Z*-*o*-(1-propenyl)aniline).

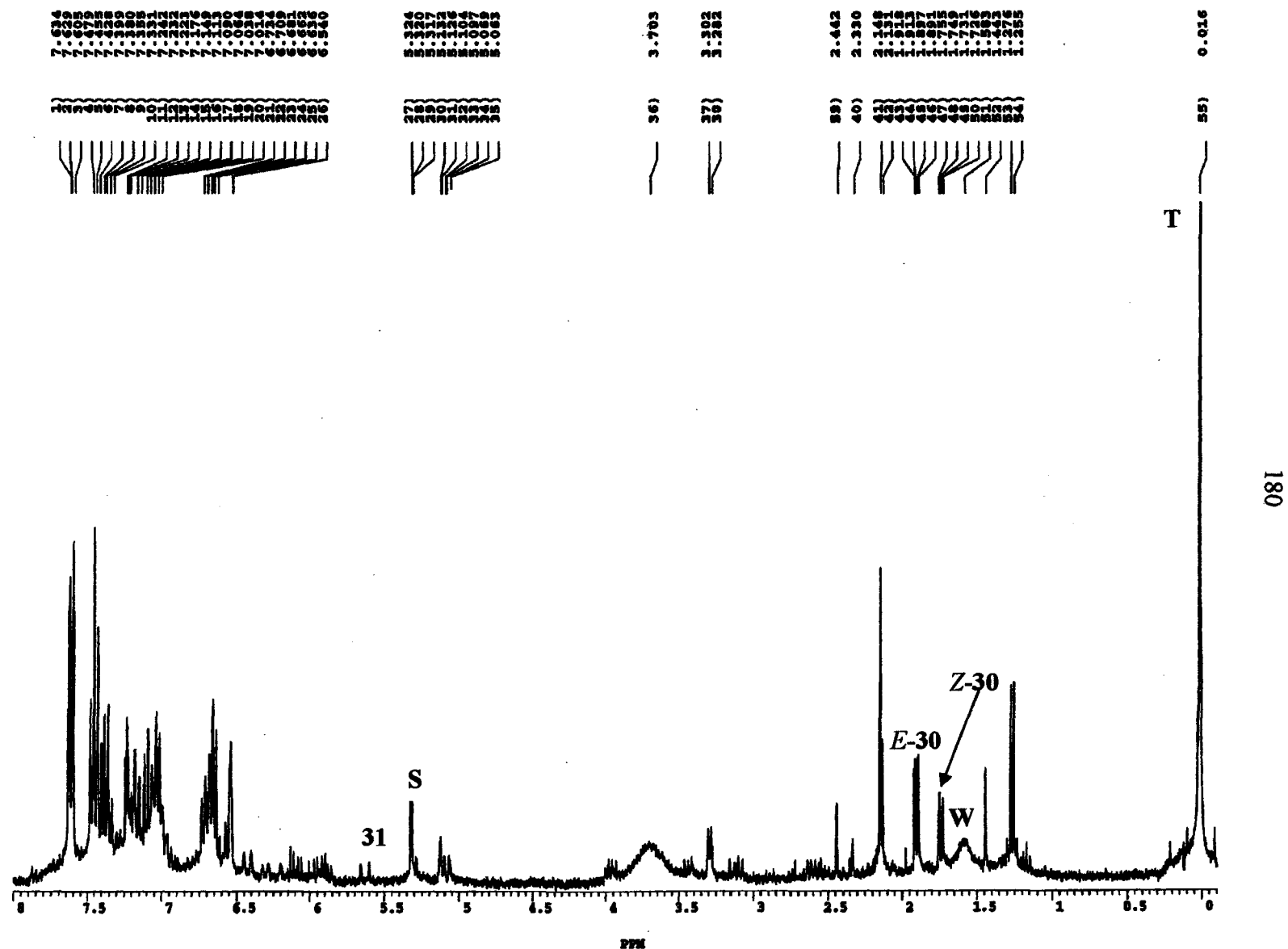


Figure B-14. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of the pyrolysis mixture from the FVP at 800 °C of *o*-allylaniline (**14**) (S: CHDCl_2 , T: tetramethylsilane, W: H_2O , E/Z-30: E/Z-*o*-(1-propenyl)aniline, 31: *o*-aminostyrene).

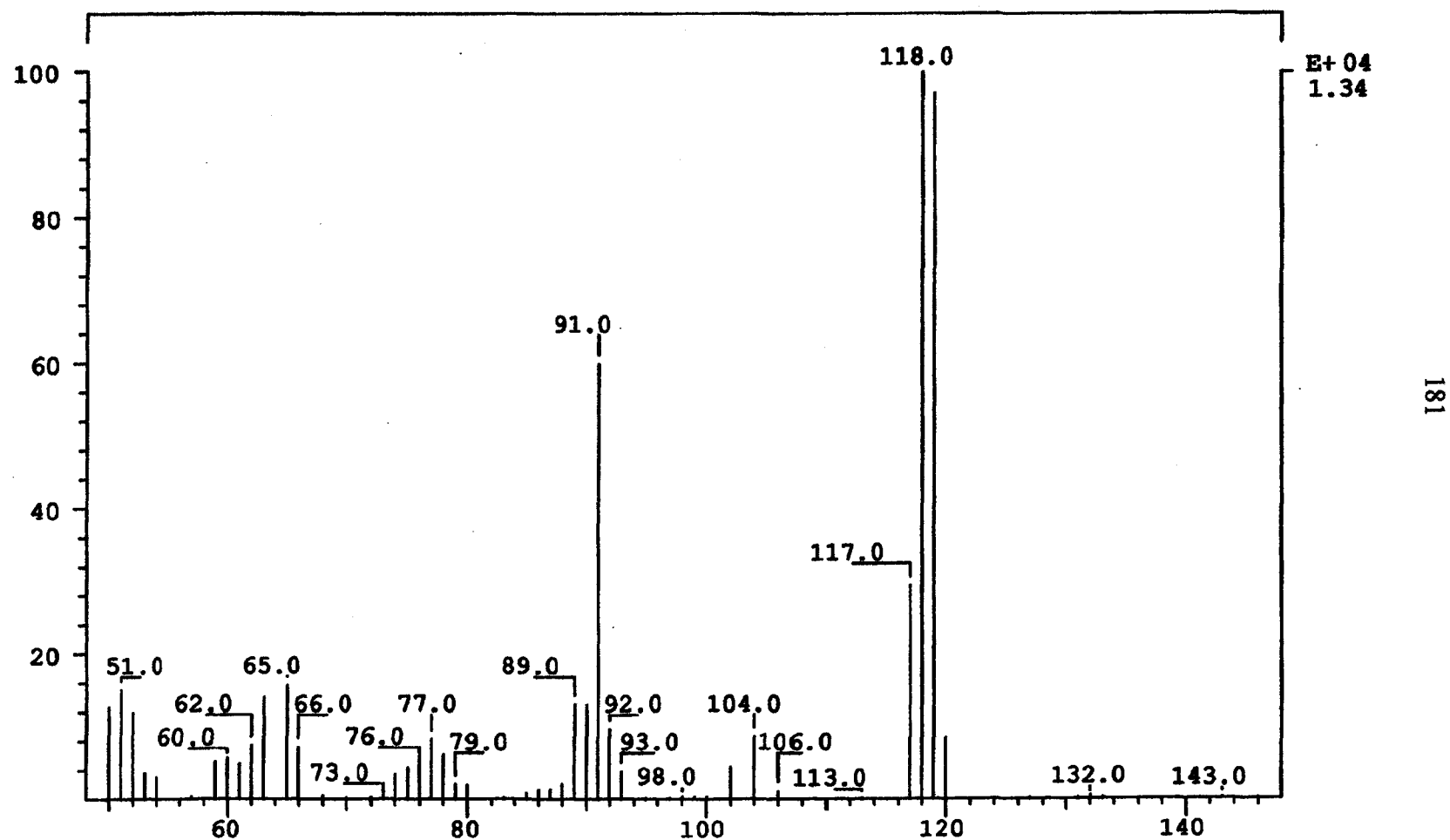


Figure B-15. GC-mass spectrum (EI, 70 eV) of the GC peak assigned to *o*-aminostyrene (31) in the pyrolysis mixture from the FVP at 800 °C of *o*-allylaniline (14).

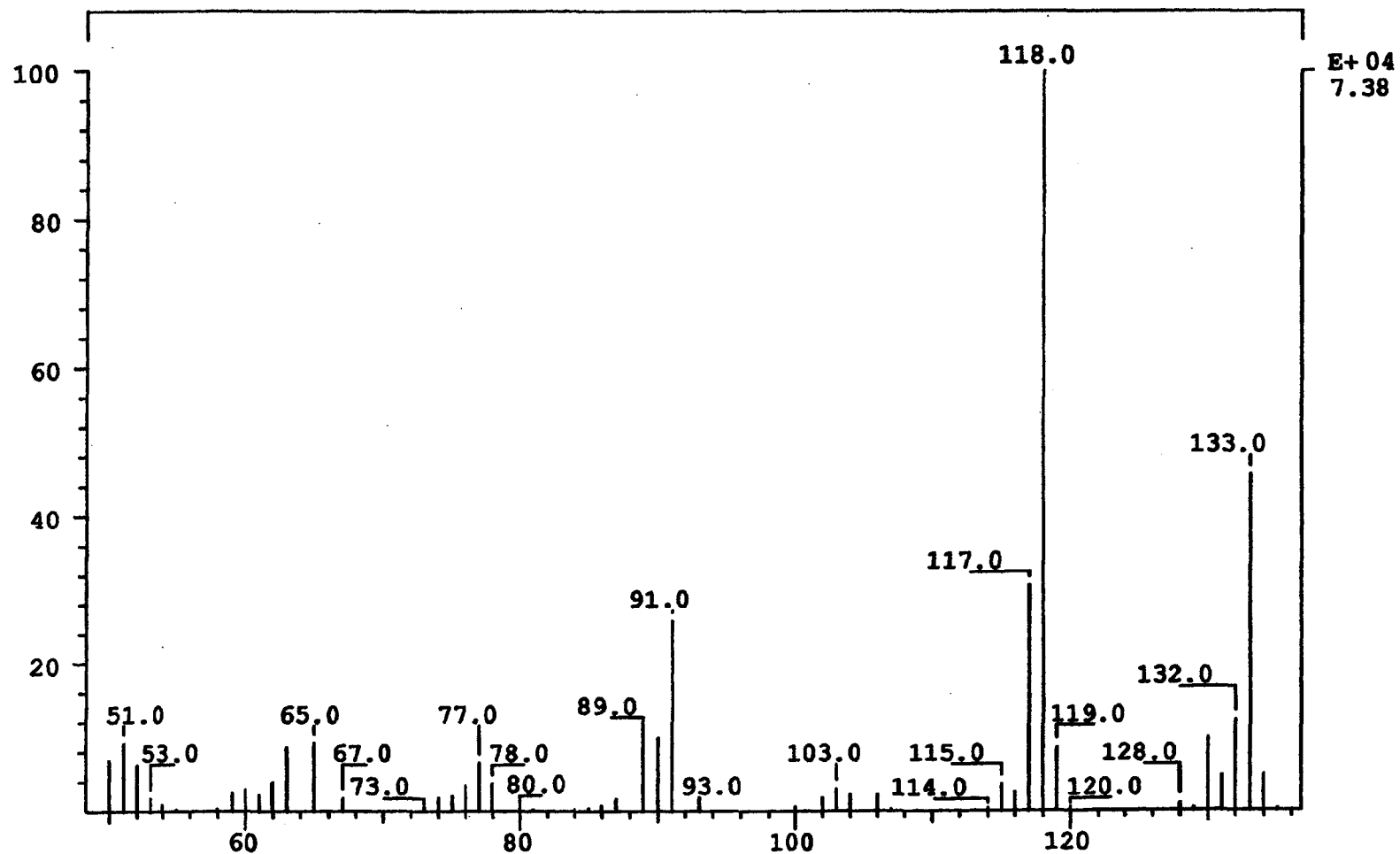


Figure B-16. GC-mass spectrum (EI, 70 eV) of the GC peak assigned to *E*-*o*-(1-propenyl)aniline (*E*-30) in the pyrolysis mixture from the FVP at 800 °C of *o*-allylaniline (14).

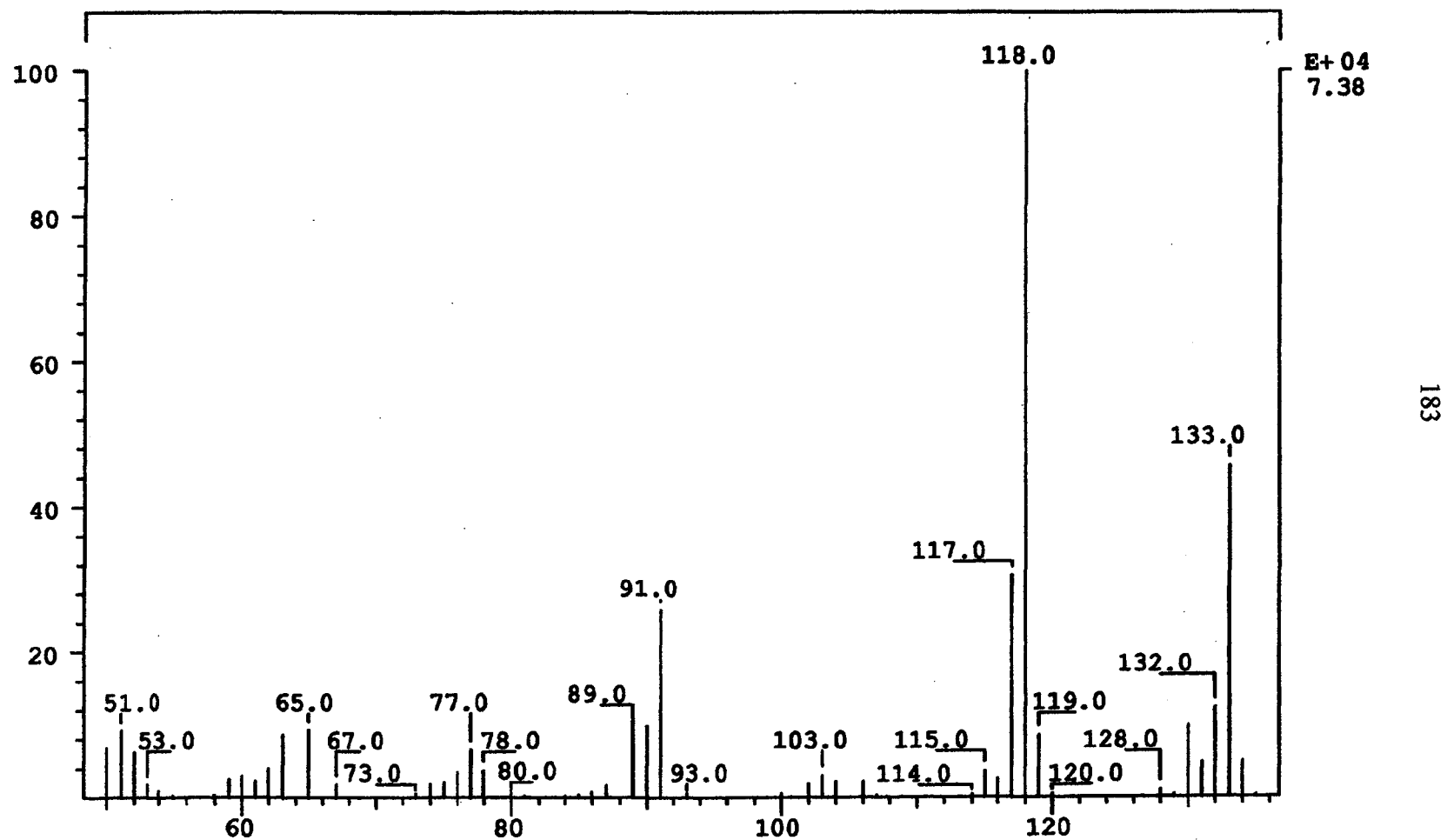


Figure B-17. GC-mass spectrum (EI, 70 eV) of the GC peak assigned to *Z*-*o*-(1-propenyl)aniline (**Z-30**) in the pyrolysis mixture from the FVP at 800 °C of *o*-allylaniline (**14**).

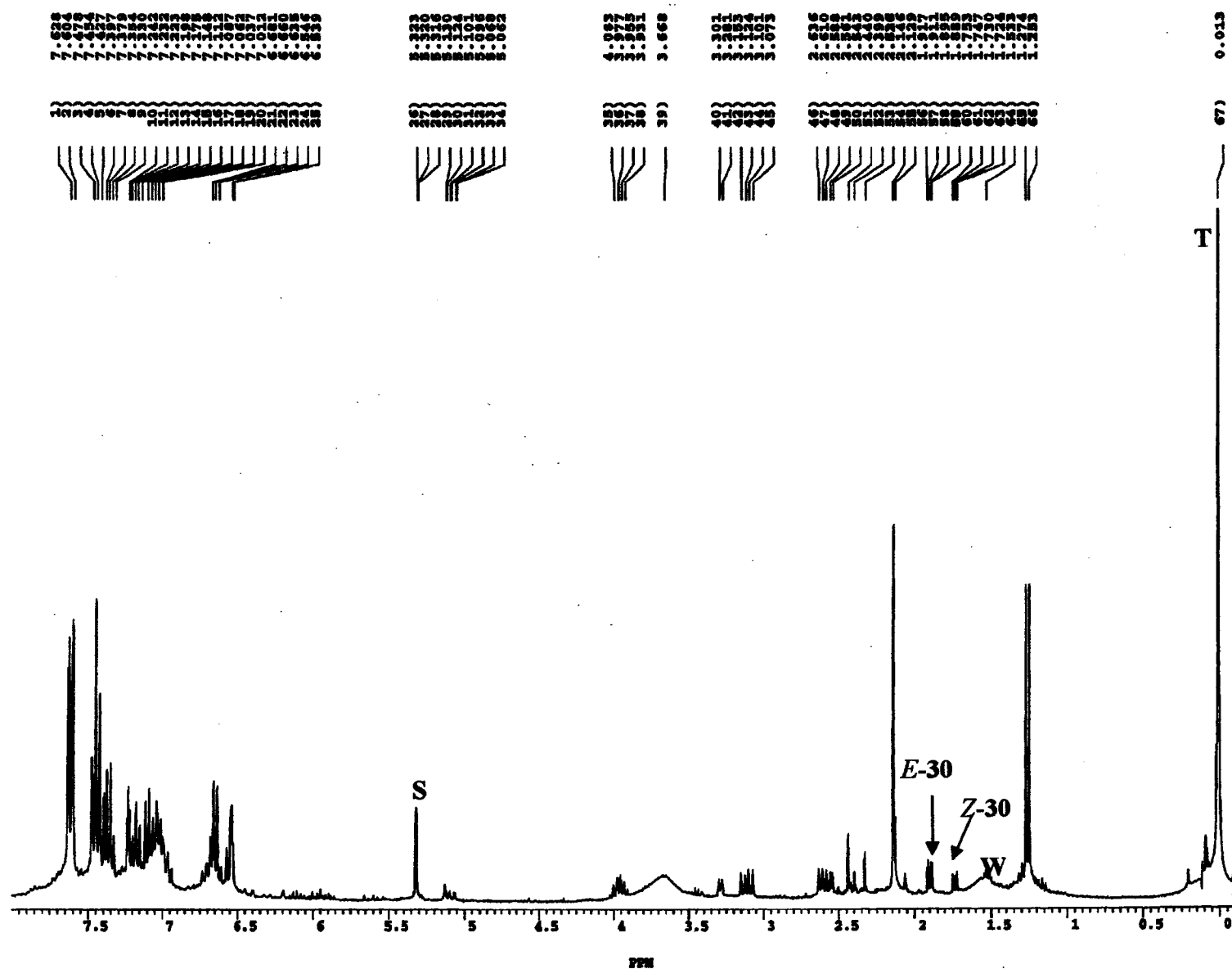


Figure B-18. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of the pyrolysis mixture from the FVP at 800 $^\circ\text{C}$ of 2-methylindoline(17) (S: CHDCl_2 , T: tetramethylsilane, W: H_2O , E/Z-30: E/Z-*o*-(1-propenyl)aniline).

APPENDIX C: FIGURES FOR CHAPTER 5

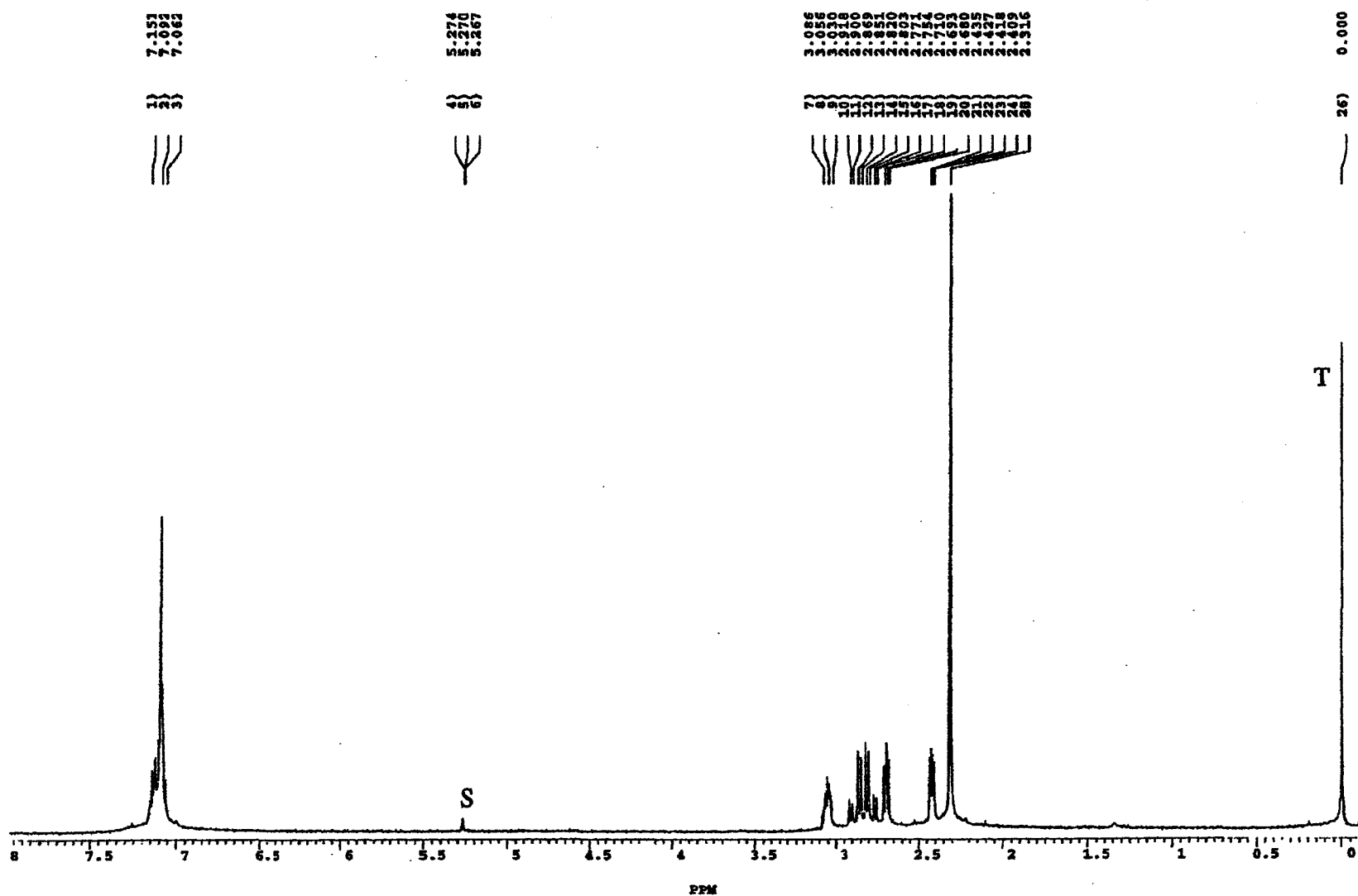


Figure C-1. ^1H NMR spectrum (300 MHz, $\text{CCl}_4:\text{CD}_2\text{Cl}_2$, 4:1 (v/v)) of 3-(*o*-tolyl)propene oxide (**6**) with durene standard (D: durene, S: CHDCl_2 , T: tetramethylsilane, W: H_2O).

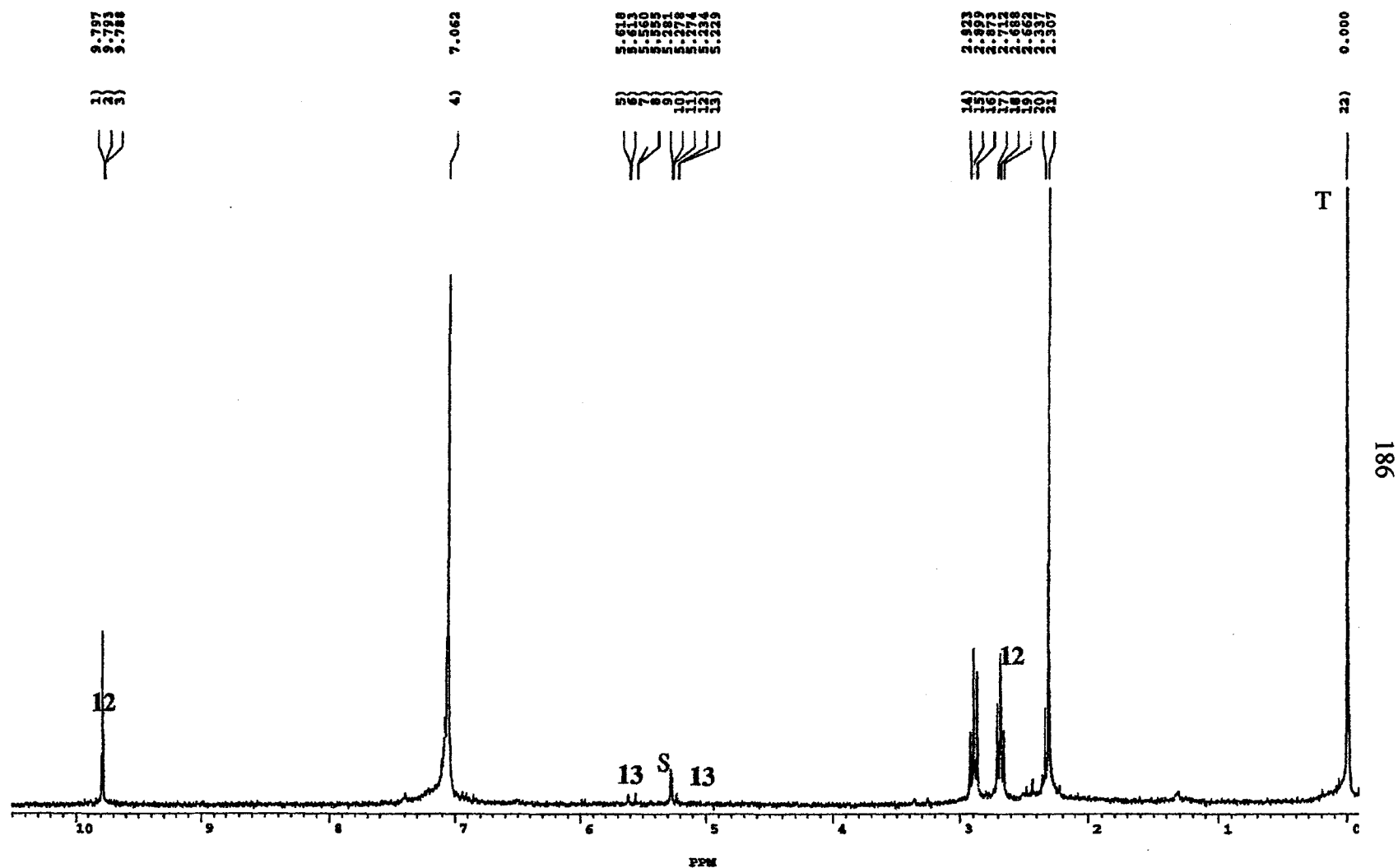


Figure C-2. ^1H NMR spectrum (300 MHz, $\text{CCl}_4:\text{CD}_2\text{Cl}_2$, 4:1 (v/v)) of the pyrolysis mixture from the FVP at 500 $^\circ\text{C}$ of 3-(*o*-tolyl)propene oxide (**6**) (**12**: 3-*o*-tolylpropionaldehyde, **13**: *o*-methylstyrene, S: CHDCl_2 , T: tetramethylsilane).

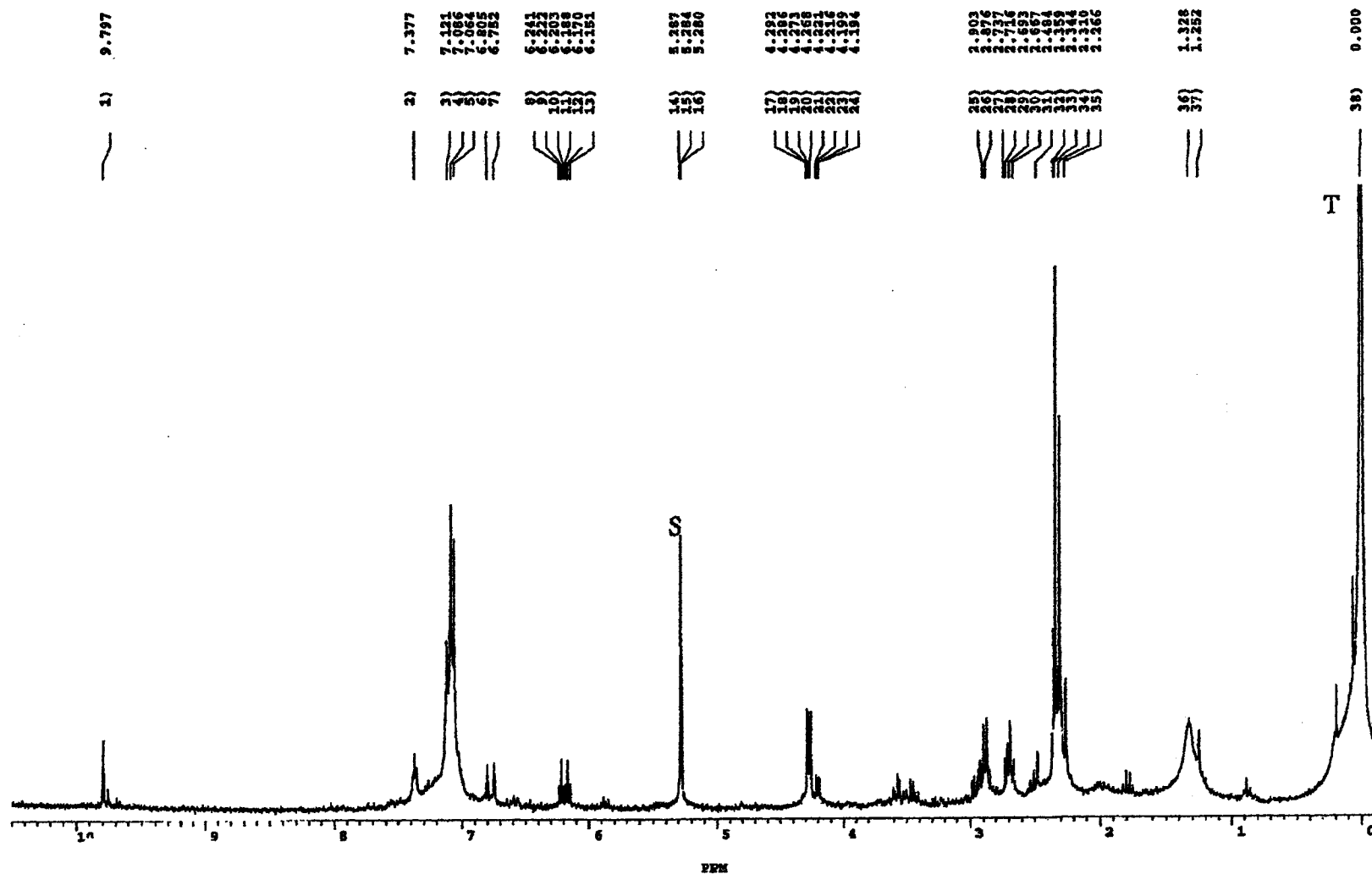


Figure C-3. ^1H NMR spectrum (300 MHz, $\text{CCl}_4:\text{CD}_2\text{Cl}_2$, 4:1 (v/v)) of the sample head residue from the FVP at 500 °C of 3-(*o*-tolyl)propene oxide (**6**) (S: CHDCl_2 , T: tetramethylsilane).

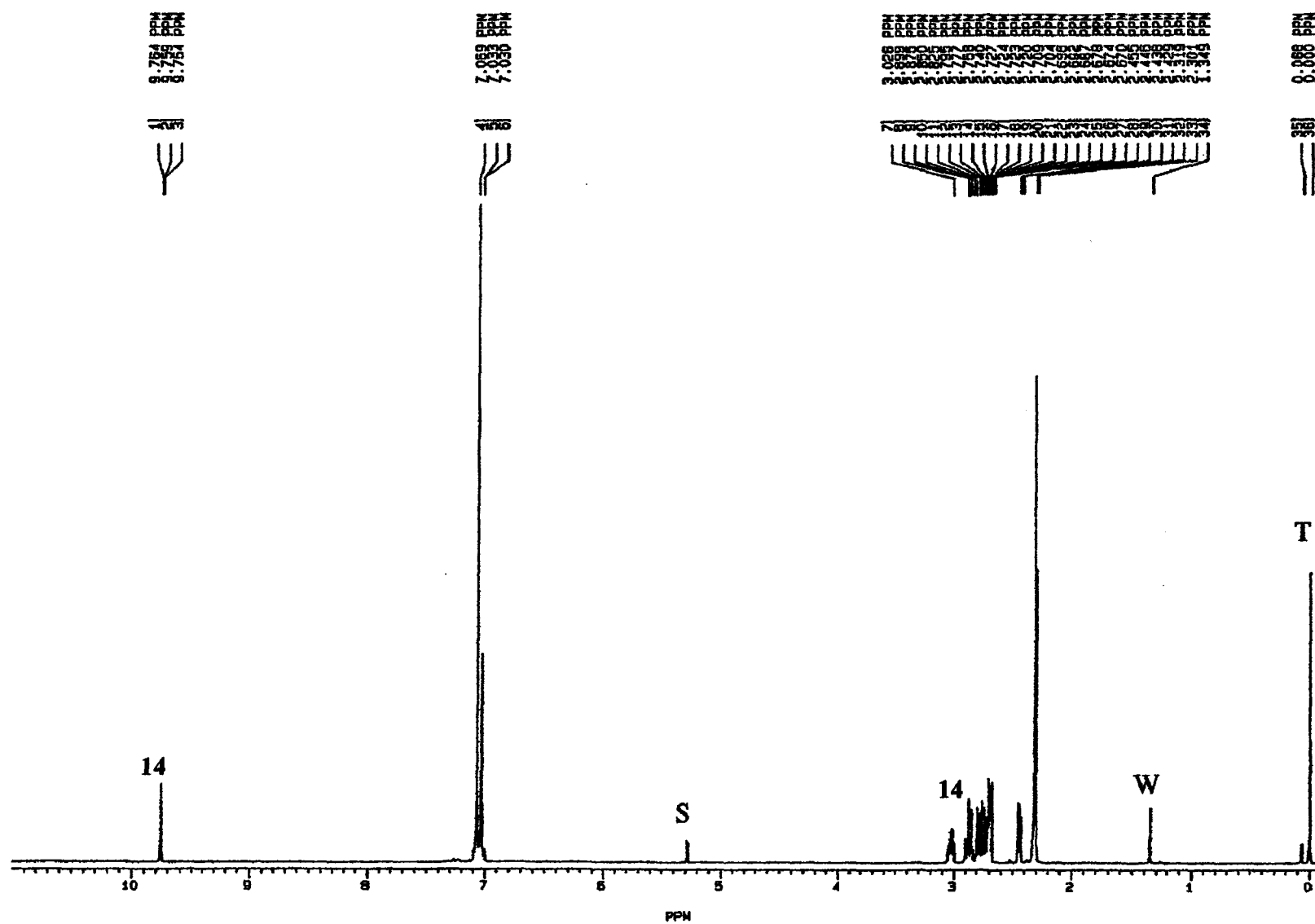


Figure C-6. ^1H NMR spectrum (300 MHz, $\text{CCl}_4:\text{CD}_2\text{Cl}_2$, 3:1 (v/v)) of the pyrolysis mixture from the FVP at 250 °C of 3-(*p*-tolyl)propene oxide (7) (14: 3-*p*-tolylpropionaldehyde, S: CHDCl_2 , T: tetramethylsilane, W: H_2O).

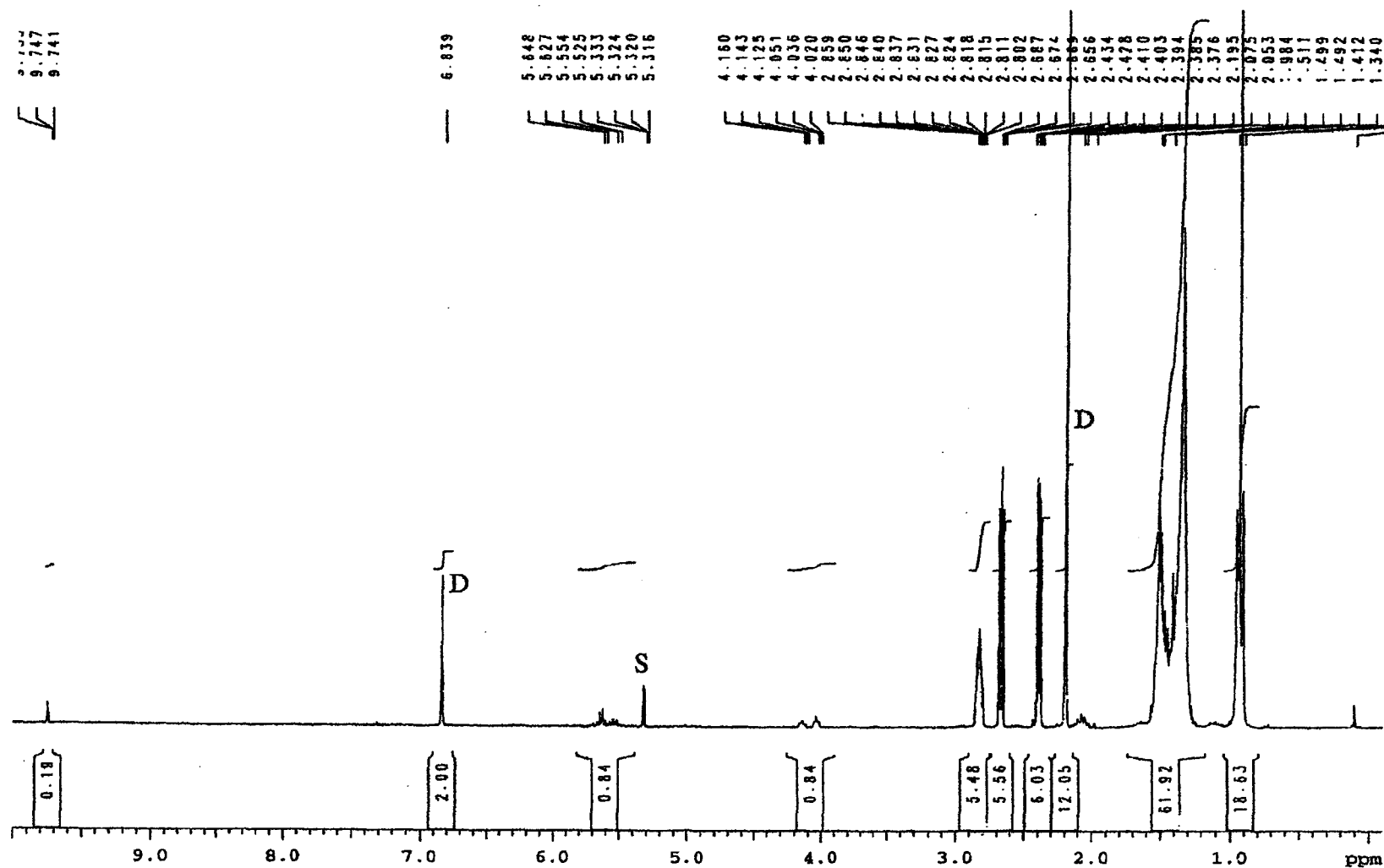


Figure C-10. ^1H NMR spectrum (300 MHz, $\text{CCl}_4:\text{CD}_2\text{Cl}_2$, 3:1 (v/v)) of the pyrolysis mixture from the FVP at 300 °C of 1-octene oxide (8) (D: durene, S: CHDCl_2).

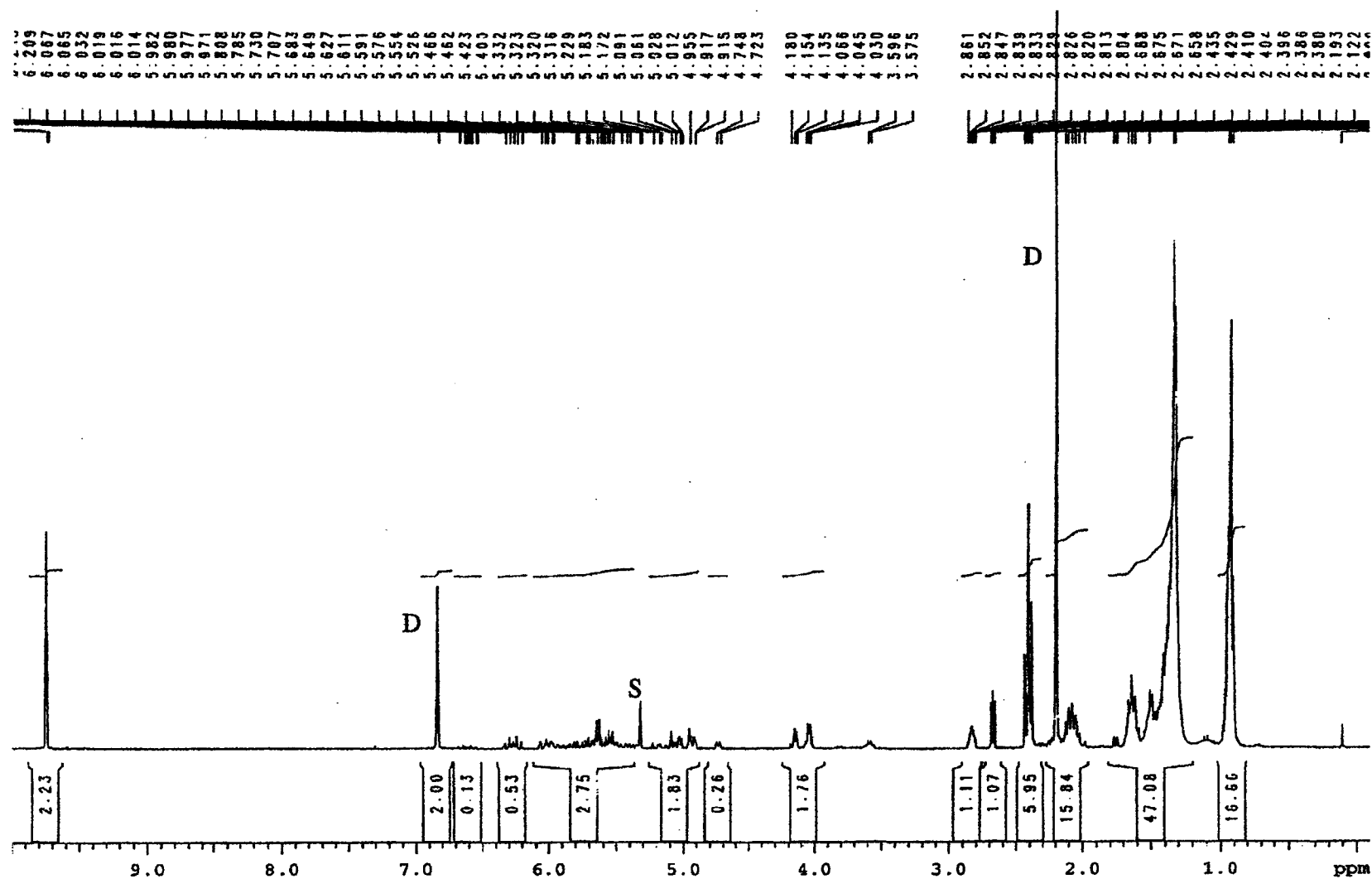


Figure C-11. ^1H NMR spectrum (300 MHz, $\text{CCl}_4:\text{CD}_2\text{Cl}_2$, 3:1 (v/v)) of the pyrolysis mixture from the FVP at 450 °C of 1-octene oxide (**8**) (D: durene, S: CHDCl_2).

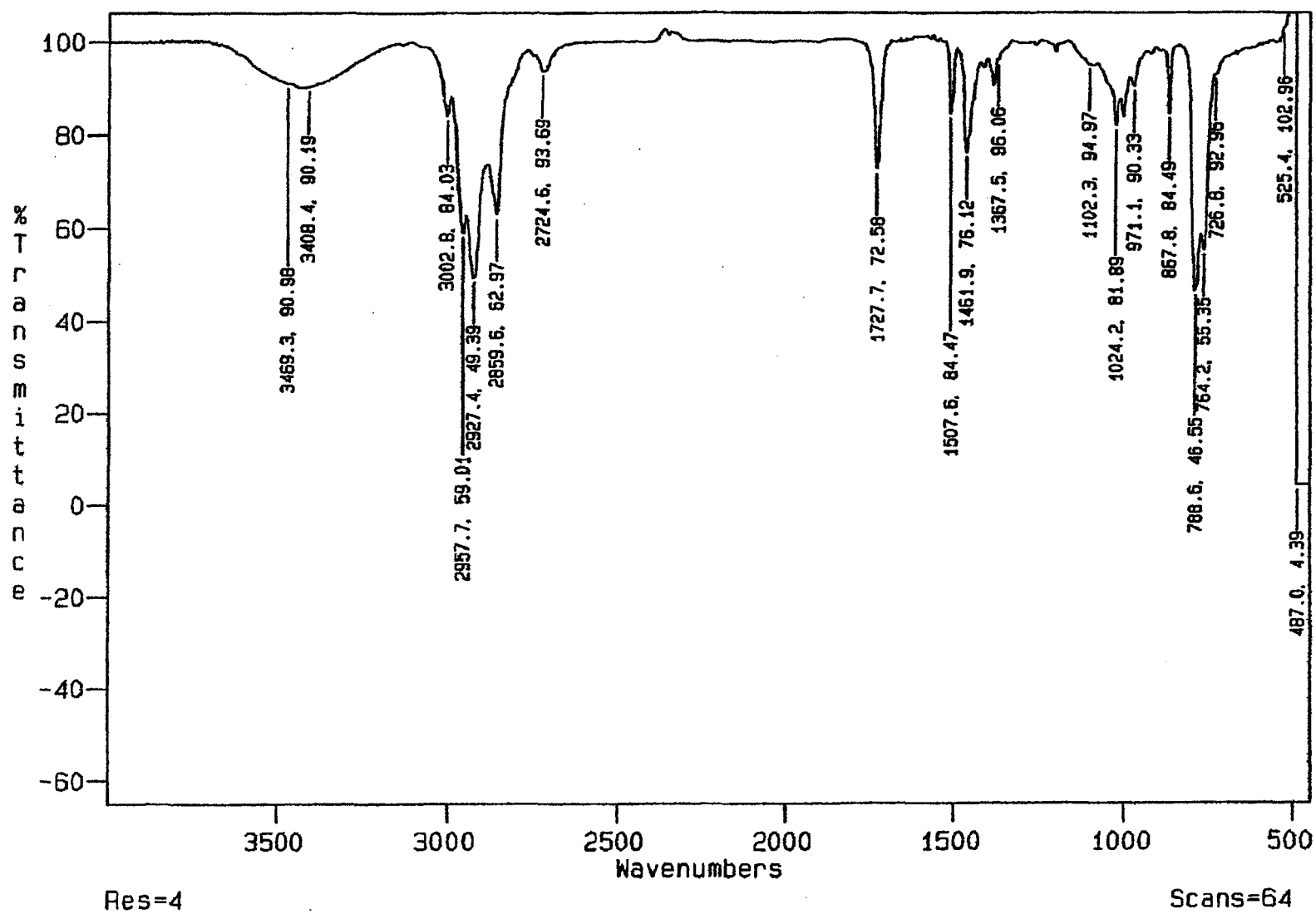


Figure C-12. IR spectrum (CCl₄) of the pyrolysis mixture from the FVP at 450 °C of 1-octene oxide (8).

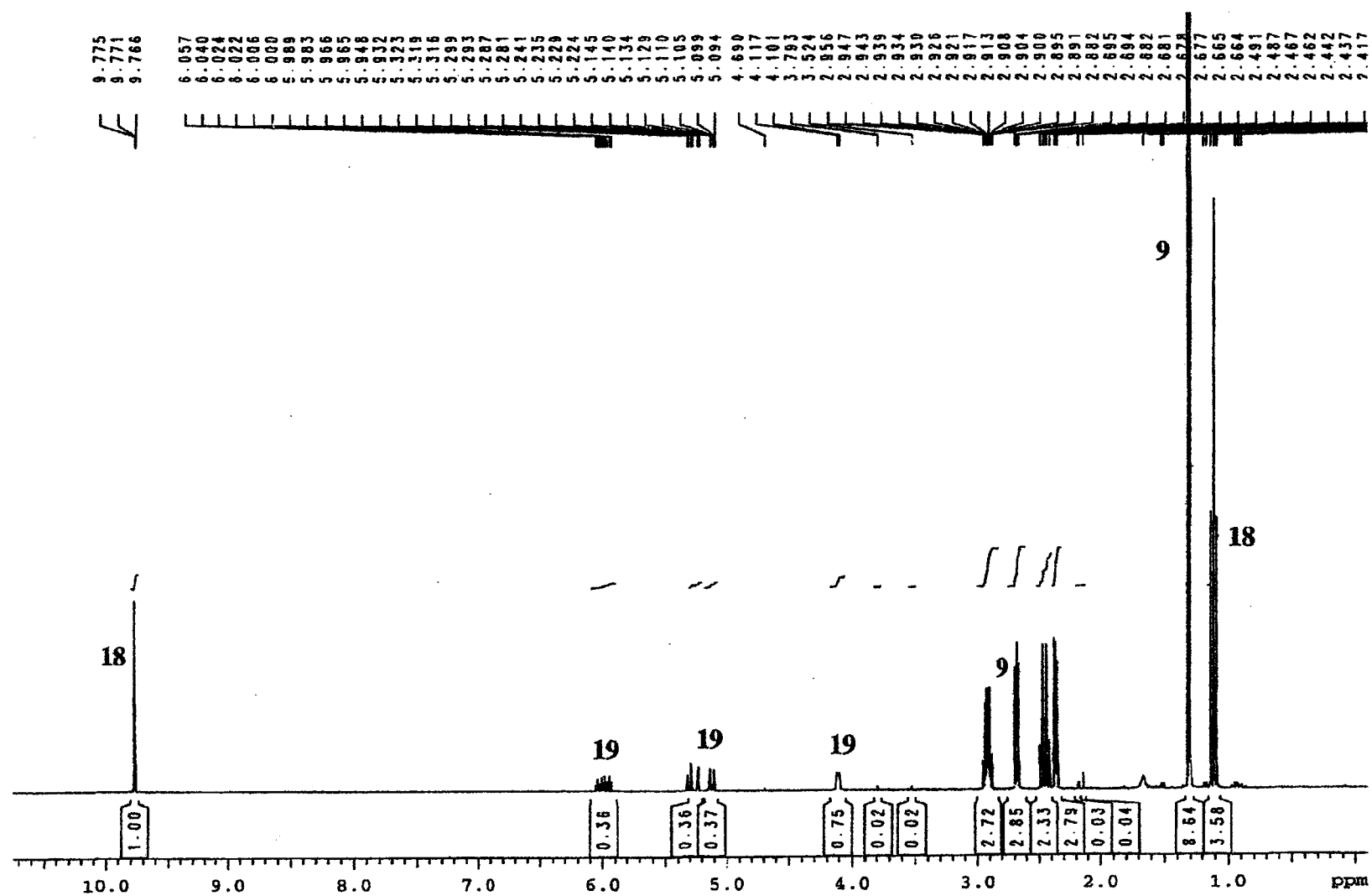


Figure C-14. ^1H NMR spectrum (300 MHz, $\text{CCl}_4:\text{CD}_2\text{Cl}_2$, 3:1 (v/v)) of the pyrolysis mixture from the FVP at 800 °C (1×10^{-5} torr) of propene oxide (9) (18: propanal, 19: allyl alcohol, S: CHDCl_2).

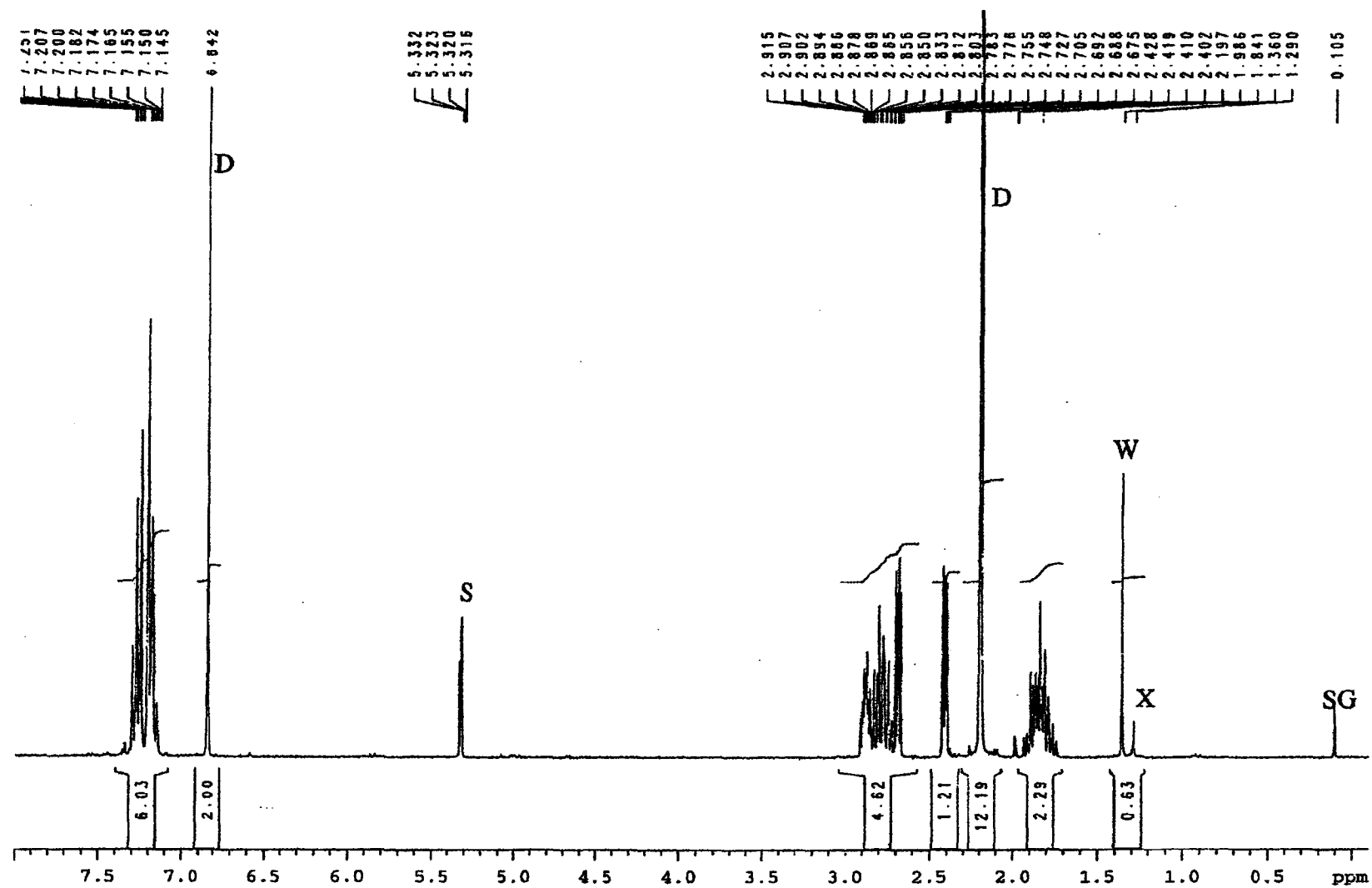


Figure C-15. ¹H NMR spectrum (300 MHz, CCl₄:CD₂Cl₂, 3:1 (v/v)) of 4-phenyl-1-butene oxide (10) with durene standard (D: durene, S: CHDCl₂, SG: silicone grease, W: H₂O, X: unknown impurity).

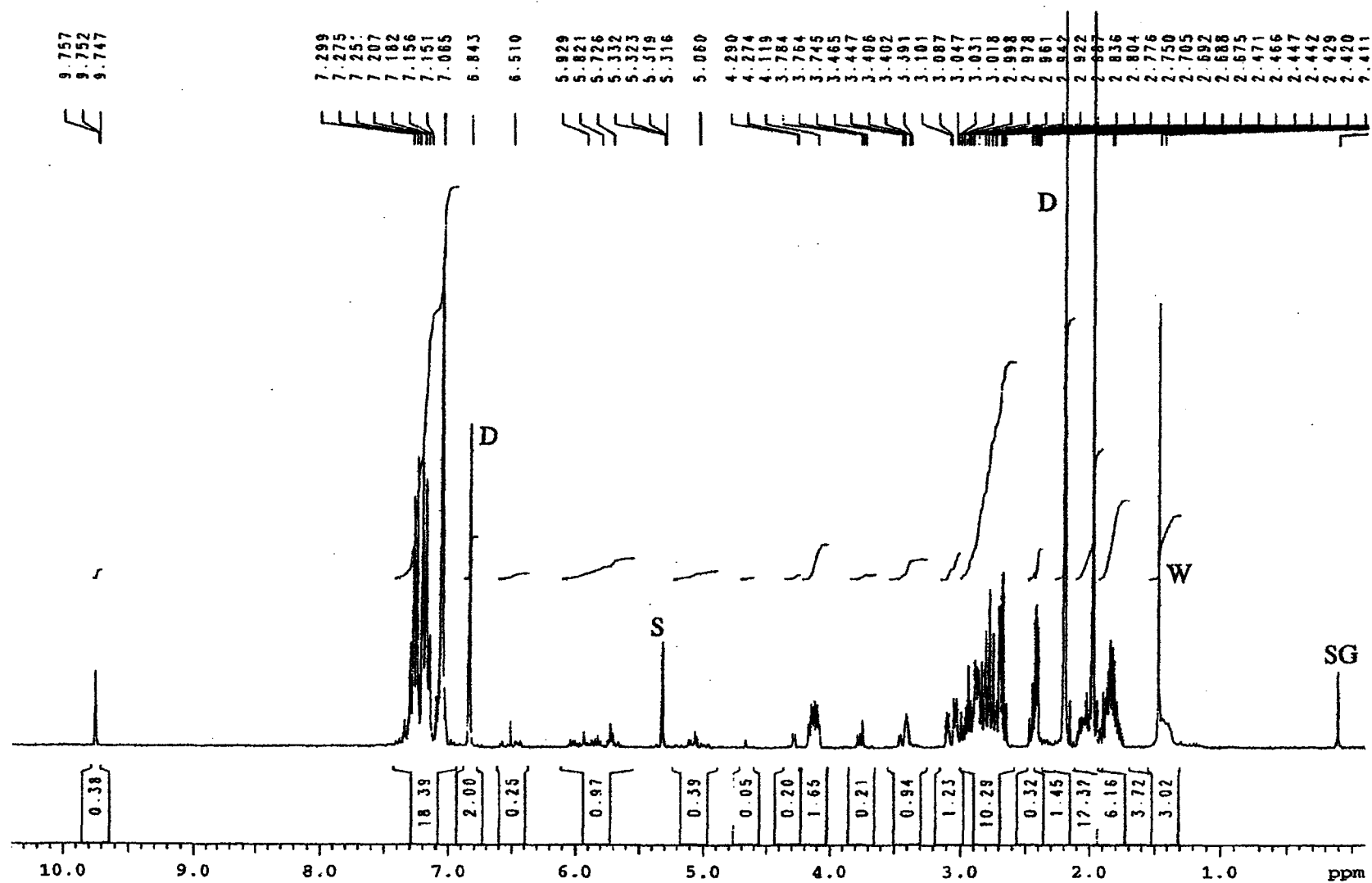


Figure C-16. ^1H NMR spectrum (300 MHz, $\text{CCl}_4:\text{CD}_2\text{Cl}_2$, 3:1 (v/v)) of the pyrolysis mixture from the FVP of 4-phenyl-1-butene oxide (10) at 400 $^\circ\text{C}$ (D: durene, S: CHDCl_2 , SG: silicone grease).

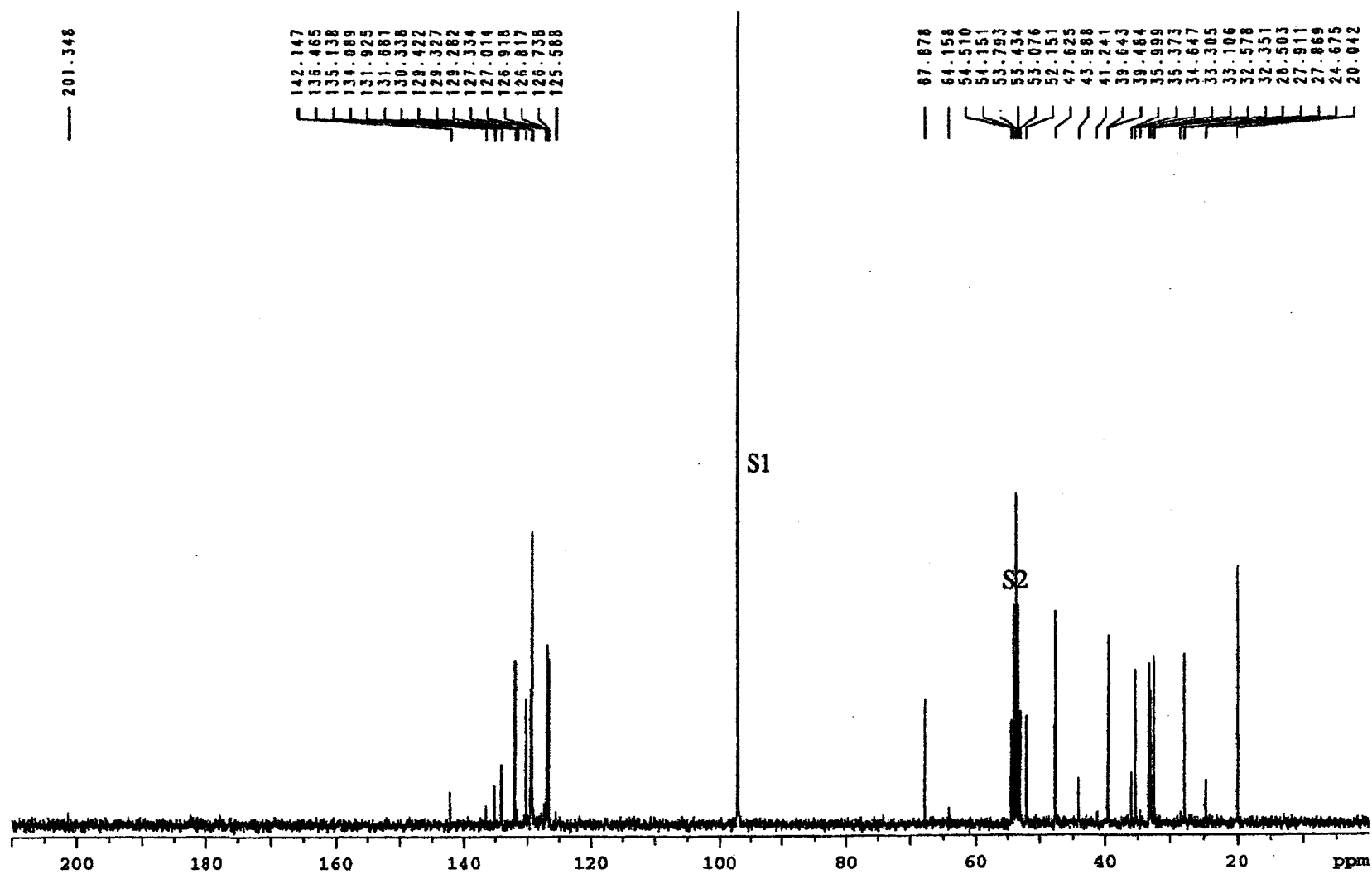


Figure C-17. ^{13}C NMR spectrum (75.5 MHz, $\text{CCl}_4:\text{CD}_2\text{Cl}_2$, 3:1 (v/v)) of the pyrolysis mixture from the FVP of 4-phenyl-1-butene oxide (**10**) 400 °C (S1: CHDCl_2 , S2: CCl_4).

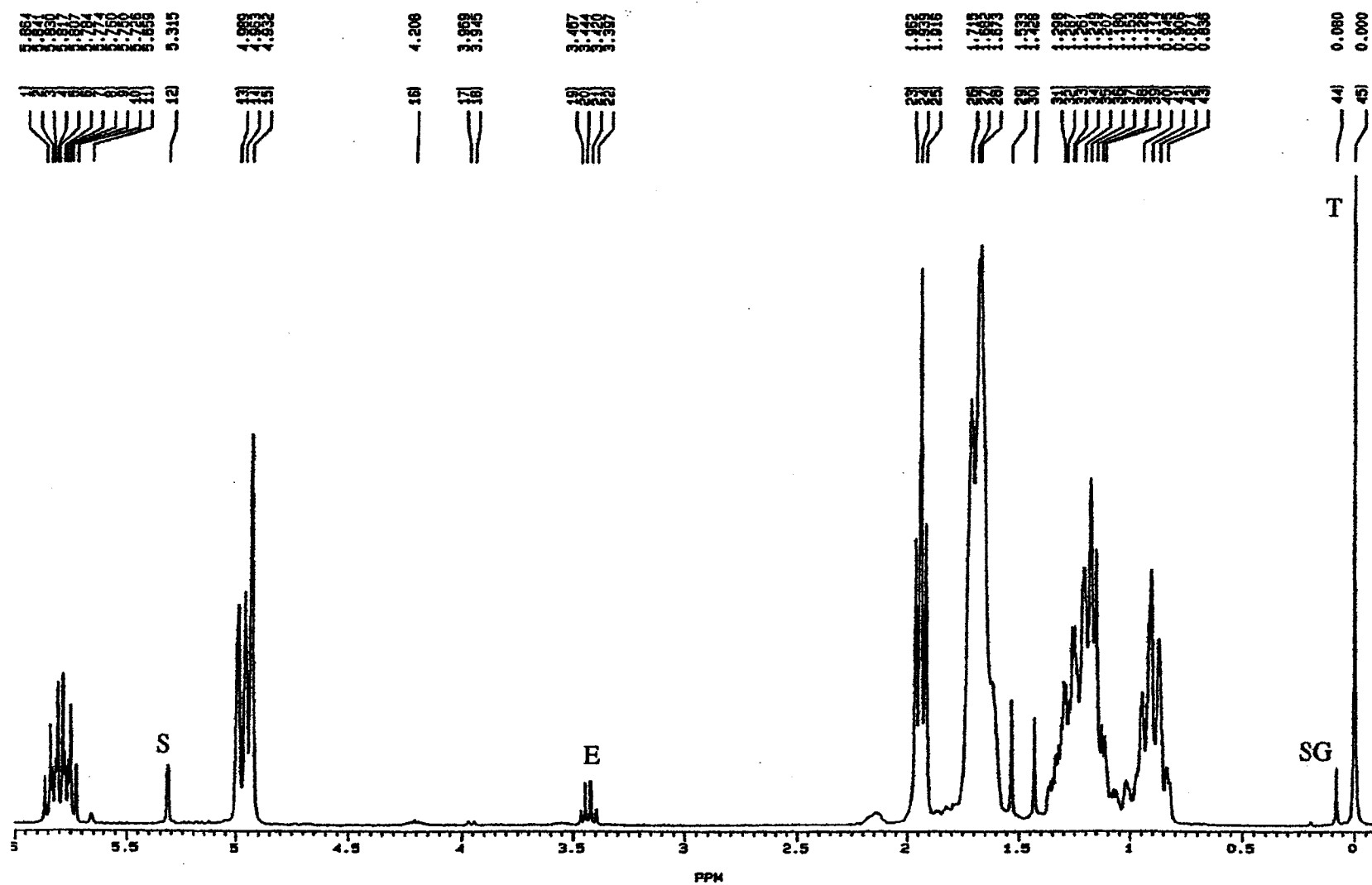


Figure C-19. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of allylcyclohexane (E: ether, S: CHDCl_2 , SG: silicone grease, T: tetramethylsilane, W: H_2O).

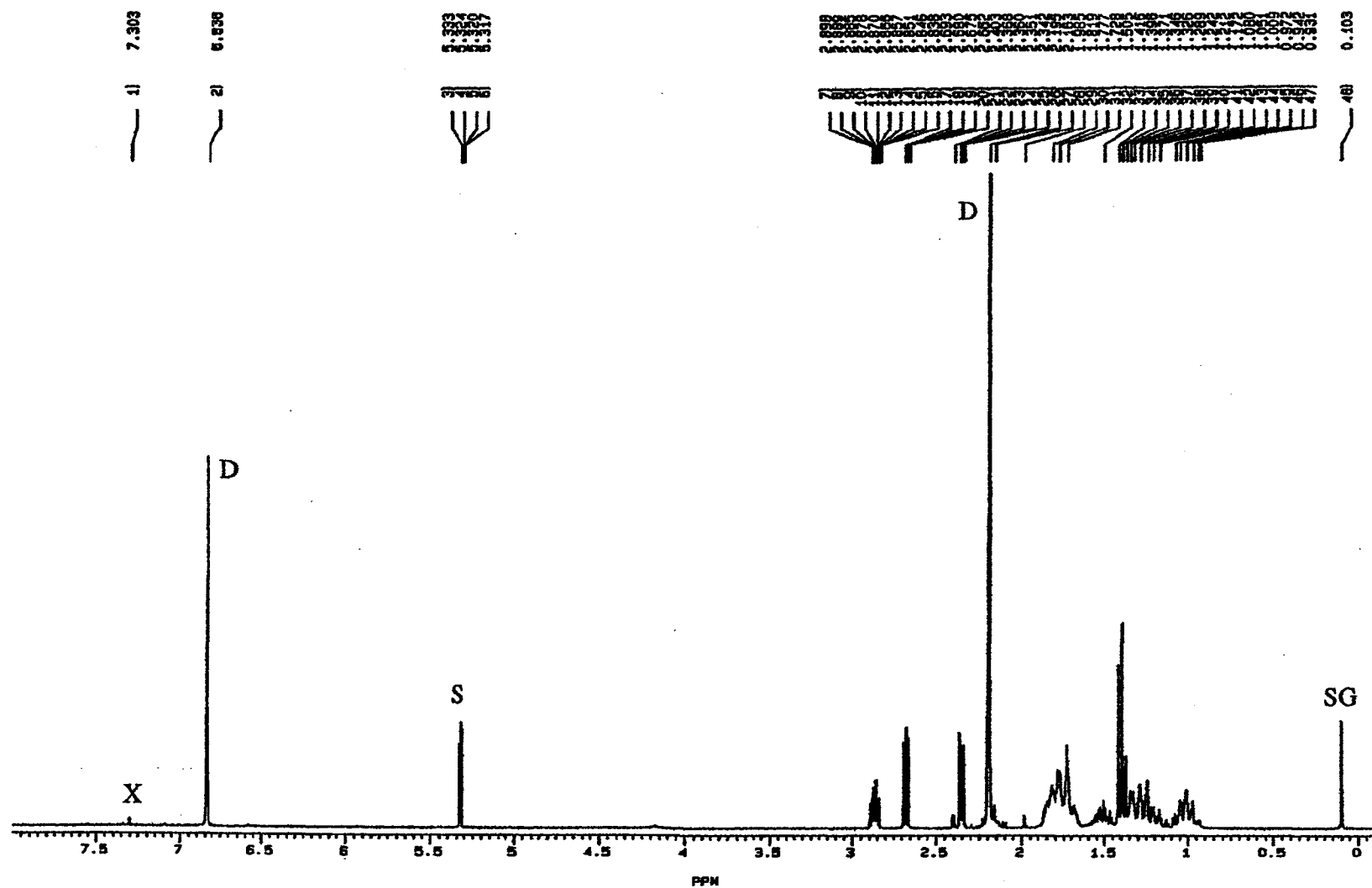
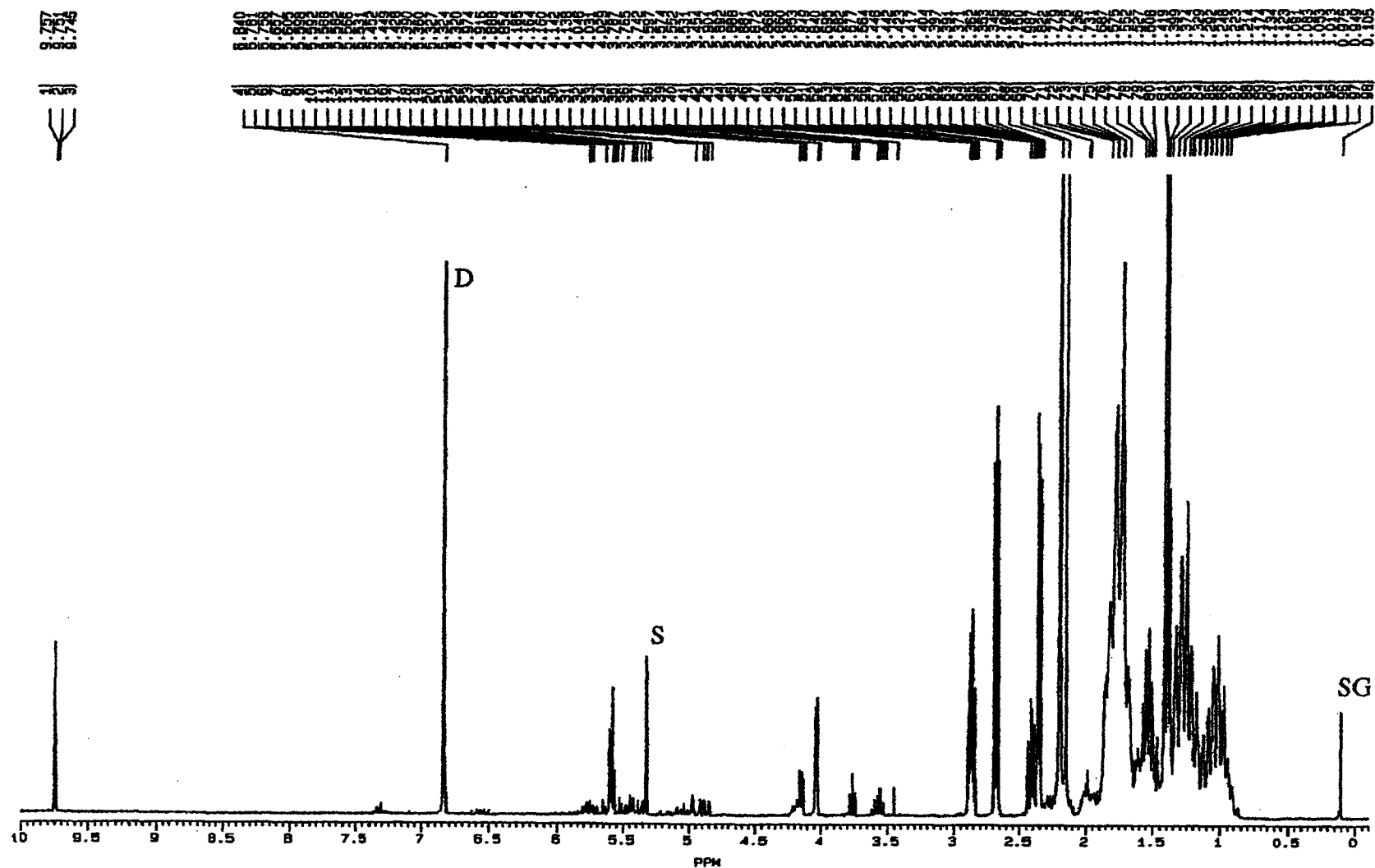


Figure C-20. ^1H NMR spectrum (300 MHz, $\text{CCl}_4:\text{CD}_2\text{Cl}_2$, 3:1 (v/v)) of 3-cyclohexylpropene oxide (11) with durene standard (D: durene, S: CHDCl_2 , SG: silicone grease, W: H_2O , X: unknown impurity).



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Figure C-21. ^1H NMR spectrum (300 MHz, $\text{CCl}_4:\text{CD}_2\text{Cl}_2$, 3:1 (v/v)) of the pyrolysis mixture from the FVP of 3-cyclohexylpropene oxide (11) at 300 °C (D: durene, S: CHDCl_2 , SG: silicone grease).

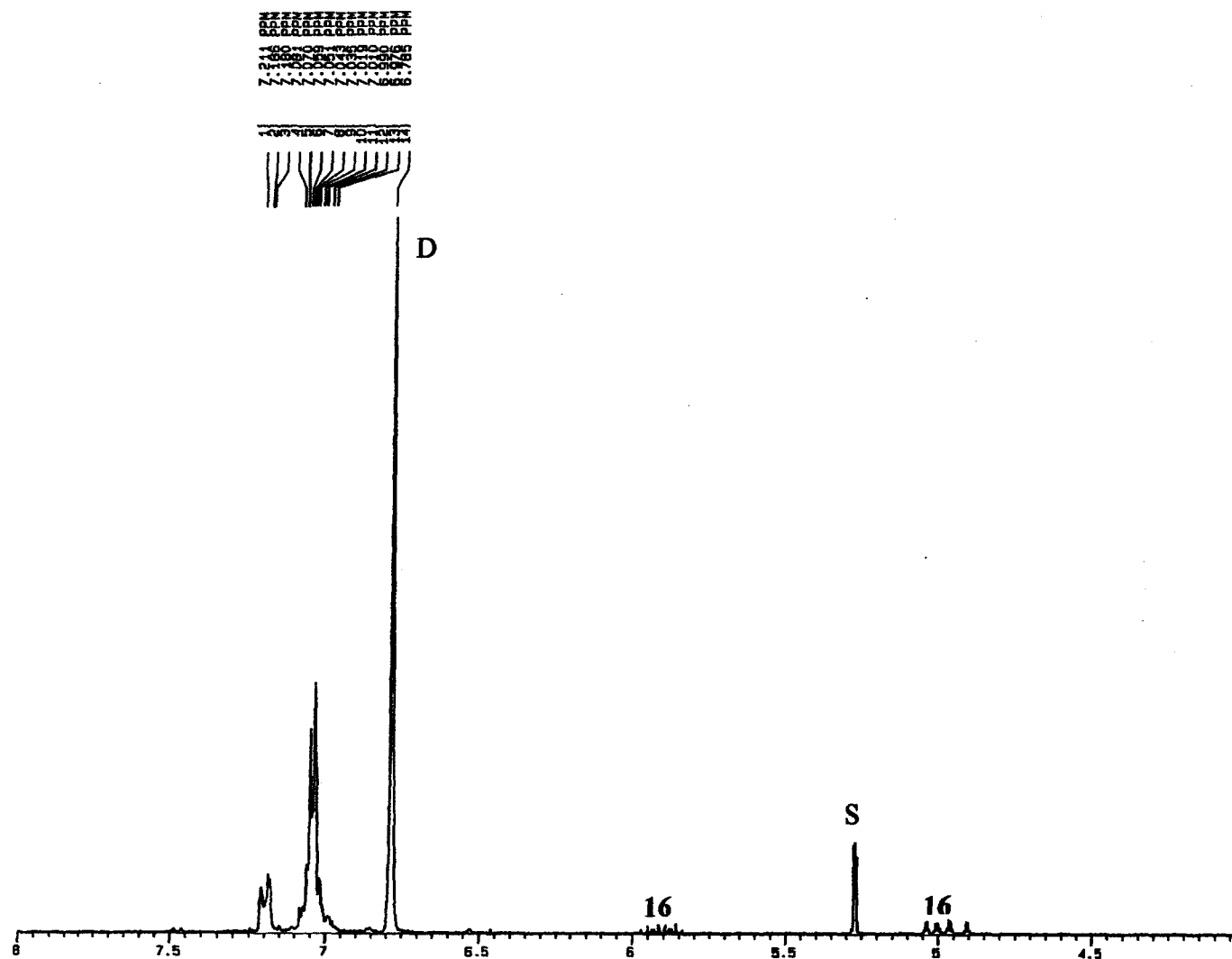


Figure D-1. ^1H NMR spectrum from 8 to 4 ppm (300 MHz, $\text{CCl}_4:\text{CD}_2\text{Cl}_2$, 4:1 (v/v)) of *o*-cyclopropylcarbinytoluene (3) with durene standard (16: *o*-allyltoluene, D: durene, S: CHDCl_2).

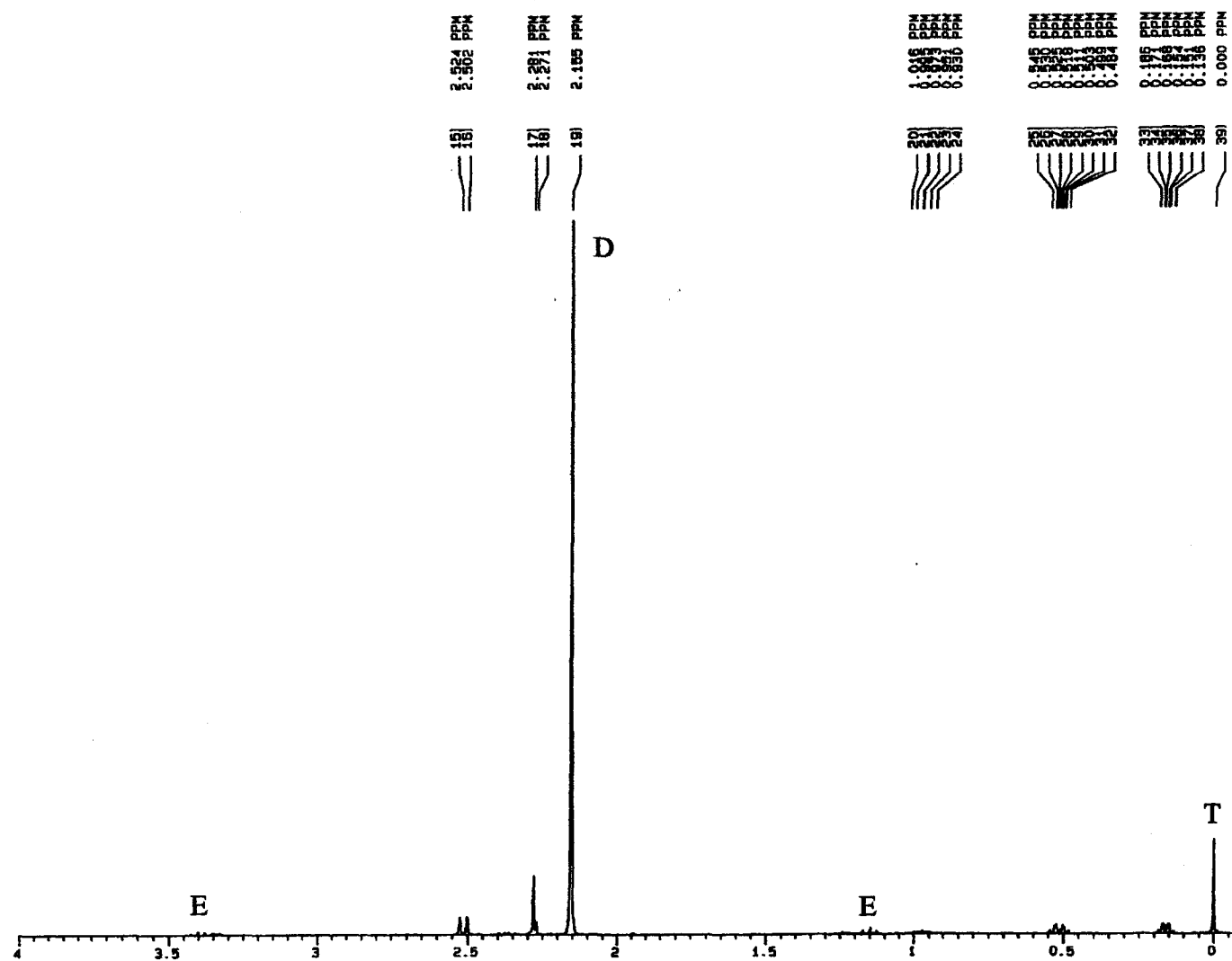


Figure D-2. ^1H NMR spectrum from 4 to -0.1 ppm (300 MHz, $\text{CCl}_4:\text{CD}_2\text{Cl}_2$, 4:1 (v/v)) of *o*-cyclopropylcarbinytoluene (3) with durene standard (D: durene, E: diethyl ether, S: CH_2Cl_2 , T: tetramethylsilane).

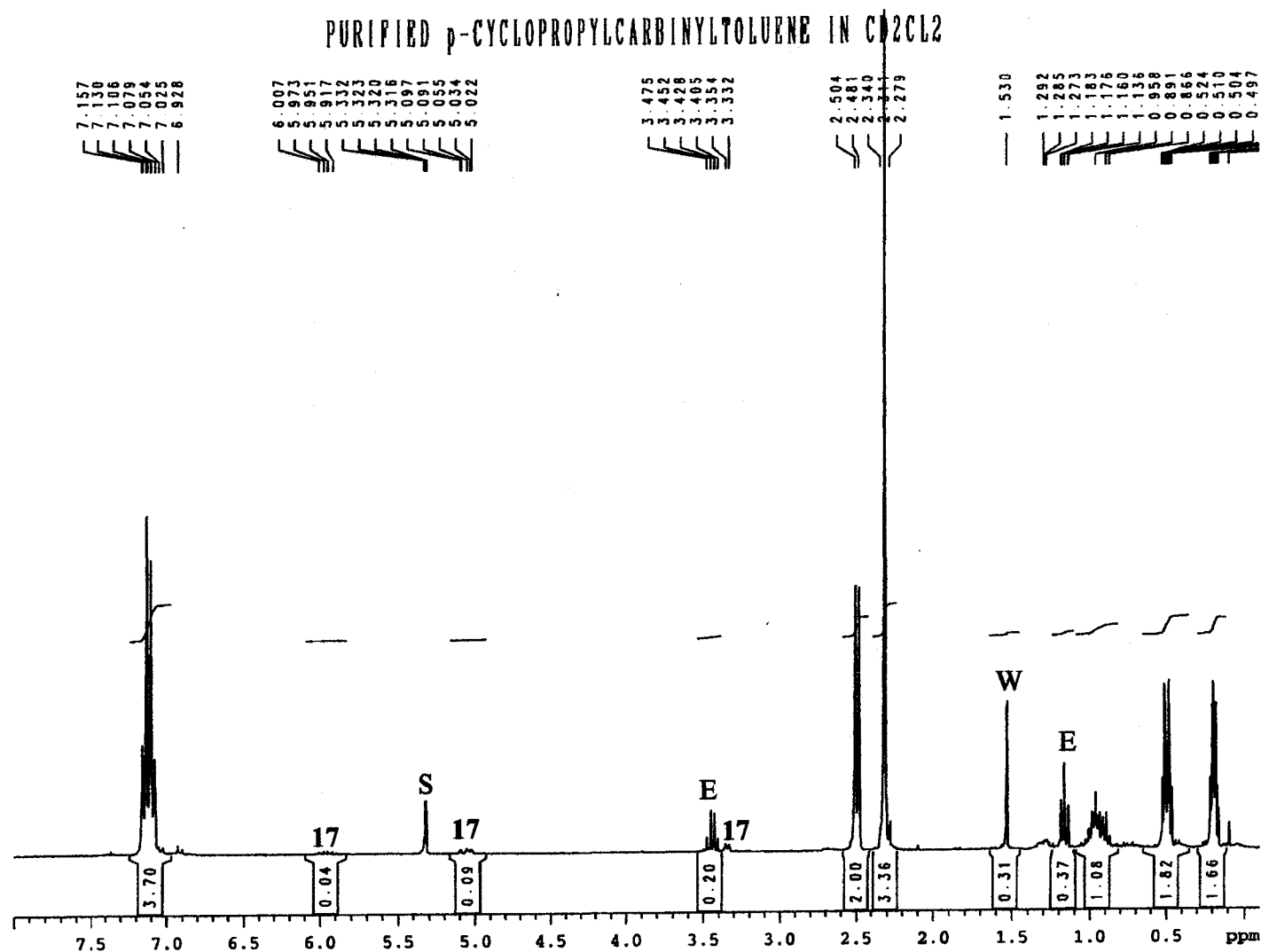


Figure D-3. ¹H NMR spectrum (300 MHz, CCl₄:CD₂Cl₂, 4:1 (v/v)) of *p*-cyclopropylcarbinyltoluene (4) (17: *p*-allyltoluene, E: diethyl ether, S: CHDCl₂, W: water).

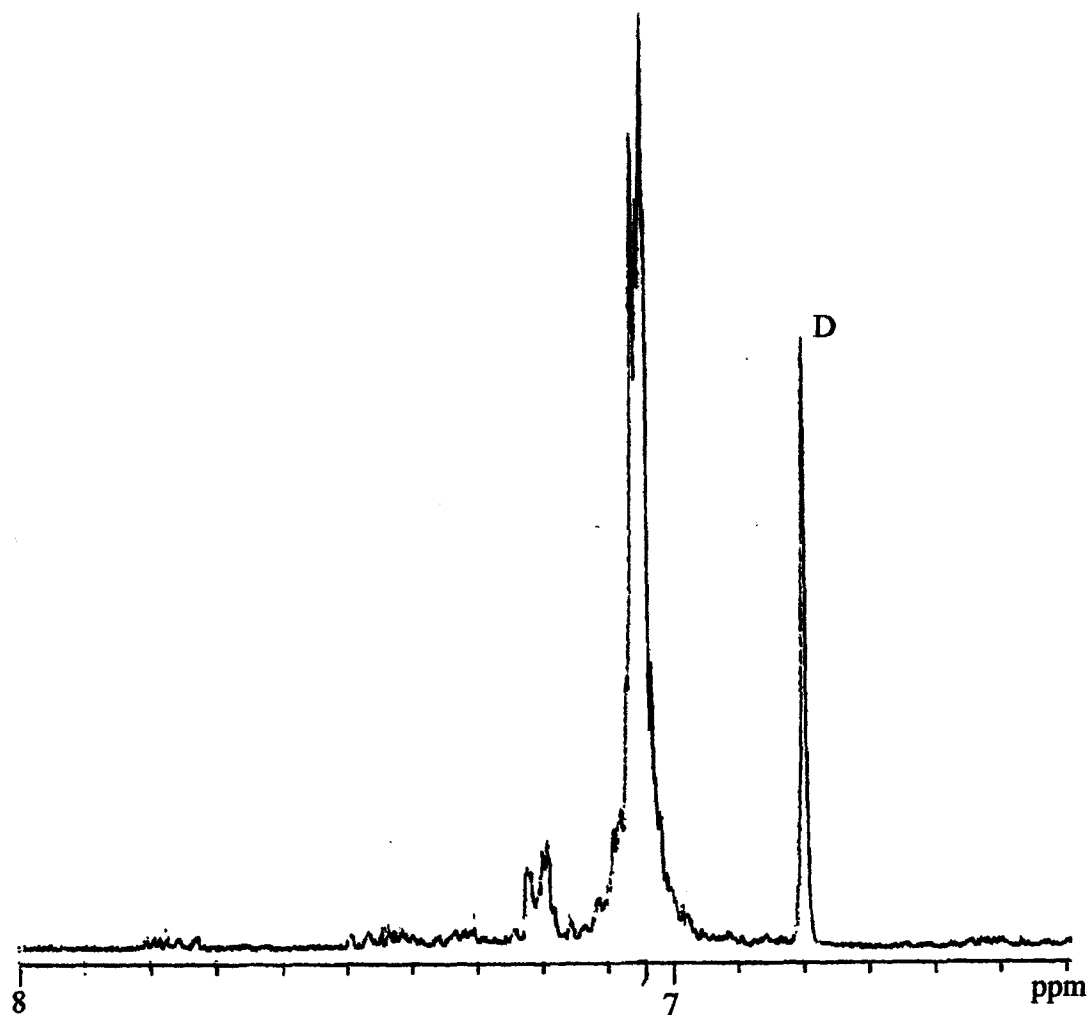


Figure D-4. ^1H NMR spectrum (300 MHz, $\text{CCl}_4:\text{CD}_2\text{Cl}_2$, 4:1 (v/v)) of the pyrolysis mixture from the FVP at 700 °C of *o*-cyclopropylcarbinylnitrobenzene (**3**) with durene standard from 8 to 7.4 ppm (D: durene).

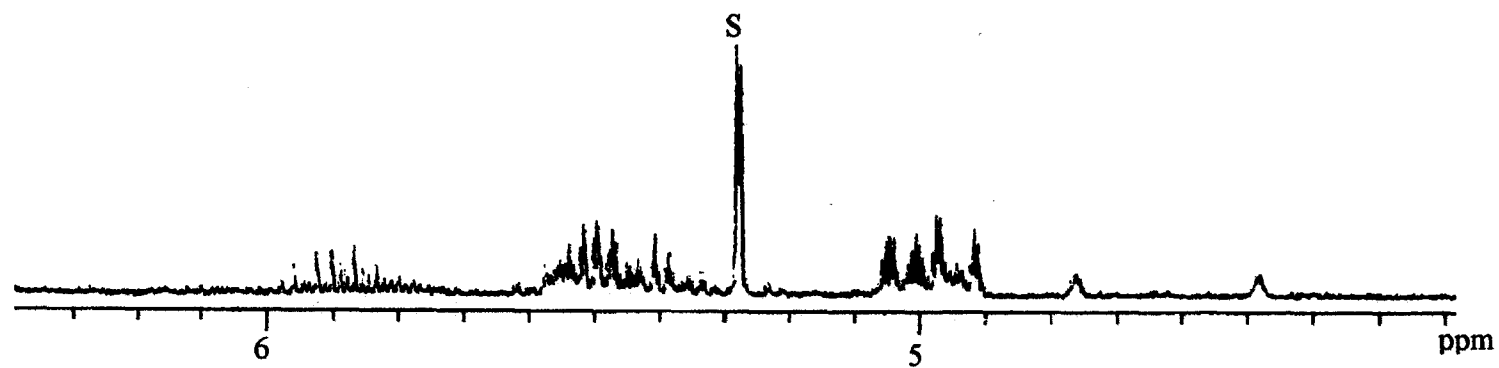


Figure D-5. ^1H NMR spectrum (300 MHz, $\text{CCl}_4:\text{CD}_2\text{Cl}_2$, 4:1 (v/v)) of the pyrolysis mixture from the FVP at 700 °C of *o*-cyclopropylcarbinytoluene (3) with durene standard from 6.4 to 4.2 ppm (S: CHDCl_2).

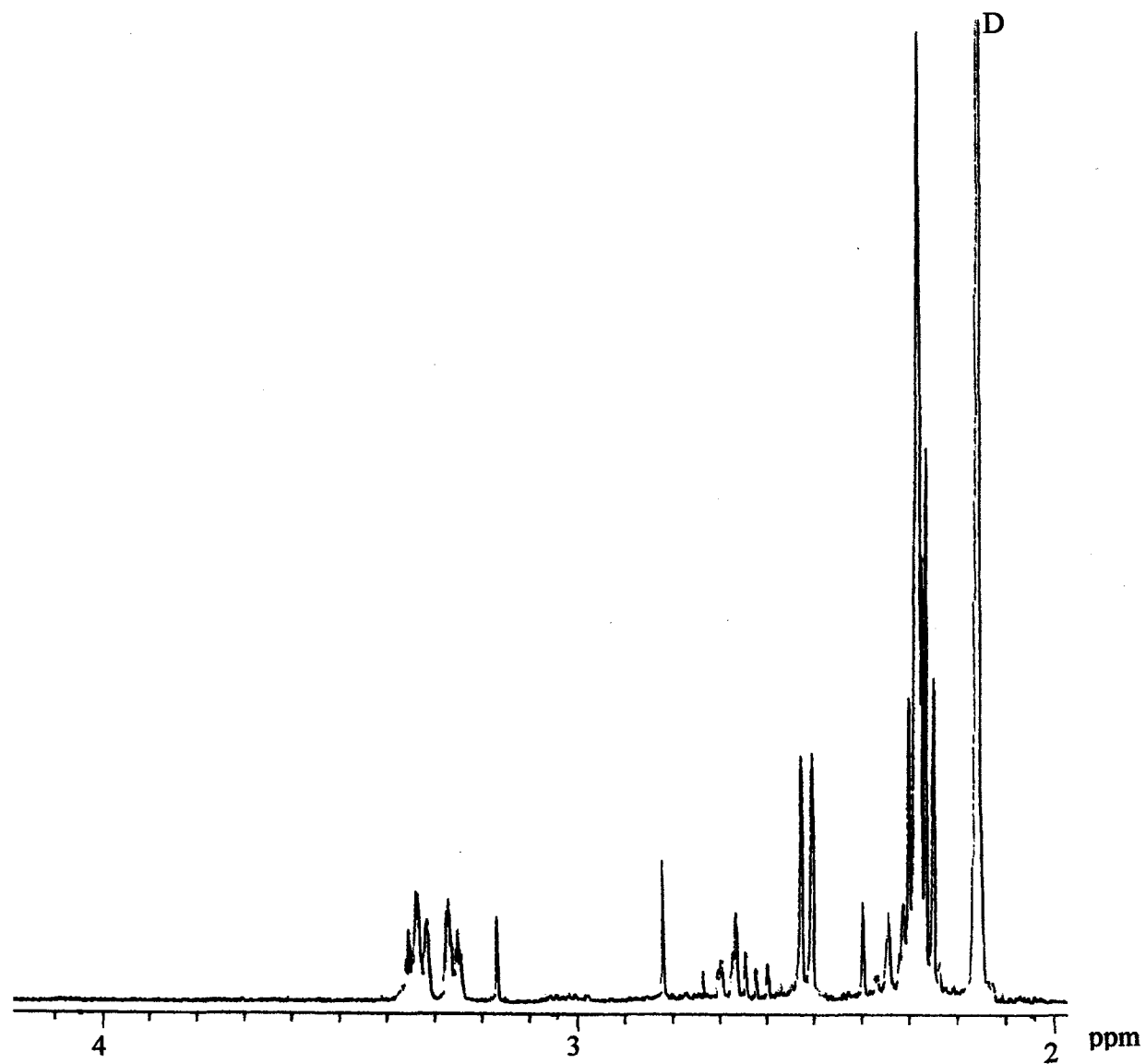


Figure D-6. ¹H NMR spectrum (300 MHz, CCl₄:CD₂Cl₂, 4:1 (v/v)) of the pyrolysis mixture from the FVP at 700 °C of *o*-cyclopropylcarbinylnitrobenzene (**3**) with durene standard from 4.2 to 2 ppm (D: durene).

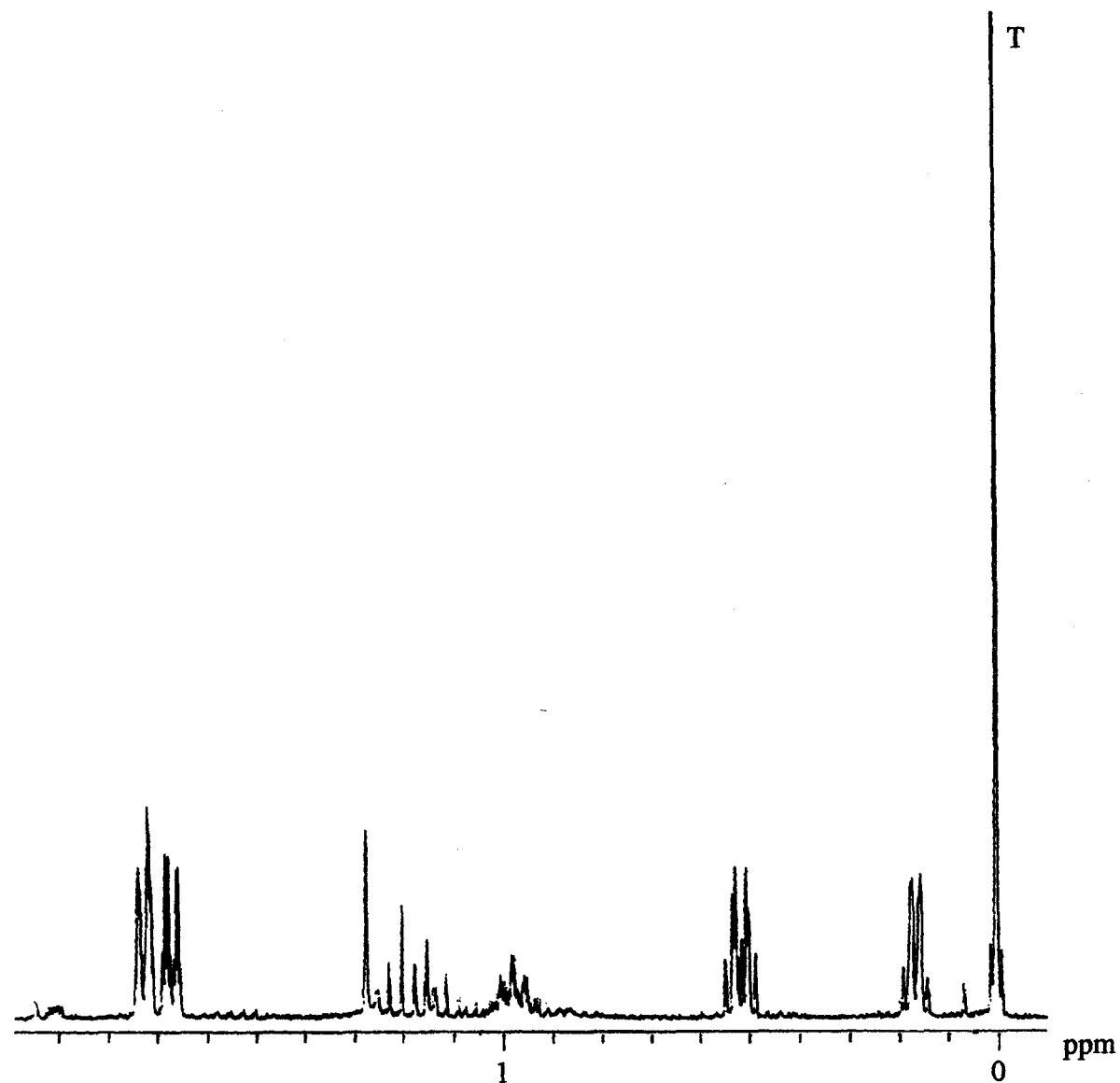


Figure D-7. ^1H NMR spectrum (300 MHz, $\text{CCl}_4:\text{CD}_2\text{Cl}_2$, 4:1 (v/v)) of the pyrolysis mixture from the FVP at 700 °C of *o*-cyclopropylcarbinytoluene (**3**) with durene standard from 2 to -0.1 ppm (T: tetramethylsilane).

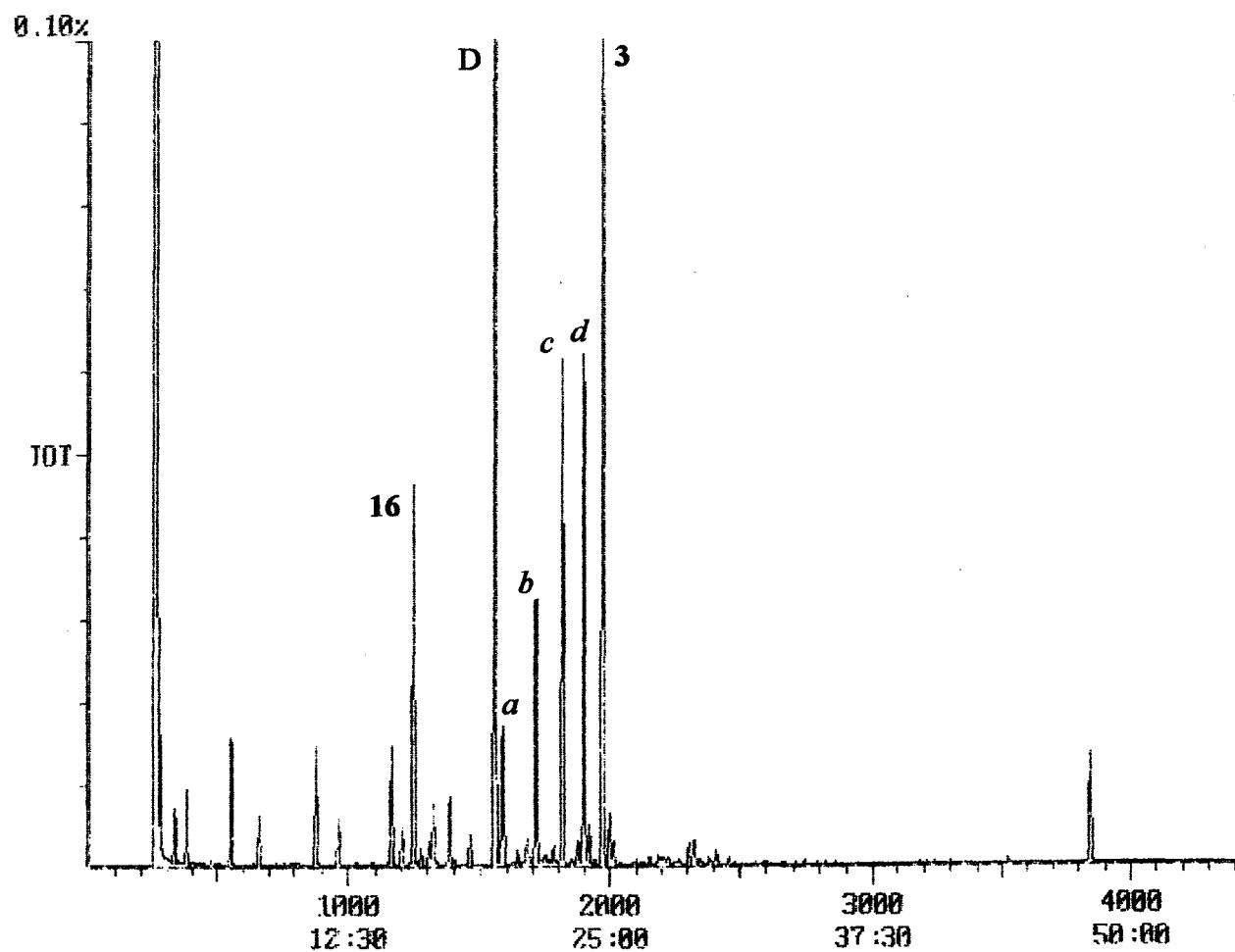


Figure D-8. GC chromatogram from the GCMS analysis of the pyrolysis mixture from the FVP at 700 °C of *o*-cyclopropylcarbinytoluene (**3**) with durene standard (**16**: *o*-allyltoluene, **D**: durene, *a-d*: isomers of **3**).

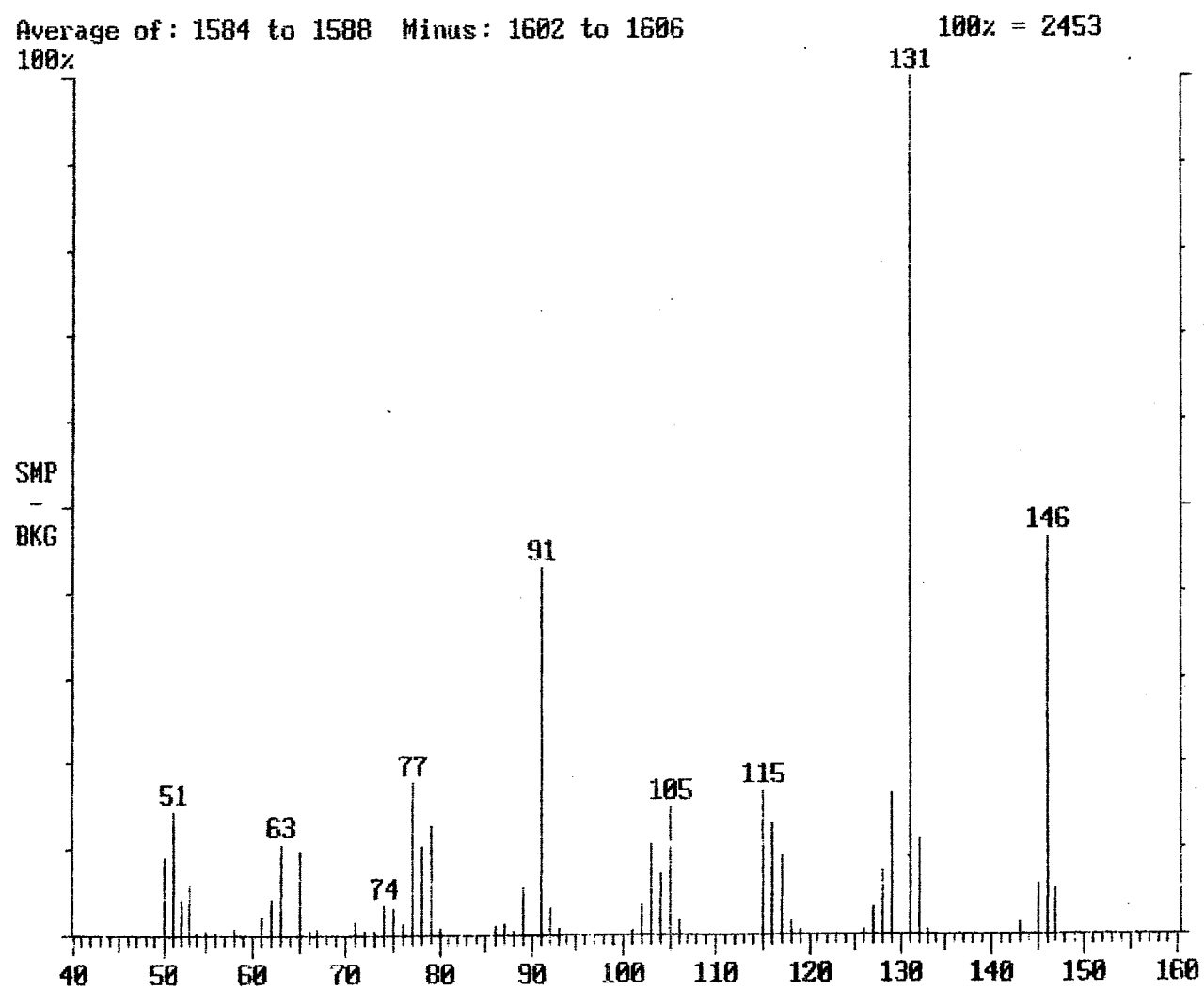


Figure D-9. GC-Mass Spectrum (EI, 70 eV) of the GC peak assigned to the first isomer of *o*-cyclopropylcarbinylnitrobenzene (**3**) to elute from the 700 °C pyrolysis mixture.

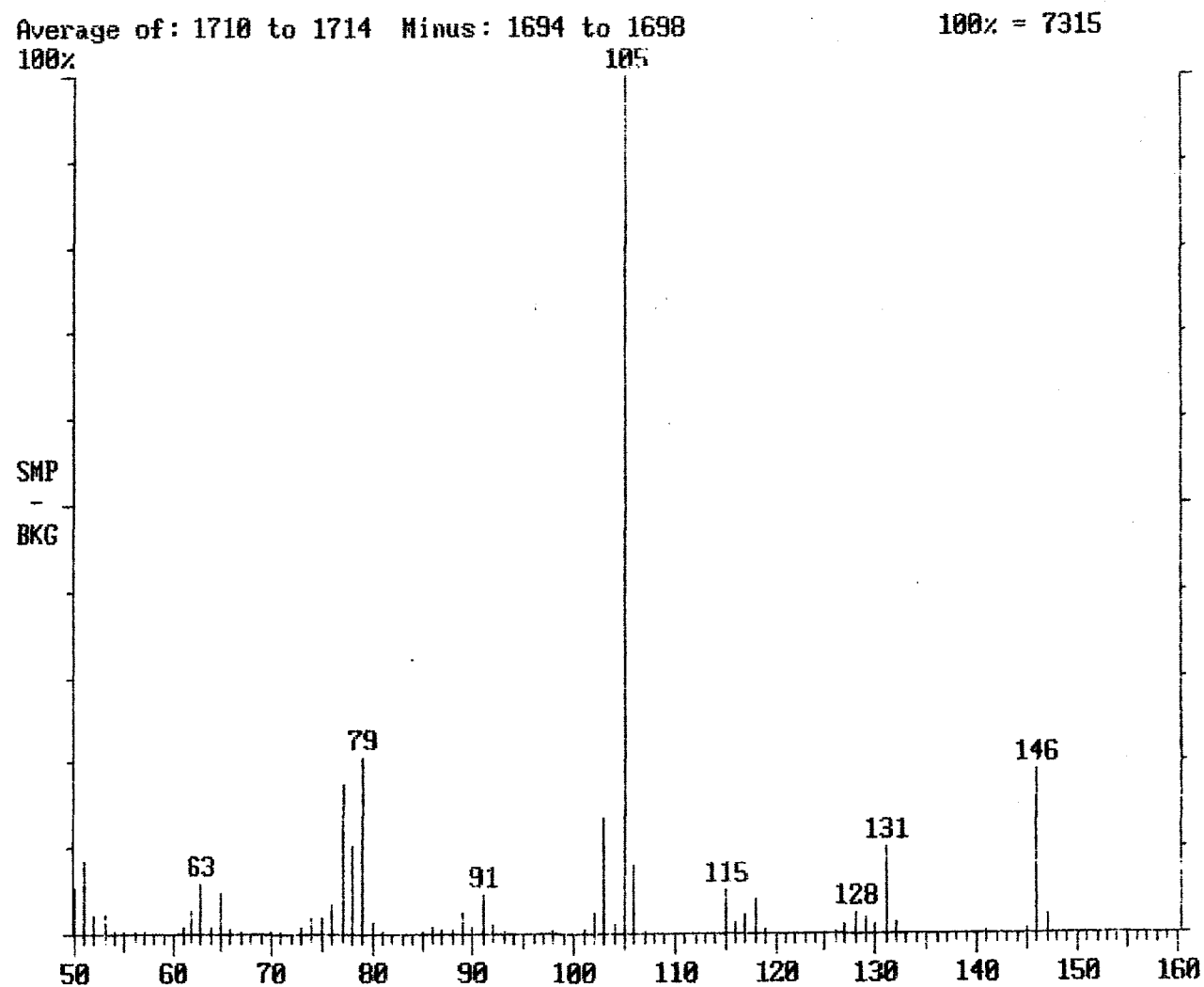


Figure D-10. GC-Mass Spectrum (EI, 70 eV) of the GC peak assigned to the second isomer of *o*-cyclopropylcarbinytoluene (**3**) to elute from the 700 °C pyrolysis mixture.

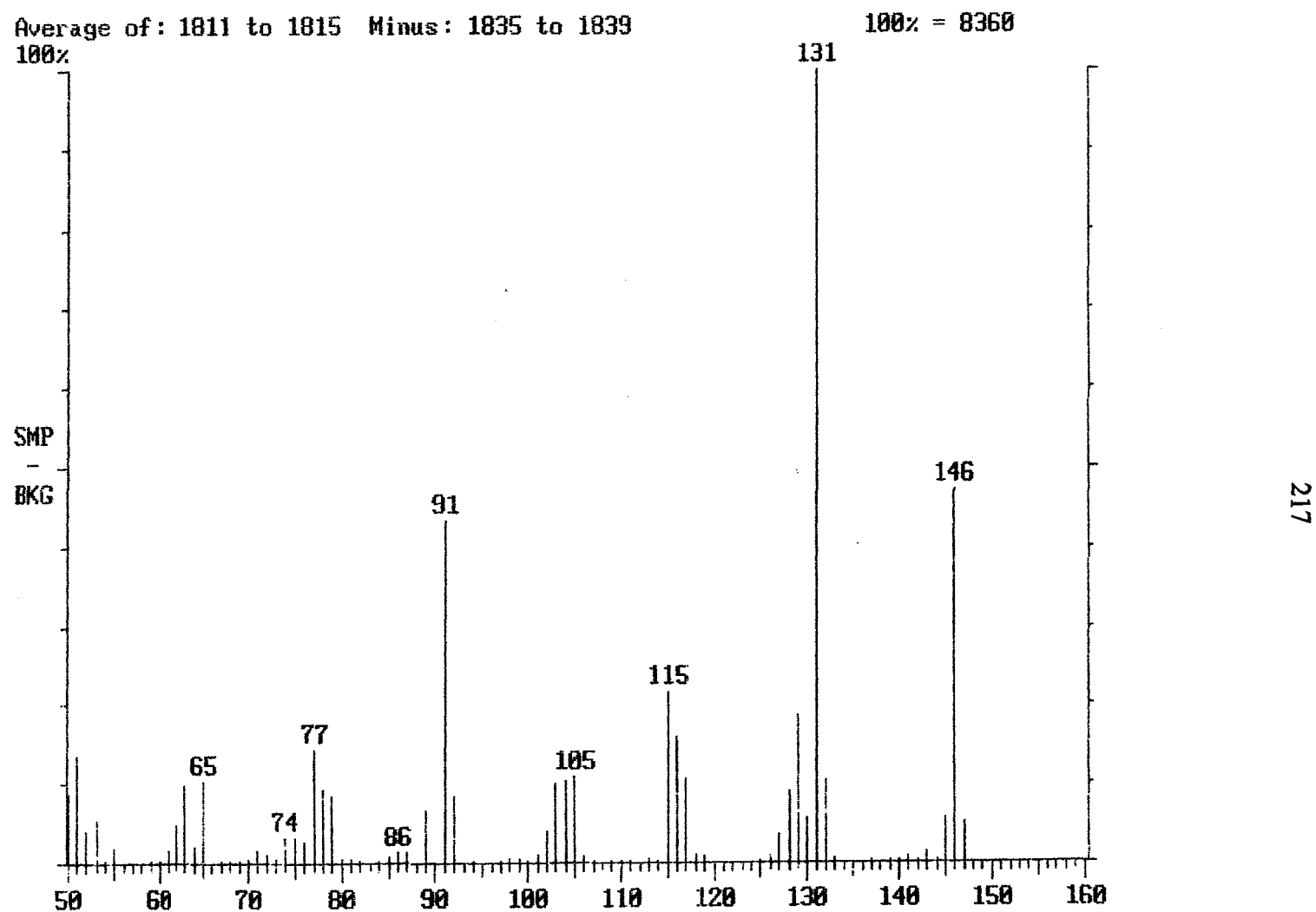


Figure D-11. GC-Mass Spectrum (EI, 70 eV) of the GC peak assigned to the third isomer of *o*-cyclopropylcarbinytoluene (**3**) to elute from the 700 °C pyrolysis mixture.

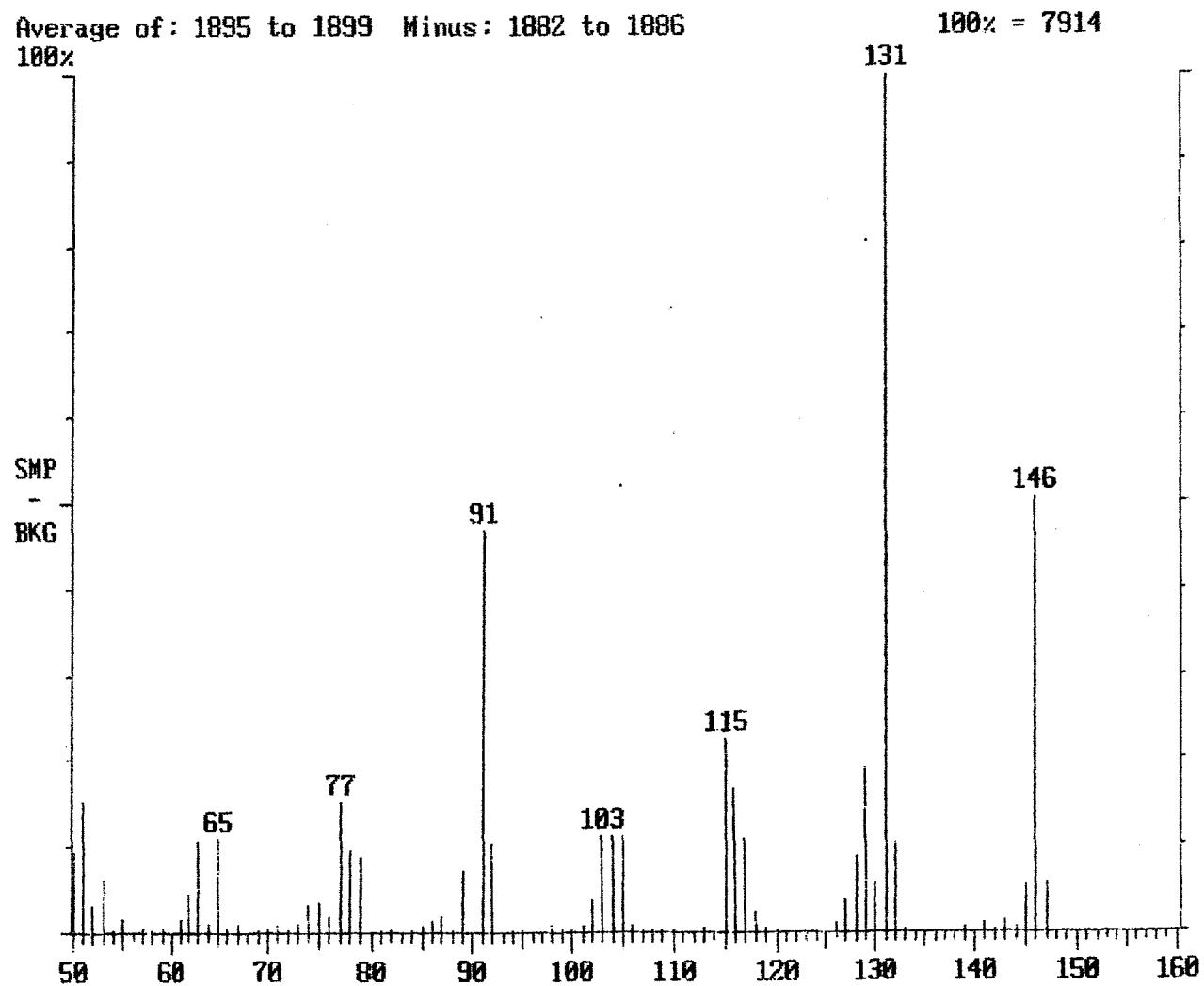


Figure D-12. GC-Mass Spectrum (EI, 70 eV) of the GC peak assigned to the fourth isomer of *o*-cyclopropylcarbinyltoluene (3) to elute from the 700 °C pyrolysis mixture.

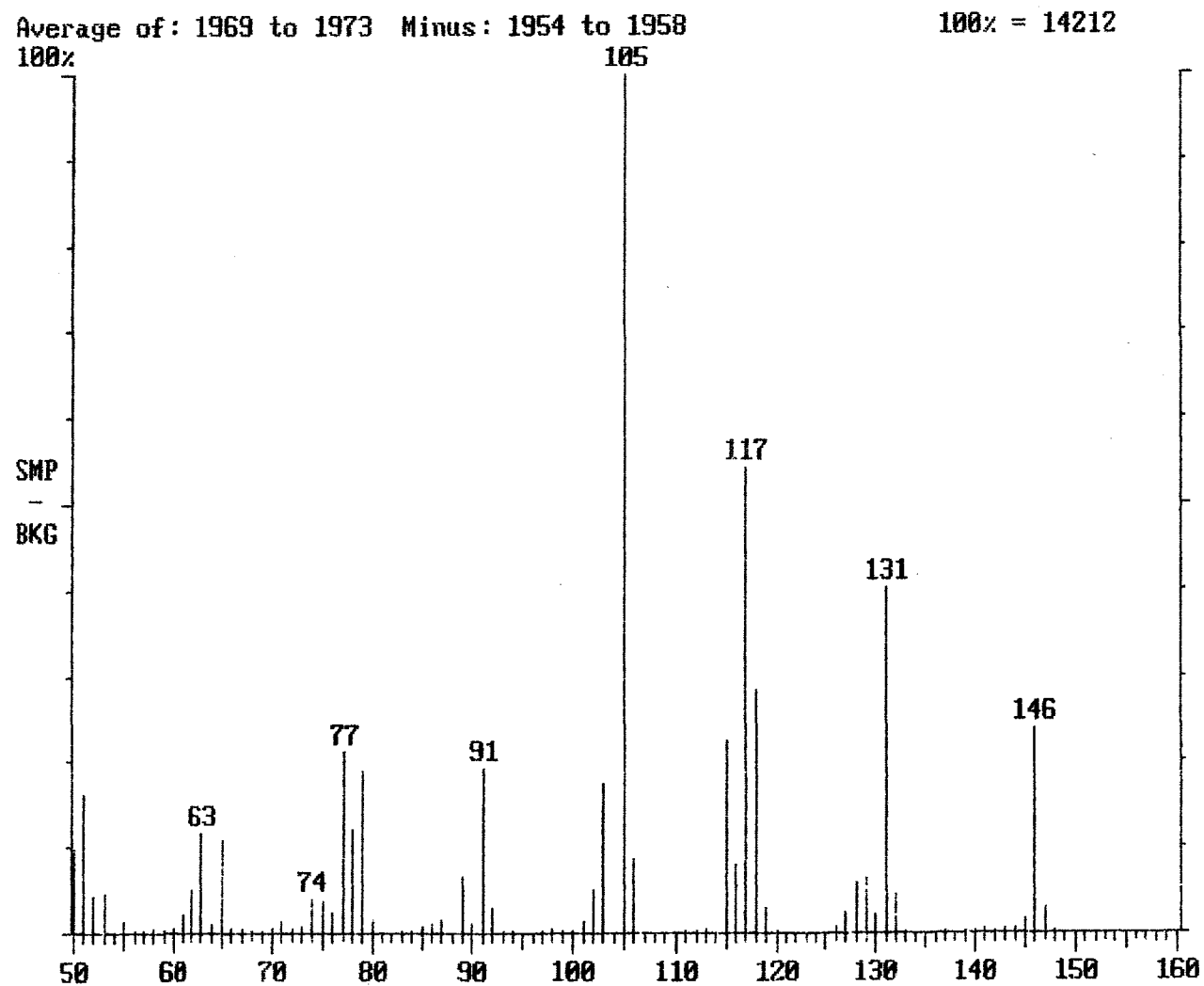


Figure D-13. GC-Mass Spectrum (EI, 70 eV) of the GC peak assigned to *o*-cyclopropylcarbinytoluene (**3**) from the 700 °C pyrolysis mixture.

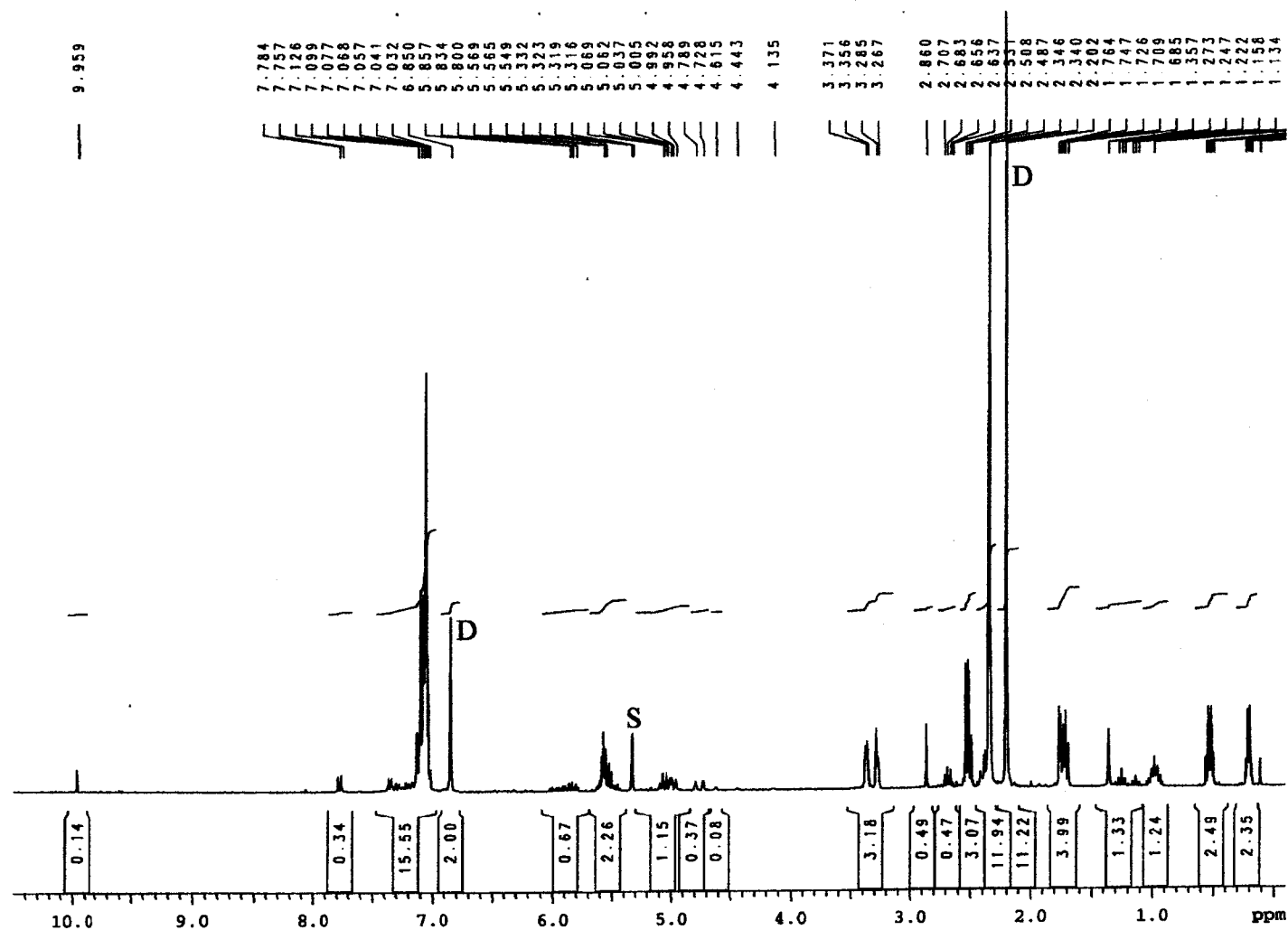


Figure D-14. ^1H NMR spectrum (300 MHz, $\text{CCl}_4:\text{CD}_2\text{Cl}_2$, 3:1 (v/v)) of the pyrolysis mixture from the FVP at 700 °C of *p*-cyclopropylcarbinylnitrobenzene (4) with durene standard (D: durene, S: CHDCl_2).

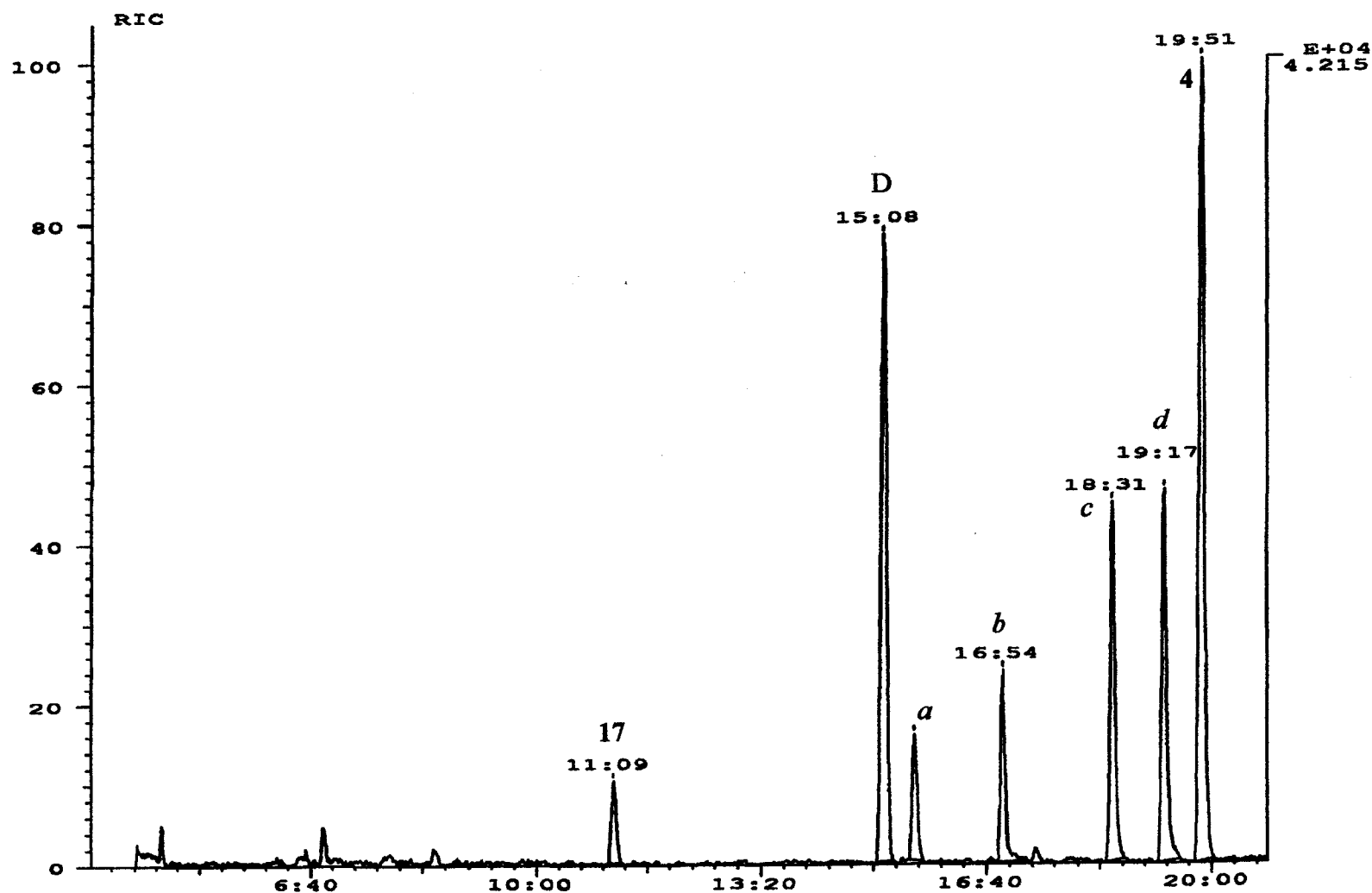


Figure D-15. GC chromatogram from the GCMS analysis of the pyrolysis mixture from the FVP at 700 °C of *p*-cyclopropylcarbinytoluene (**4**) with durene standard (**17**: *p*-allyltoluene, **D**: durene, *a-d*: isomers of **4**).

SPEC: ADP-095.MS
 Samp: p-CFCT FVE @ 700 C W/ SM @ 0 C W/ DURME
 Comm: STANDARD IN CCL4
 Mode: +LMR UP LR
 Oper:
 Base: 131.0
 Norm: 131.0
 Peak: 1000.00 AUU

Date: 01-Apr-95
 Time: 15:35
 Start: 14:44:59
 Elapse: 1240
 7200

Inlet: 50 > 500
 Masses: 53
 Peaks: 53

Inten: 1951
 RIC: 6962

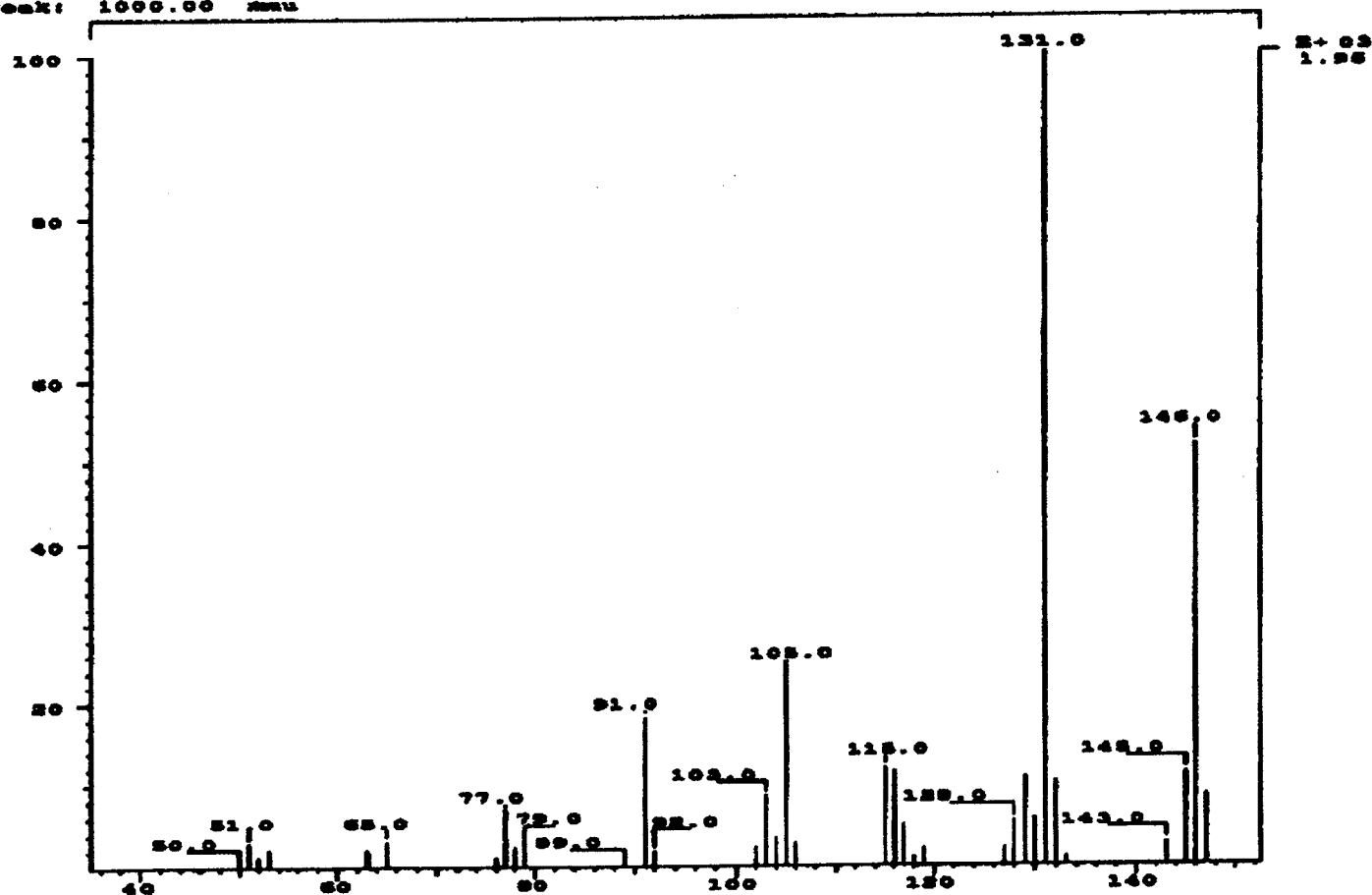


Figure D-16. GC-Mass Spectrum (EI, 70 eV) of the GC peak assigned to the first isomer of *p*-cyclopropylcarbinytoluene (4) to elute from the 700 °C pyrolysis mixture.

SPEC: ABF-092.ms 01-Apr-98 Elapse: 16:54 1352
 Sump: p-CPT FVP @ 700 C W/ SH @ C W/ DURENE Start: 14:44:59 7200
 Conn: STANDARD IN GCL4
 Mode: +LGR UP LR
 Oper:
 Base: 105.0 Inten: 4937 Inlet: 50 > 600
 Norm: 105.0 RIC: 10324 Masses: 55
 Peak: 1000.00 m/z

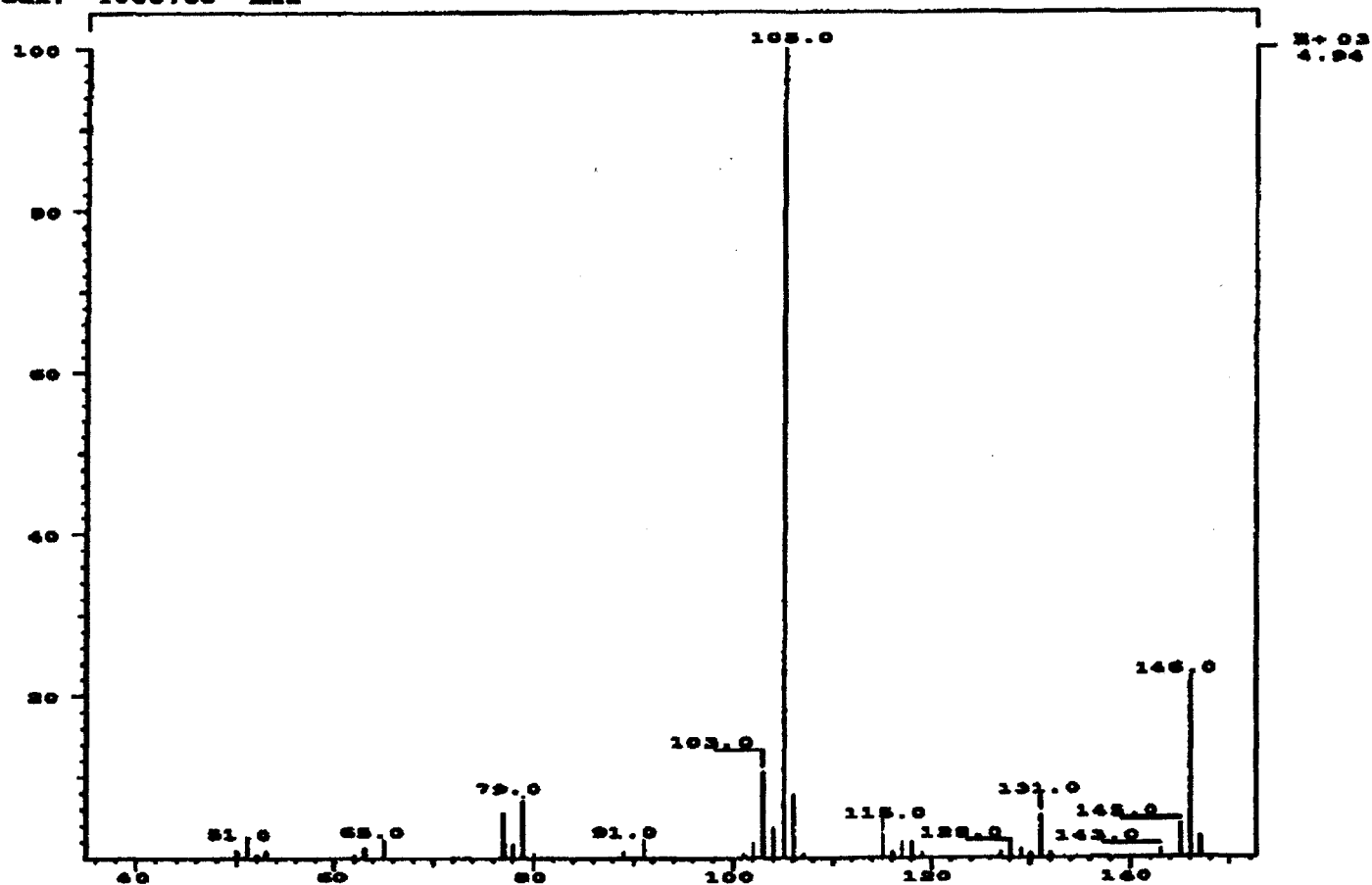


Figure D-17. GC-Mass Spectrum (EI, 70 eV) of the GC peak assigned to the first isomer of *p*-cyclopropylcarbinyltoluene (4) to elute from the 700 °C pyrolysis mixture.

SPEC: ABF-092.ms 01-Apr-95 Elapse: 18:31 1481
 Samp: p-CFCT FVP @ 700 C W/ SN @ 0 C W/ DURHAM Start: 14:44:59 7200
 Comm: STANDARD IN CCL4
 Mode: +LHR UP LR
 Oper:
 Base: 131.0 Inten: 4802 Inlet: 50 > 599
 Norm: 131.0 RIC: 18998 Masses: 59
 Peak: 1000.00 m/z

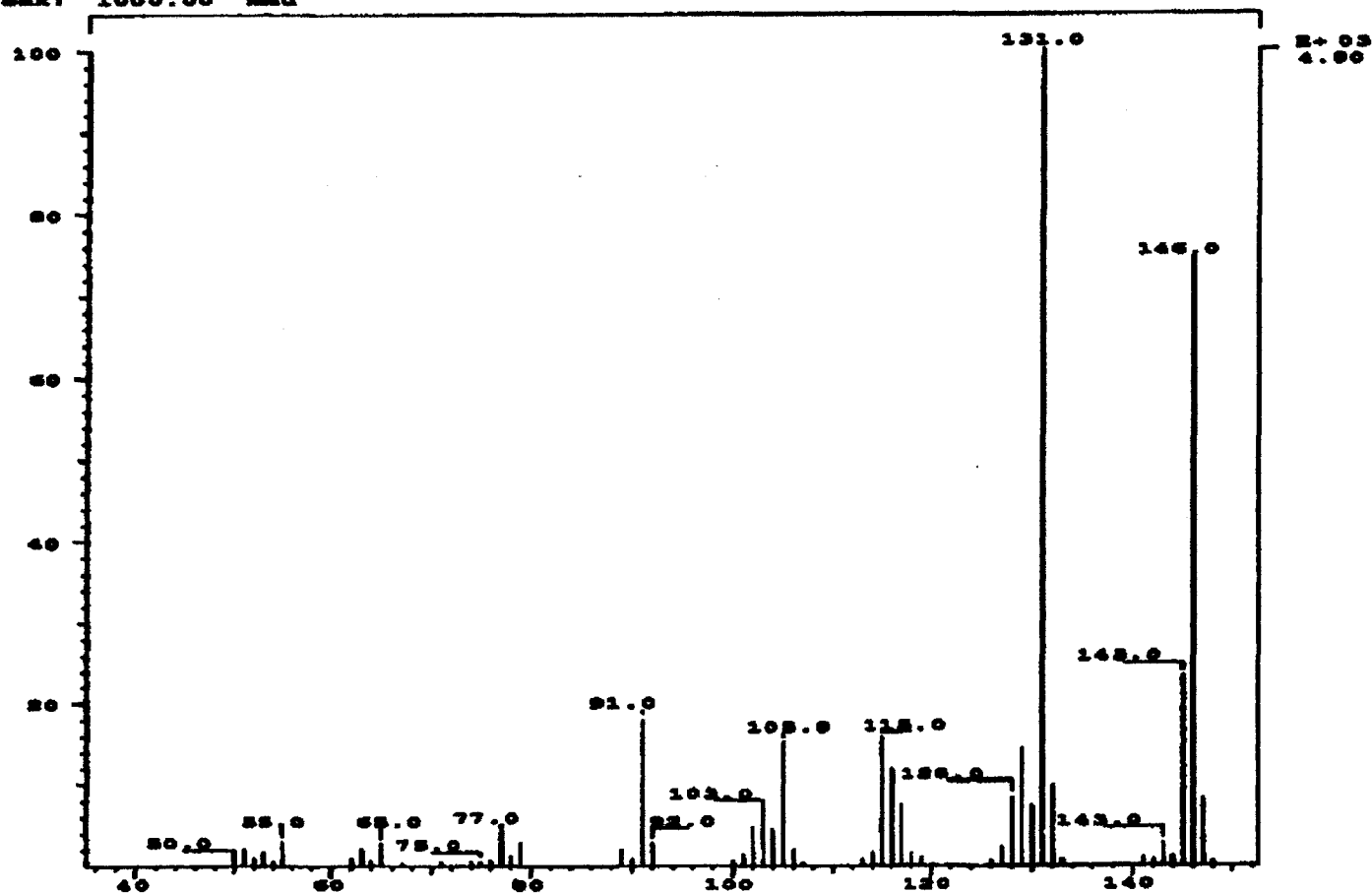


Figure D-18. GC-Mass Spectrum (EI, 70 eV) of the GC peak assigned to the first isomer of *p*-cyclopropylcarbinytoluene (4) to elute from the 700 °C pyrolysis mixture.

SPEC: AMF-022.ms 01-Apr-98 Elapse: 19:17 1843
 Samp: p-CPCT FVP @ 700 C W/ SH @ 0 C W/ DURENE Start: 14:44:59 7500
 Comp: STANDARD IN CCL4
 Mode: +LNR UP LR
 Oper:
 Base: 131.0 Inten: 4941 Inlet: 80 > 600
 Norm: 131.0 RIC: 19761 Masses: 70
 Peak: 1000.00 msu

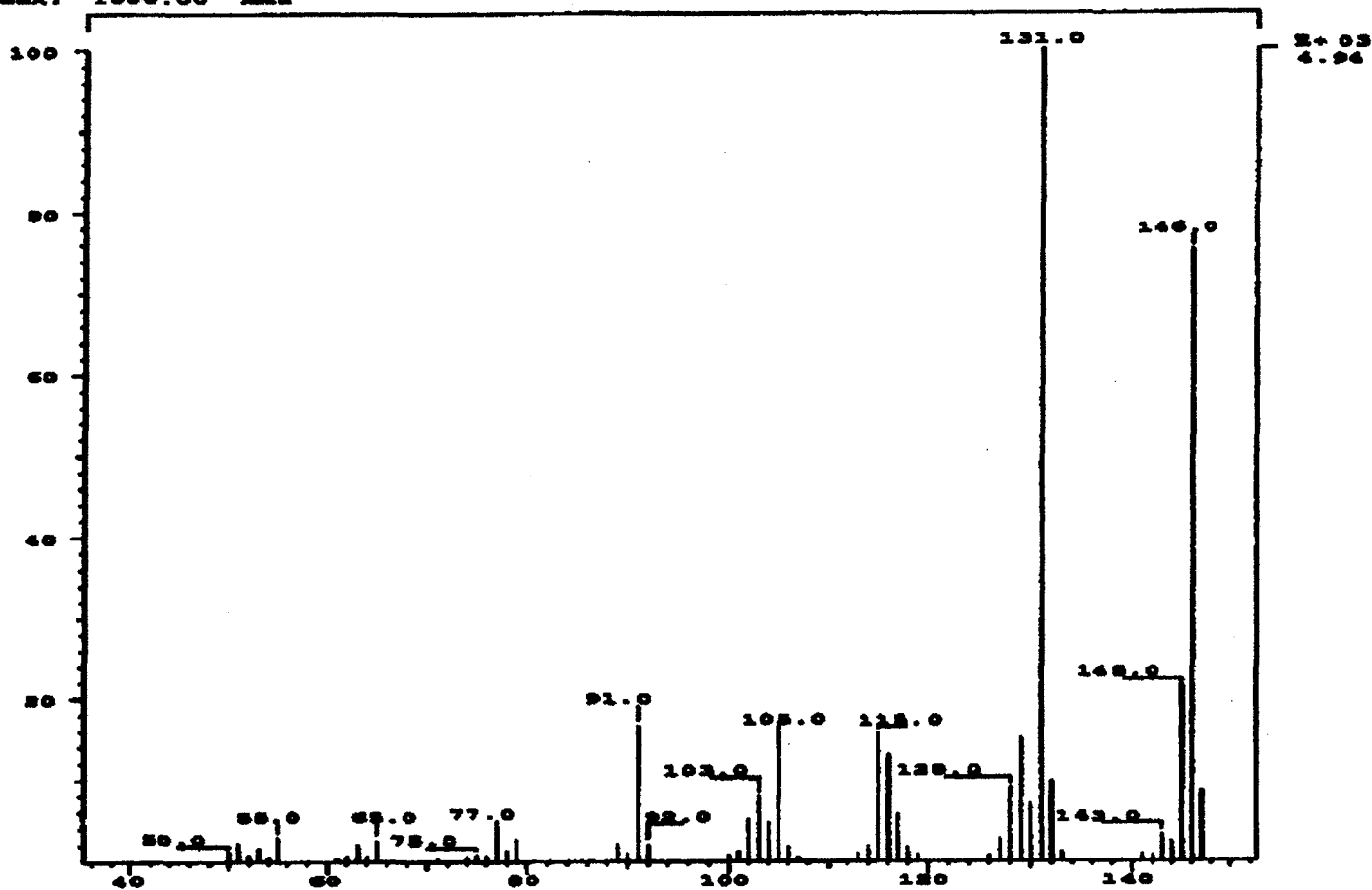


Figure D-19. GC-Mass Spectrum (EI, 70 eV) of the GC peak assigned to the first isomer of *p*-cyclopropylcarbinytoluene (4) to elute from the 700 °C pyrolysis mixture.

SPEC: ABF-022.ms 01-Apr-98 Elapse: 19:01 1588
 Samp: p-CPCT FVP @ 700 C W/ SM @ 0 C W/ DURENE Start: 14:44:59 7200
 Conn: STANDARD IN CGL4
 Mode: LMR UP LR
 Oper:
 Base: 105.0 Inten: 2055 Inlet: 50 > 600
 Norm: 105.0 RIC: 42803 Masses: 120
 Peak: 1000.00 mru #peaks: 120

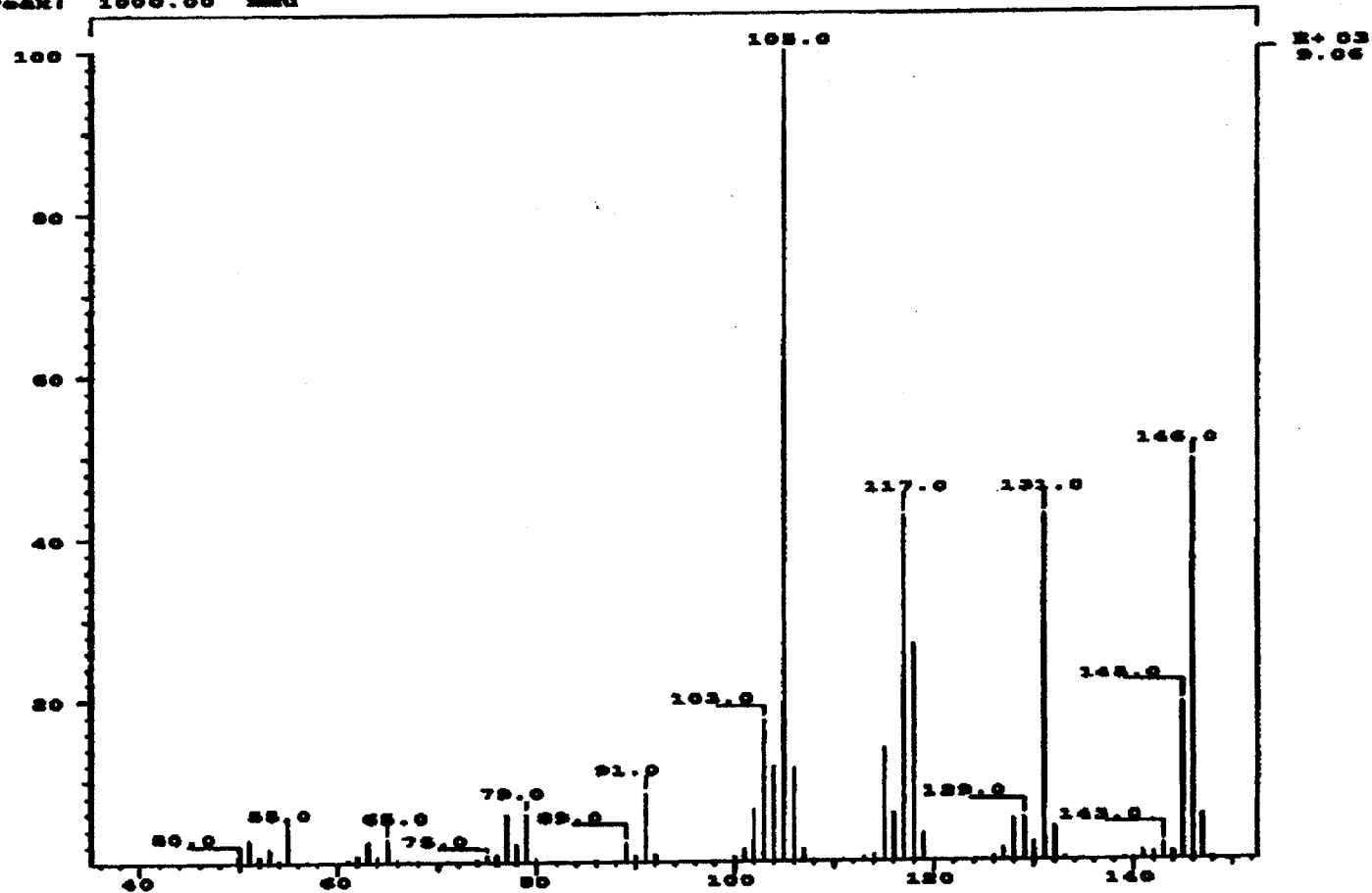


Figure D-20. GC-Mass Spectrum (EI, 70 eV) of the GC peak assigned to *p*-cyclopropylcarbinytoluene (4) from the 700 °C pyrolysis mixture.

APPENDIX E. FIGURES FOR CHAPTER 7.

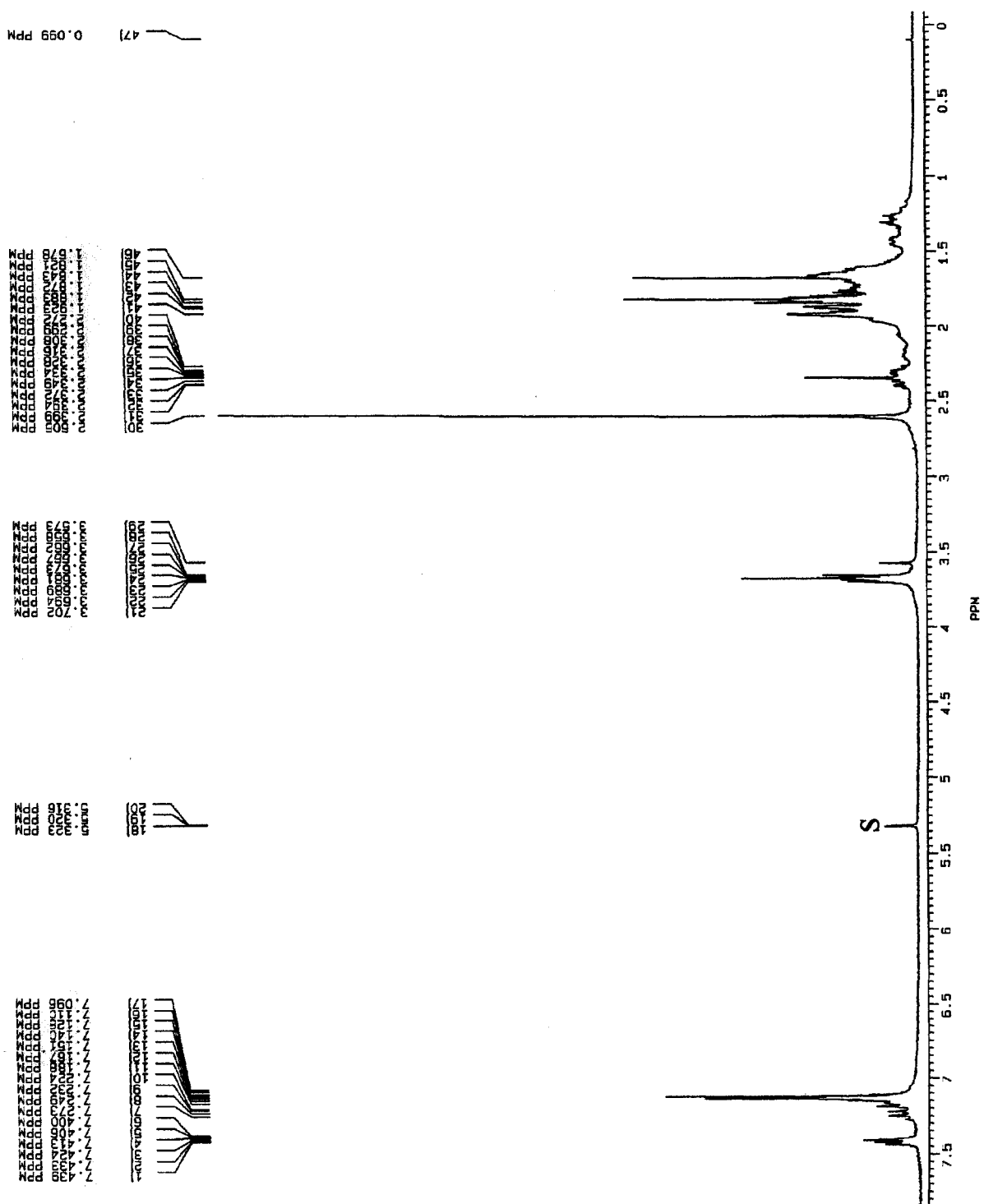


Figure E-1. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of 1-o-tolylcyclohexanol (26) (S: CD_2Cl_2).

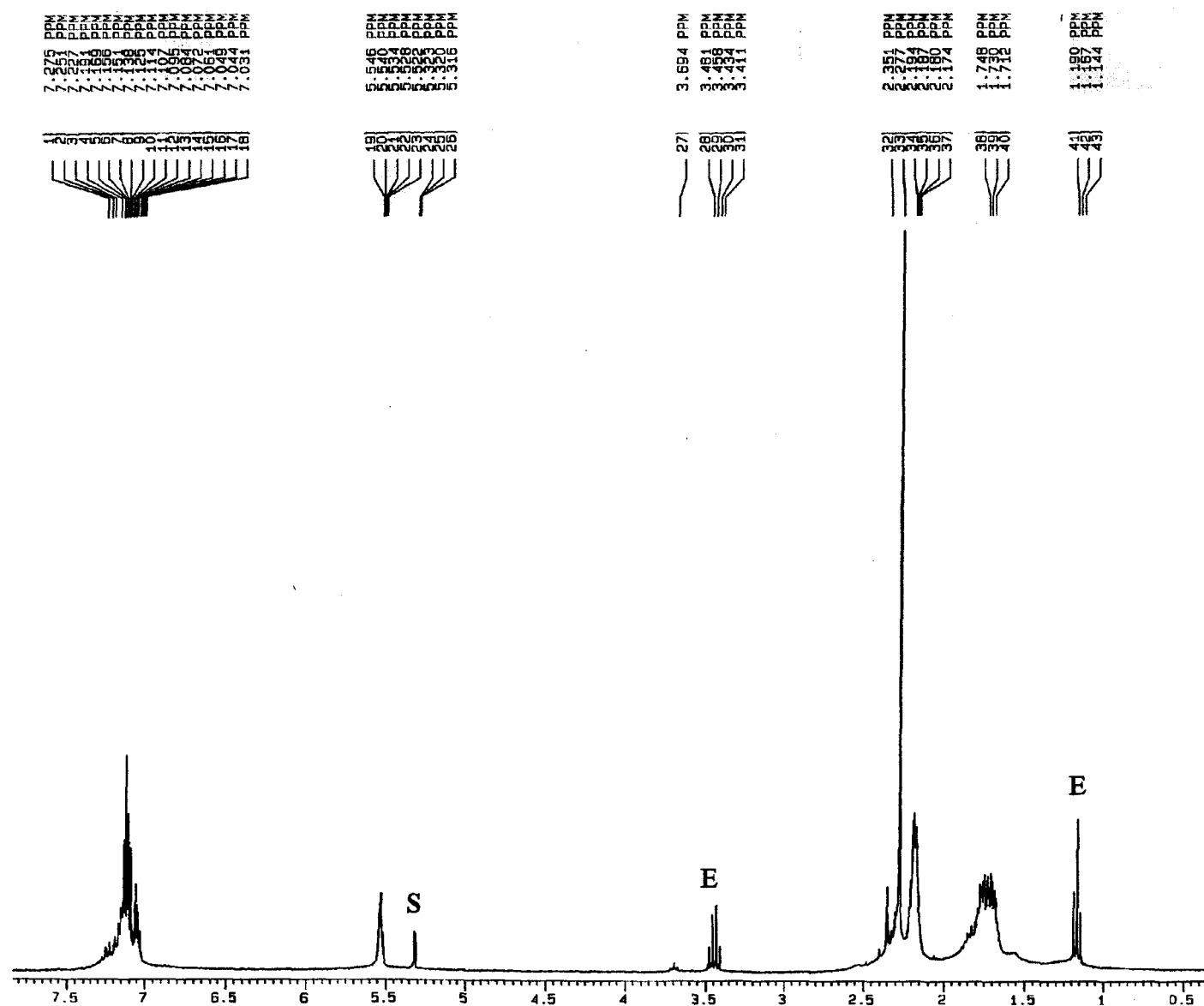


Figure E-2. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of 1-*o*-tolylcyclohexene (27) (S: CD_2Cl_2 , E: diethyl ether).

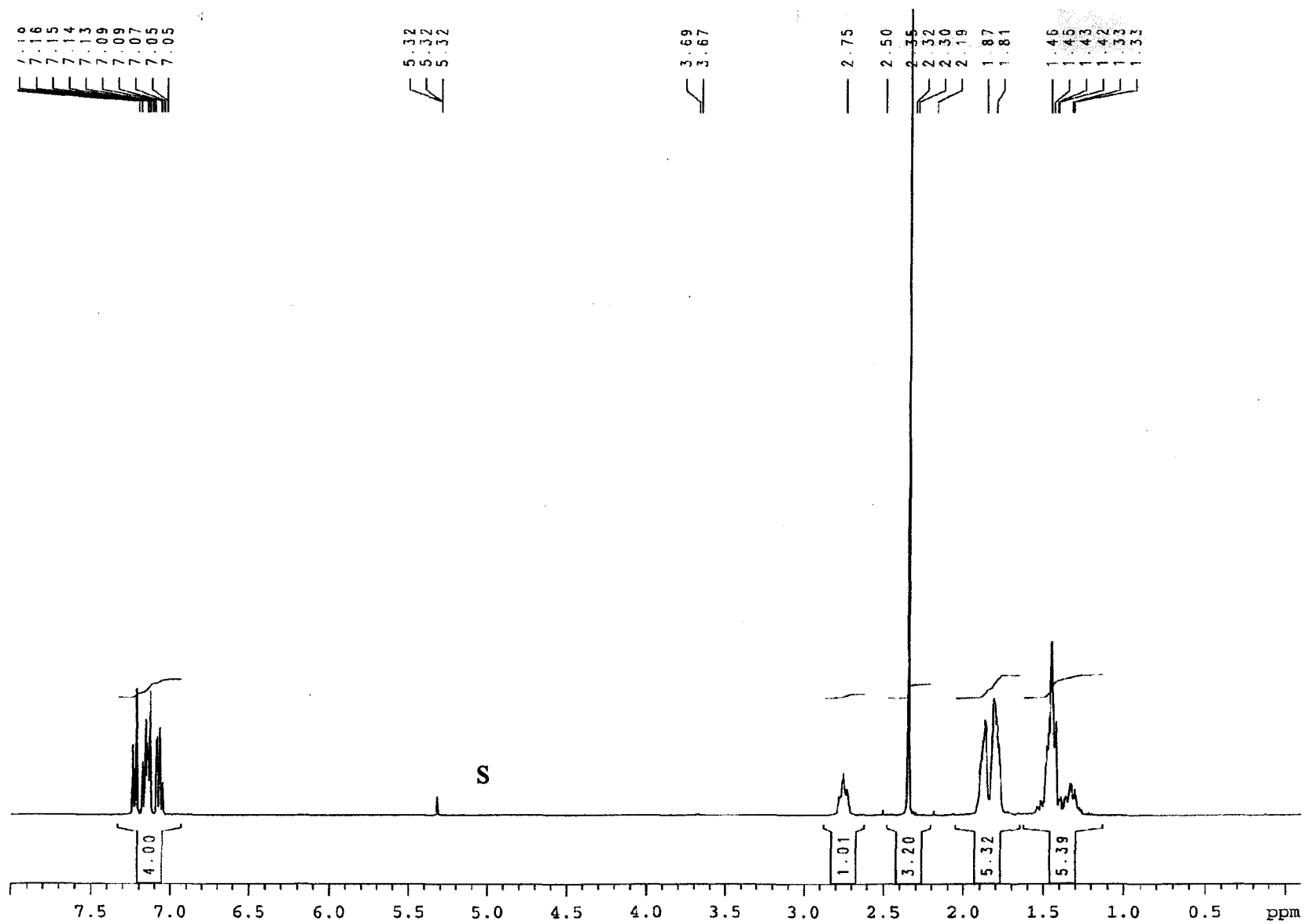


Figure E-3. ^1H NMR spectrum (400 MHz, CD_2Cl_2) of *o*-cyclohexyltoluene (**5**) (S: CD_2Cl_2).

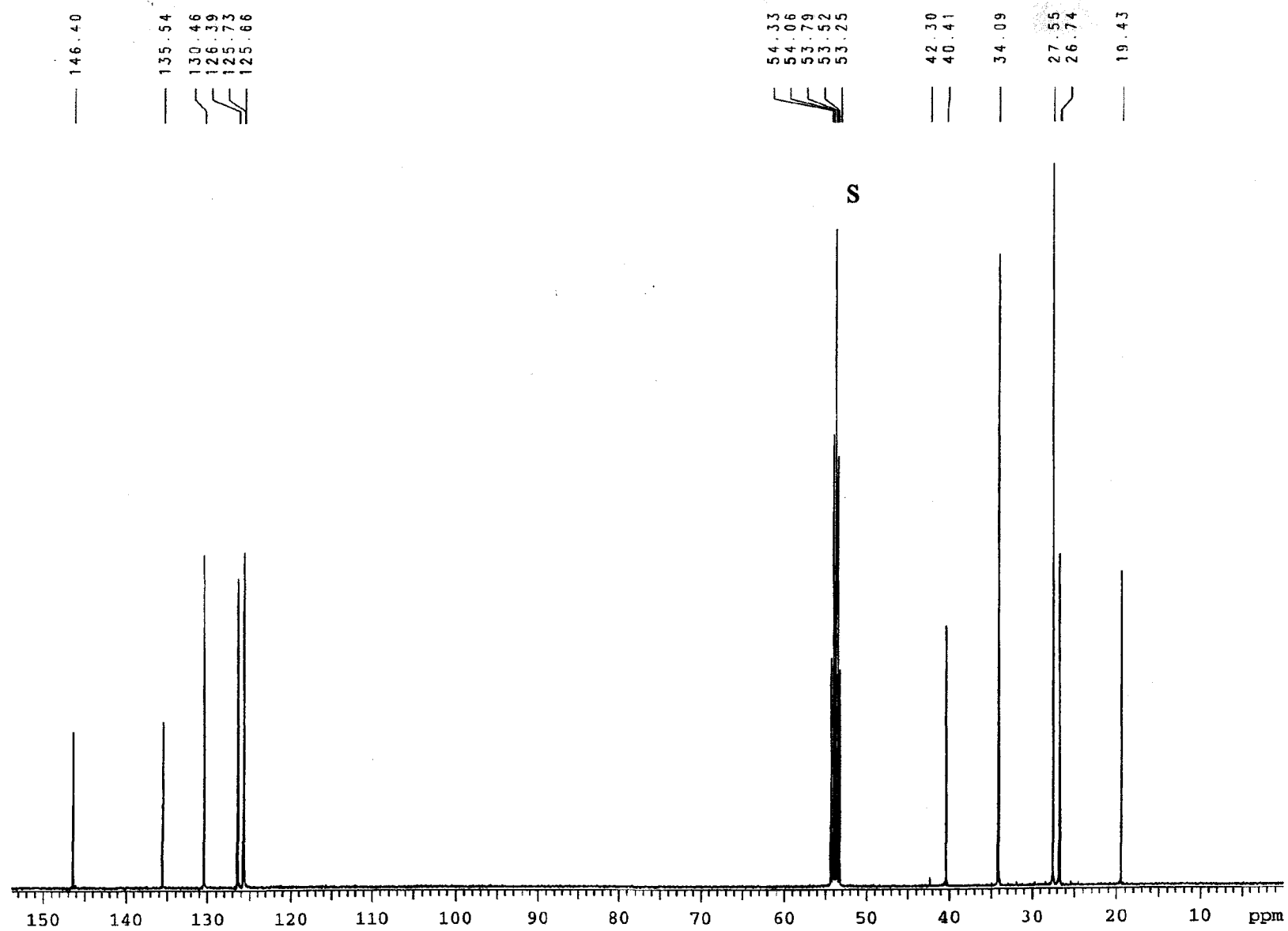


Figure E-4. ^{13}C NMR spectrum (100 MHz, CD_2Cl_2) of *o*-cyclohexyltoluene (**5**) (S: CD_2Cl_2).

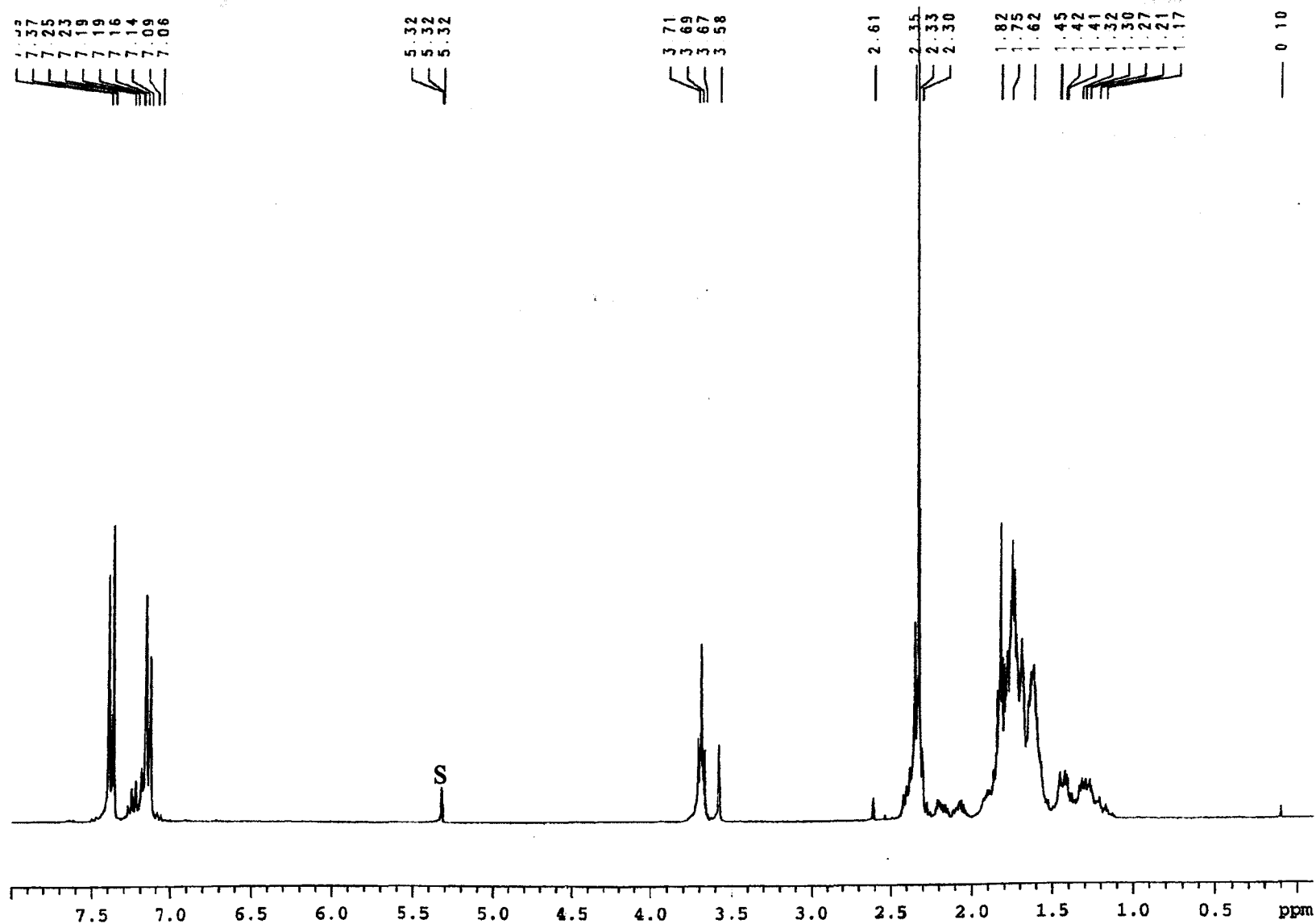


Figure E-5. ¹H NMR spectrum (300 MHz, CD₂Cl₂) of 1-*p*-tolylcyclohexanol (**28**) (S: CD₂Cl₂).

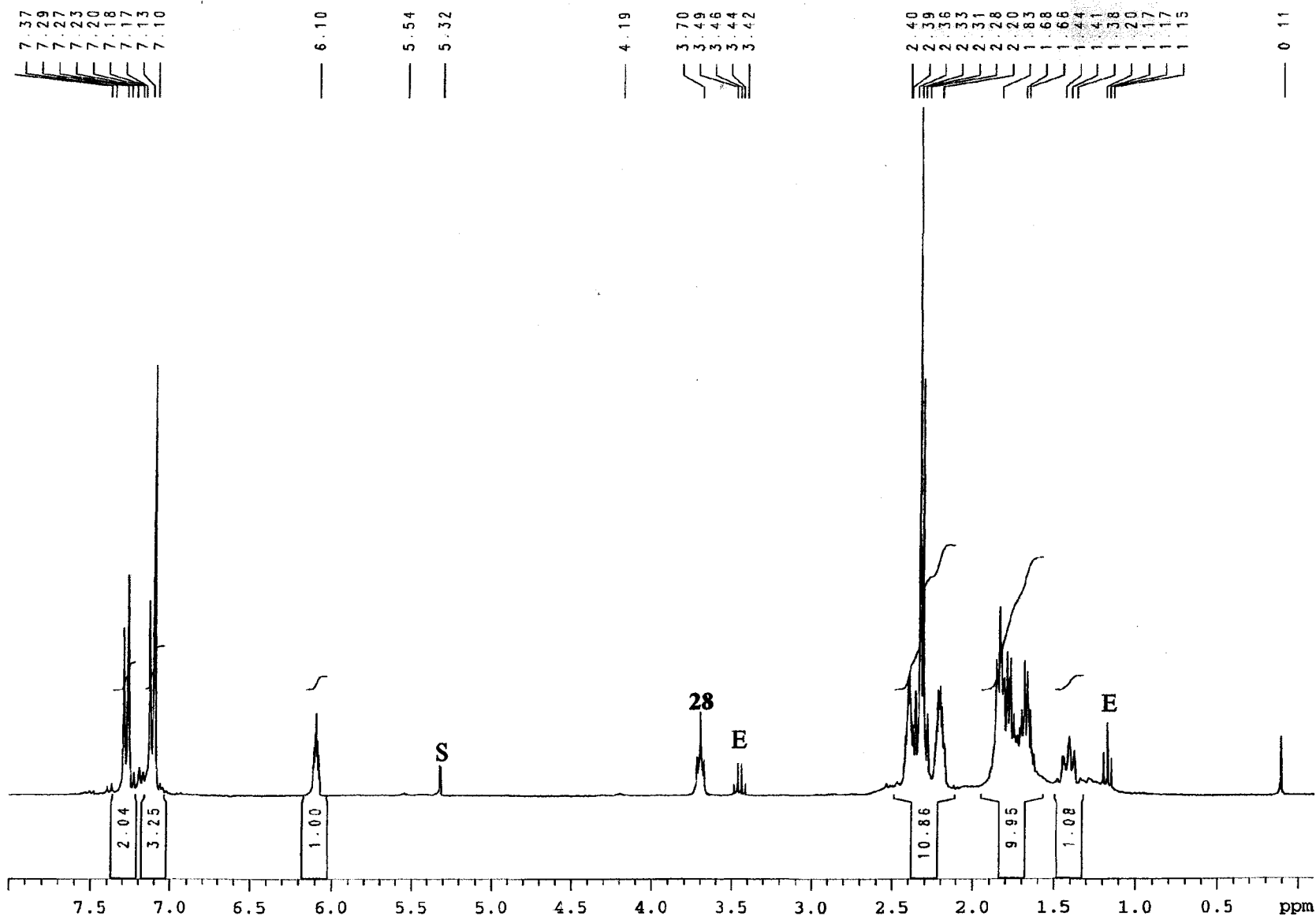


Figure E-6. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of 1-*p*-tolylcyclohexene (29) (S: CD_2Cl_2 , E: diethyl ether, 28: 1-*p*-tolylcyclohexanol).

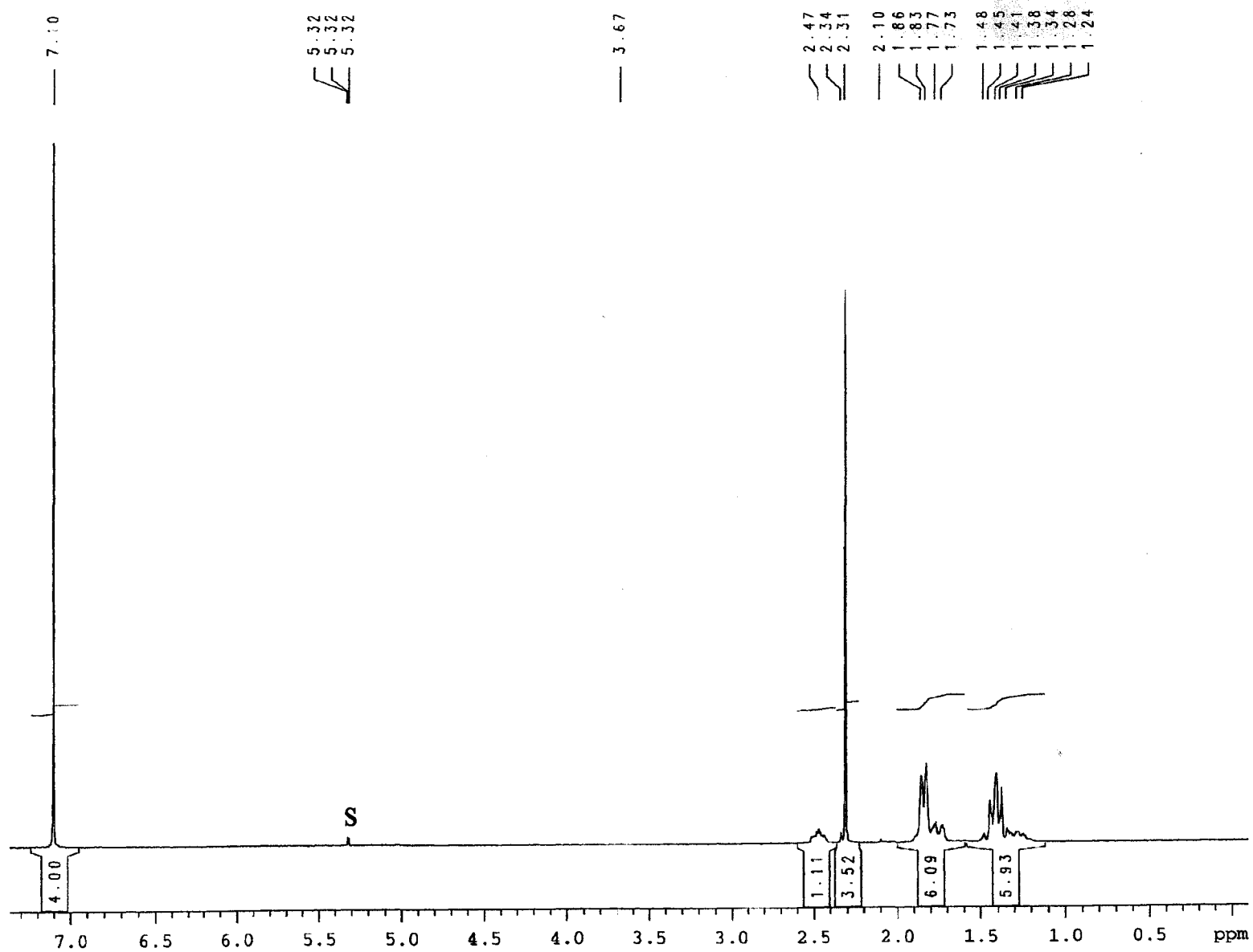


Figure E-7. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of *p*-cyclohexyltoluene (6) (S: CD_2Cl_2)

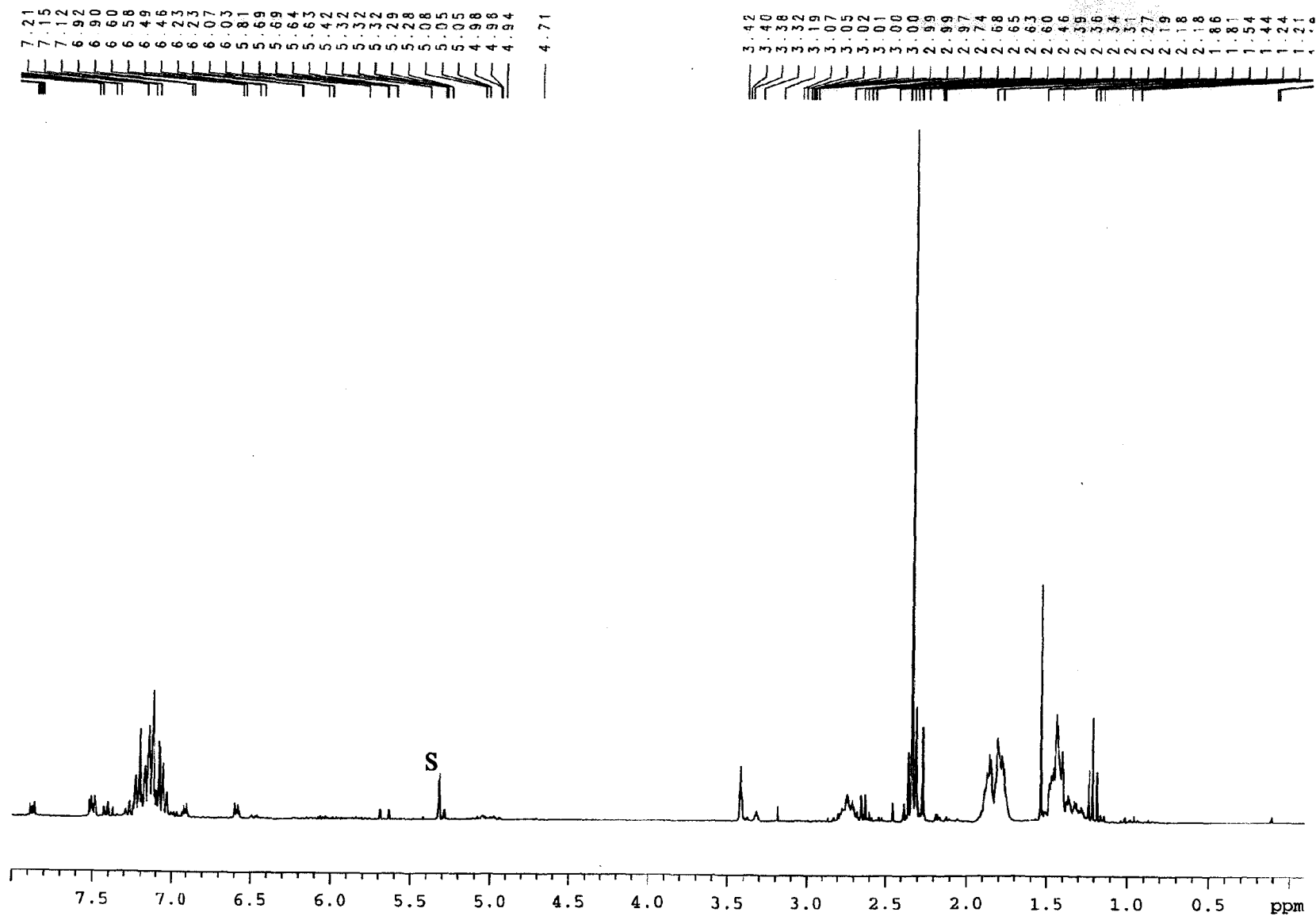


Figure E-8. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of the pyrolysis mixture from the FVP at 800 °C of *o*-cyclohexyltoluene (5) (S: CD_2Cl_2).

SPEC: abf-097.ms 09-Jun-95 Elapse: 10:29.2 839
Samp: o-CYCLOHEXYL TOLUENE FVP @ 800 C IN CD2C Start : 7:43:54 2609
Comm: 2
Mode: +LMR UP LR
Oper:
Base: 115.0 Inten : 185413 Inlet :
Norm: 115.0 RIC : 463292 Masses: 50 > 232
Peak: 1000.00 mmu #peaks: 53

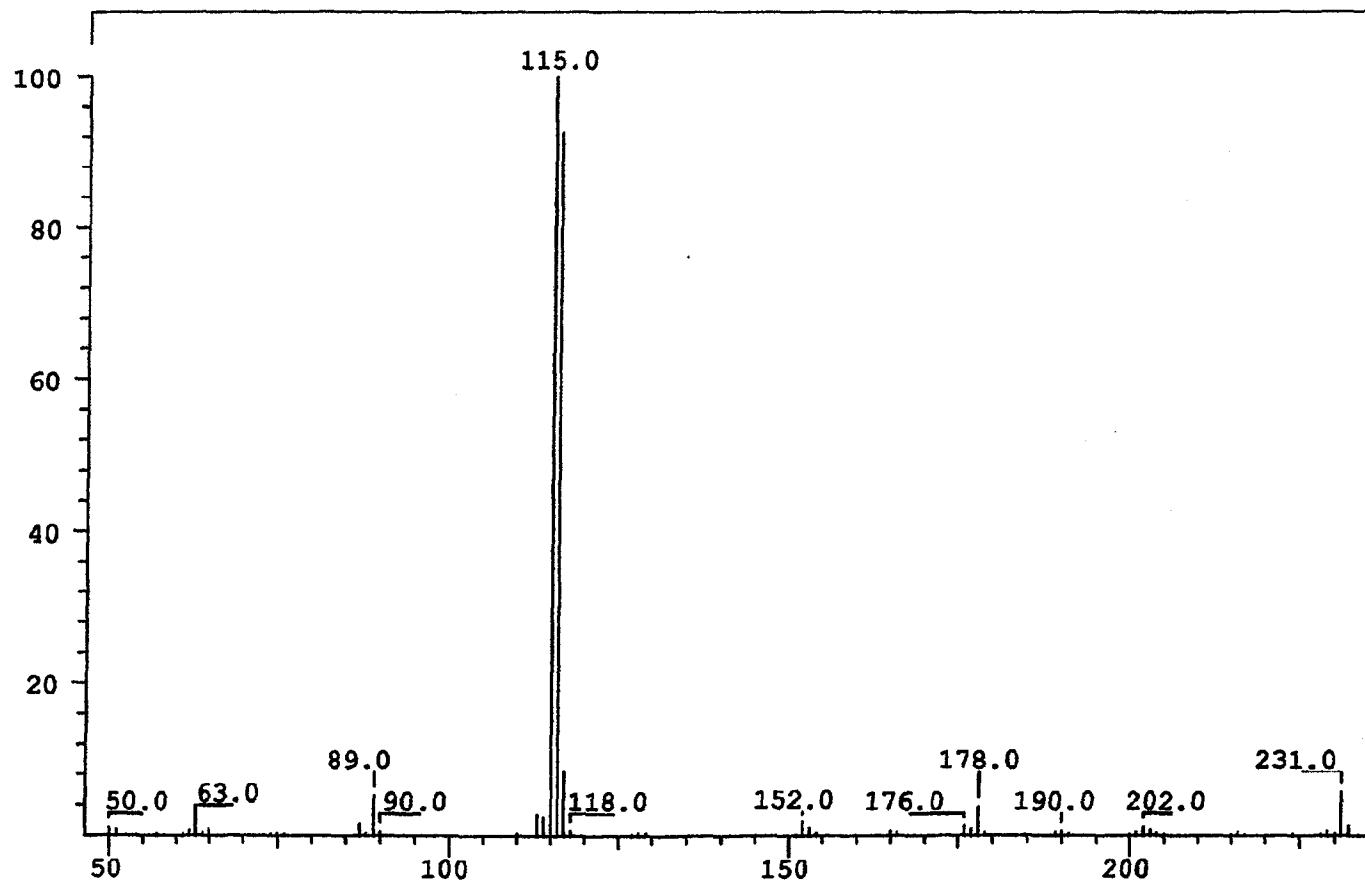


Figure E-9. GC-mass spectrum (EI, 70 eV) of the GC peak assigned to indene (7) in the FVP at 800 °C of 5.

SPEC: abf-097.ms 09-Jun-95 Elapse: 10:43.4 858
 Samp: o-CYCLOHEXYL TOLUENE FVP @ 800 C IN CD2C Start : 7:43:54 2609
 Comm: 2
 Mode: +LMR UP LR
 Oper:
 Base: 117.0 Inten : 30070 Inlet :
 Norm: 117.0 RIC : 115469 Masses: 50 > 461
 Peak: 1000.00 mmu #peaks: 67

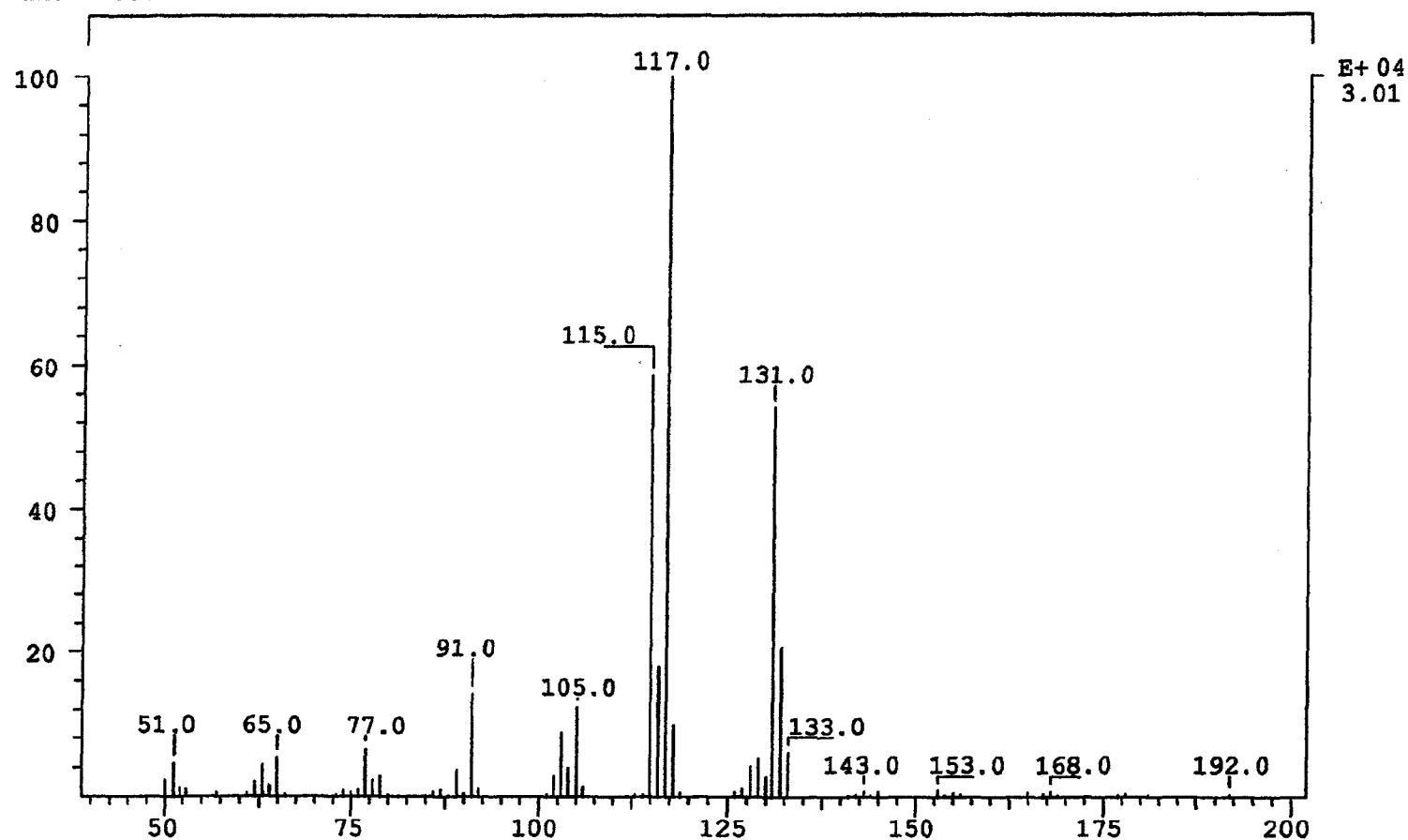


Figure E-10. GC-mass spectrum (EI, 70 eV) of the GC peak assigned to *o*-allyltoluene (9) in the FVP at 800 °C of 5.

SPEC: abf-097.ms 09-Jun-95 Elapse: 12:22.4 990
 Samp: o-CYCLOHEXYL TOLUENE FVP @ 800 C IN CD2C Start : 7:43:54 2609
 Comm: 2
 Mode: +LMR UP LR
 Oper:
 Base: 117.0 Inten : 19631 Inlet :
 Norm: 117.0 RIC : 66043 Masses: 50 > 247
 Peak: 1000.00 mmu #peaks: 72

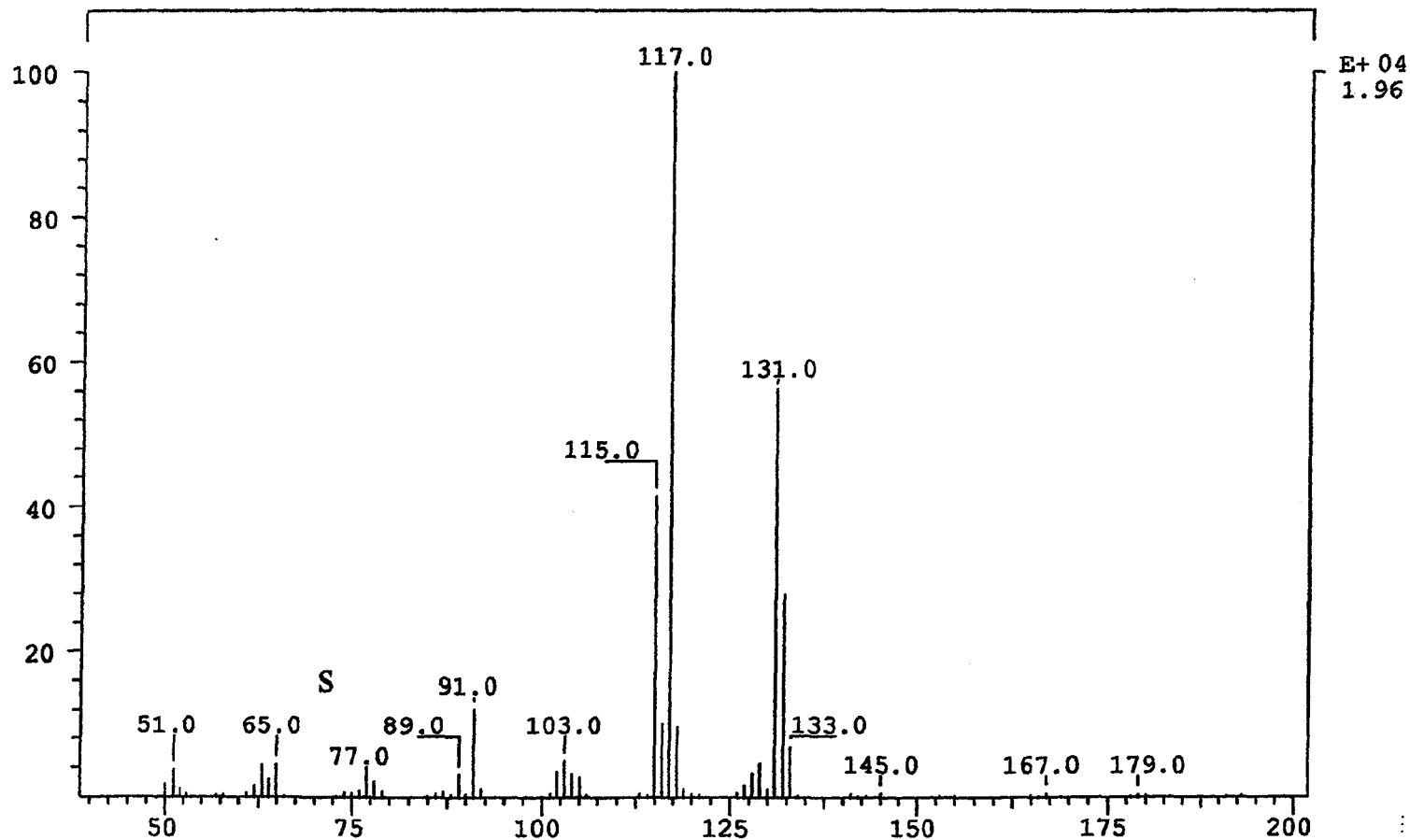


Figure E-11. GC-mass spectrum (EI, 70 eV) of the GC peak assigned to 1-(2-methylphenyl)-1-hexene (15) in the FVP at 800 °C of 5.

SPEC: abf-097.ms 09-Jun-95 Elapse: 27:30 2200
 Samp: o-CYCLOHEXYL TOLUENE FVP @ 800 C IN CD2C Start : 7:43:54 2609
 Comm: 2
 Mode: +LMR UP LR
 Oper:
 Base: 105.0 Inten : 35101 Inlet :
 Norm: 105.0 RIC : 130390 Masses: 50 > 523
 Peak: 1000.00 mmu #peaks: 87

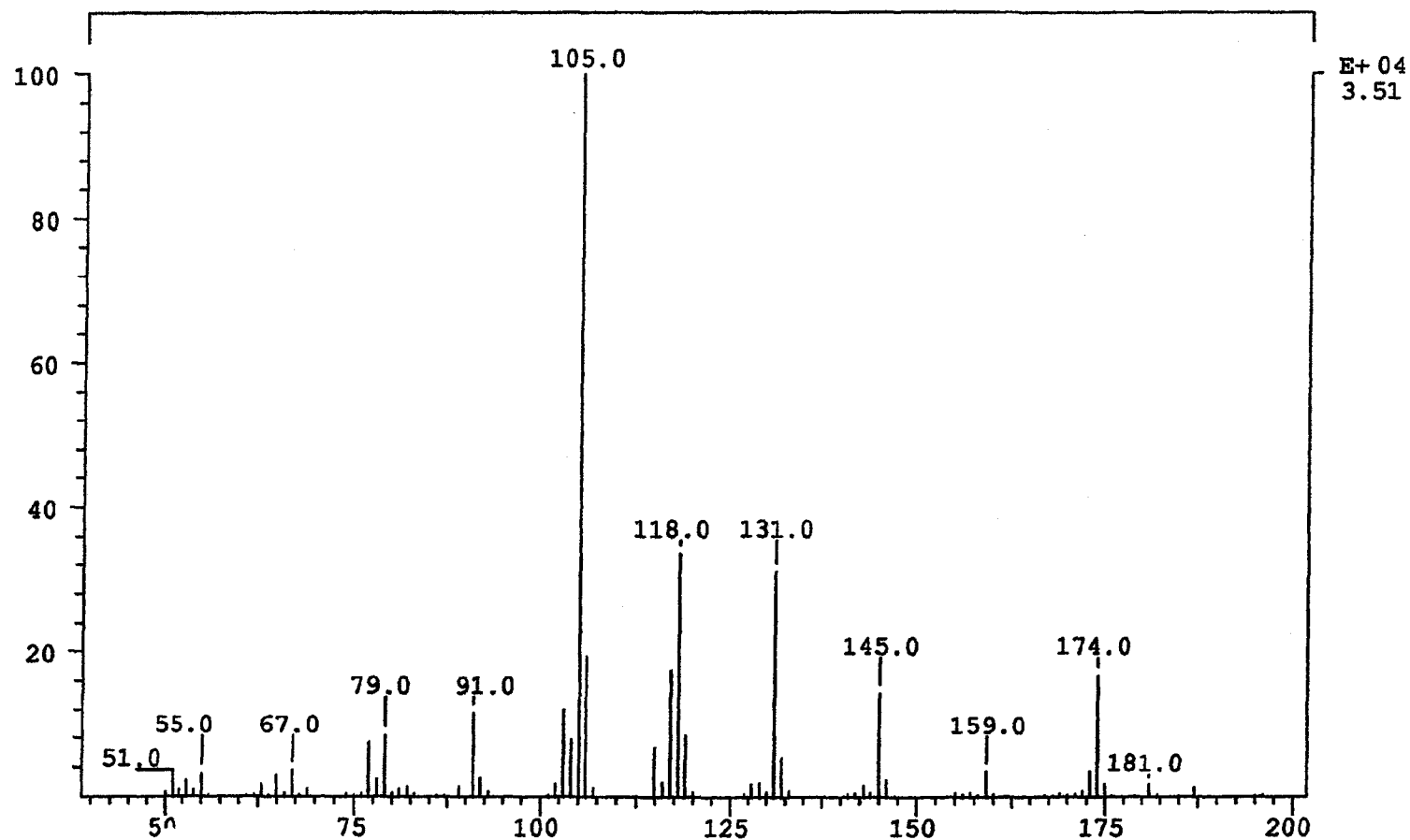


Figure E-12. GC-mass spectrum (EI, 70 eV) of the GC peak assigned to *o*-cyclohexyltoluene (5) in the FVP at 800 °C of 5.

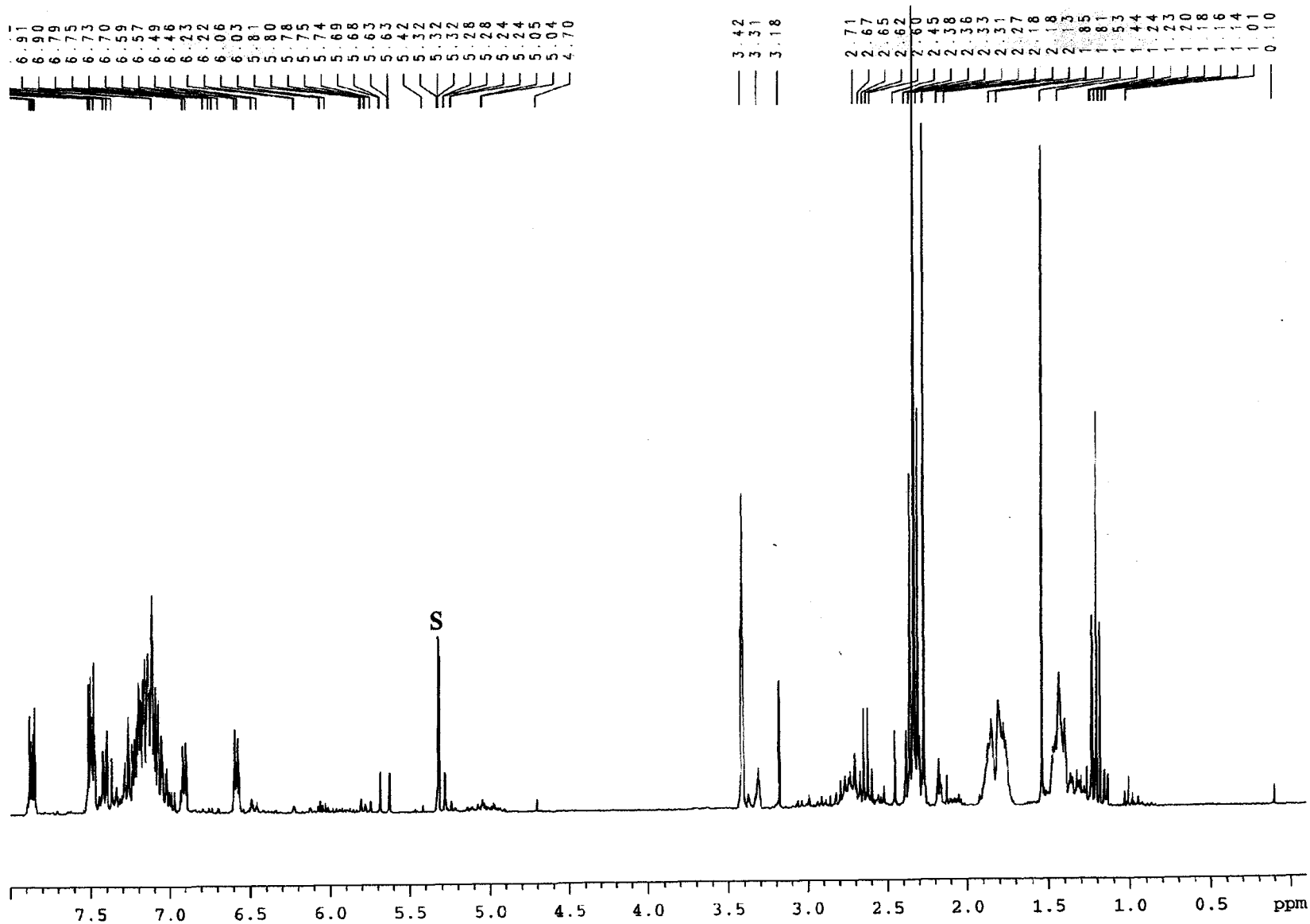


Figure E-13. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of the pyrolysis mixture from the FVP at 850 °C of *o*-cyclohexyltoluene (5) (S: CD_2Cl_2).

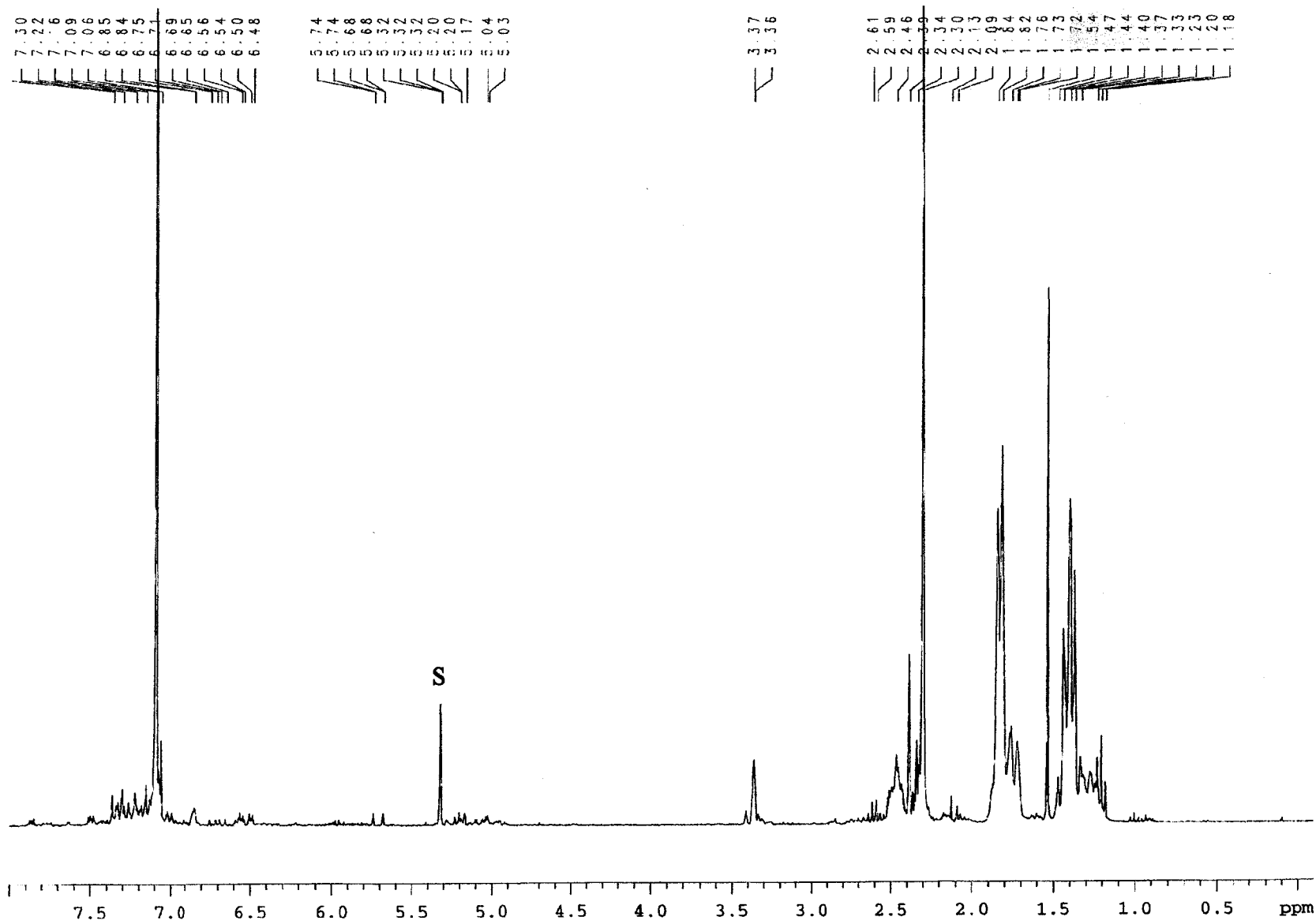


Figure E-14. ^1H NMR spectrum (300 MHz, CD_2Cl_2) of the pyrolysis mixture from the FVP at 800 °C of *p*-cyclohexyltoluene (6) (S: CD_2Cl_2).

SPEC: ABF-099.ms
 Samp: FVP OF p-CT @ 800 C IN CD2CL2
 Mode: +LMR UP LR
 Oper:
 Base: 115.0 Inten : 15037
 Norm: 115.0 RIC : 65575
 Peak: 1000.00 mmu

20-Jun-95 Elapse: 10:07.5 810
 Start : 15:17:27 2897
 Inlet :
 Masses: 50 > 231
 #peaks: 62

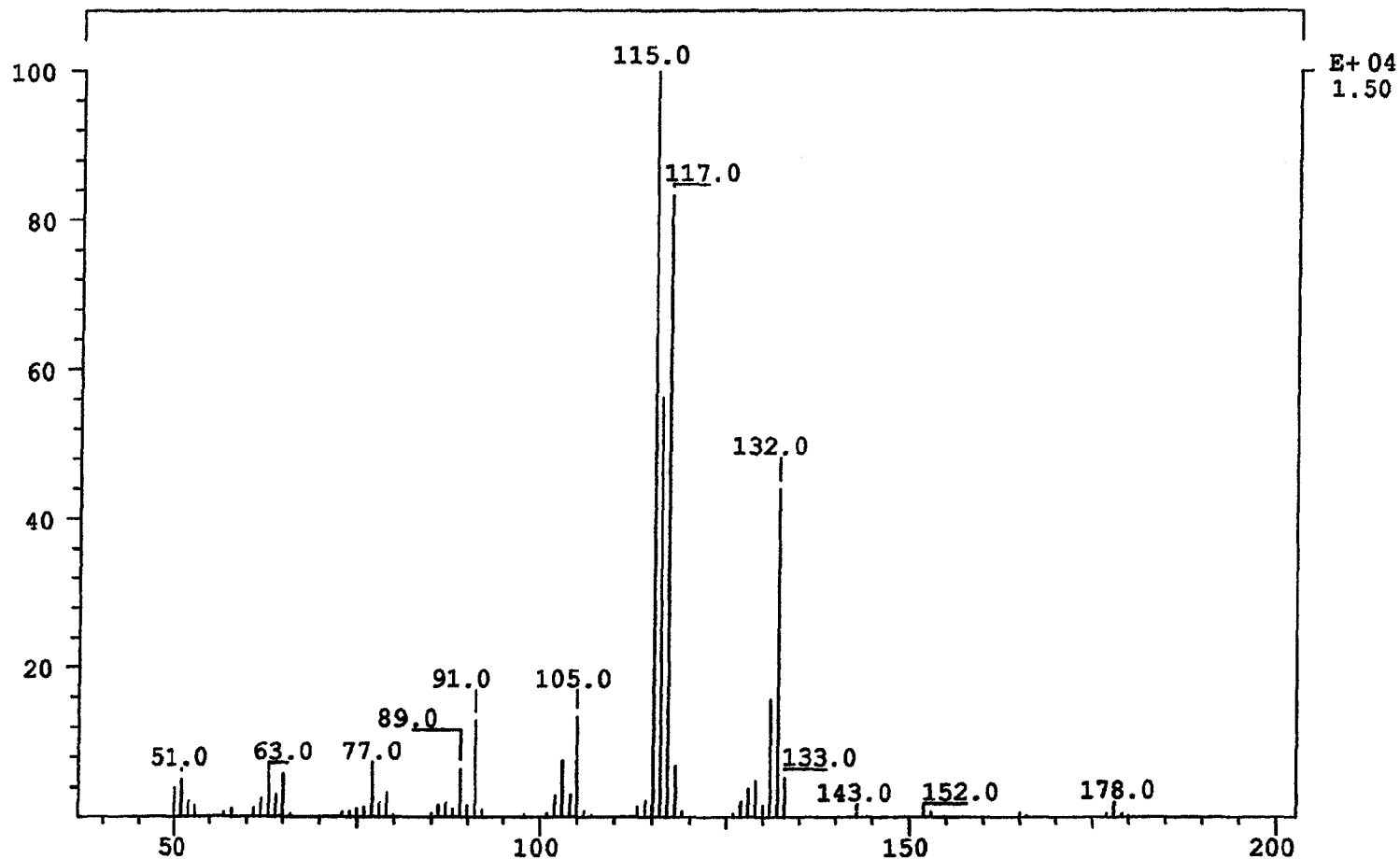


Figure E-15. GC-mass spectrum (EI, 70 eV) of the GC peak assigned to *p*-allyltoluene (**18**) in the FVP at 800 °C of **6**.

SPEC: ABF-099.ms 20-Jun-95 Elapse: 16:24 1312
Samp: FVP OF p-CT @ 800 C IN CD2CL2 Start : 15:17:27 2897
Mode: +LMR UP LR
Oper:
Base: 130.0 Inten : 64382 Inlet :
Norm: 130.0 RIC : 208664 Masses: 50 > 246
Peak: 1000.00 mmu #peaks: 61

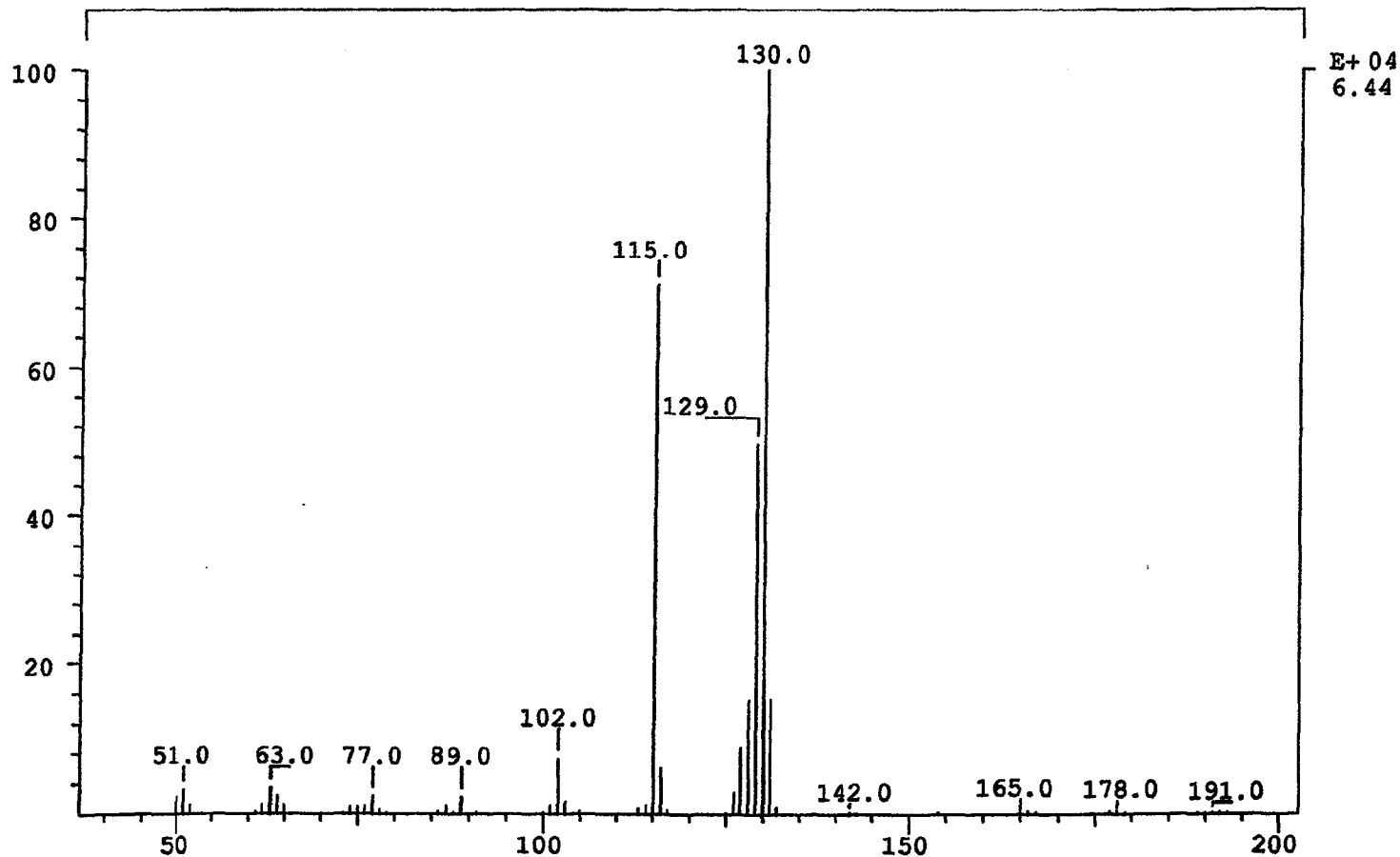


Figure E-16. GC-mass spectrum (EI, 70 eV) of the GC peak assigned to 6-methylindene (16) in the FVP at 800 °C of 6.

SPEC: ABF-099.ms
Samp: FVP OF p-CT @ 800 C IN CD2CL2
Mode: +LMR UP LR
Oper:
Base: 105.0
Norm: 105.0
Peak: 1000.00 mmu

20-Jun-95

Elapse: 26:51 2148
Start : 15:17:27 2897

Inten : 13138
RIC : 48436

Inlet :
Masses: 50 > 204
#peaks: 73

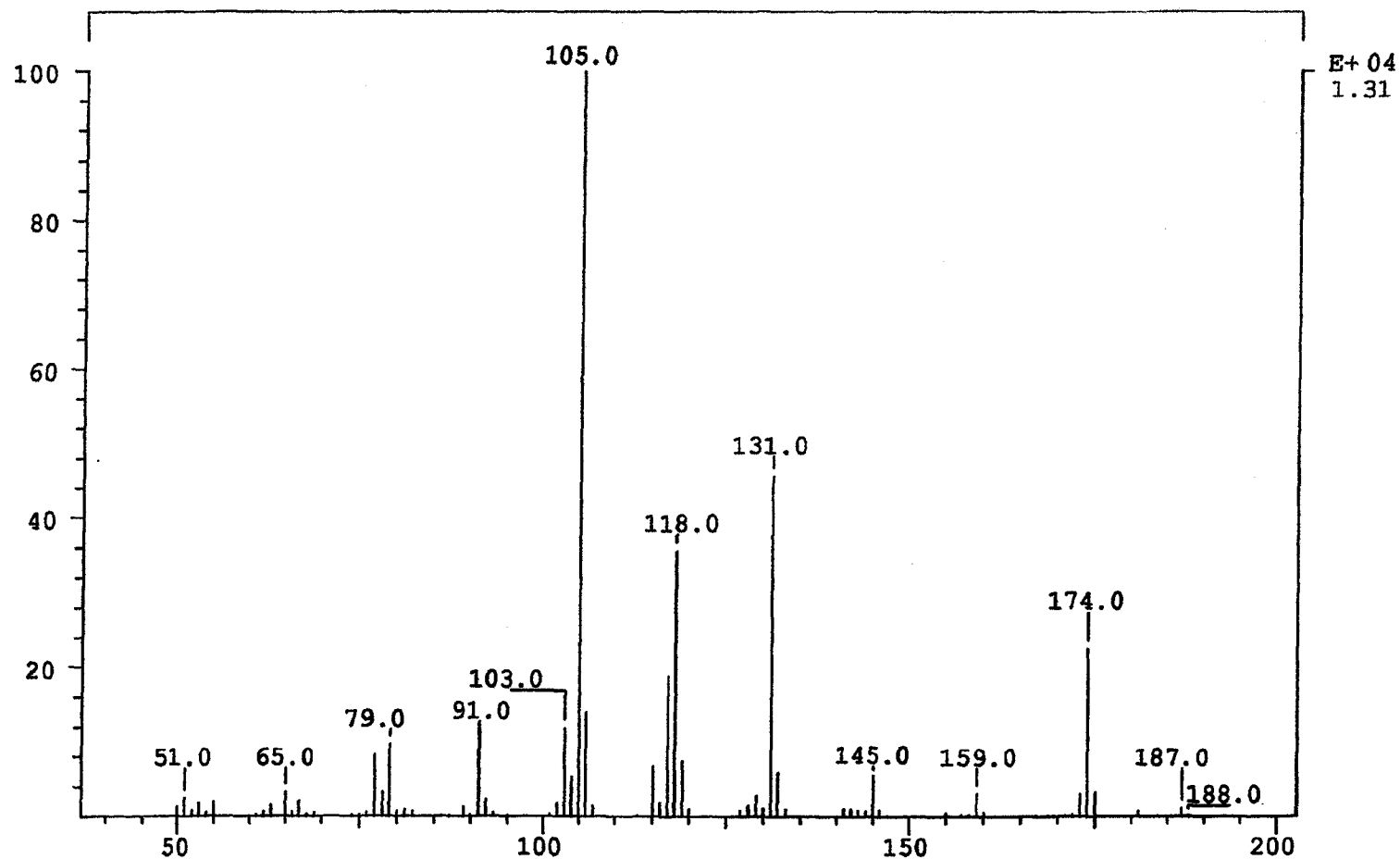


Figure E-17. GC-mass spectrum (EI, 70 eV) of the GC peak assigned to 1-(4-methylphenyl)-1-hexene (19) in the FVP at 800 °C of 6.

SPEC: ABF-099.ms
Samp: FVP OF p-CT @ 800 C IN CD2CL2
Mode: +LMR UP LR
Oper:
Base: 131.0
Norm: 131.0
Peak: 1000.00 mmu

20-Jun-95

Elapse: 29:56 2395
Start : 15:17:27 2897

Inlet :
Masses: 50 > 207
#peaks: 75

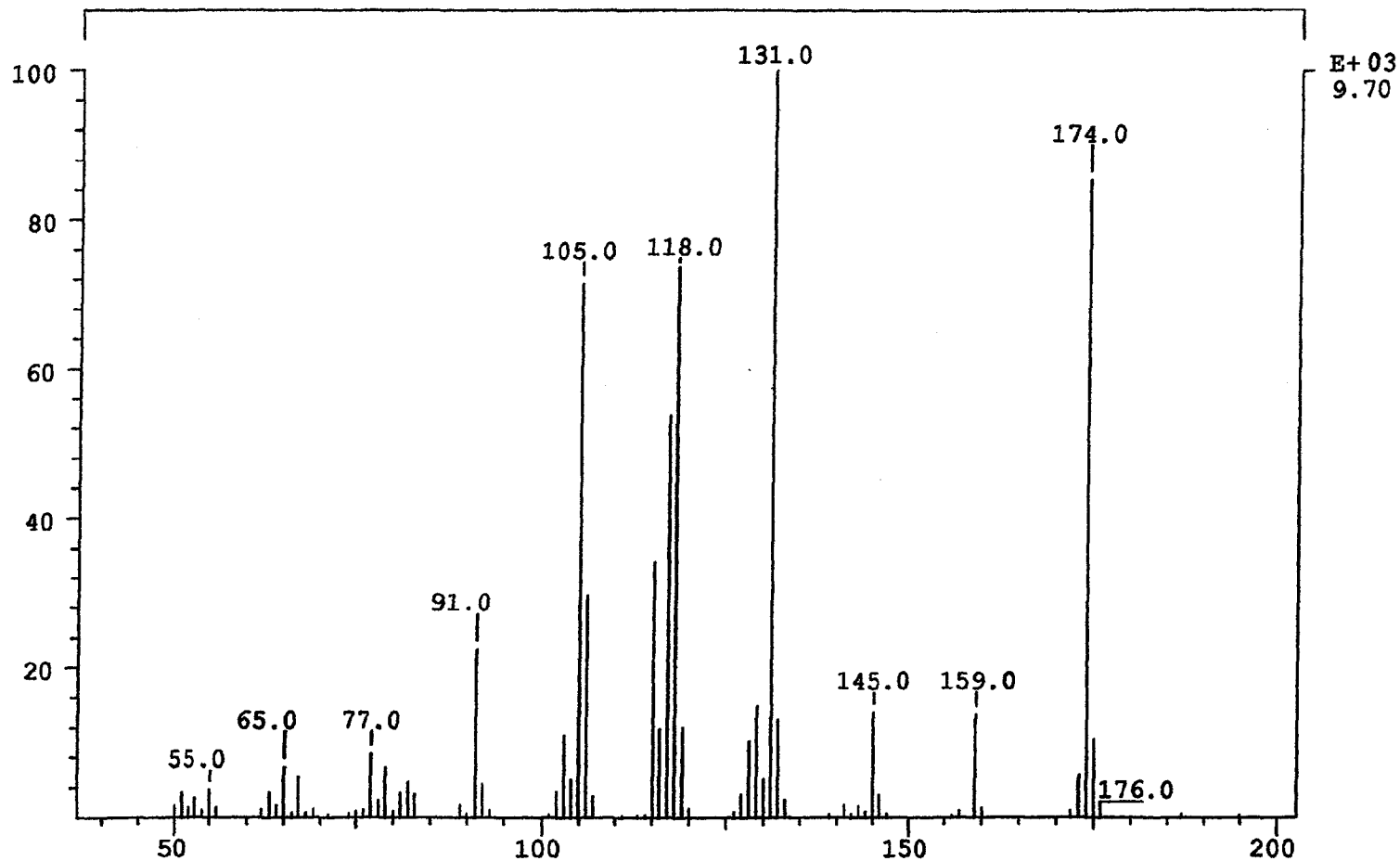
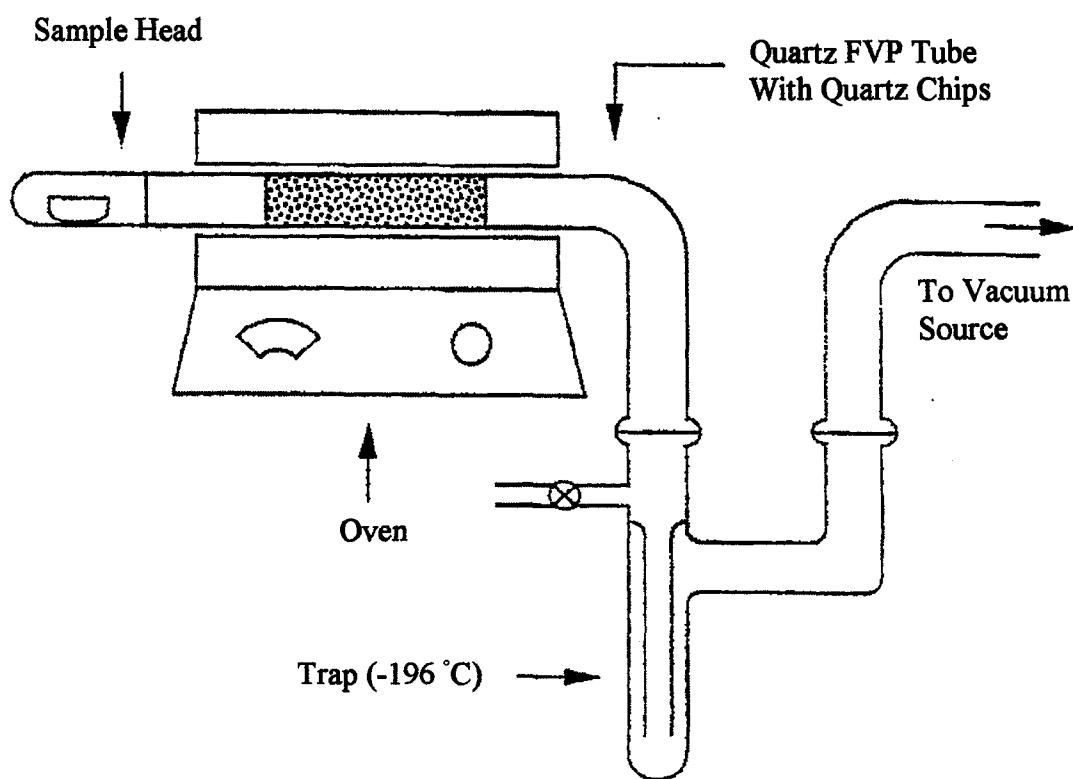


Figure E-18. GC-mass spectrum (EI, 70 eV) of the GC peak assigned to *p*-cyclohexyltoluene (6) in the FVP at 800 °C of 6.

**APPENDIX F. GENERAL SCHEMATIC DIAGRAM OF
THE FLASH VACUUM APPARATUS**



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I dedicate this dissertation to my mother, who taught me to believe in myself, and to my wife and children, who remind me to believe in myself everyday.