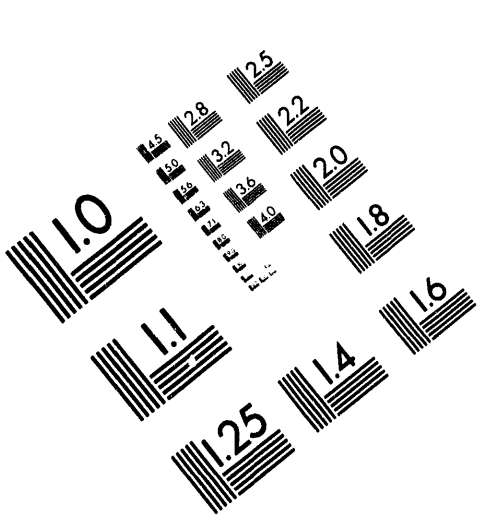

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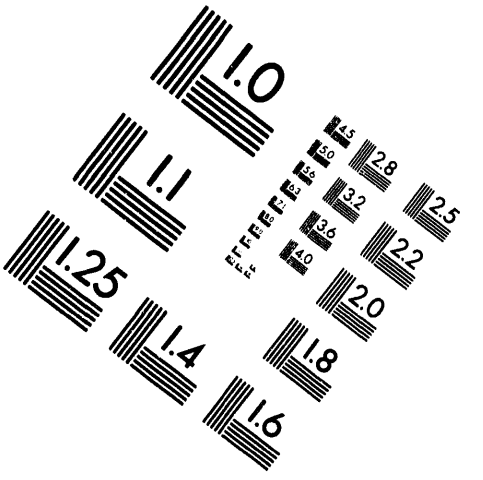

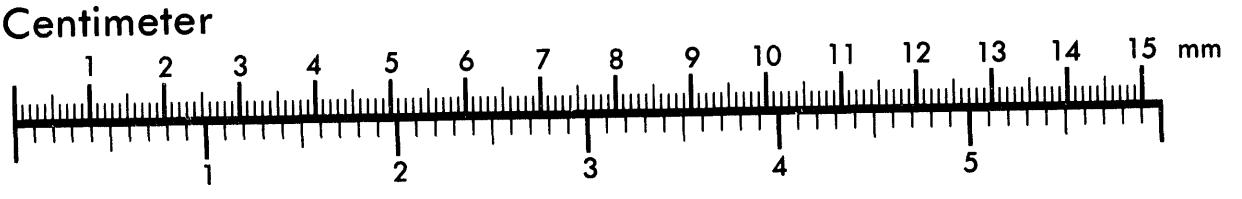

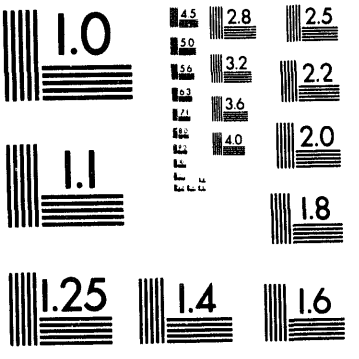

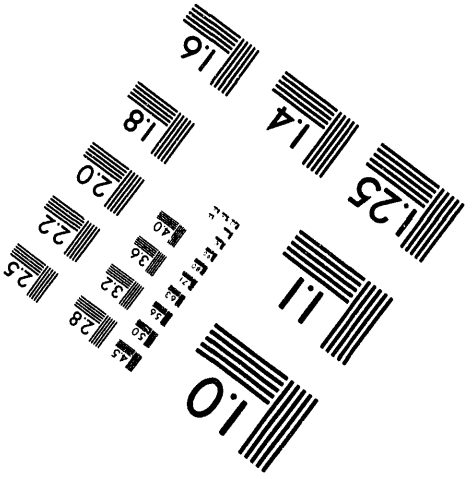

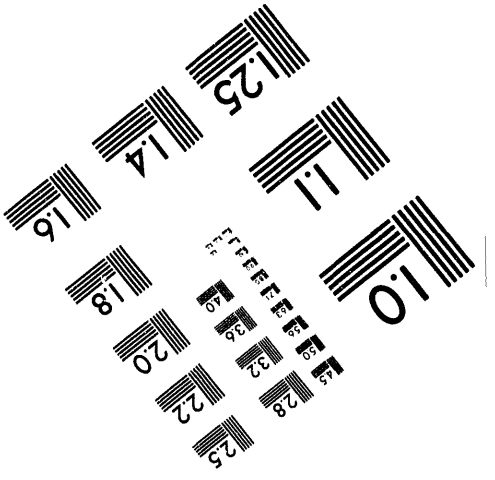

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IS-T 1685

The Mechanism of the Oligomerization of Thiophene-based Para-quinodimethanes

by

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MS Thesis submitted to Iowa State University

Ames Laboratory, U.S. DOE

Iowa State University

Ames, Iowa 50011

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DISCLAIMER

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GENERAL INTRODUCTION

For the last decade, the Trahanovsky research group has focused on the study of various reactive molecules such as *o*-quinodimethanes (*o*-QDM's) and *p*-quinodimethanes (*p*-QDM's) derived from benzene, furan, and thiophene. These types of molecules are reactive and dimerize or polymerize at room temperature. One of the group's interests is to understand the dimerization mechanism of these molecules.

Paper 1 describes the preparation and dimerization product analyses of 2-ethylidene-5-methylene-2,5-dihydrothiophene. Insights provided by these results into the mechanism of the dimerization of 2,5-dimethylene-2,5-dihydrothiophene are discussed.

In paper 2, a convenient synthesis of cyclooctadecane is presented.

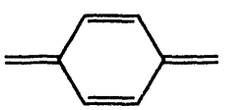
EXPLANATION OF THESIS FORMAT

This thesis consists of two complete papers in the style suitable for publication in journals published by the American Chemical Society. As such, each paper has its own numbering system and reference section following the text. The research described in the results and experimental section was done by the author unless otherwise indicated. Detailed analytical data and spectra are contained in a appendix following each section.

PAPER 1. CHARACTERIZATION AND OLIGOMERIZATION OF 2,5-DIMETHYLENE-2,5-DIHYDROTHIOPHENE AND 2-ETHYLIDENE-5-METHYLENE-2,5-DIHYDROTHIOPHENE

INTRODUCTION

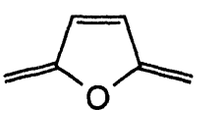
Considerable attention has been focused on *para*-quinodimethanes, a large and important class of reactive molecules. Szwarc was the first to observe that the pyrolysis of *p*-xylene at low pressure leads to the formation of a white polymeric material which he suggested was formed via the reactive intermediate *p*-QDM **1**,



1

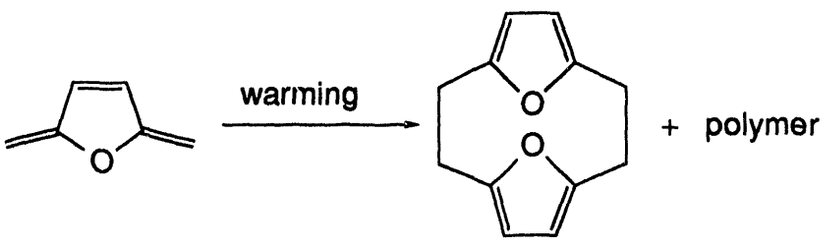
p-xylylene.[1] Errede and co-workers showed that solutions of *p*-xylylene (**1**) could be prepared at low temperatures (-78°C) and reactions of **1** with a variety of molecules were studied.[2] Pearson and co-workers have subsequently prepared **1** and the naphthalene-based and 9,10-anthracene-based *p*-QDM's by the pyrolytic cleavage of the corresponding paracyclophanes and reported their ^{1}H NMR, IR, and UV-visible spectra.[3]

The first heterocyclic *p*-QDM's were reported by Winberg et al. in 1960.[4] 2,5-Dimethylene-2,5-dihydrofuran (O-monomer **2**) was prepared from



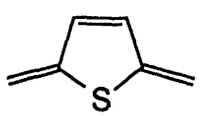
2

(5-methyl-2-furfuryl)trimethylammonium ion by a 1,6-elimination reaction of the Hofmann type involving removal of a proton from the methyl group and elimination of trimethylamine. O-Monomer **2** was isolated at -78°C and upon warming a dimer, [2.2](2,5)furanophane (OO-dimer **3**), and polymer were formed.



2 **3**

The sulfur analog, 2,5-dimethylene-2,5-dihydrothiophene (S-monomer **4**) was first obtained by Anderson by pyrolysis of 5-ethyl-2-methylthiophene at 825°C and collection of the monomer in a liquid-nitrogen cooled trap.[5] On warming to room temperature polymeric poly(2,5-dimethylene-2,5-dihydrothiophene) formed spontaneously. S-Monomer **4** was not directly observed.

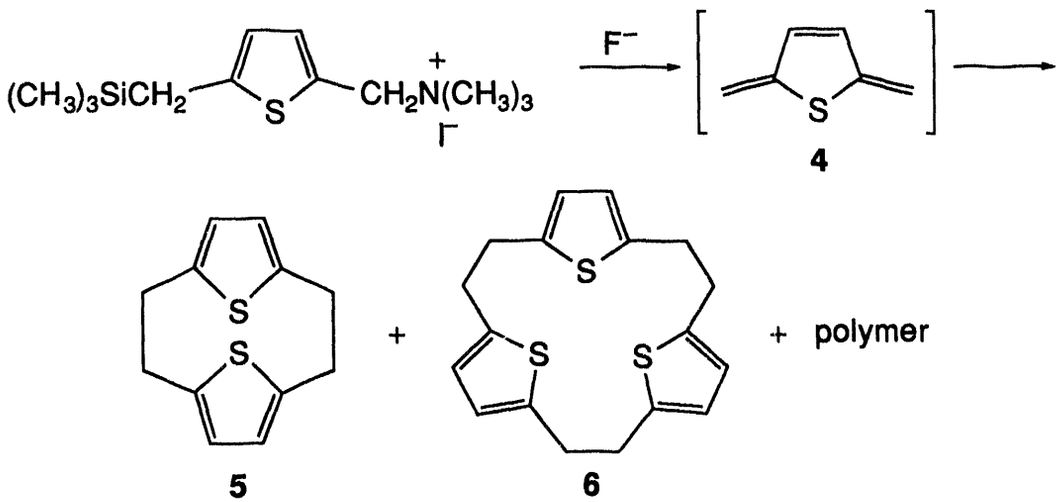


4

Winberg et al. prepared S-monomer **4** by a procedure analogous to that used to prepare O-monomer **2**. However, the sulfur analog appeared to be much more reactive than the oxygen monomer as **4** could not be observed by this method.[4] The only products isolated from this reaction were a dimer, [2.2](2,5)thiophenophane (SS-dimer **5**), and polymer.

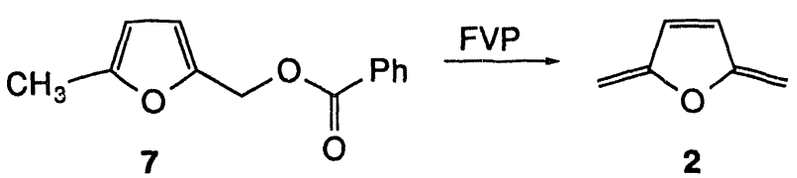
Ito, Nakatsuka, and Saegusa reported that the fluoride-ion induced 1,6-elimination from the appropriate trimethylsilyl-trimethylammonium ion can be used to prepare *p*-xylylene (**1**), O-monomer **2**, and S-monomer **4**.[6] O-Monomer **2** was sufficiently long-lived to be observed by ^{1}H NMR in the reaction mixture. In the sulfur case, a mixture of SS-dimer **5** and SSS-trimer **6** were produced.

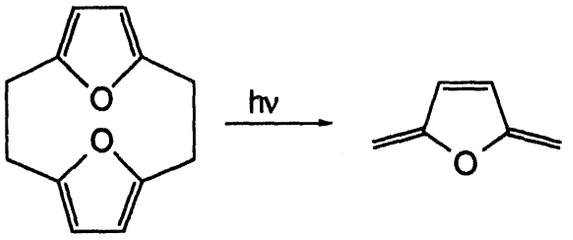
This is the first report of SSS-trimer **6** which includes its melting point, and ^{1}H NMR, UV, and mass spectra. SSS-Trimer **6** had been reported in 1974 by Mizogami and co-workers as a byproduct in a cross-breeding Hofmann reaction, but the report includes no physical characteristics of SSS-trimer **6**.[7]



The structure of SS-dimer **5** was studied as early as 1965 by Kamenar and Prout.[8] The ^{1}H NMR of OO-dimer **3** was studied in 1967 by Sutherland and co-workers.[9] The structures of both dimers **3** and **5** were determined from three-dimensional X-ray data by Randaccio and co-workers.[10]

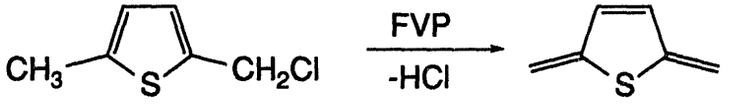
O-Monomer **2** was also prepared by the flash vacuum pyrolysis (FVP) of **7**,[11] and by the [6+6] photocleavage of OO-dimer **3**.[12] In both cases **2** was observed at room temperature by ^{1}H NMR[11] or UV-vis[12] spectroscopy.





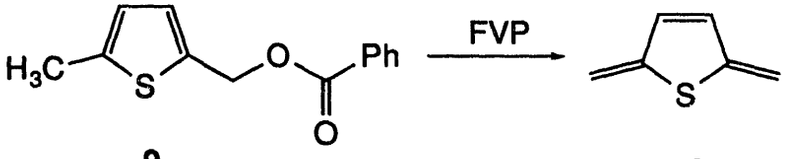
3 **2**

The direct observation of S-monomer **4** was reported only recently by Schweig and co-workers.[13] S-Monomer **4** was prepared by the FVP of **8** and characterized by UV photoelectron, UV/VIS, and IR spectroscopy. S-Monomer **4** was also observed when generated by the FVP of SS-dimer **5**.[13]



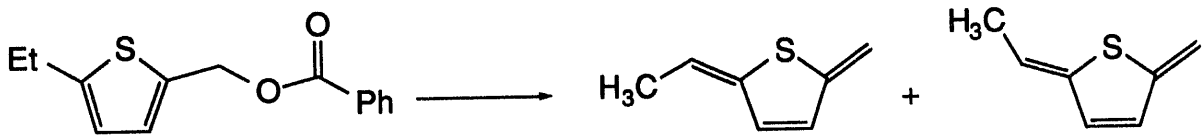
8 **4**

We have found that S-monomer **4** can be prepared in good yield by the FVP of 5-methyl-2-thiophenemethyl benzoate (**9**). We have obtained the ^{1}H and ^{13}C NMR spectra of **4** at low temperatures, observed **4** by GC/IR and GC/MS, and studied the oligomerization of **4**. In addition, in order to fully understand the mechanism of the



9 **4**

dimerization and trimerization of **4**, the oligomerization of a mixture of the methyl derivatives of **4**, E, and Z-2-ethylidene-5-methylene-2,5-dihydrothiophene (**11a** = E, **11b** = Z), which was also prepared by FVP of 5-ethyl-2-thiophenemethyl benzoate (**10**), was also studied. The results of this work are reported herein.

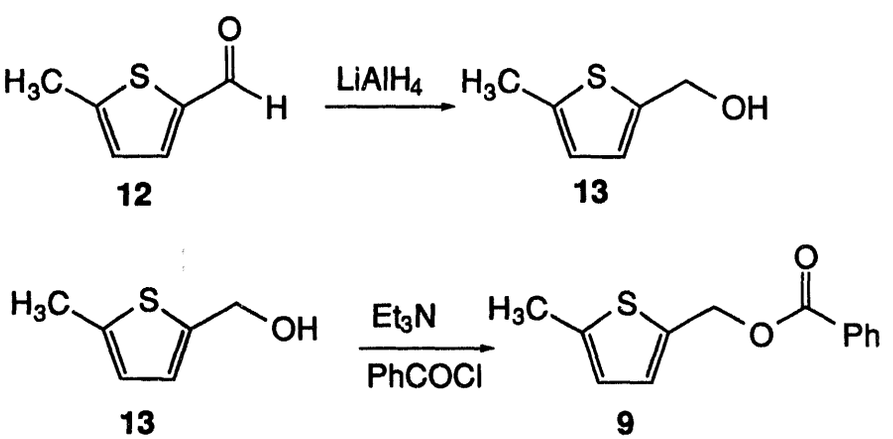


10 **11a** **11b**

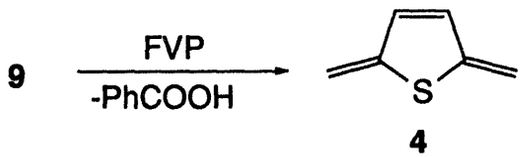
RESULTS AND DISCUSSION

Preparation and Flash Vacuum Pyrolysis of 5-Methyl-2-thiophenemethyl Benzoate (9)

5-Methyl-2-thiophenemethyl benzoate (**9**) was prepared in high yield by the reduction of 5-methyl-2-thiophenecarboxaldehyde (**12**) with lithium aluminum hydride followed by the esterification of the resulting alcohol (**13**) with benzoyl chloride in the presence of triethylamine.



FVP of benzoate **9** at 650°C and *ca.* 10^{-5} torr produced in *ca.* 75% yield S-monomer **4**, which appeared as a yellow band in the cold trap at 77 K. Benzoic acid and a small amount of a white polymer were also produced. Carbon disulfide-chloroform was added to the trap and the mixture was then warmed to -78°C. This provided a solution of **4** which was relatively stable under these conditions.



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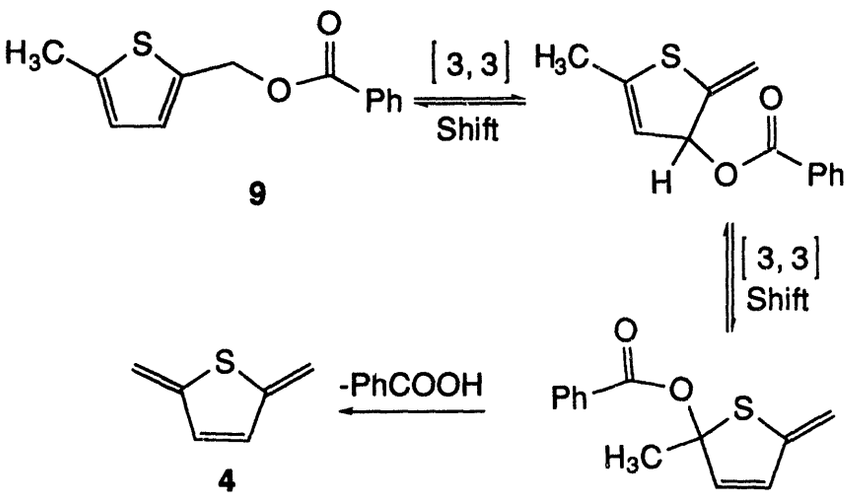
The structure of **4** was confirmed by its spectral properties. The ^{1}H NMR spectrum (at -70°C) shows three singlets at δ 6.52, 5.24, and 5.02. The ^{13}C NMR spectrum (at -70°C) also shows three peaks at δ 150.5, 136.6, and 104.7. The IR and mass spectra, obtained by GC/IR and GC/MS, are also consistent with structure **4**.

When a 0.1 *M* solution of S-monomer **4** was allowed to warm to room temperature, SS-dimer **5**, SSS-trimer **6**, and polymer were produced. The structures of products **5** and **6** were indicated by their spectral properties, which agree well with the available literature data.[4,6] The ratio of SS-dimer **5** to SSS-trimer **6** was found to be 1 to 3.0 as measured by GC[14].

Evidence for formation of an SSSS-tetramer with a molecular weight of 440 was obtained by GC-MS[14]. Quantitative GC showed 1.88 mg (0.0042 mmol, 0.677 mol %, based on amount of initial monomer) of the SSSS-tetramer.

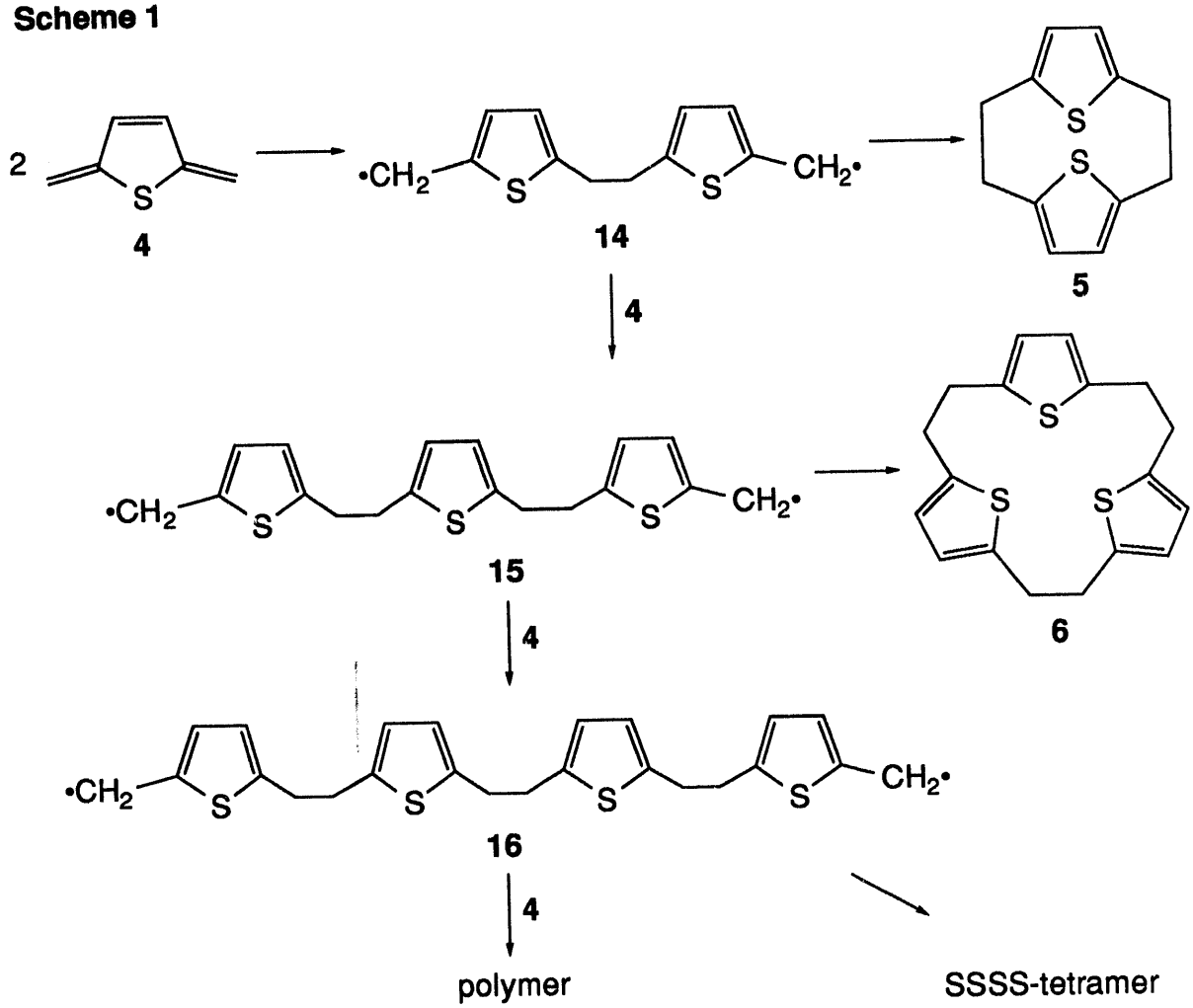
A high dilution experiment was carried out to explore the possibility of obtaining a greater yield of SS-dimer **5**[14]. A preparative-scale pyrolysis (2.0 g) of benzoate **9** was carried out with S-monomer **3** being dissolved in 1.025 L of carbon disulfide, which resulted in a 0.0066 M solution of the S-monomer. After five days at room temperature, the mol ratio of SS-dimer **5** to SSS-trimer **6** produced was 8.8:1, as measured by GC.

The formation of 2,5-dimethylene-2,5-dihydrothiophene (**4**) by FVP of the thiophene benzoate **9** is explained by a mechanism proposed for the furan analog, two [3,3] sigmatropic shifts followed by β elimination of benzoic acid.[11,15]



A concerted or two-step diradical mechanism could be proposed for conversion of S-monomer **4** to its corresponding SS-dimer **5**. However, a thermal concerted [π^6s + π^6s] cycloaddition is not allowed by the Woodward-Hoffmann rules[16] and is thus unlikely. Moreover, formation of a large amount of SSS-trimer **6** is easily explained by a diradical mechanism. We propose, therefore, the mechanism presented in Scheme 1.

Scheme 1



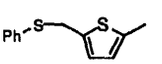
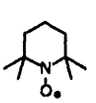
In this mechanism two molecules of **4** combine to give diradical **14** which can close to give SS-dimer **5** or react with another molecule of **4** to give diradical **15**, the precursor of SSS-trimer **6**. The production of a small amount of SSSS-tetramer is consistent with diradical **15** reacting with a molecule of **4** to give diradical **16** which can close to give an SSSS-tetramer. Each diradical could either close to give an oligomer or react with a molecule of **4** to give the next higher diradical. As the diradical becomes larger, closure to give an oligomer should be less likely since it

should be more difficult for the two radical sites to encounter each other. Apparently diradical **16** and the larger diradicals lead primarily to polymer.

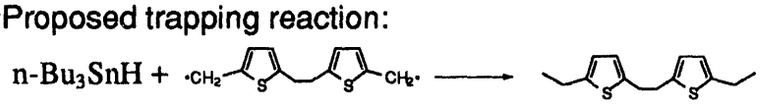
Attempted Trapping of Diradical Intermediate 14

Conventional trapping agents. In order to attempt to obtain evidence for a diradical mechanism for dimerization and trimerization of S-monomer (**4**), a series of trapping experiments along with their control reactions was carried out. The results are listed in Table 1.

Table 1. Summary of Trapping Experiment Results .

Trapping agent	Ratio trapping agent : S-monomer **4**		Product(s)
1,4-Cyclohexadiene	400	1	dimer **5** + trimer **6**
9,10-Dihydroanthracene	40	1	dimer **5** + trimer **6**
Dimethyl maleate	20	1	dimer **5** + trimer **6**
Phenylsilane	16	1	dimer **5** + trimer **6**
Styrene	10	1	dimer **5** + trimer **6**
Thiophenol	19	1	 **17**
Tri-n-butyltin hydride[a]	100	1	Several tin compounds, no compound **18**[a]
TEMPO[b] 	2	1	Structure could not be determined[b]

[a]Proposed trapping reaction:

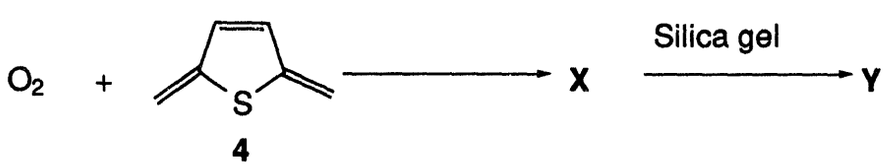


14 **18**

[b]After preparative HPLC separation of the product mixture, ^{1}H NMR and mass spectra of the major component were obtained, but its structure could not be determined from these data.

No evidence for trapping of an intermediate diradical was obtained with any of these trapping agents. In the cases where the normal oligomerization products were obtained, if there is a diradical intermediate it must cyclize before the agent can react with it.

Oxygen as a trapping agent. Since oxygen is a scavenger of free radicals[17], it was used to attempt to trap diradical intermediate **14**. Oxygen was bubbled through a series of solutions of 0.1 M monomer **4** for 5, 10, 20, 50, 60, and 180 seconds. At the same time nitrogen was bubbled through a series of the same monomer concentration solutions for comparable time periods. ^{1}H NMR spectroscopy was used to examine the reaction products. It was found that a new compound, **X**, was obtained when oxygen was bubbled through the S-monomer solution. Separation of compound **X** was attempted, but compound **Y** was obtained instead. We believe **X** is an oxygen-containing compound, but we could not determine the structure of either **X** or **Y**. ^{1}H NMR spectra of **X** and **Y** are presented in the appendix (see appendix, Figure **A-6**, **7**).

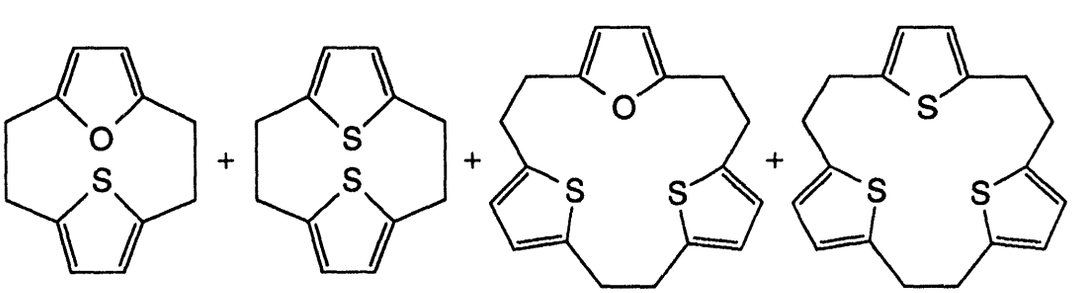


4

The ^{1}H NMR spectrum ($CDCl_3$) of compound **X** shows a pair of singlets at 6.865 and 4.988 ppm in a 1 to 2 ratio. These singlets increased as the time of oxygen bubbling increased (see appendix, Figure **A-8**, **9**). GC analysis of both the oxygen and nitrogen bubbling experiments shows that the dimer **5** to trimer **6** ratio is different. In the oxygen case, the ratio of dimer **5** to trimer **6** is higher than in the nitrogen case (see appendix, Figure **A-10**, **11**). In these experiments, we believe oxygen added to S-monomer **4** directly to form compound **X**. With oxygen the

oligomerization process is complete within 11 hours (see appendix, Figure **A-12**), but with nitrogen, it takes a longer time (48 h) to consume the monomer. No evidence for a trapped diradical was found.

Trapping by 2,5-dimethylene-2,5-dihydrofuran (2). Although the above radical trapping reactions failed, trapping by O-monomer **2** was successful. O-Monomer **2** was selected as a potential trap of diradical intermediate **14**, because it is similar both in size and reactivity to S-monomer **4**.[14] O-Monomer **2** was prepared by FVP of **7** at 560 °C and *ca.* 10^{-5} torr[11,15] and the solution in CS_2 was stored at -78 °C overnight. The following day S-monomer **4** was prepared, the solutions mixed, and the relative concentrations of the monomers in the mixture were determined by ^1H NMR spectroscopy. The mixture was allowed to react at room temperature overnight until none of S-monomer **4** remained. However, due to the differences in reactivity, much of O-monomer **2** remained after all S-monomer **4** was gone. The excess O-monomer **2** was selectively destroyed by the addition of acetic acid. The excess acid was easily removed by basic workup without damage to the oligomerization products. Four compounds containing the thiophene moiety were produced: OS-dimer **19**,[18] SS-dimer **5**, OSS-trimer **20**, and SSS-trimer **6**. Relative yields of each depended on the ratio of monomers used and are summarized in Table 2.



19 **5** **20** **6**

Table 2. Summary of Yields of Products in the Co-oligomerization of O-Monomer **2** and S-Monomer **4**

Product	Run 1 1:1 ratio[a]	Run 2 3:1 ratio[a]		Run 3 6:1 ratio[a]	
	Relative Yield, mole %[b]	Relative Yield, mole %[b]	Absolute Yield, mg[c]	Absolute Yield, %[d]	Relative Yield, mole %[b]
OS-dimer **19**	34.2	56.6	44.1	18.1	58.3
SS-dimer **5**	24.1	12.6	25.6	19.5	31.3
OSS-trimer **20**	10.4	12.6	7.2	3.8	6.2
SSS-trimer **6**	31.3	18.2	5.1	3.8	4.2

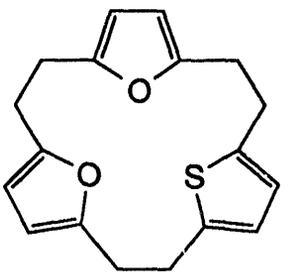
[a]Ratio of O-monomer **2** to S-monomer **4**.

[b]Relative yields are moles per 100 moles of products based on only the OS, SS, OSS, and SSS products and were determined by GC analysis (response factors proportional to weight were assumed).

[c]Absolute yields in Run 3 were determined by GC using biphenyl as an internal standard.

[d]Absolute yield based on moles of S-monomer **4** available (this assumes a 75% yield from benzoate **9**).

Some OO-dimer **3** was also produced, but amounts varied due to the variation in the length of time the solution of monomers was allowed to stand before the acetic acid treatment to destroy the excess O-monomer **2**. It should be noted that only a trace of OOS-trimer **21** was observed (by GC-MS) and no OOO-trimer **22** was observed. The products were separated by careful column chromatography on silica gel with



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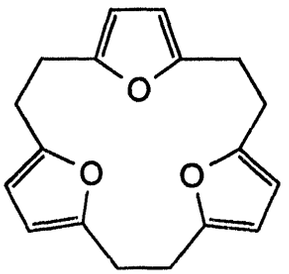
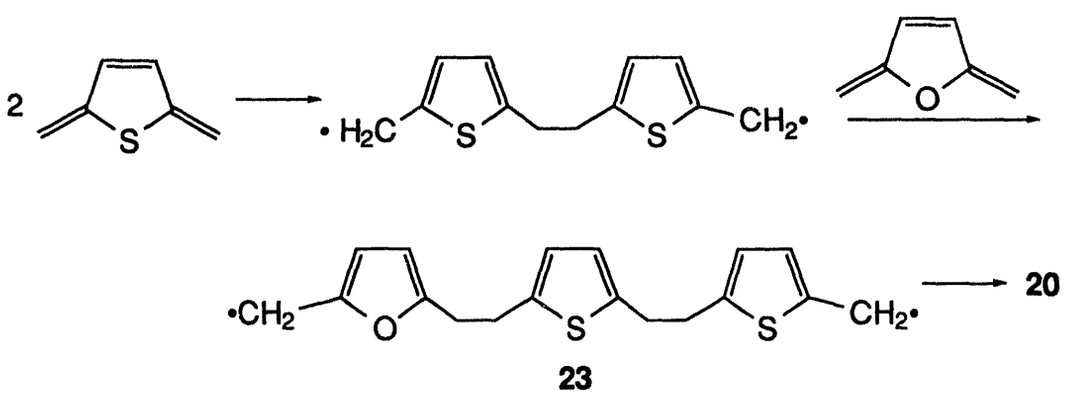


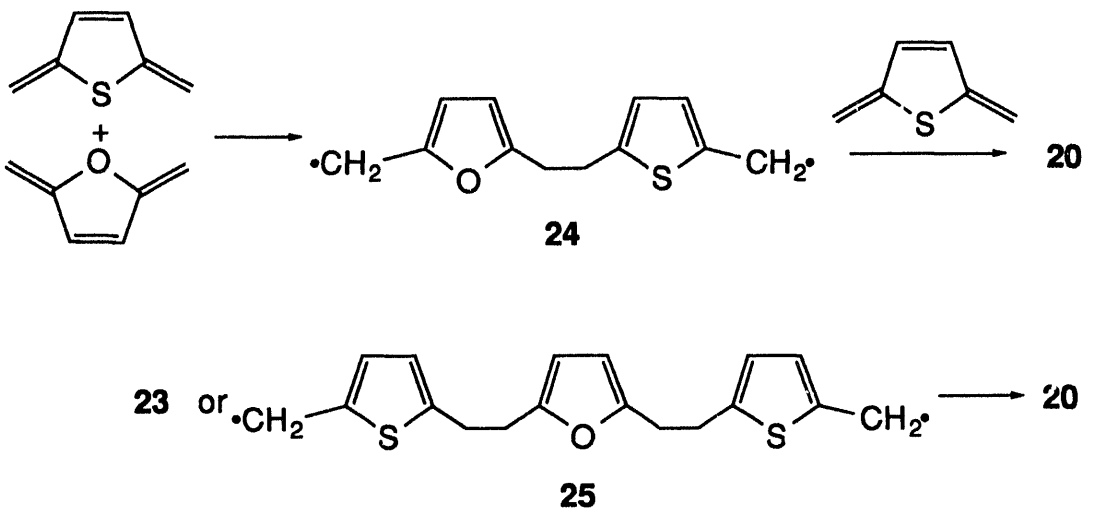
22

hexanes. OSS-Trimer **20** was not previously known, and its structure is indicated by its spectral properties.

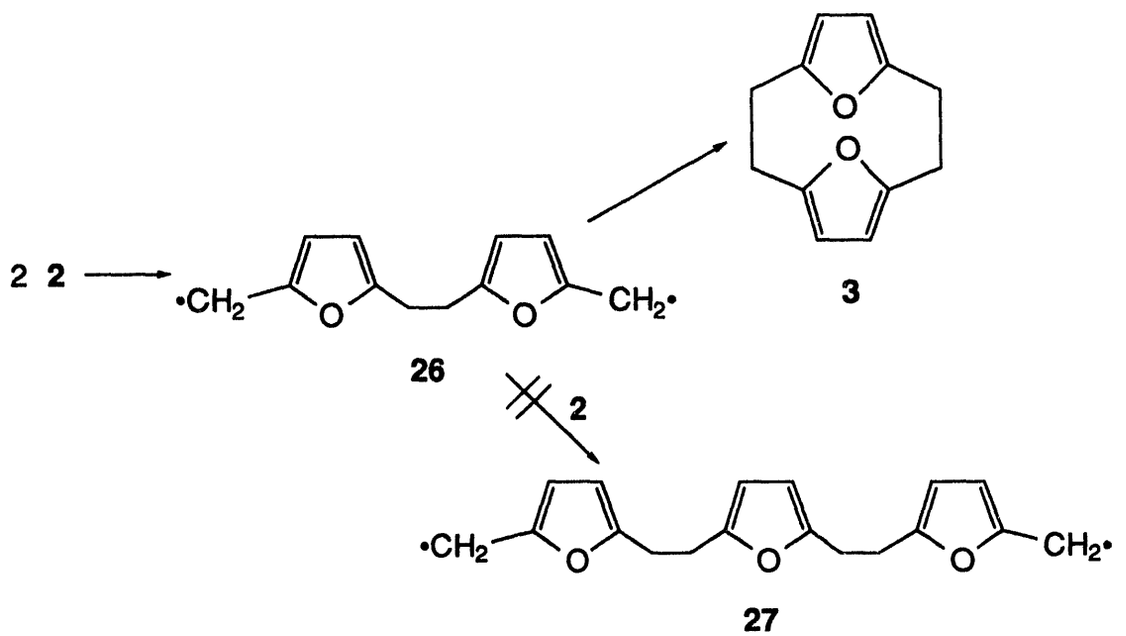
We think the formation of OSS-trimer **20** is consistent with the proposed mechanism. Thus the following sequence accounts for the formation of OSS-trimer **20**. OSS-Trimer **20** could also result from OS-diradical **24**, which could react with S-monomer **4** to form either OSS-diradical **23** or **25**, both of which could close to give OSS-trimer **20**.



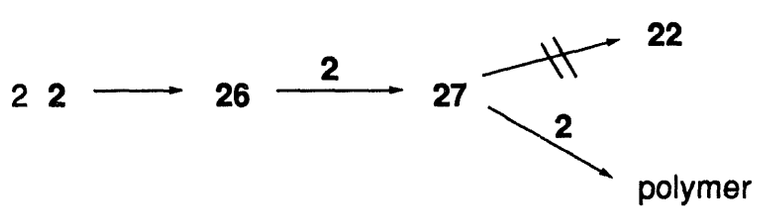
23



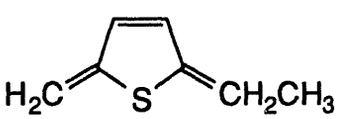
Because O-monomer **2** is in higher concentration (3:1 O-monomer : S-monomer), one might expect a comparable amount of OOS-trimer **21** to be produced. However GC-MS showed only a trace of this product. OS-Diradical **24** is probably formed but the rate of closure to give OS-dimer **19** is faster than the rate of addition to another monomer. This agrees with the results of the oligomerization of O-monomer **2** which produces only OO-dimer **3** and polymer. One explanation for the absence of OOO-trimer **22** is that once OO-diradical **26** is formed, it rapidly closes to OO-dimer **3** rather than picking up a third O-monomer **2** molecule.



The polymer produced in this reaction could be formed by an independent route such as free radical polymerization. Another possible explanation is that if OO-diradical **26** picks up a third O-monomer **2** molecule, the resulting OOO-diradical **27** reacts with another molecule of O-monomer **2** leading to polymer faster than closing to OOO-trimer **22**.



Intramolecular disproportionation products from oligomerization of 2-ethylidene-5-methylene-2,5-dihydrothiophene (11) as evidence for a diradical intermediate. In an attempt to provide direct evidence for the diradical mechanism for the oligomerization of thiophene-based *p*-QDM's, we focused our attention on the trapping of diradical intermediate **14**. Of the trapping agents we used, only 2,5-dimethylene-2,5-dihydrofuran (**2**) trapped the diradical. The other trapping agents failed probably because a) the diradical intermediate is too short lived and too reactive for the radical trapping agent, and b) some of the trapping agents, such as oxygen and thiophenol, reacted directly with the very reactive **4**. In an attempt to gain more evidence for an intermediate diradical in the oligomerization of thiophene-based *p*-QDM's, it was decided to study 2-ethylidene-5-methylene-2,5-dihydro-thiophene (**11**). Other studies have shown that diradicals with α-methyl groups

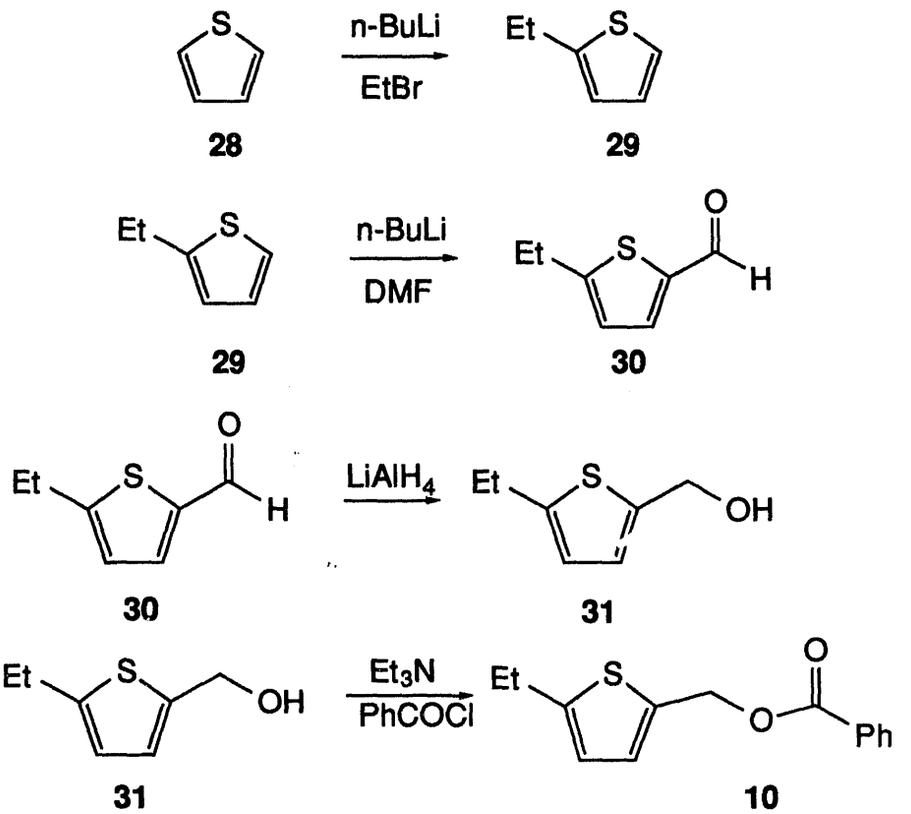


11

can give rise to intramolecular disproportionation products.[19,20] Observation of such a product from **11** would be good evidence for the existence of a diradical intermediate.

2-Ethylidene-5-methylene-2,5-dihydrothiophene (**11**) was prepared by flash vacuum pyrolysis of 5-ethyl-2-thiophenemethyl benzoate (**10**) which was obtained in high yield as shown in Scheme 2.

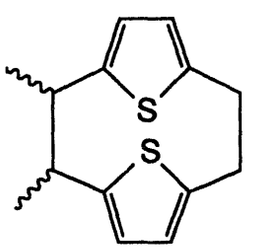
Scheme 2



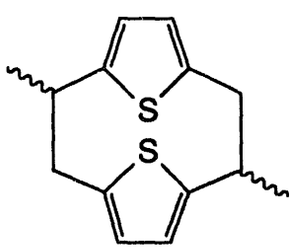
5-Ethyl-2-thiophenecarboxaldehyde (**30**) was prepared by alkylation of thiophene (**28**) with butyllithium (BuLi) / ethylbromide (EtBr) and followed by formylation of 2-ethylthiophene (**29**) with butyllithium (BuLi) / dimethylformamide (DMF). The aldehyde **30** was reduced with lithium aluminum hydride to give 5-ethyl-2-thiophenemethanol (**31**) which was esterified to give 5-ethyl-2-thiophenemethyl benzoate (**10**).

About 40% of 2-ethylidene-5-methylene-2,5-dihydrothiophene (**11**) was obtained from flash vacuum pyrolysis of **10** at 680°C and *ca.* 10^{-5}. Product **11** appeared as a dark yellow band in the liquid nitrogen trap at 77K. Benzoic acid and white polymer were also produced.

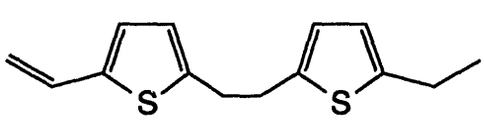
The ^1H NMR spectrum of compound **11** shows that its exists as two isomers (E=**11a** , Z=**11b**) in a ratio of *ca.* 3:1. When a *ca.* 0.05 M solution (1:1 CS_2 : $CDCl_3$) of S-monomer (**11**) was allowed to warm to room temperature, SS-cyclic dimers **33a**, and **33b**, acyclic dimers **34a** and **34b**, and SSS-cyclic trimers **36a** and **36b** were produced. SSS-Acyclic trimers were not observed. The results are summarized in Table 3.



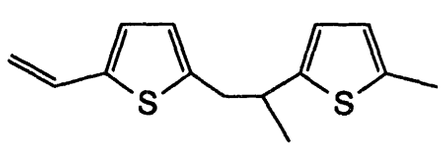
33a



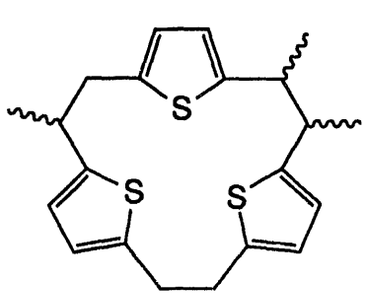
33b



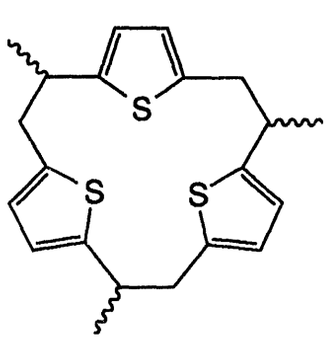
34a



34b



36a



36b

Table 3. Summary of Oligomerization Products of 2-Ethylidene-5-methylene-2,5-dihydrothiophene (**11**)[a]

Product	Relative yield[b], %
SS-cyclic dimers **33a** (cis, trans)[c]	37
SS-cyclic dimers **33b** (cis, trans)[c]	
SS-acyclic dimers **34a**[d]	19.5
SS-acyclic dimers **34b**[d]	
SSS-cyclic trimers **36a** (cis, trans)[e]	43.4
SSS-cyclic trimers **36b** (cis, trans)[e]	

[a]A 0.05 M of **11** (a 3 to 1 mixture of the E-isomer, **11a**, to the Z-isomer, **11b**) in a 1:1 mixture of CS_2 : $CDCl_3$ as solvent was oligomerized.

[b]Isolated yields after flash chromatography.

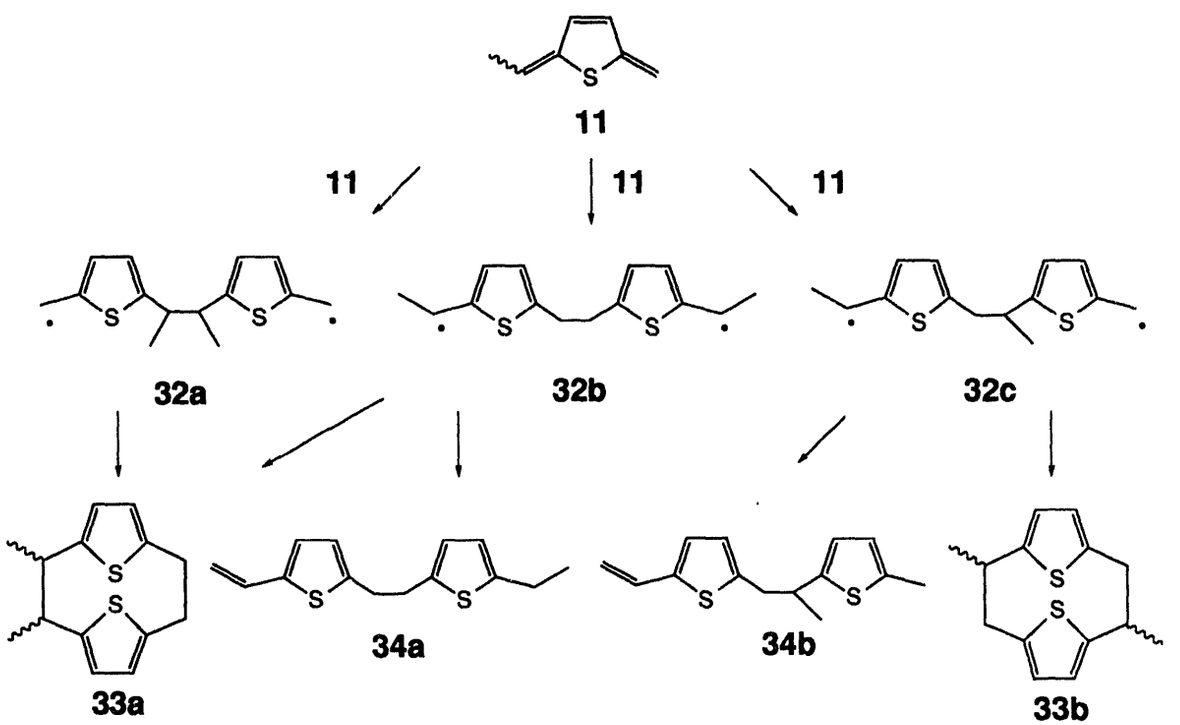
[c]The mixture of isomers was isolated and identified by ^1H NMR, ^{13}C NMR and GC/MS (see appendix, Figure **A-17**, **18**, **19**, **20**). Based on ^{13}C spectrum, both cis and trans isomers exist.

[d]The mixture of isomers was isolated and identified by ^1H NMR, COSY, ^{13}C NMR and GC/MS (see appendix, Figure **A-21**, **22**, **23**, **24**). The ratio of two acyclic dimers, **34a** and **34b**, is *ca.* 2.2 : 1 based on ^1H NMR analysis.

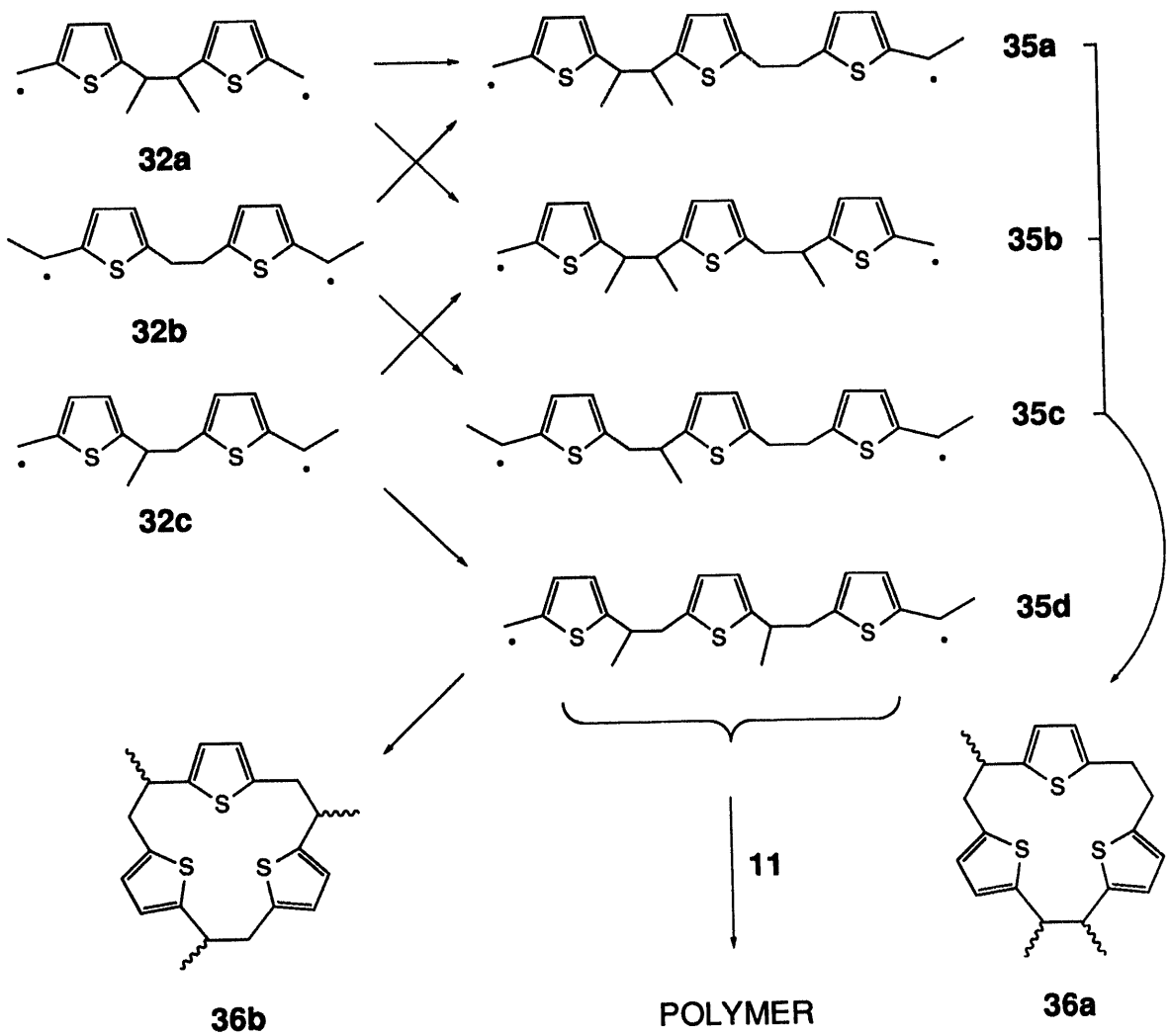
[e]The mixture of isomers was isolated and identified by ^1H NMR and GC/MS (see appendix, Figure **A-25**, **26**).

Formation of acyclic dimers **34a** and **34b** strongly support the proposed diradical mechanism.[20,21] Scheme 3 accounts for the formation of **33a**, **33b**,**34a** and **34b**, Scheme 4 accounts for the formation of **36a**, **36b**.

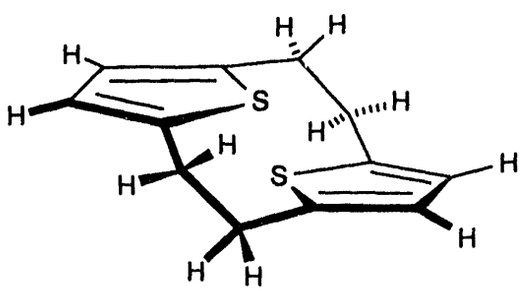
Scheme 3



Scheme 4

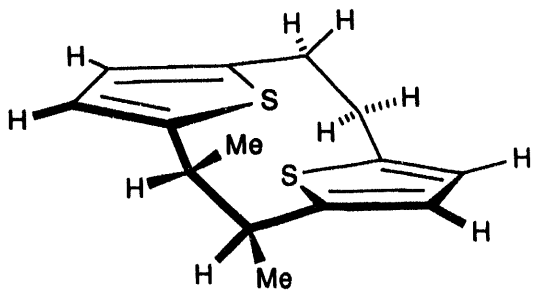


In an attempt to further understand the composition of the mixture of dimers **33a** and **33b**, a quantitative ^{13}C NMR experiment [22] using $Cr(acac)_3$ in deutereochloroform ($CDCl_3$) was performed on the mixture. Analysis of these data showed 16 singlets in the thiophene carbon region (δ 159.8-147.9) (appendix Figure **A-19**). This is consistent with the conclusion that each constitutional isomer exists in 3 stereoisomeric forms, 1 cis isomer and two trans isomers. The parent dimer **5** has been shown to exist in the stepped anti comformation.[8,10] The ^1H NMR signal for

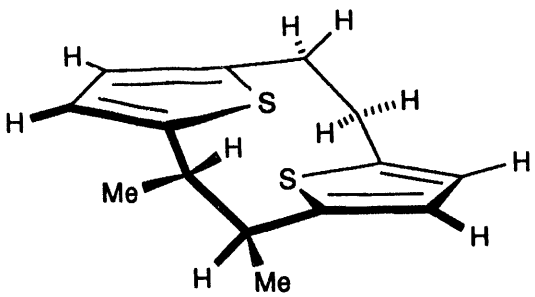


Stepped anti structure

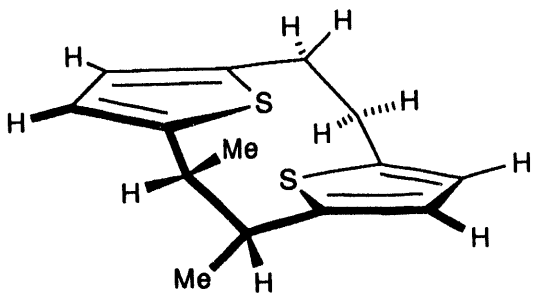
the ethano bridge of **5** is an AA'BB' pattern. Analysis of the temperature dependence of these ^1H NMR spectra of **5** shown that the barrier to interconversion of these forms is larger than 27 kcal / mol[23]. Thus, a mixture of **33a** and **33b** should consist of the following six isomers.



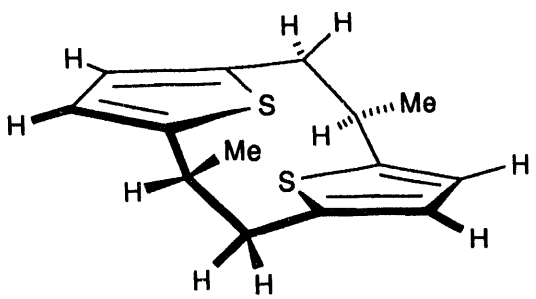
33a-cis



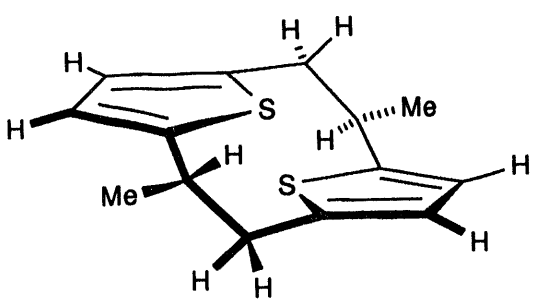
33a-trans-A



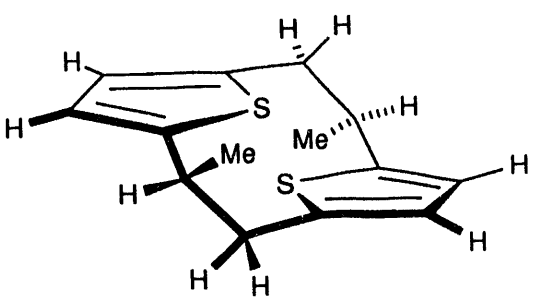
33a-trans-B



33b-cis

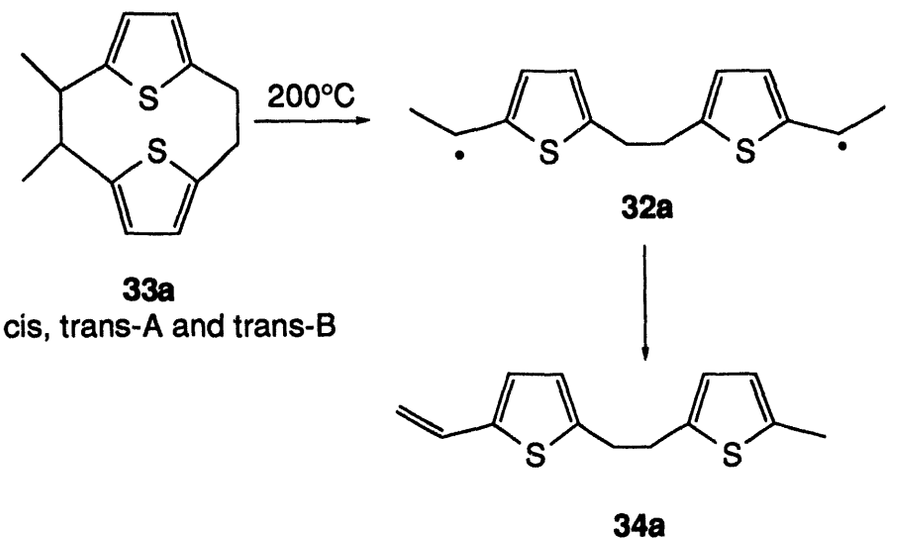


33b-trans-A



33b-trans-B

In the GC studies of the interconversion of cyclic dimers and acyclic dimers, the mixture of cyclic dimers **33a** (cis, trans A and trans B) decomposed at high injector temperatures of the gas chromatograph. Using a high injector temperature (T=200°C), GC of dimers **33a** (cis, trans A and trans B) decomposed to diradical

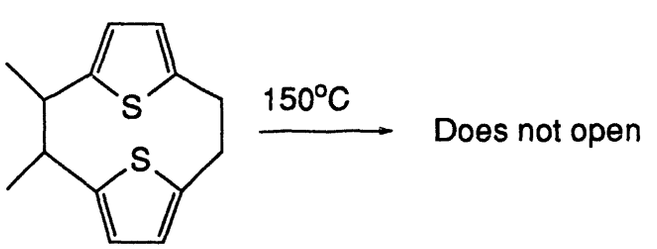


33a
cis, trans-A and trans-B

32a

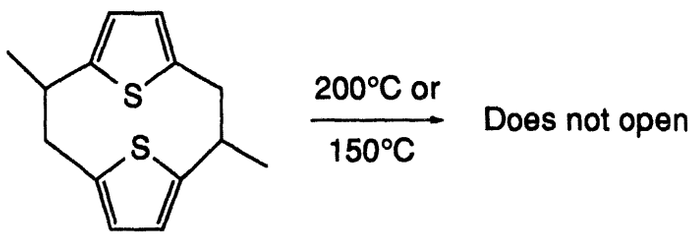
34a

32a, which transferred hydrogen atom to form compound **34a**. This gave a 1 : 1.6 cyclic dimers to acyclic dimer ratio (see appendix, Figure **A-26**). Using a relatively low injector temperature (T=150°C), no significant amount of **34a** was obtained, which indicates that **33a** was stable under these conditions.



33a
cis, trans-A and trans-B

With the lower injector temperature (150°C) an 8.8 : 1 cyclic dimers to acyclic dimer ratio was obtained (see appendix, Figure **A-27**). Even at higher temperatures, dimer **33b** does not open probably because the dimer is less congested.



33b
cis, trans-A and trans-B

EXPERIMENTAL SECTION

Methods and Materials

The pyrolysis apparatus[21] and some general methods[24] have been described previously. ^1H NMR spectra were obtained from Nicolet 300 spectrometer. Chemical shifts are reported in parts per million (δ) from tetramethylsilane (TMS) and deuterochloroform ($CDCl_3$). ^{13}C NMR spectra were obtained from Nicolet 300 and VXR-300 spectrometers. Infrared spectra (IR) were measured with IBM/98 spectrometer. High resolution mass spectrum (MS) was measured with an Associated Electronic Industries MS-902 instrument. GC/MS were recorded on a Finnigan 4000 GC/MS with Inco data system. Gas chromatographic analysis were performed on a Hewlett-Packard model 5840A gas chromatograph (GC) equipped with a 30 meter, DB-1 capillary column from J&W scientific and a flame ionization detector. Elemental analyses were carried out by Galbraith laboratories, Knoxville, Tennessee. Commercial thiophene, ethyl bromine, n-butyllithium, N,N-dimethyl formamide (DMF), lithium aluminum hydride($LiAlH_4$), triethylamine, 5-methyl-2-thiophenecarboxaldehyde, and benzyol chloride were purchased from Aldrich Chemical Company.

5-Methyl-2-thiophenemethyl Benzoate (9)

To a stirred slurry of 1.774 g (0.0467 mol) of lithium aluminum hydride ($LiAlH_4$) in 150 mL of dry ether at 0°C was slowly added a solution of 11.77 g (0.0933 mol) of 5-methyl-2-thiophenecarboxaldehyde (**12**) in 50 mL dry ether. The mixture was stirred at room temperature for 30 min. A standard workup[25] gave 10.86 g (0.0847 mol, 92%) of 5-methyl-2-thiophenemethanol (**13**): ^1H NMR ($CDCl_3$, 300 MHz) (see

appendix, Figure **A-14**) δ 6.68 (d, J = 3 Hz, 1 H), 6.50 (m, 1 H), 4.64 (s, 2 H), 2.46 (s, 3 H) [lit[26] ^{1}H NMR δ 6.65 (2 H), 4.52 (s, 2 H), 2.18 (s, 3 H)].

A solution of 12 mL (0.103 mol) of benzoyl chloride in 60 mL of dry ether was added dropwise over a 50-min period to a stirred solution of 10.86 g (0.086 mol) of 5-methyl-2-thiophenemethanol (**13**) and 12 mL distilled triethylamine in 150 mL of dry ether. After stirring at room temperature for over night (*ca.* 20 h), 100 mL distilled water was added and the layers were separated. The aqueous layer was extracted with ether (4x25 mL). The combined ether layers was washed successively with 1 M hydrochloric acid (3x50 mL), saturated sodium bicarbonate (3x50 mL), and saturated sodium chloride (3x50 mL). After drying ($MgSO_4$) and concentrating, 18.7 g (0.081 mol) of 5-methyl-2-thiophenemethyl benzoate (**9**) was recovered (95%). (b.p. 124°C, 0.45 mmHg): IR (thin film) 3080, 2960, 2930, 1725, 1610, 1455, 1270, 1100, 800, 710 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) (see appendix, Figure **A-15**) δ 8.08 (m, 2 H), 7.40 (m, 3 H), 6.90 (d, J = 3.6 Hz, 1 H), 6.56 (m, 1 H), 5.37 (s, 2 H), 2.44 (s, 3 H).

5-Ethyl-2-thiophenemethyl benzoate (10)

To a stirred slurry of 0.3760 g (0.0099 mol) of lithium aluminum hydride ($LiAlH_4$) in 40 mL of dry ether at 0°C was slowly added a solution of 2.777g (0.0198 mol) of 5-ethyl-2-thiophenecarboxaldehyde (**30**) in 20 mL dry ether. The mixture was stirred at room temperature for 1 h. A standard work up[23] gave 2.512 g (0.0177 mol) of 5-ethyl-2-thiophenemethanol (**31**) (89%). ^{1}H NMR ($CDCl_3$, 300 MHz) (see appendix, Figure **A-28**) δ 6.818 (d, J=3.3Hz, 1H), 6.648 (d, J=3.6Hz, 1H), 4.746 (s, 2H), 2.861 (q, J=7.2Hz, J=7.8Hz, 2H), 1.648 (broad, 1H). IR (thin film) (see appendix, Figure **A-29**): 3333, 2966, 2930, 1456, 1207, 1005, 804 cm^{-1}.

A solution of 2.81 g (0.01999 mol) of benzoyl chloride in 25 mL of dry ether was added dropwise over a 30 min period to a stirred solution of 2.512 g (0.0177 mol) of 5-ethyl-2-thiophenemethanol (**31**) and 2.9 g (0.0287 mol) of triethylamine in 40 mL of dry ether. After stirring at room temperature for overnight (16-18 h) 50 mL distilled water was added and the layers were separated. The aqueous layer was extracted with ether (4x25 mL). The combined ether layers was washed successively with 1M hydrochloric acid (3x50 mL) and saturated sodium chloride (3x50 mL). After drying over magnesium sulfate ($MgSO_4$) and concentrating, 3.6 g (0.0146 moles) of 5-ethyl-2-thiophenemethyl benzoate (**10**) (82%) was recovered. Pure compound was obtained by silica column 1:100 ethyl acetate and hexane as eluent. (b.p 145°C, 1.2 mmHg). ^1H NMR ($CDCl_3$, 300 MHz) (see appendix, Figure **A-30**) δ 8.072 (m, 2H), 7.451 (m, 3H), 6.909 (d, J=3.3Hz, 1H), 6.683 (d, J=3.6Hz, 1H), 5.435 (s, 2H), 2.848 (q, J=7.5Hz, 2H), 1.307 (t, J=7.5Hz, 3H). ^{13}C NMR ($CDCl_3$,75.5 MHz) δ 166.10, 149.22, 135.05, 132.89, 129.87, 129.57, 128.18, 128.05, 122.88, 61.29, 23.44, 15.76. IR (thin film) cm^{-1} (see appendix, Figure **A-31**): 3063, 2968, 2934, 1718, 1603, 1450, 1267, 1096, 1069, 1026, 806, 712. High resolution mass spectrum: calculated m/z 246.0715, measured m/z 246.0720. Elemental analysis calcd 68.3 % C, 5.73% H, measured 68.4% C, 6.06% H.

2-Ethylthiophene (29)[27]

To a stirred 5.26 g (0.0625 mol) of thiophene (**28**) in 9:1 THF and HMPA (100 mL) at -78°C was slowly added 1.98 M, 35 mL of n-butyl lithium (n-BuLi). After stirring for 2 h, 4.7 mL of distilled ethylbromide was added to the same flask. The reaction mixture was stirred at room temperature for over night. After the reaction was complete, hydrochloric acid (0°C) was added to the reaction mixture until the

solution was turn yellow. The solution was transferred to the separatory funnel. Organic layer was extracted with saturate sodium bicarbonate (2X50 mL) and saturate sodium chloride (2X50 mL). After dry over magnum sulfate ($MgSO_4$) and concentrating, 5.66 g (0.051 moles) of 2-ethylthiophene (**29**) was recovered (81%). ^1H NMR ($CDCl_3$, 300 MHz) (see appendix, Figure **A-32**) δ 7.107 (d, J=4.2Hz, 1H), 6.912 (m, 1H), 6.791(m, 1H), 2.874 (q, J=7.5Hz, 2H), 1.316 (t, J=7.2Hz, 3H) Pure ethylthiophene (**29**) can be obtained by distillation (b. p 138°C). [lit[28]: b. p. 134°C. lit[29]: ^1H NMR δ 7.1 (1H), 6.9 (1H), 6.79 (1 H), 2.8 (2H), 1.3 (3H)].

5-Ethyl-2-thiophenecarboxaldehyde (30)

To a 4.0 g (0.0357 mol) of distilled 2-ethylthiophene which was in 9 to 1 THF and HMPA (100 mL) at -78°C 1.9 M (23 mL) of n-butyllithium (n-BuLi) was slowly added. After stirring about 45 min, 28 mL of dimethylformamide (DMF) was added to the solution. The reaction mixture was slowly allowed to warm up to room temperature and stirred for overnight. A standard work up gave 4.0 g (0.0285 mol) of 5-ethyl-2-thiophenecarboxaldhyde (**30**) (80%). Pure compound can be obtained from distillation (b. p 60°C, 0.15 mmHg) [lit:[30] b. p. 103-104°C, 9 mmHg]. ^1H NMR ($CDCl_3$, 300 MHz) (see appendix, Figure **A-33**) δ 9.818 (s, 1H), 7.619 (d, J=3.6Hz, 1H) 6.925 (d, J=3.9Hz, 1H), 2.931 (q, J=7.5Hz, 2H), 1.352 (t, J=7.5Hz, 3H) [lit:[30] ^1H NMR ($CDCl_3$) δ 9.79 (s), 7.761(J=3.7 Hz), 6.9 (J=3.7 Hz), 2.89 (J=7.4 Hz), 1.31 (J=7.4 Hz)]. IR (thin film) (see appendix, Figure **A-34**) cm-1: 2966, 1663, 1464, 1452, 1227, 1082, 812, 758, 669.

General Pyrolysis Procedure [21]

The oven was maintained at temperatures ranging 640-660°C for 5-methyl-2-thiophenemethyl benzoate (**9**) and 679-690°C for 5-ethyl-2-thiophenemethyl benzoate (**10**). A sample of the benzoate in a pyrex boat was placed in the sample chamber and the system was evacuated to *ca.* 10^{-5} torr. The sample chamber was heated to 60-90°C during the pyrolysis. A condenser cooled to *ca.* -20°C was inserted between the furnace and the liquid nitrogen-cooled trap to collect the benzoic acid formed as a byproduct as well as any unreacted benzoate. The liquid nitrogen-cooled trap was used to collect the more volatile products. Upon completion of the pyrolysis a solvent or solvent mixture was deposited into the trap through a side arm. Nitrogen gas was then introduced into the system and the trap was warmed to -78°C. The cold pyrolysate was then transferred to other vessels for further study at -78°C or allowed to warm to room temperature.

Pyrolysis of 5-Methyl-2-thiophenemethyl Benzoate (9)

A 0.3360 g (0.0136 mol) of **9** was pyrolyzed at 640°C in the normal manner. Upon completion, 5 mL of a 1:1 mixture of carbon disulfide (CS_2) and deuterochloroform ($CDCl_3$) was distilled into the trap, which resulted in a 0.10 *M* solution of 2,5-dimethylene-2,5-dihydrothiophene (**4**). A quantitative low temperature ^1H NMR analysis of the pyrolysate using dibromoethane as a standard showed the presence of **4** in 74.4% yield. After allowing the pyrolysate to stand at room temperature overnight, substantial amounts of [2.2](2,5)thiophenophane (SS-dimer **5**, 14.7 mol %) and [2.2.2](2,5)thiophenophane (SSS-trimer **6**, 44.3 mol%)

were formed. The products were separated by column chromatography on silica gel (1: 100 ethyl acetate to hexanes).

2,5-Dimethylene-2,5-dihydrothiophene (**4**): ^{1}H NMR (see appendix, Figure **A-1**) (1:1 $CS_2/CDCl_3$, 300 MHz) δ 6.52 (s, 2 H), 5.24 (s, 2 H), 5.02 (s, 2 H); ^{13}C NMR[14] (see appendix, Figure **A-2**) (1:1 CD_3COCD_3, 22.5 MHz) δ 150.5, 136.6, 104.7; GC-IR[14] (see appendix, Figure **A-3**) 3101, 3001, 1589 (intense), 1192, 837 (intense) cm^{-1} [lit[13] IR (Ar 15 K) 1586.6, 1187.4, 840.8, 831.2, 801.6 cm^{-1}]; GC-MS m/e (relative intensity) (see appendix, Figure **A-4**) 112 (4.94), 111 (8.51), 110 (100.00), 109 (40.59), 95 (5.4), 84 (23.36), 77 (14.31), 74 (4.26), 71 (12.90), 69 (14.92), 66 (54.29), 65 (13.86), 63 (6.49), 58 (25.78), 55 (10.33), 51 (30.51), 50 (24.22), 47 (2.09).

13,14-Dithiatricyclo[8.2.1^{3,6}]tetradeca-4,6,10,12-tetraene ([2.2](2,5)thiophenophane, SS-dimer **5**). m.p. 190-191°C [lit[6] m.p. 194-197°C] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.725 (s, 4 H), 3.22 (m, 4 H), 2.87 (m, 4 H) [lit[6] ^{1}H NMR ($CDCl_3$) δ 6.75 (s, 4 H), 3.04 (AA'BB' m, 8 H)]; ^{13}C NMR[14] ($CDCl_3$, 75.45 MHz) δ 151.2, 126.8, 32.2; GC-MS m/e (relative intensity) 222 (0.58), 221 (2), 220 (15), 112 (5), 111 (8), 110 (100.00), 109 (9), 84 (5), 77 (5), 66 (15), 58 (5). [lit[6] mass spectrum m/e (relative intensity) 220 (24), 110 (100)]; high resolution mass spectrum[1], calcd for $C_{12}H_{12}S_2$ 220.0380, measured 220.03818.

19,20,21-Trithiatetracyclo[14.2.1.1^{3,6}.1^{9,12}]heneicosa-4,6,10,12,-16,18-hexaene ([2.2.2](2,5)thiophenophane, SSS-trimer **6**). m.p. 125-126°C [lit[6] m.p. 126.5-127°C]; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.60 (s, 6 H), 3.00 (s, 12 H) [lit[6] ^{1}H NMR ($CDCl_3$) δ 6.60 (s, 6 H), 3.01 (s, 12 H)]; ^{13}C NMR[14] ($CDCl_3$, 75.45 MHz) δ 140.3, 124.4, 31.2; GC-MS m/e (relative intensity) 332 (0.83), 331 (1), 330 (9), 222 (0.5), 221 (2), 220 (9), 112 (5), 111 (8), 110 (100), 84 (5), 77 (3), 66 (13) [lit[6] mass

spectrum m/e (relative intensity) 330 (100), 220 (36), 110 (61)]; high resolution mass spectrum[14], calcd for $C_{18}H_{18}S_3$ 330.05707, measured 330.05712.

Evidence for SSSS-tetramer. A 0.781 g (0.00336 moll) quantity of **9** was pyrolyzed at 680°C in the normal manner[14]. Upon completion, 10 mL of CS_2 was distilled into the trap. After warming to -78°C, the solution was transferred to a flask containing 0.112 g (0.000724 mol) biphenyl. A GC trace of the cold solution was obtained, and multiple ion detection GC-MS showed the expected SS-dimer **5** and SSS-trimer **6**, as well as a 1.88 mg (0.677 mol%, based on amount of initial monomer) of a compound having a molecular weight of 440, and fragments at m/e 330 and 220.

Preparation of SS-Dimer 5 by High Dilution Experiment

A 2.10 g (0.00902 mol) quantity of **9** was pyrolyzed at 625°C in the normal manner[21]. Upon completion, 25 mL CS_2 was distilled into the trap. After warming to -78 °C, the solution was added to 1 L of CS_2, which resulted in a 0.00660 *M* solution of S-monomer **4**. After 5 d at room temperature, the product ratio of S-monomer **4** to SS-dimer **5** to SSS-trimer **6** was 1.00:32.89:5.58 as determined by GC.

Pyrolysis of 5-ethyl-2-thiophenemethyl benzoate (10)

A 0.1439 g (0.0005845 mol) of quantity of **10** was pyrolysed at 680°C in the normal manner[21]. Upon the completion, 4.4 mL of 1:1 mixture of carbon disulfide (CS_2) and deuterochloroform ($CDCl_3$) was distilled into the trap, which resulted in a 0.05 M solution of 2-ethylidene-5-methylene-2,5-dihydrothiopene (**11**). (see appendix, Figure **A-13**).

A quantitative low temperature ^1H NMR analysis of the pyrolysate using diphenylmethane as a standard showed that the presence of **11a** in 34% yield and **11b** in 9% yield. After allowing the pyrolysate to stand at room temperature under argon for *ca.* 3 days, substantial amount of [2.2](2,5)thiophenophane (SS-dimer) **33**, acyclic dimer **34**, and [2.2.2](2,5)thiophenophane (SSS-trimer) **36** were formed. The products were separated by flash column (silica). Ethyl acetate and hexane (1:200) were used as eluent.

2-Ethylidene-5-methylene-2,5-dihydrothiophene (isomer **11-a**, E form): ^1H NMR ($CDCl_3$, 300 MHz) δ 6.435 (d, J=6Hz, 1H), 6.399 (d, J=5.7Hz, 1H), 5.635 (q, J=7.2Hz, 1H), 5.147 (s, 1H), 4.979 (s, 1H), 1.803(d, J=7.2Hz, 3H).

2-Ethylidene-5-methylene-2,5-dihydrothiopene (isomer **11- b**, Z form): ^1H NMR ($CDCl_3$, 300 MHz) δ 6.49-6.4 (d, J=6.6Hz, 2H), 5.4 (q, J=6.9Hz, 1H), 5.1 (s, 1H), 4.9 (s, 1H), 1.9 (d, J=7.5Hz, 3H).

trans, cis-(2,3-Dimethyl)-13,14-dithiatricyclo[8.2.$1^{3,6}$]tetradeca-4,6,10, 12-tetraene ([2.2](2,5)thiophenophane, SS-dimer **33a**-cis, **33a**-trans); trans, cis-(2,8-dimethyl)-13,14-dithiatricyclo[8.2.$1^{3,6}$]tetradeca-4,6,10,12-tetraene ([2.2](2,5)thiophenophane, SS-dimer **33b**-cis, **33b**-trans): ^1H NMR ($CDCl_3$, 300 MHz) δ 6.8-6.6 (m, 8H), 3.7-2.3 (m, 12H), 1.6-1.2 (several d, J=6.9 Hz, 12H); GC/MS: *m/e* (relative intensity) 248 (M^+, 4), 124 (100), 97.1 (6.02), 65.0 (2.82), 39.1 (5.17). ^{13}C NMR ($CDCl_3$, 75.5 MHz, 7 mg of $Cr(acac)_3$ was added) δ 159.78, 158.07, 157.26, 157.16, 156.73, 156.19, 155.94, 154.12, 150.54, 150.46, 150.23, 149.59, 149.55, 148.80, 148.39, 147.93 (16 quaternary carbons), 126.94,126.26, 125.87, 125.82, 125.32, 125.26, 124.57, 124.38, 122.82, 122.48, 122.26 (11 signals), 47.02, 44.96, 43.64, 41.69, 41.47, 39.77, 39.57 (7 signals), 36.98, 32.37, 32.31, 31.68, 31.11 (5 signals), 19.49, 19.30, 18.56, 17.19, 16.17, 12.46 (6 signals).

5-Ethyl-5'-vinyl-2,2'-ethylenedithiophene (acyclic dimer **34a**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.7 (m, 2H), 6.5 (m, 2H), 6.7 (q, J=17.1Hz, J=10.8Hz, 1H), 5.48 (d, J=17.1Hz, 1H), 5.08 (d, J=10.8Hz, 1H), 3.1 (s, 4H), 2.8 (q, J=7.5Hz, 2H), 1.3 (t, J=7.2Hz, 3H), ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 145.6, 143.3, 141.2, 140.96, 130.2, 125.8, 124.8, 124.2, 122.8, 112.2, 32.5, 32.2, 23.5, 16.0.

5-Methyl-5'-vinyl-2,2'-propylenedithiophene (acyclic dimer **34b**): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.7 (m, 2H), 6.5 (m, 2H), 6.7 (q, J=17.4Hz, 1H), 5.48 (d, J=17.4Hz, 1H), 5.08 (d, J=10.8Hz, 1H), 3.25-2.9 (m, 3H), 2.4 (s, 3H), 1.3 (d, J=6.9Hz, 3H), ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 145.6, 143.3, 141.2, 140.96, 130.2, 125.8, 124.8, 124.2, 122.8, 112.2, 40.1, 37.6, 29.8, 22.2, GC/MS m/e (relative intensity) 248.2 (8), 125.1 (100), 123 (35).

(2,3,14-Trimethy)19,20,21-trithiatetracyclo[14.2.1.1^{3,6}.1^{9,12}]heneicosa-4,6,10,12,16,18-hexaene ([2.2.2](2,5)thiophenophane, SSS-trimer **36a**); (3,9,15-trimethy)19,20,21-trithiatetracyclo[14.2.1.1^{3,6}.1^{9,12}]heneicosa-4,6,10,12,16,18-hexaene ([2.2.2](2,5)thiophenophane, SSS-trimer **36b**): GC/MS: *m/e* (relative intensity) 372.5 (M^+, 0.3), 234.1 (11), 123.0 (54), 111 (100). ^{1}H NMR ($CDCL_3$, 300 MHz) δ 6.63-6.55 (m, 12H), 3.47 (s, 4H), 3.0-3.2 (m, 14H), 1.37-1.27 (m, 18H).

Trapping Experiments

The conventional trapping experiment. To a 0.5 mL of S-monomer **4** solution (0.1 M), 0.3615 g of purified 9, 10 dihydroanthracene and 4.5 mL of CCl_4 were added. This results in a 1 to 40 monomer to 9, 10-dihydroanthracene ratio. To a 0.5 mL of S-monomer solution **4** (0.1M), 0.3606 g of anthracene in 4.5 mL of CCl_4 was added. Both reactions were allowed to stand at room temperature overnight.

GC, GCMS, and NMR were used to analyze the final products. The same procedure was applied to the rest of the conventional trapping experiment mentioned in the paper. The results are summarized in Table 1.

Oxygen was used as trapping agent. To 6 NMR tubes, 0.5 mL of S-monomer **4** (0.1M) solution was added to each tube. Oxygen then was bubbled through the monomer solution at different time period: 5, 10, 20, 50, 60, and 180 sec. To 6 NMR tubes, 0.5 mL of S-monomer **4** (0.1M) solution was added to each tube and nitrogen was bubbled to each tube at different time: 5, 10, 20, 50, 60, and 180 sec. ^{1}H NMR was used to follow both reactions. After standing at room temperature for 2 d, GC was used to analyze the products.

Co-oligomerization of O-Monomer (2) and S-Monomer (4). Preparation of O-monomer[15] **2** and S-monomer **4**[14]. A 1.77 g (0.00819 mol) quantity of 5-methyl-2-furfuryl benzoate (**7**) was pyrolyzed at 560°C in the normal manner. Upon completion, 17 mL of CS_2 was distilled into the trap. After warming to -78°C, the solution containing 2,5-dimethylene-2,5-dihydrofuran, O-monomer **2**, was stored at -78°C.

A 0.370 g (0.00159 mol) quantity of 5-methyl-2-thiophenemethyl benzoate (**9**) was pyrolyzed at 680°C in the normal manner. Upon completion, 10 mL of CS_2 was distilled into the trap. After warming to -78°C, the solution containing S-monomer **4** was combined with the O-monomer **2** solution and allowed to stand at room temperature overnight. Integration of the ^{1}H NMR obtained just before warming showed the ratio of O-monomer **2** to S-monomer **4** to be 5.6 :1.

Oligomerization Products. After standing at room temperature overnight, a number of dimers and trimers derived from S-monomer **4** were formed, as well as OO-dimer **3** (identified by GC/MS) and polymer. Yields were determined by GC

analysis using biphenyl as an internal standard. The compounds and yields are summarized in Table 2.

It should be noted that using a 1:1 ratio of O-monomer **2** to S-monomer **4** gave the highest relative yield of trimers but that using a 3:1 ratio gave a greater OSS-trimer **20** to SSS-trimer **6** ratio.

Because excess O-monomer **2** remained for several days after all of the S-monomer **4** had reacted, the excess O-monomer **2** was destroyed by adding an equal volume of glacial acetic acid to the reaction mixture. This mixture was allowed to stand for 30-90 min. Excess acetic acid was removed by first adding ethyl ether, then extraction with water (2x50 mL) followed by saturated sodium bicarbonate extractions until the ether solution was basic. After drying ($MgSO_4$) and concentrating the products were dissolved in a minimum amount of hexanes. Separation by careful column chromatography on silica gel (hexanes) yielded pure samples of all five products. The sulfur containing products not mentioned above were identified by the following data.

13-Oxa-14-thiatricyclo[8.2.1.$1^{3,6}$]tetradeca-4,6,10,12-tetraene[14] (OS-dimer **19**). ^{1}H NMR ($CDCl_3$, 300 MHz) (see appendix, Figure **A-35**) δ 6.93 (s, 2 H), 5.96 (s, 2 H), 2.90 (m, 8 H) [lit.[15] ^{1}H NMR ($CDCl_3$) δ 6.92 (s, 2 H), 5.94 (s, 2 H), 2.88 (m, 8 H)]; ^{13}C NMR ($CDCl_3$, 75.45 MHz) δ 154.9, 151.6, 128.3, 108.5, 33.1, 31.0; GC-MS m/e (relative intensity) 206 (1.28), 205 (3.17), 204 (24.40), 112 (4.69), 111 (7.48), 110 (100.00), 94 (29.94), 84 (3.70), 77 (7.36), 66 (22.20), 51 (17.82) [lit.[18] mass spectrum m/e 110, 94].

19-Oxa-20,21-dithiatetracyclo[14.2.1.1^{3,6}.1^{9,12}]heneicosa-4,6,10,12,-16,18-hexaene[14] (OSS-Trimer **20**). m.p. 79.5-84°C; ^{1}H NMR ($CDCl_3$, 300 MHz) (see appendix, Figure **A-36**) δ 6.58 (q, AB, 2 H), 5.98 (s, 4 H), 2.96 (m, 12 H); ^{13}C

NMR ($CDCl_3$, 75.5 MHz) (see, appendix, Figure **A-37**) δ 152.4, 141.4, 140.5, 124.2, 123.9, 106.7, 32.0, 29.7, 29.2; high resolution mass spectrum, calcd for $C_{18}H_{18}OS_2$ 314.07991, measured 314.07872.

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APPENDIX

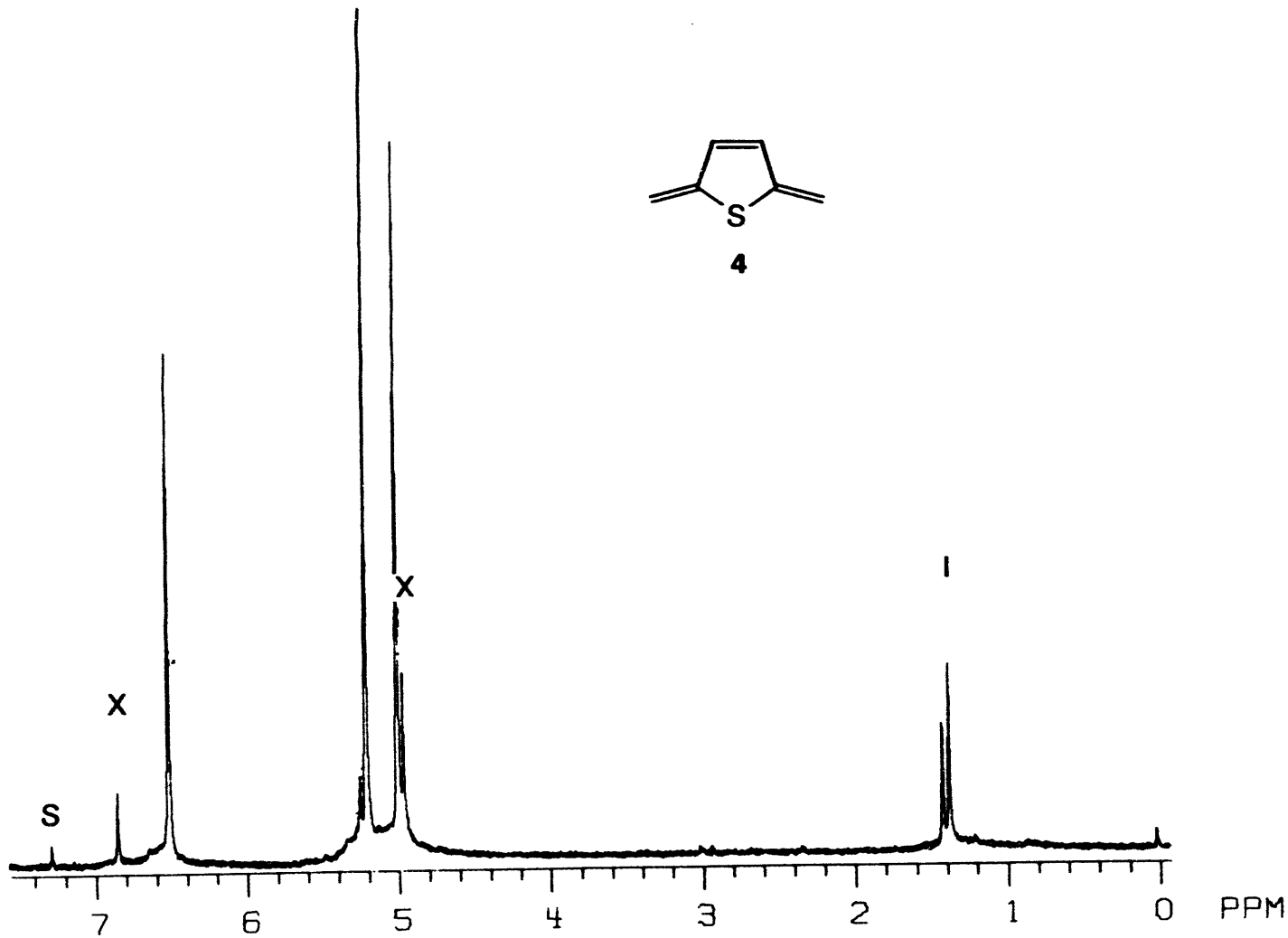


Figure A-1. ^1H NMR spectrum (300 MHz, $CDCl_3$) of 2,5-dimethylene-2,5-dihydrothiophene (**4**) (S: chloroform, I: impurities, X: compound **X**).

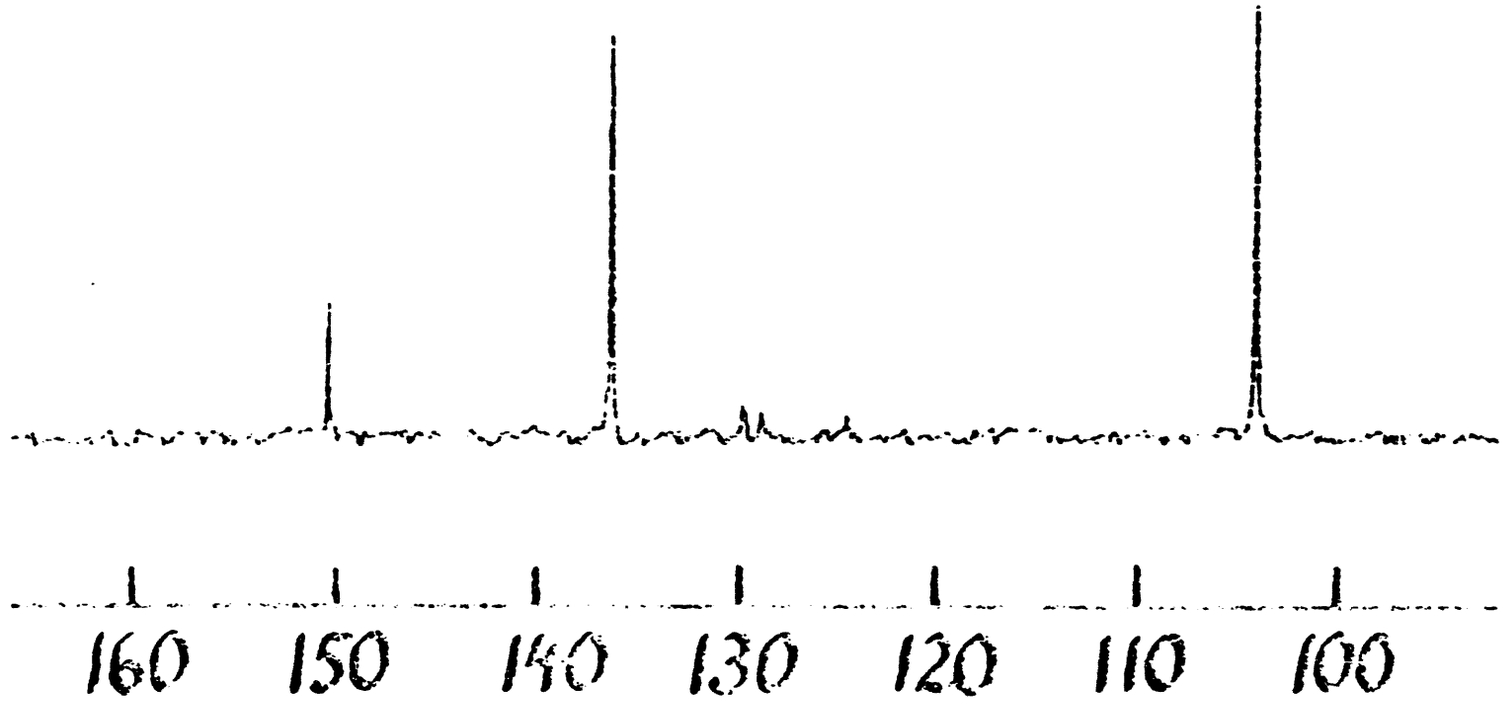


Figure A-2. ^{13}C NMR spectrum (22.5 MHz, CD_3COCD_3) of S-monomer **4** at -70°C.

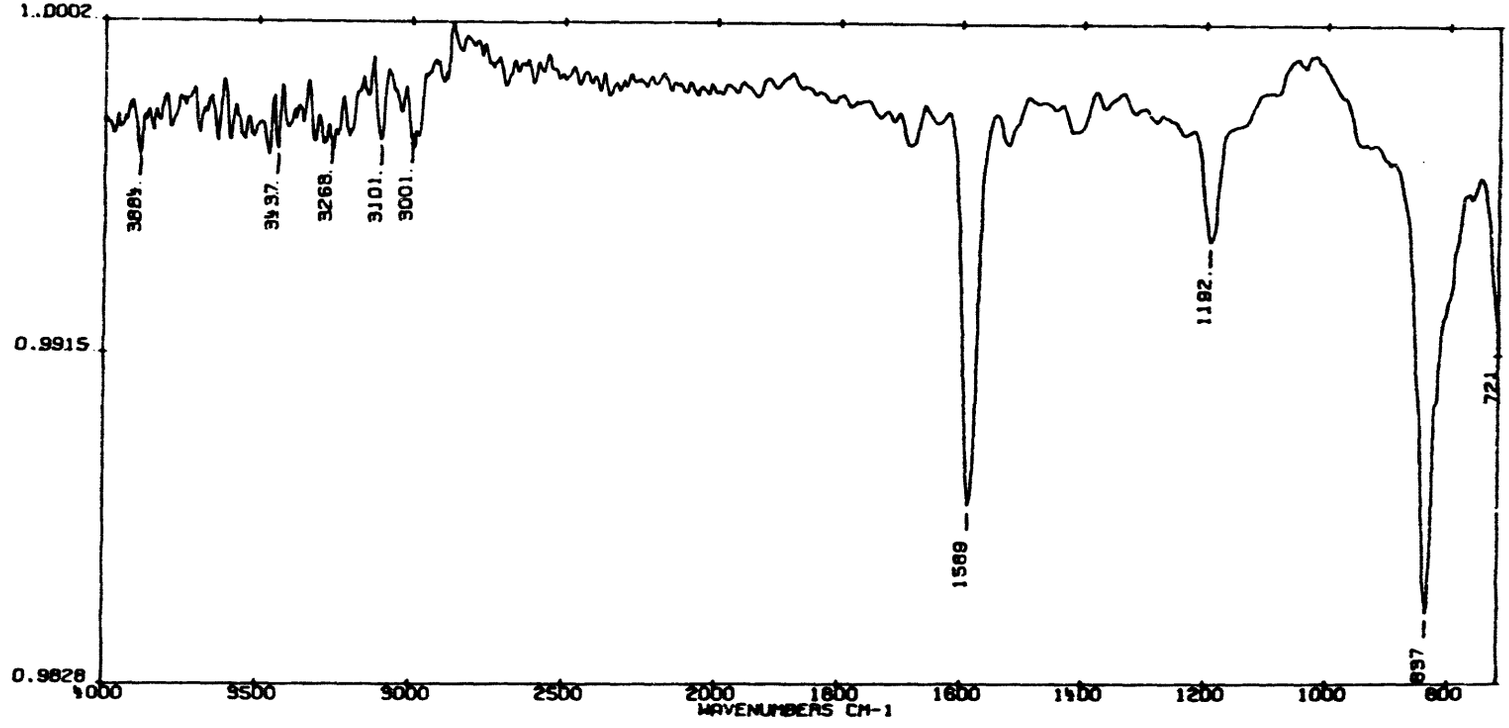


Figure A-3. GC/IR of S-monomer **4**.

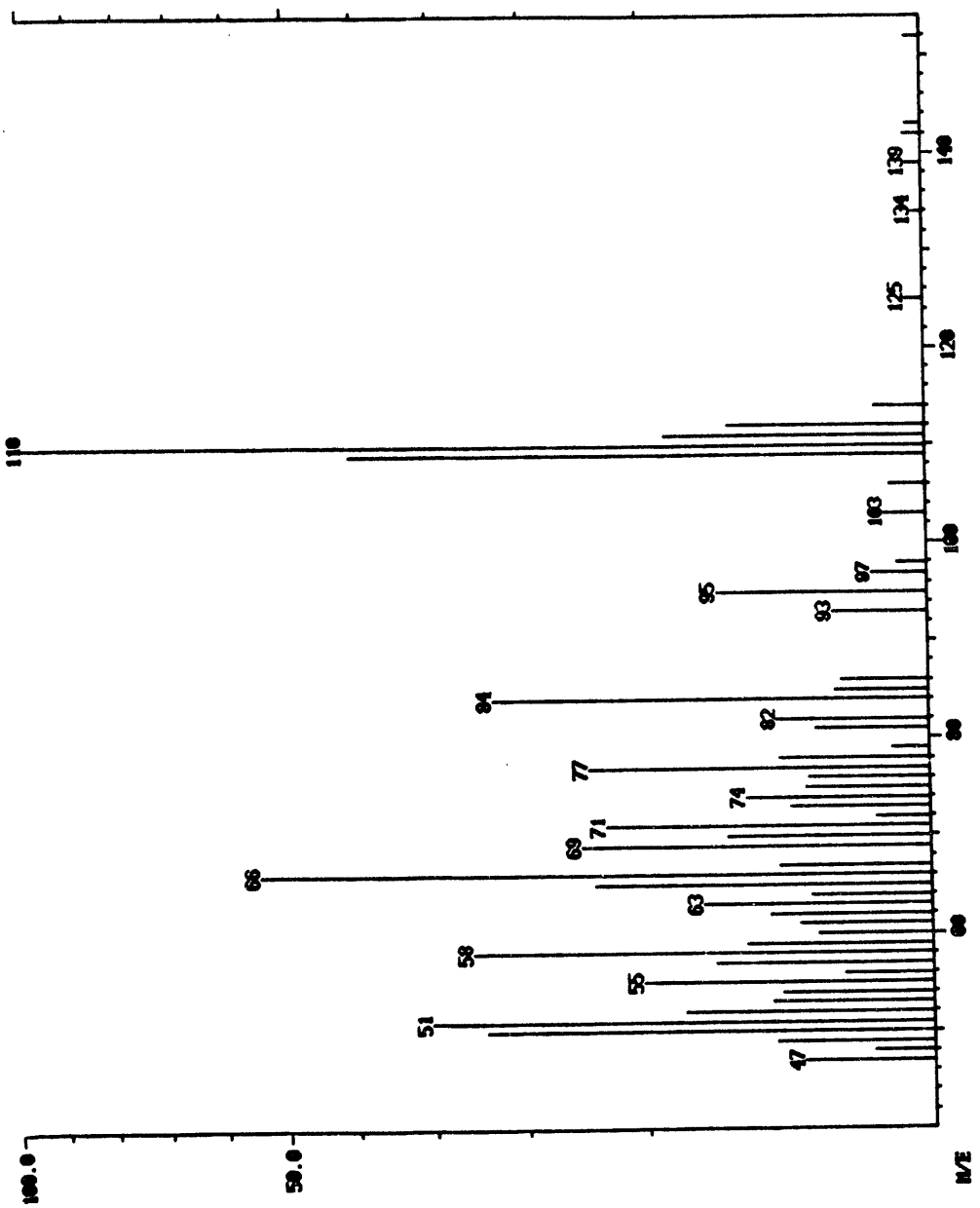


Figure A-4. GC/MS of S-monomer 4.

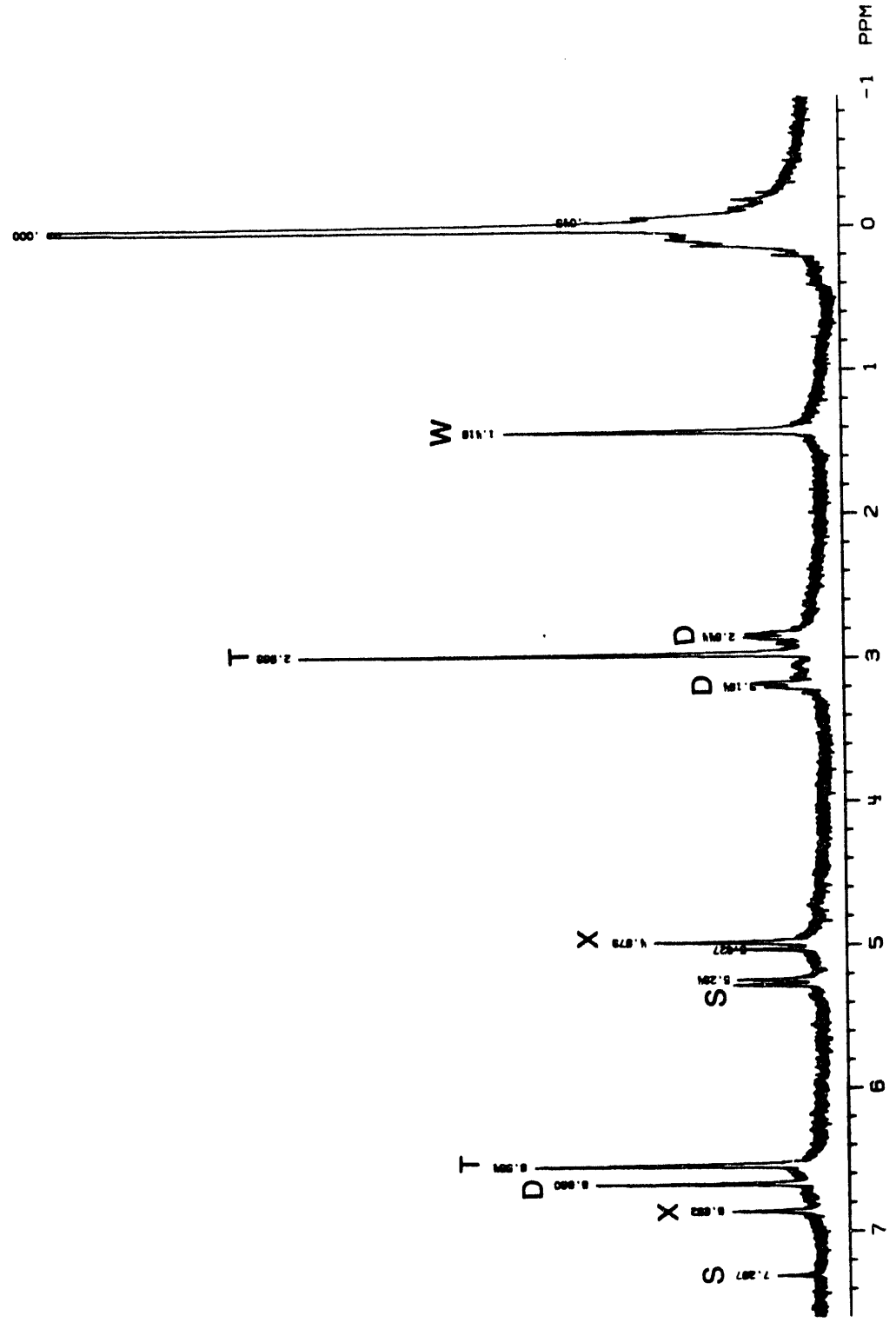


Figure A-5. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of the oligomerization products of 2,5-dimethylene-2,5-dihydrothiophene (**4**) (11 hours passed after nitrogen was bubbled through the monomer **4** solution for 1 min; D: dimer, T: trimer; S: chloroform, S: methylene chloride, W: H_2O, X: compound **X**).

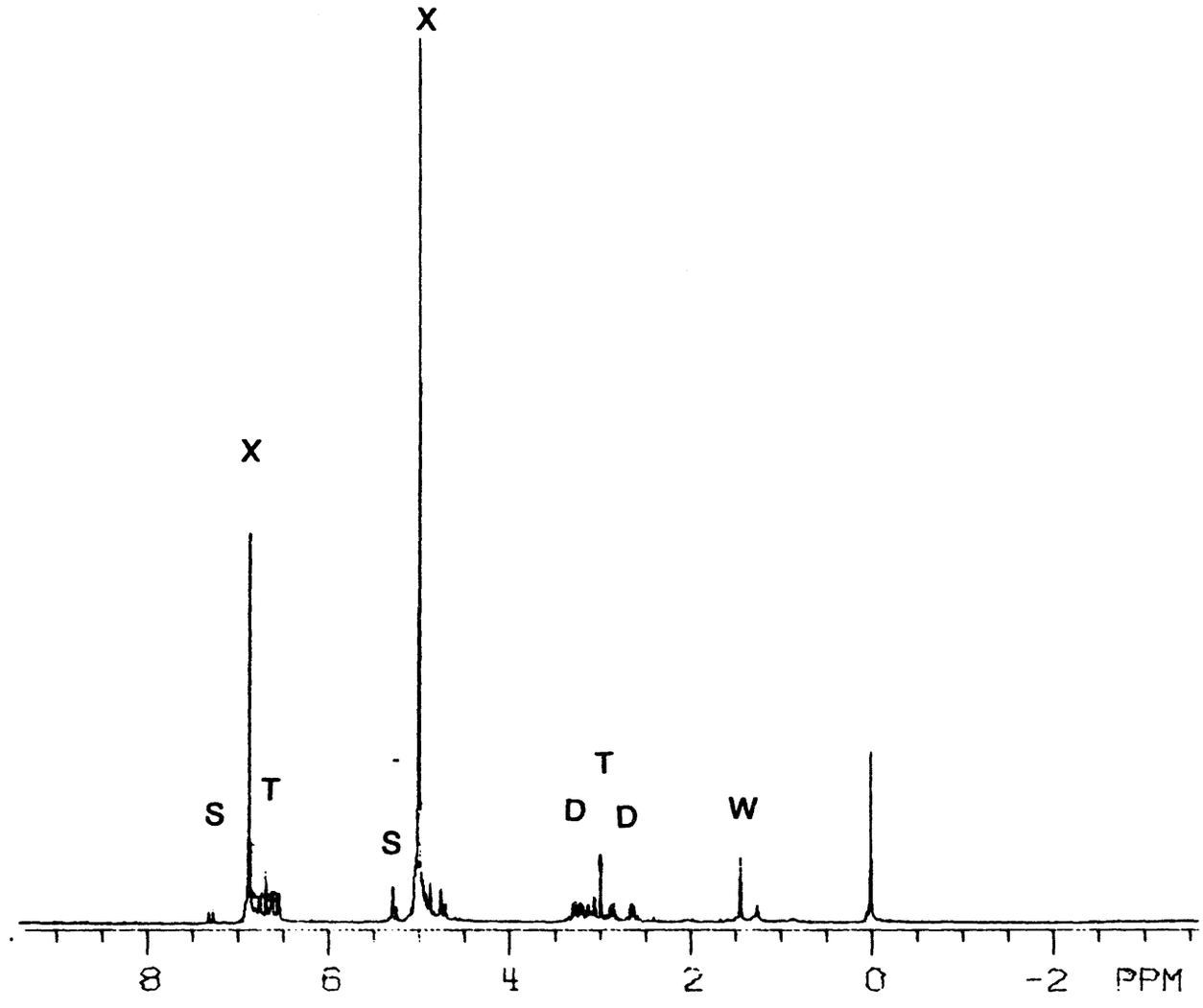


Figure A-6. ^1H NMR spectrum (300 MHz, $CDCl_3$) of compound **X** (Oxygen was bubbled through the monomer **4** solution. D: dimer. T: trimer, S: chloroform, S: methylene chloride, W: H_2O).

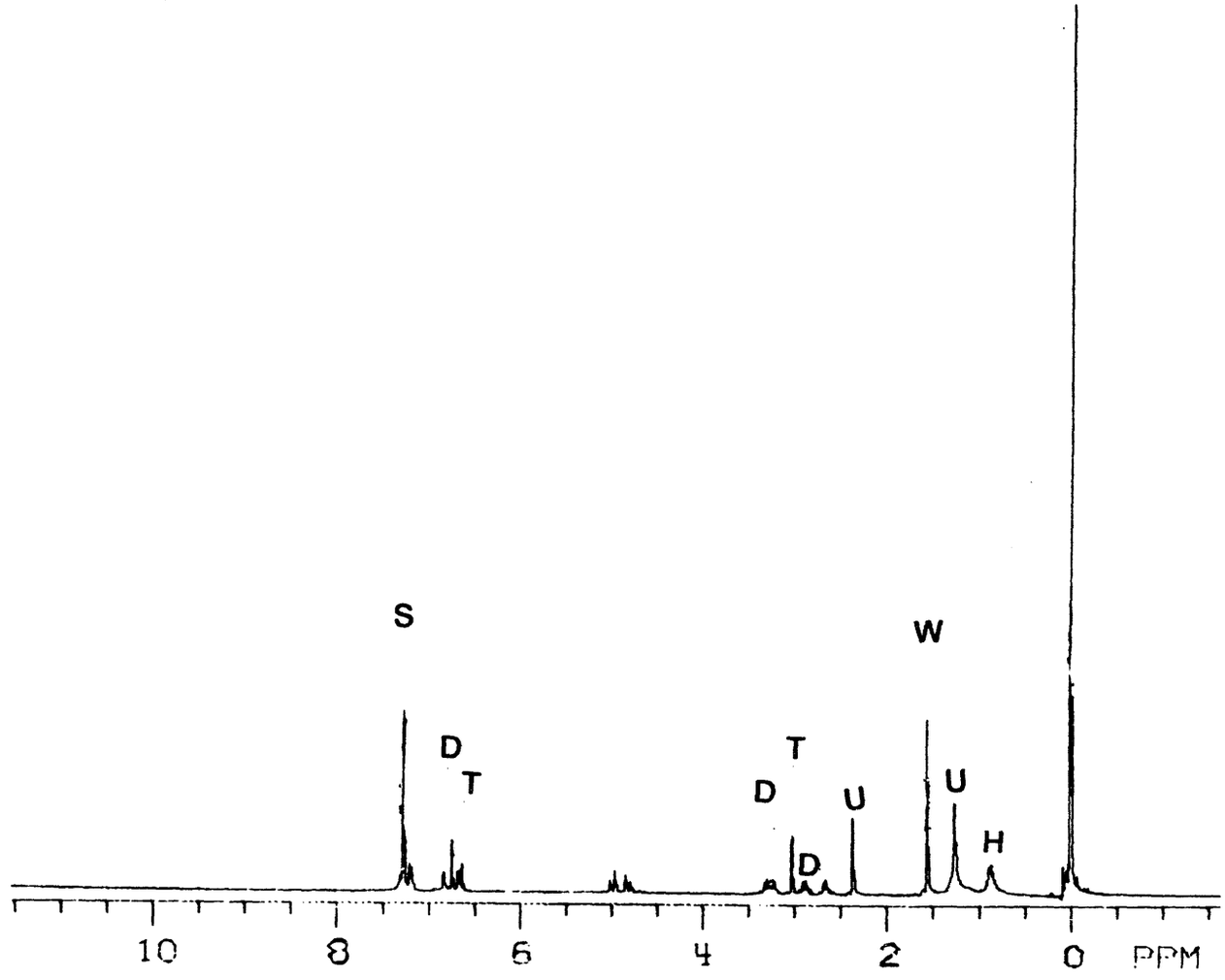


Figure A-7. ^1H NMR spectrum (300 MHz, $CDCl_3$) of compound **Y** (D: dimer, T: trimer, S: chloroform, W: H_2O, H: high boiling residue from hexane, the eluent, U: unknown compound).

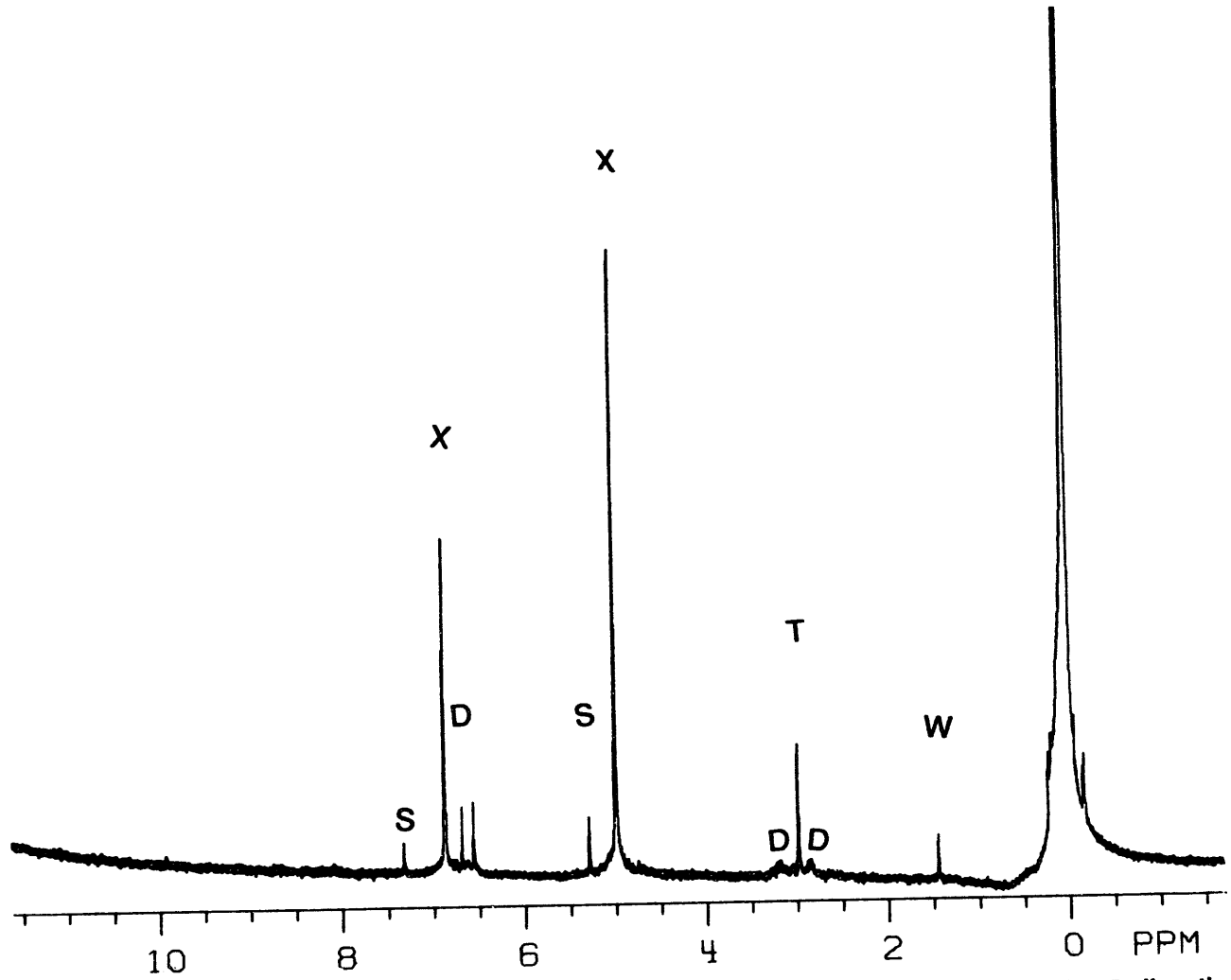


Figure A-8. ^1H NMR spectrum (300 MHz, $CDCl_3$) of the oligomerization products of 2,5-dimethylene-2,5-dihydrothiophene (**4**) (Oxygen was bubbled through the monomer **4** solution for 1 min; D: dimer, T: trimer, S: chloroform, S: methylene chloride, W: H_2O, X: compound **X**).

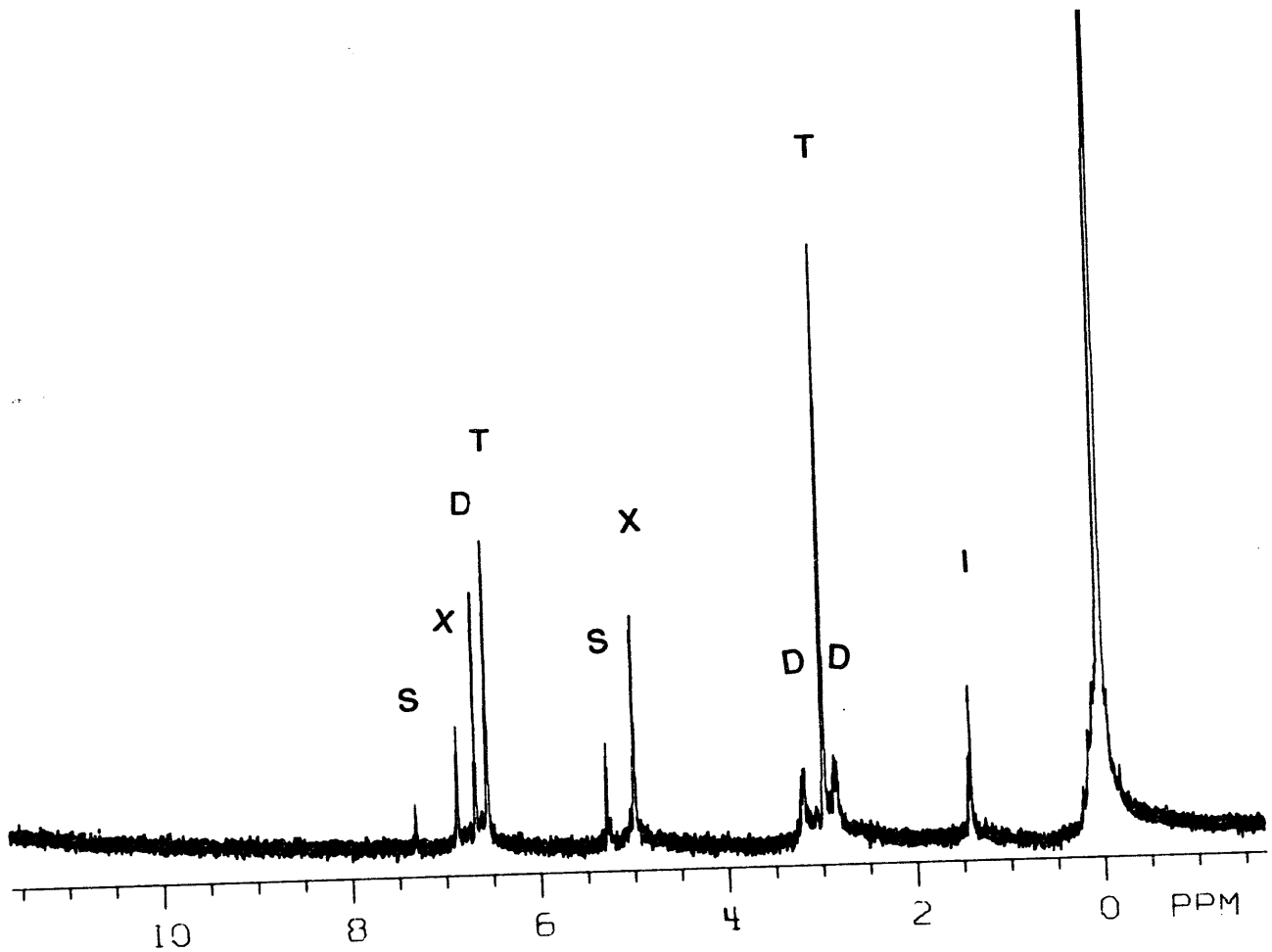


Figure A-9. ^1H NMR spectrum (300 MHz, $CDCl_3$) of the oligomerization products of 2,5-dimethylene-2,5-dihydrothiophene (**4**) (Nitrogen was bubbled through the monomer **4** solution for 1 min; D: dimer, T: trimer, S: chloroform, S: methylene chloride, I: impurities, X: compound **X**).

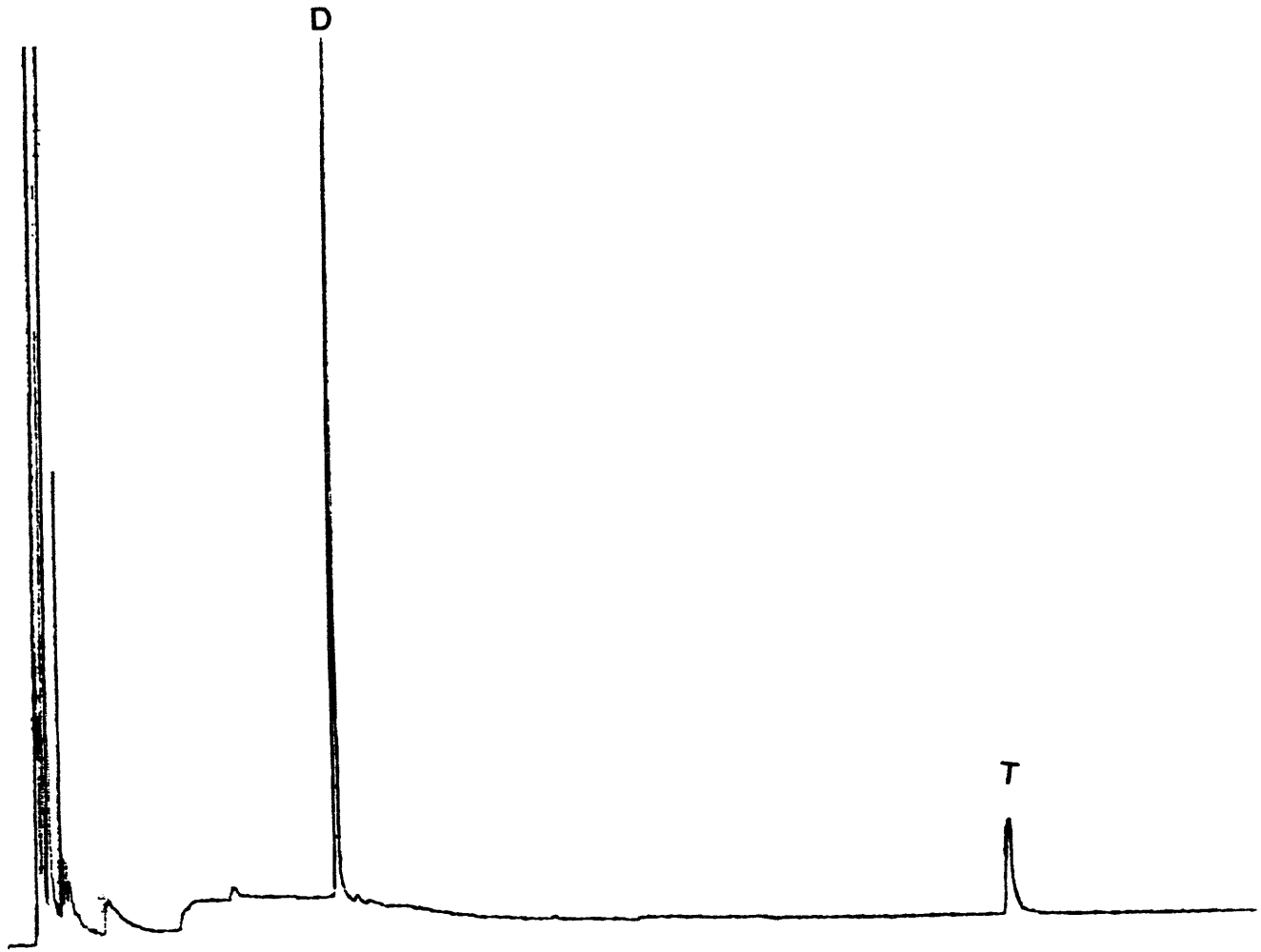


Figure A-10. Gas chromatograph (DB-1, temperature program 100°C, 5 min, 10°C/min, 200°C, 35 min; Oxygen was bubbled through the monomer **4** solution for 1 min) of the oligomerization products of 2,5-dimethylene-2,5-dihydrothiophene (**4**) (D: dimer, T: trimer).

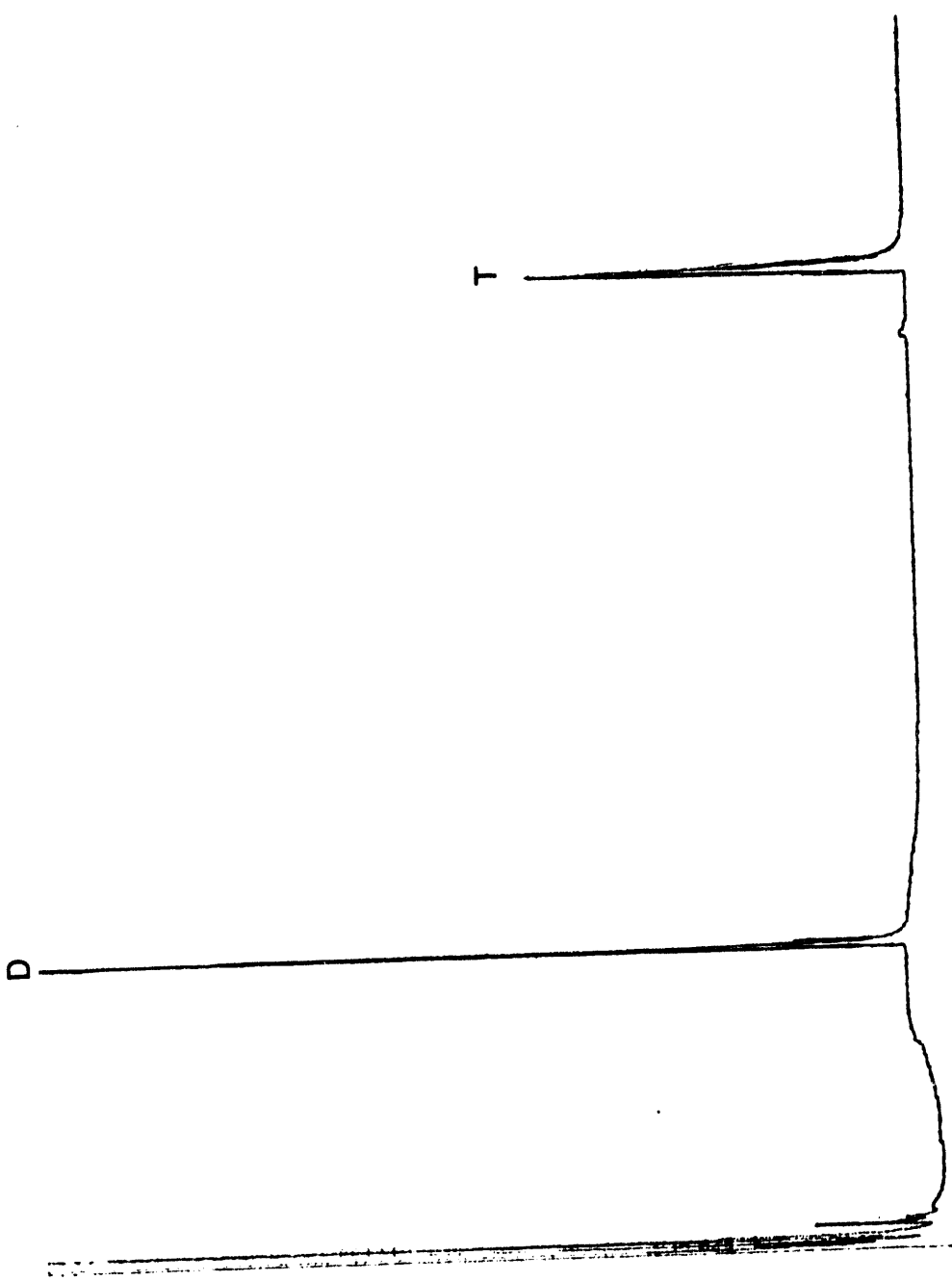


Figure A-11. Gas chromatograph (DB-1, temperature program 100°C, 5 min, 10°C/min, 200°C, 35 min; Nitrogen was bubbled through the monomer **4** solution for 1 min) of the oligomerization products of 2,5-dimethylene-2,5-dihydrothiophene (**4**) (D: dimer, T: trimer).

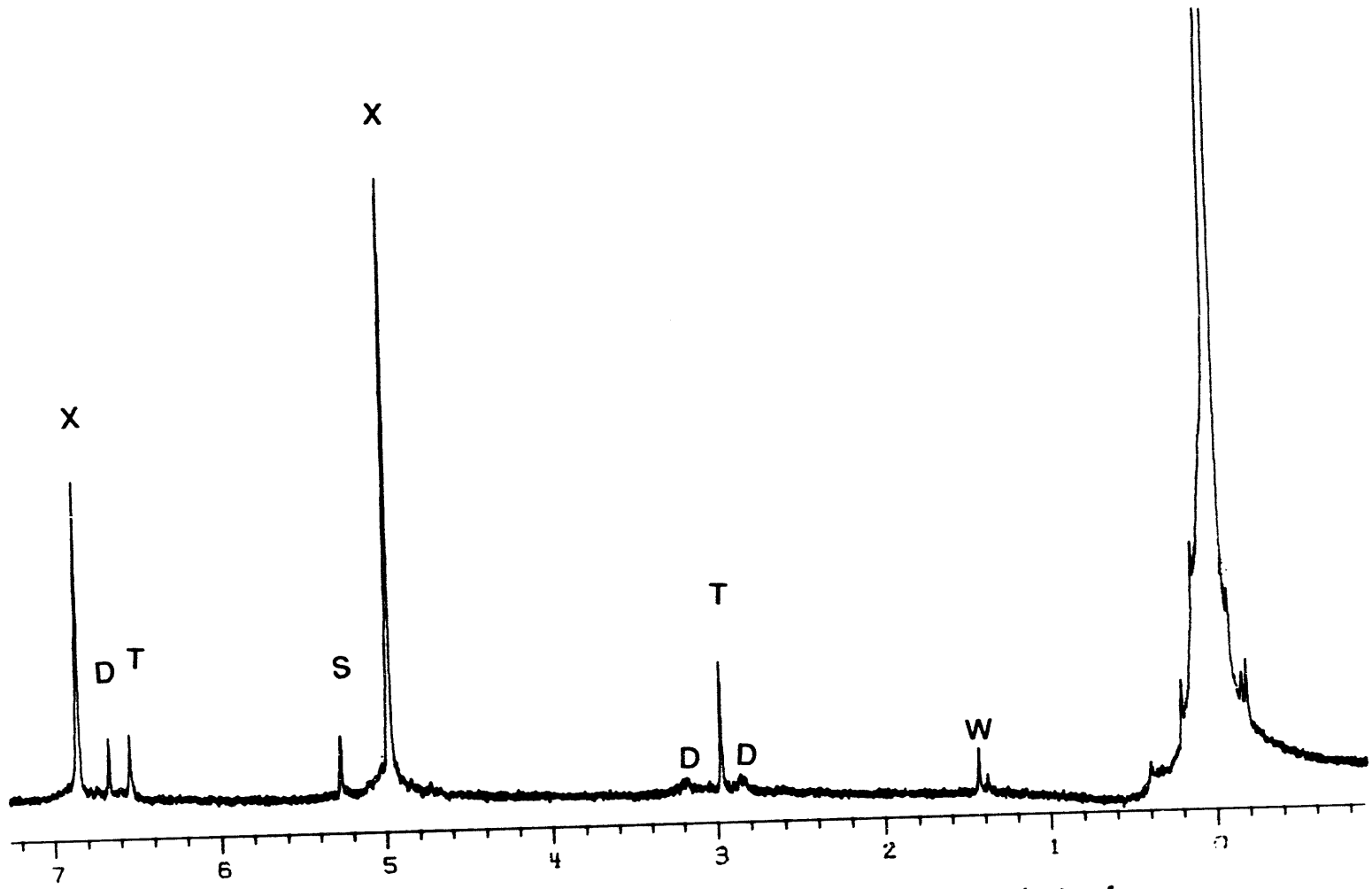


Figure A-12. ^1H NMR spectrum (300 MHz, $CDCl_3$) of the oligomerization products of 2,5-dimethylene-2,5-dihydrothiophene (**4**) (11 hours passed after oxygen was bubbled through the monomer **4** solution for 1 min; D: dimer, T: trimer; S: methylene chloride, W: H_2O, X: compound **X**).

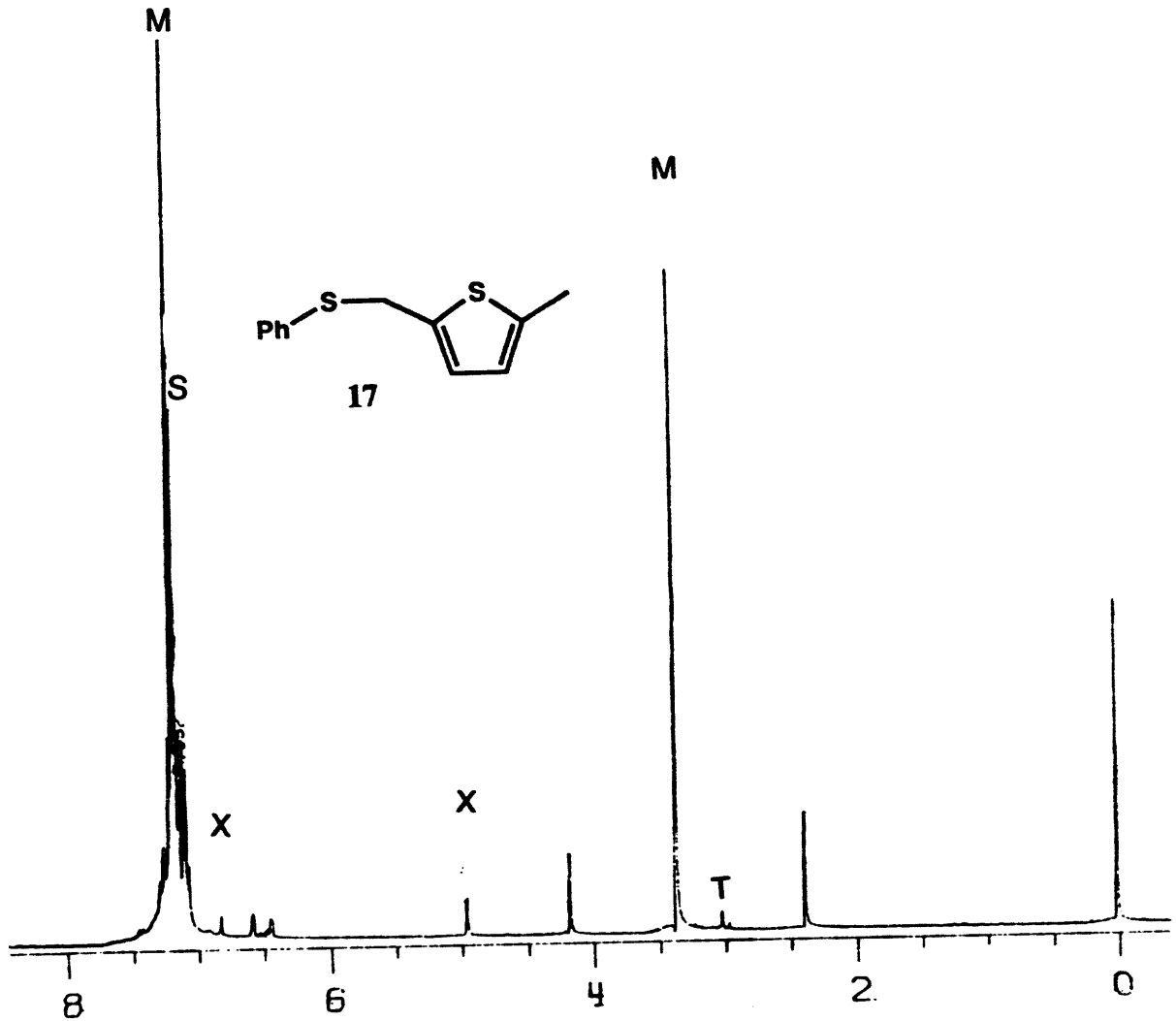


Figure A-13. ^1H NMR spectrum (300 MHz, $CDCl_3$) of compound **17** (S: chloroform, X: compound **X**, D: dimer, T: trimer, M: thiophenol).

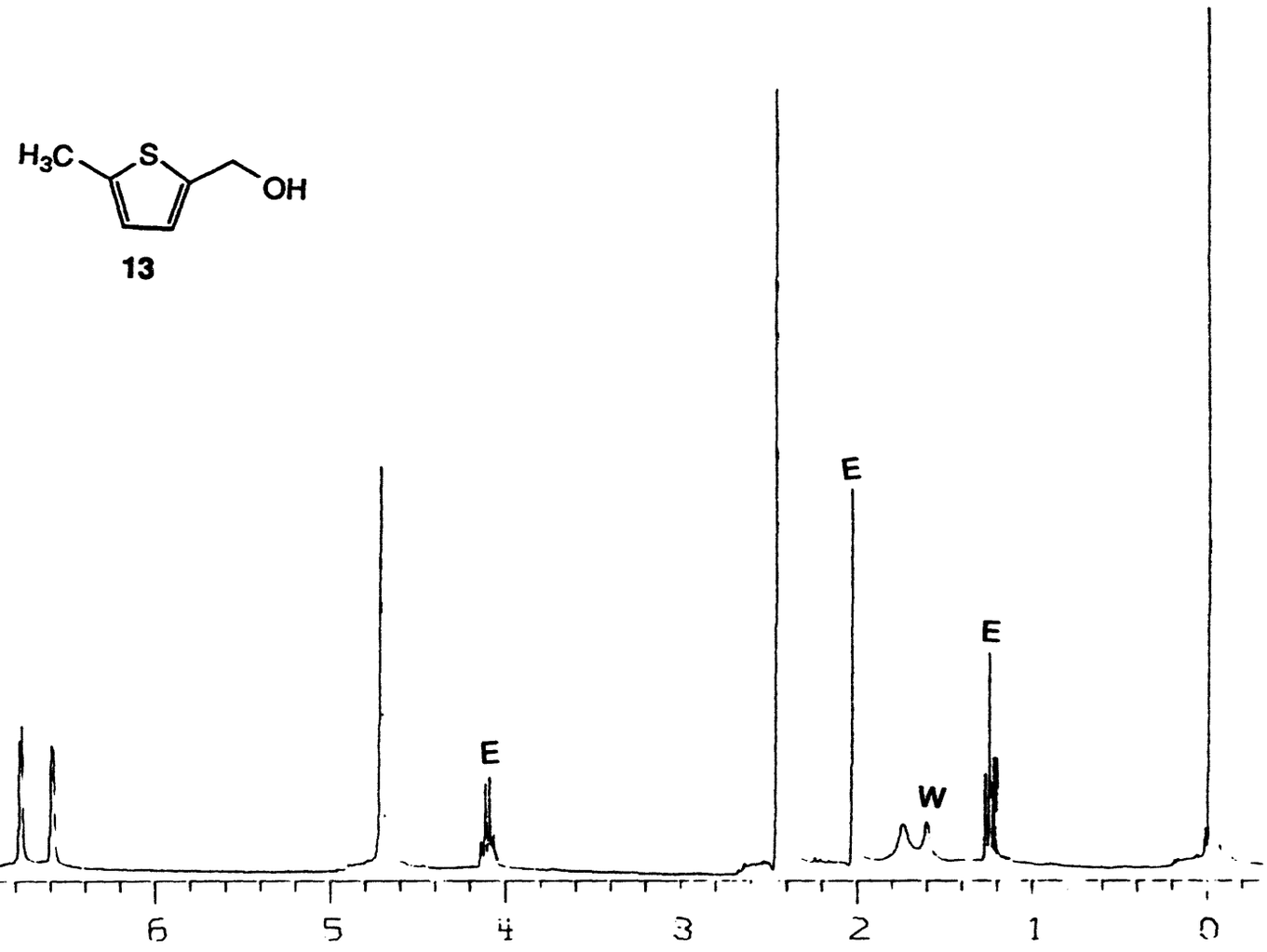


Figure A-14. ^1H NMR spectrum (300 MHz, $CDCl_3$) of 5-methyl-2-thiophenemethanol (**13**) (S: chloroform, W: H_2O, E: ethyl acetate).

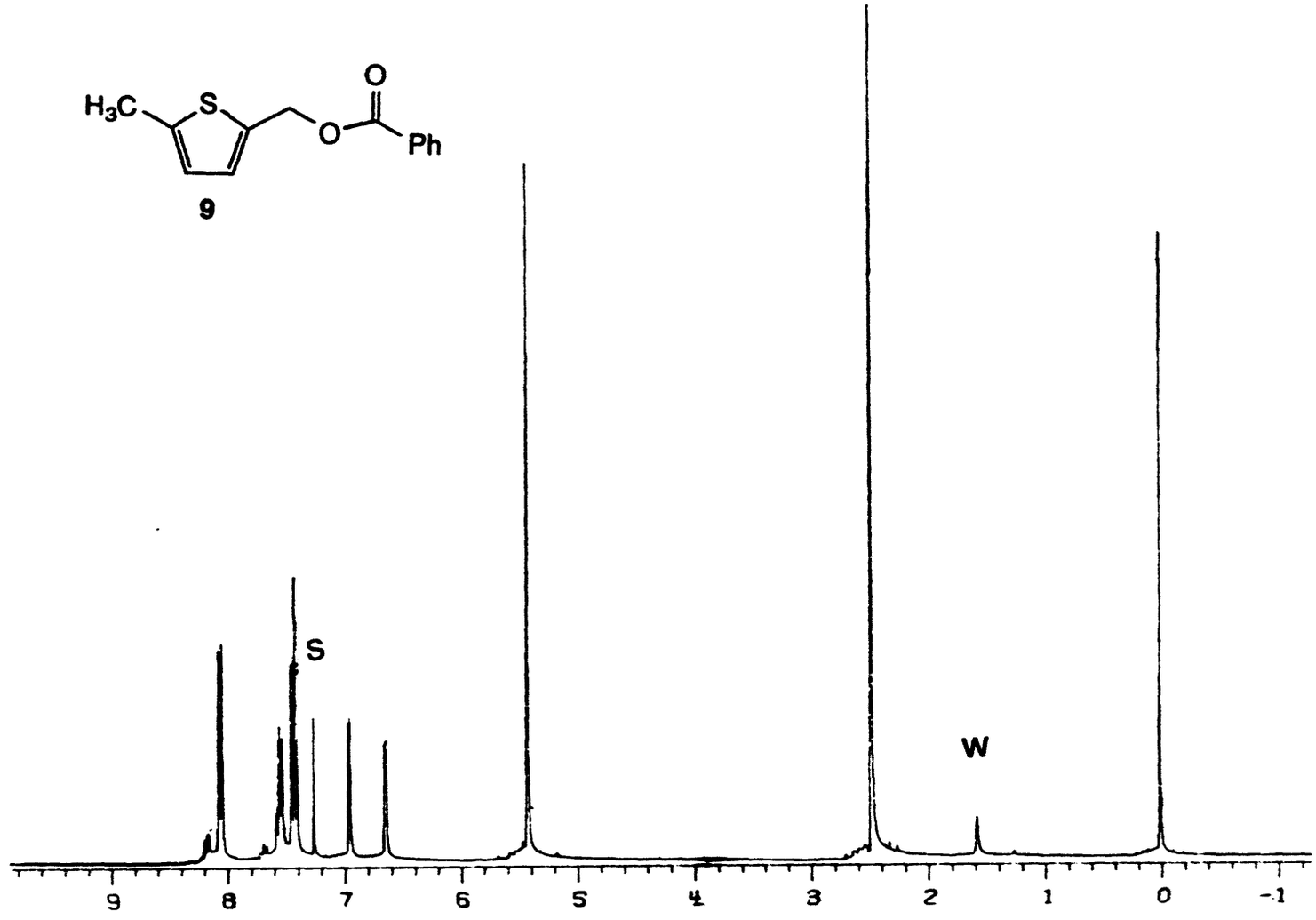


Figure A-15. ^1H NMR spectrum (300 MHz, $CDCl_3$) of 5-methyl-2-thiophenemethyl benzoate (**9**) (S: chloroform, W: H_2O).

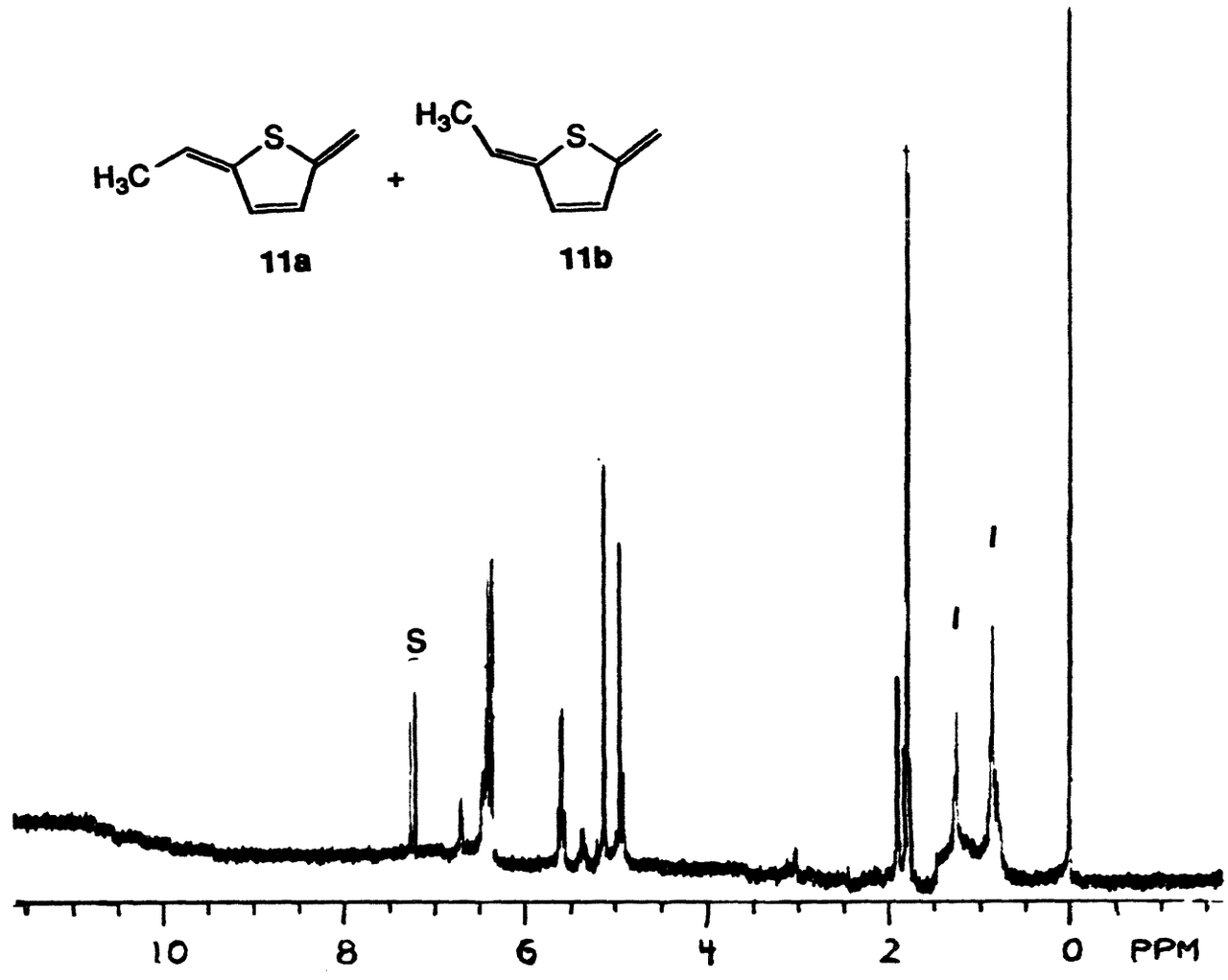


Figure A-16. ^1H NMR spectrum (300 MHz, $CDCl_3$) of 2-ethylidene-5-methylene-2,5-dihydrothiophene (**11**) (S: chloroform, I: material from grease).

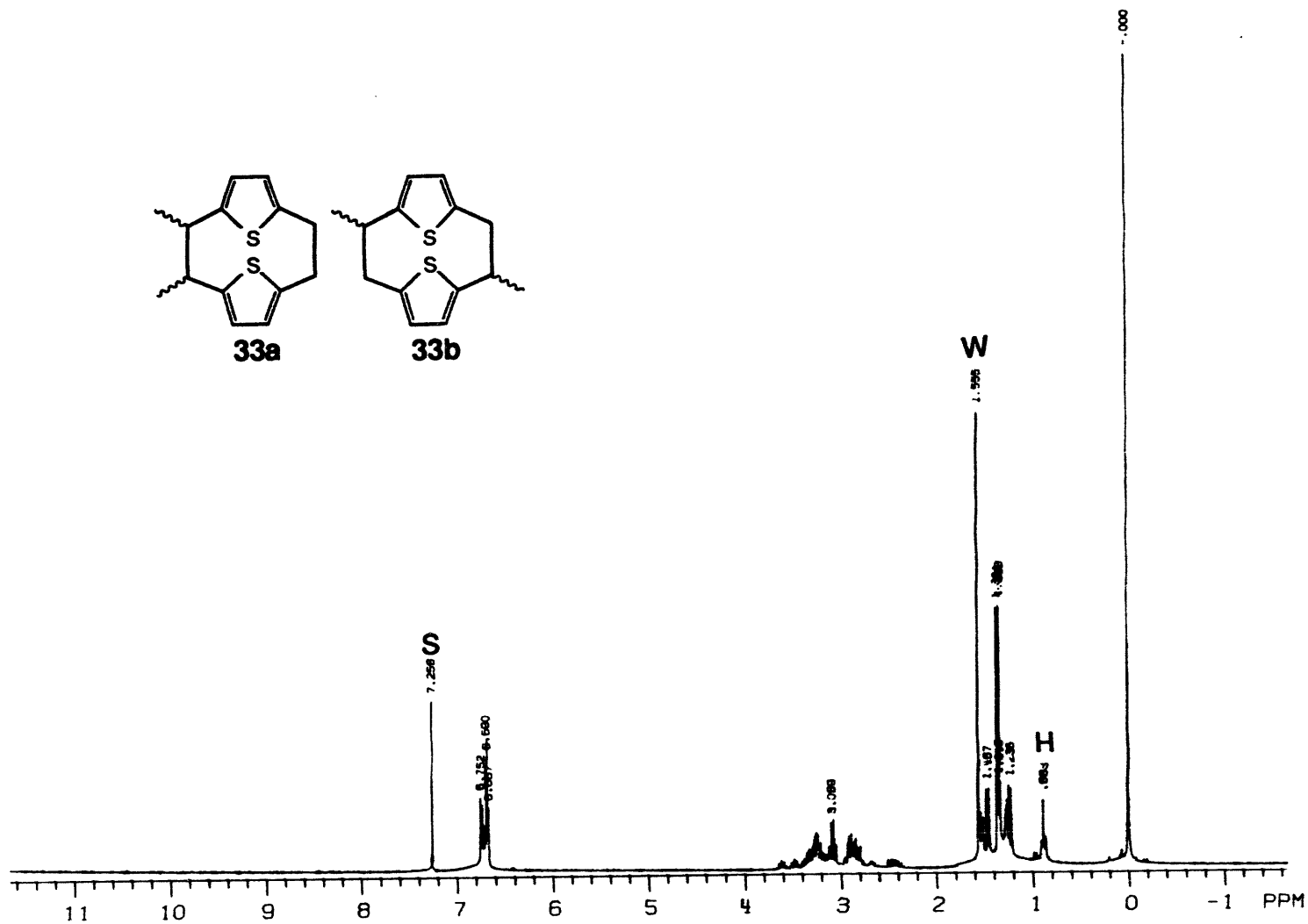


Figure A-17. ^1H NMR spectrum (300 MHz, $CDCl_3$) of pure dimers **33a** and **33b** (S: chloroform, W: H_2O, H: high boiling residue from hexane, the eluent).

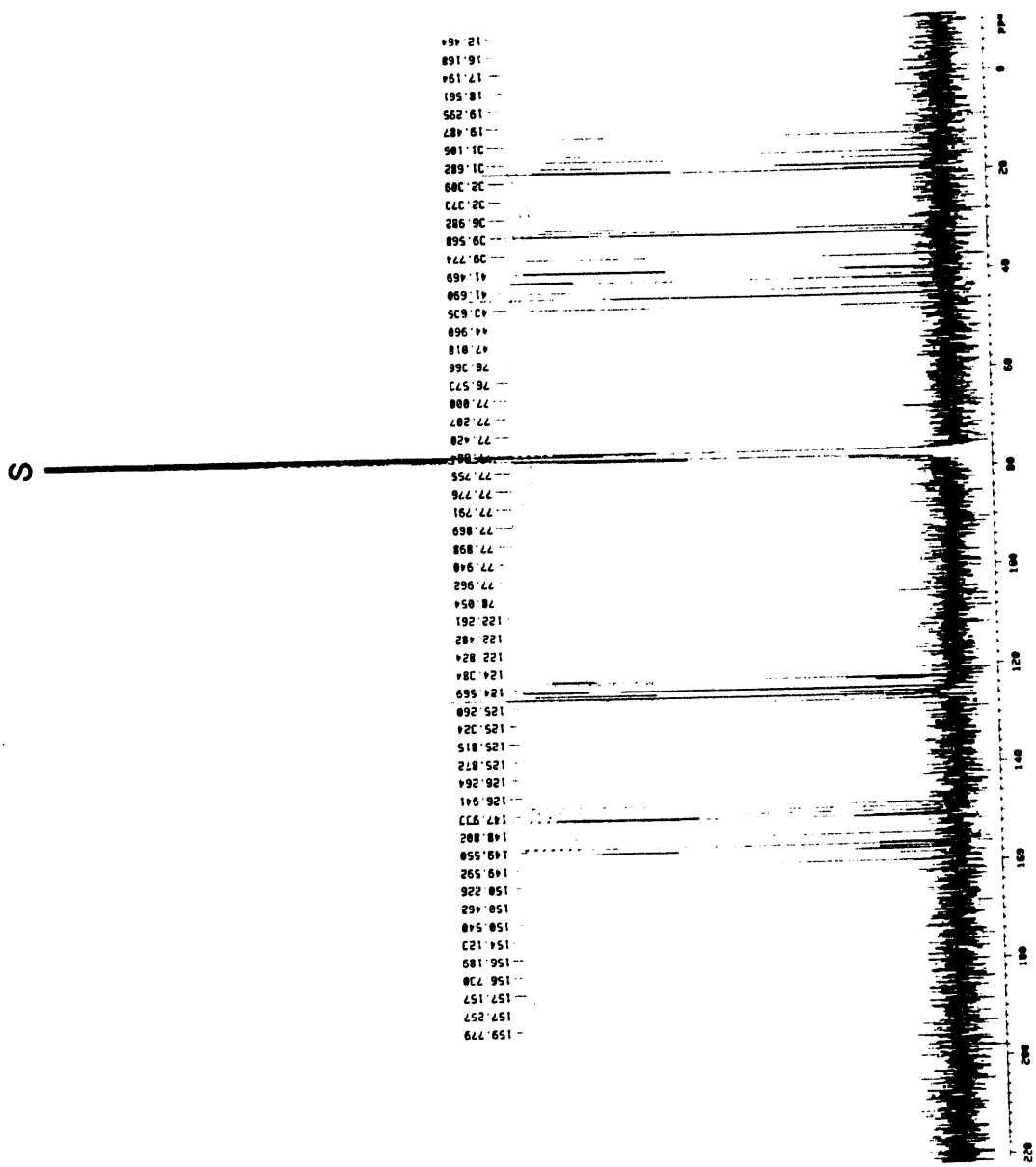


Figure A-18. ^{13}C spectrum (75.5 MHz, $CDCl_3$) of dimers **33a** and **33b** (S: chloroform, Chromium(III) acetylacetonate was added).

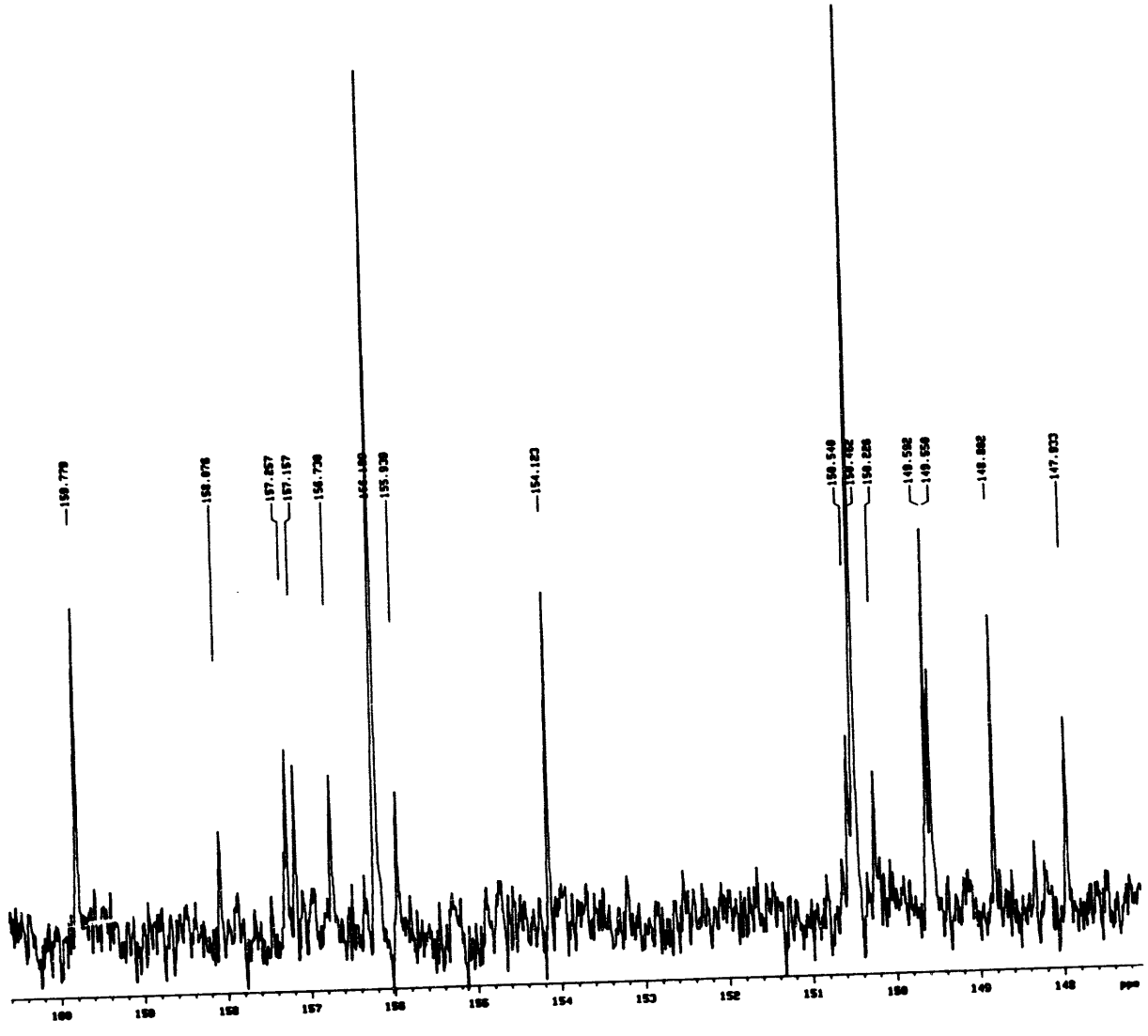


Figure A-19 Blown up ^{13}C spectrum of Figure A-18 (δ 160-145).

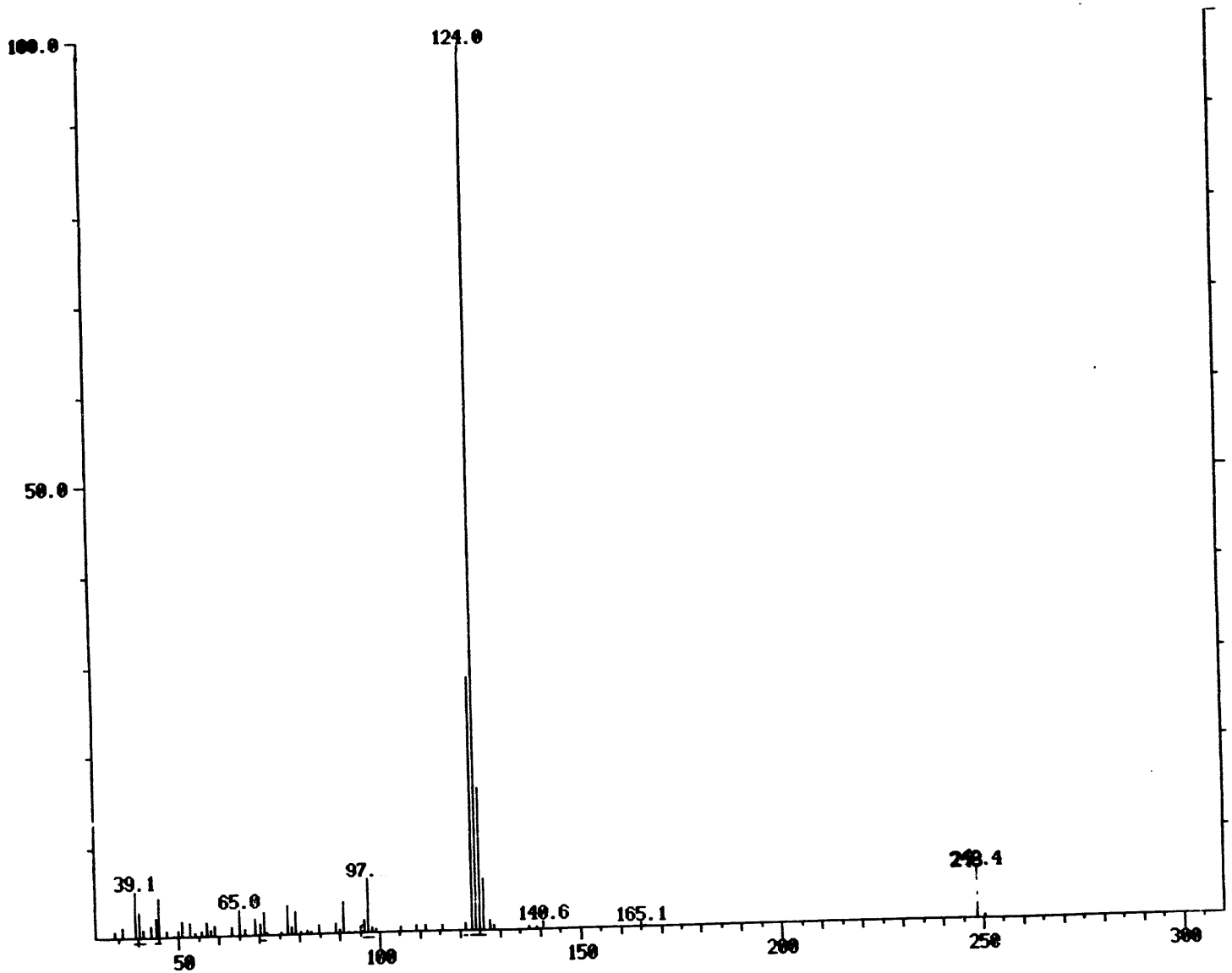


Figure A-20. GC/MS of dimers **33a** and **33b**.

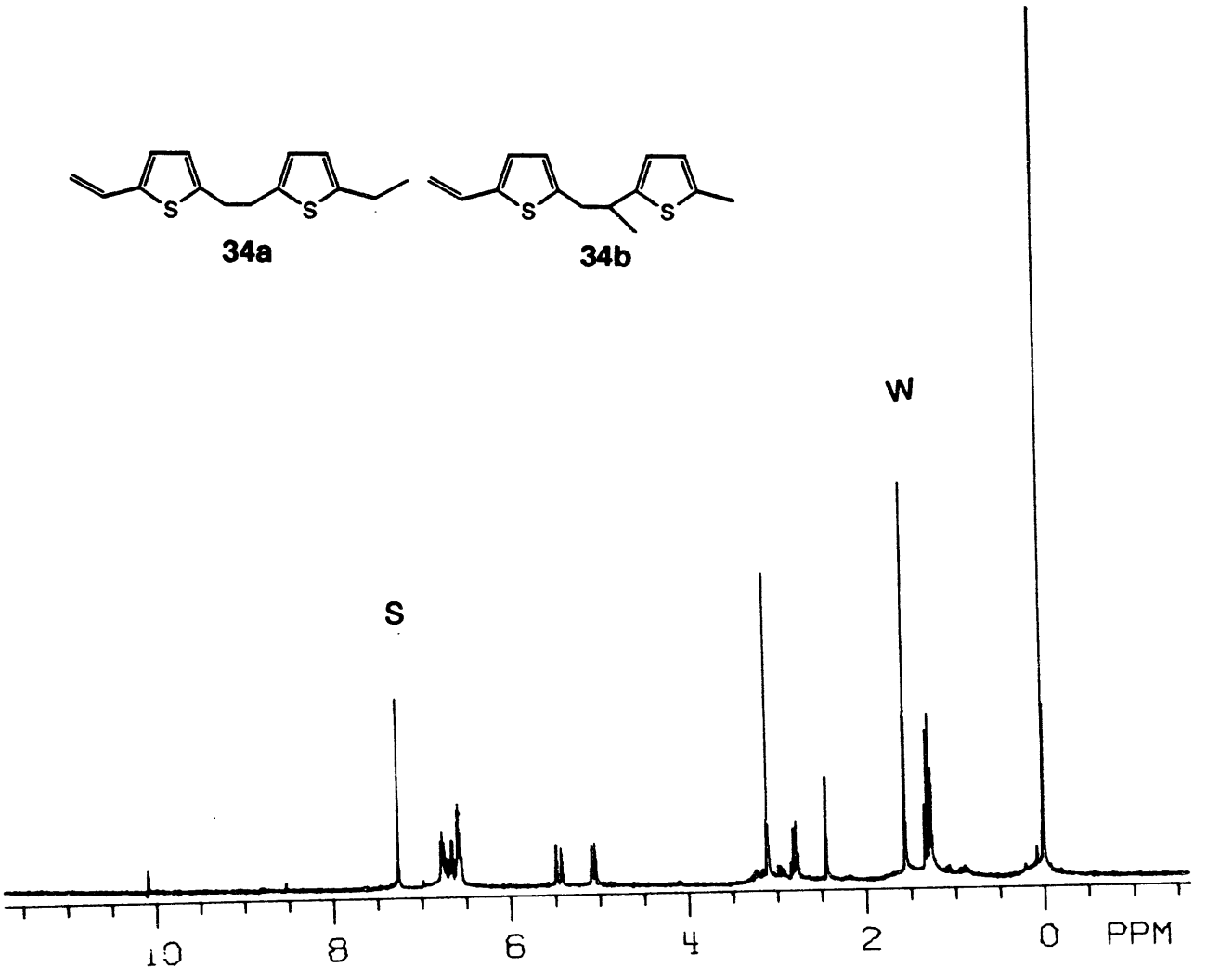


Figure A-21. ^1H NMR spectrum (300 MHz, $CDCl_3$) of acyclic dimers **34a** and **34b** (S: chloroform, W: H_2O).

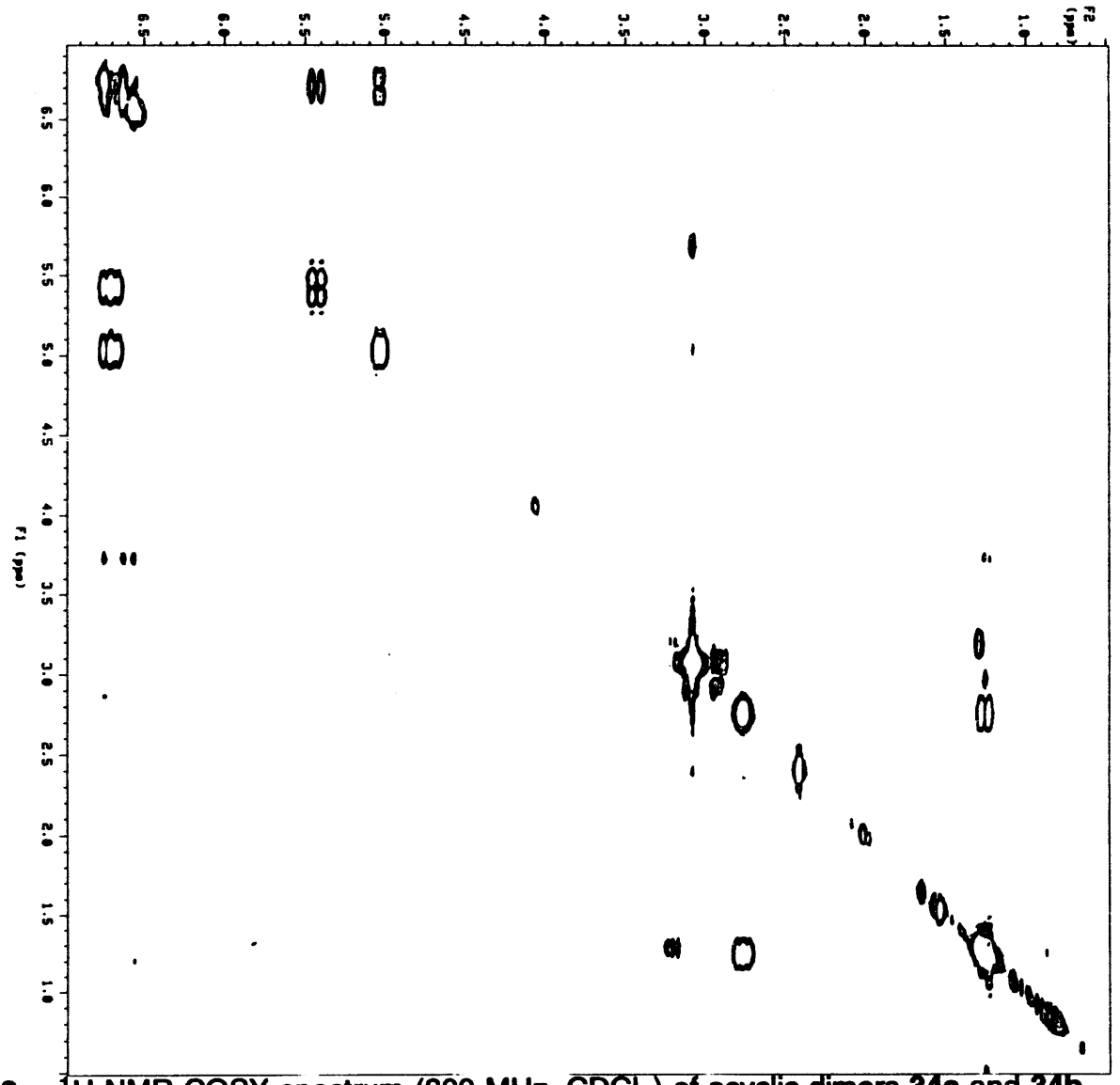


Figure A-22. ^{1}H NMR COSY spectrum (300 MHz, $CDCl_3$) of acyclic dimers **34a** and **34b**.

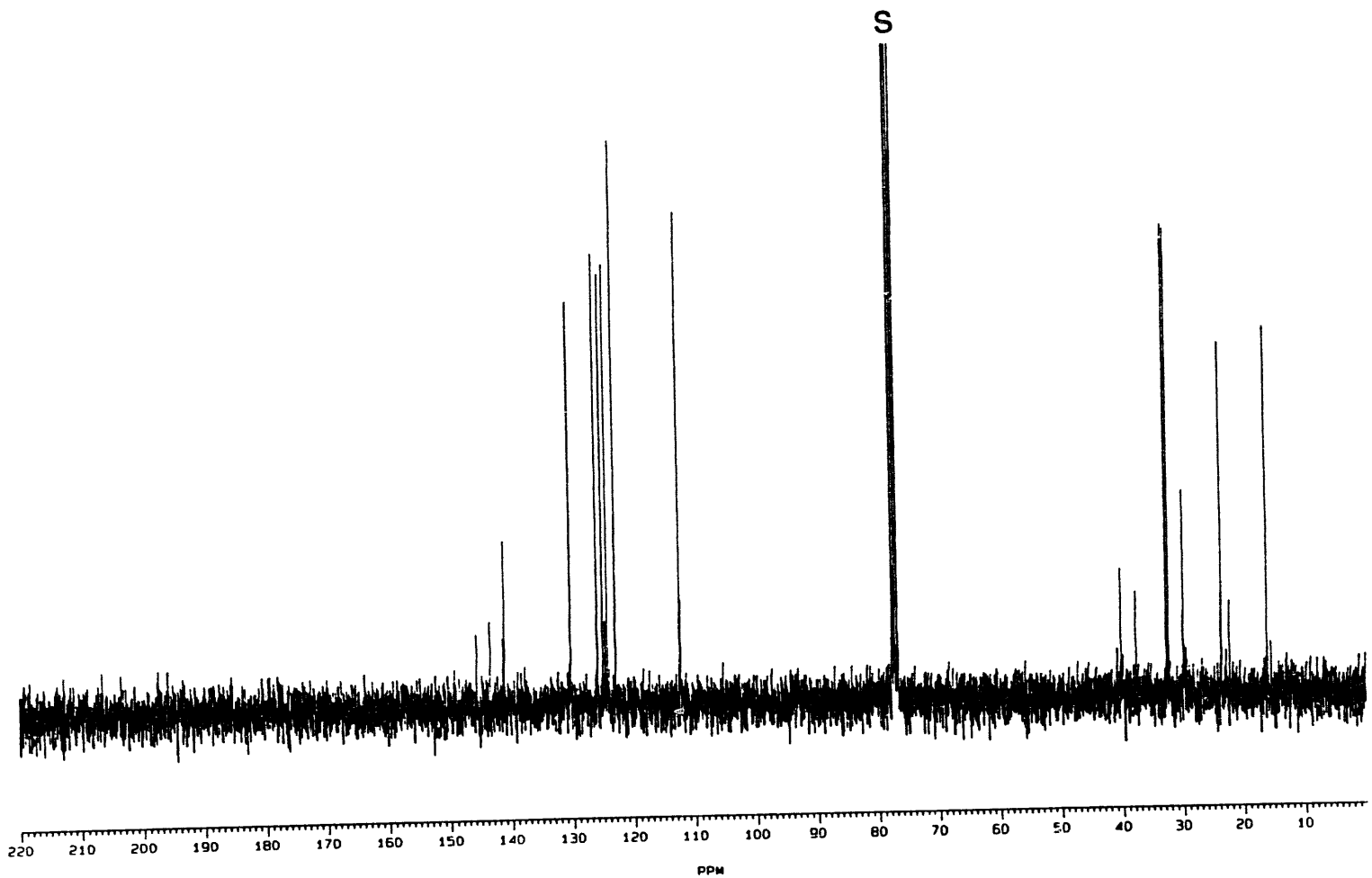


Figure A-23. ^{13}C spectrum (75.5 MHz, $CDCl_3$) of acyclic dimers **34a** and **34b** (S: chloroform).

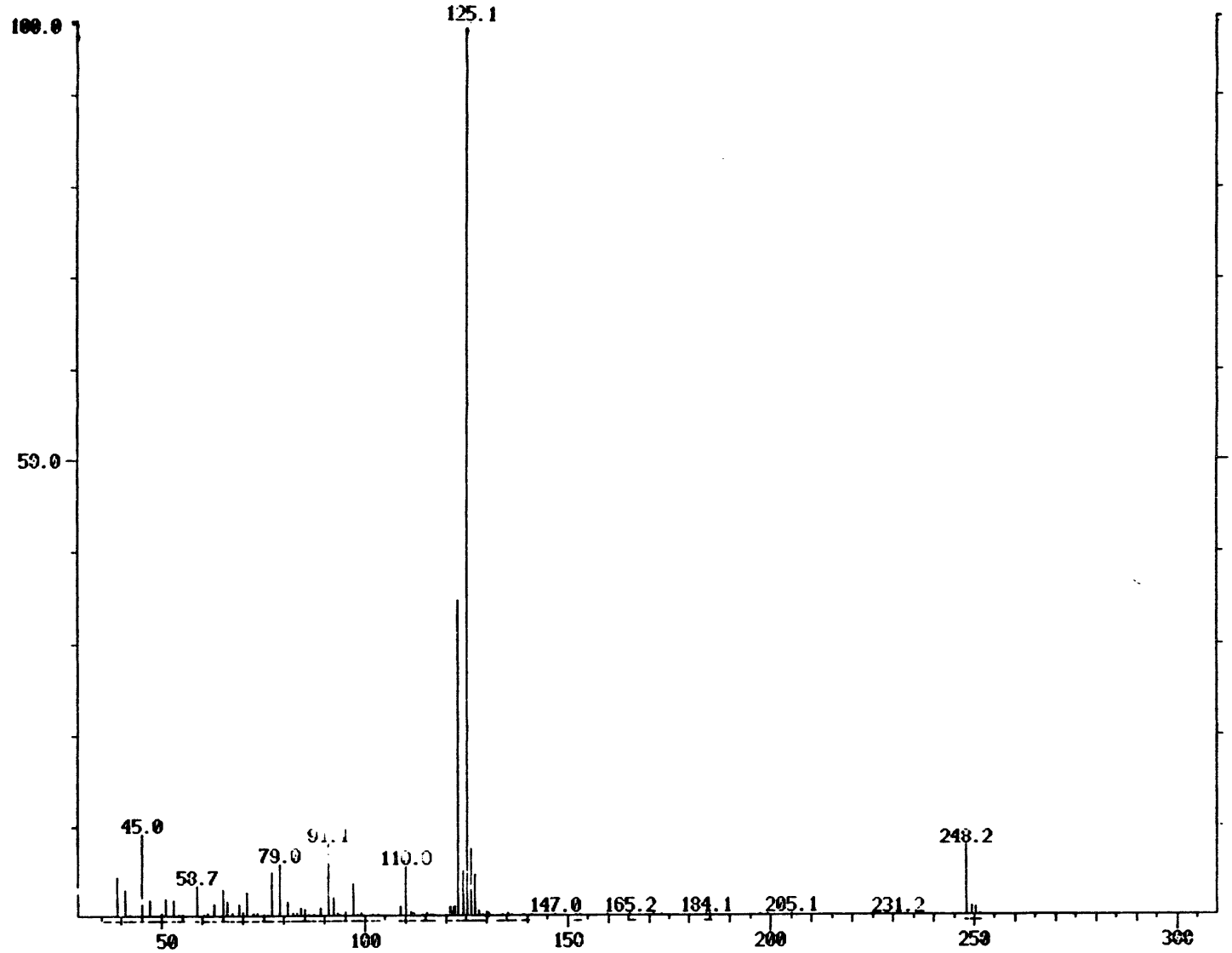


Figure A-24. GC/MS of acyclic dimers **34a** and **34b**.

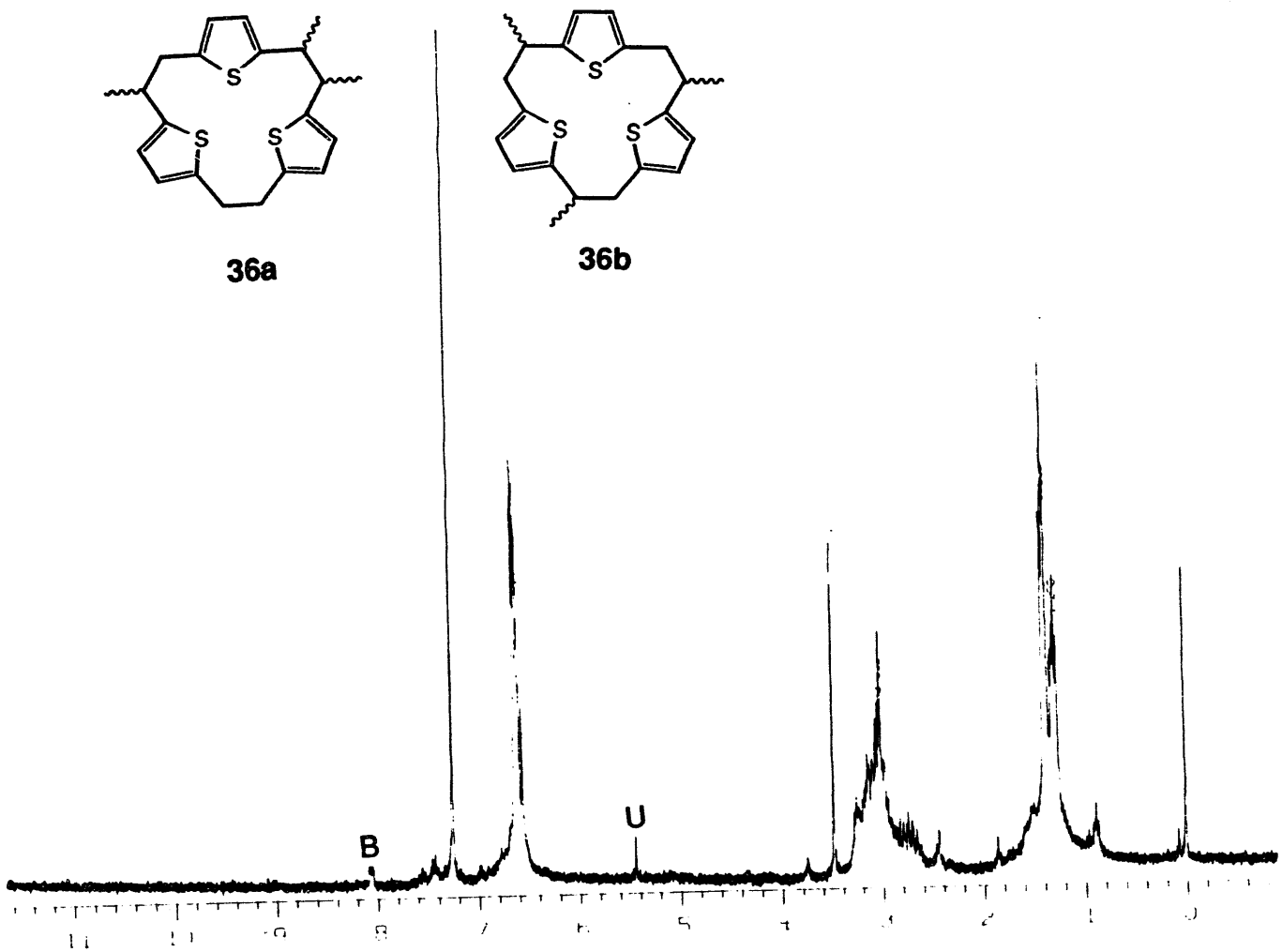


Figure A-25. ^1H NMR spectrum (300 MHz, $CDCl_3$) of trimers **36a** and **36b** (S: chloroform, B: benzoic acid, U: unknown compound).

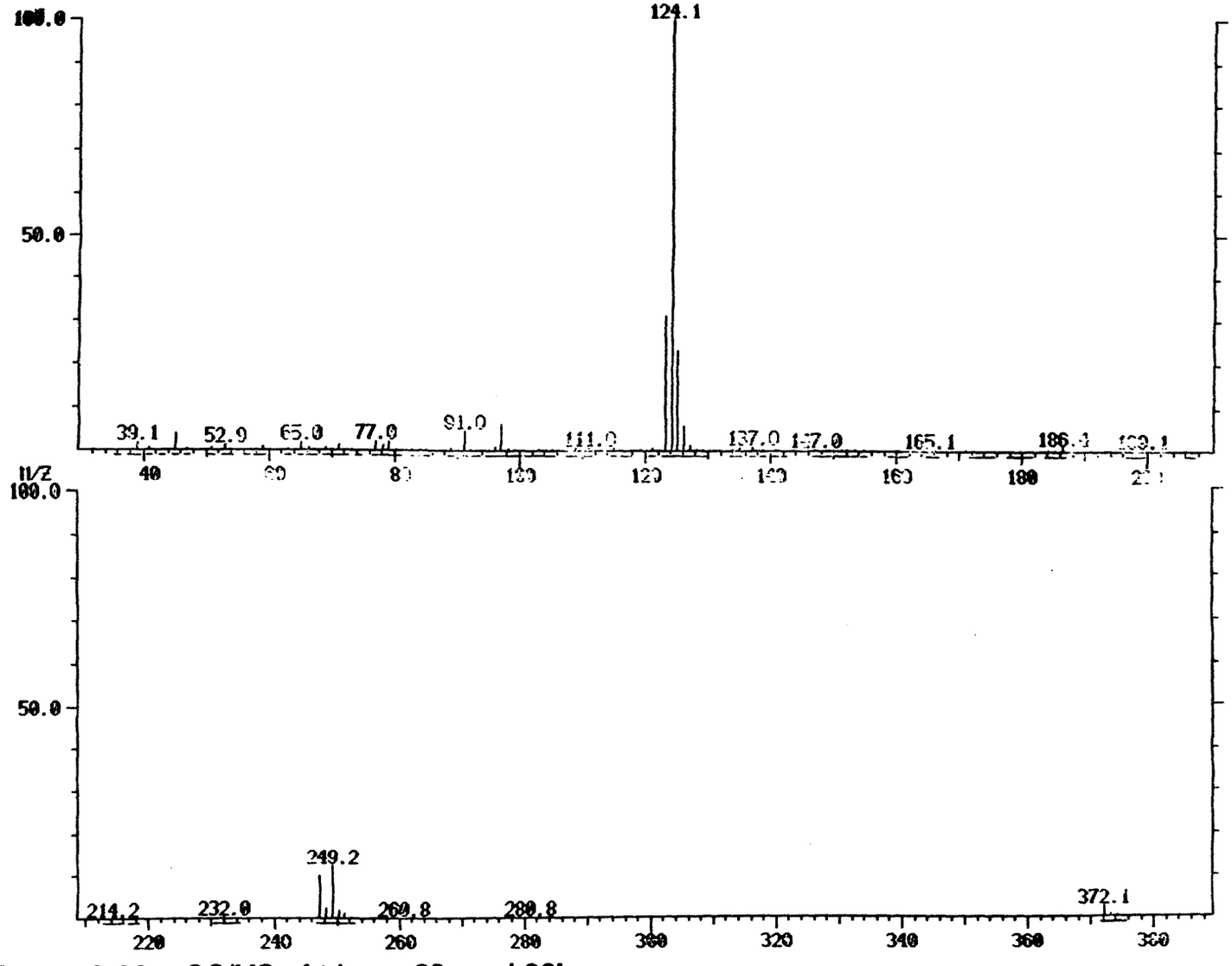


Figure A-26. GC/MS of trimers **36a** and **36b**.

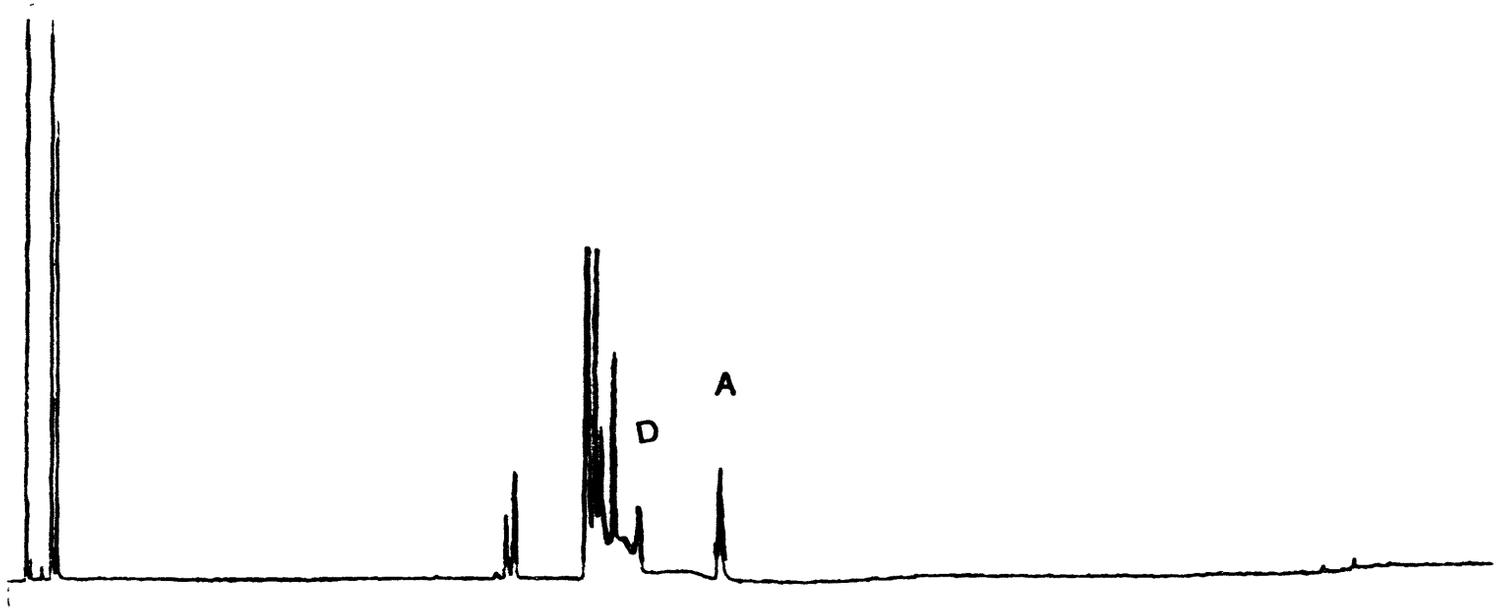


Figure A-27. Gas chromatograph of dimers **33a** and **33b** and acyclic dimers **34a** (DB-1, temperature program 100°C, 2 min, 2.0°C/min, 135°C, 10°C/min, 200°C, 10 min, 10°C/min, 250°C, 10 min; Injector temperature = 200°C, A: acyclic dimer; D: dimer).

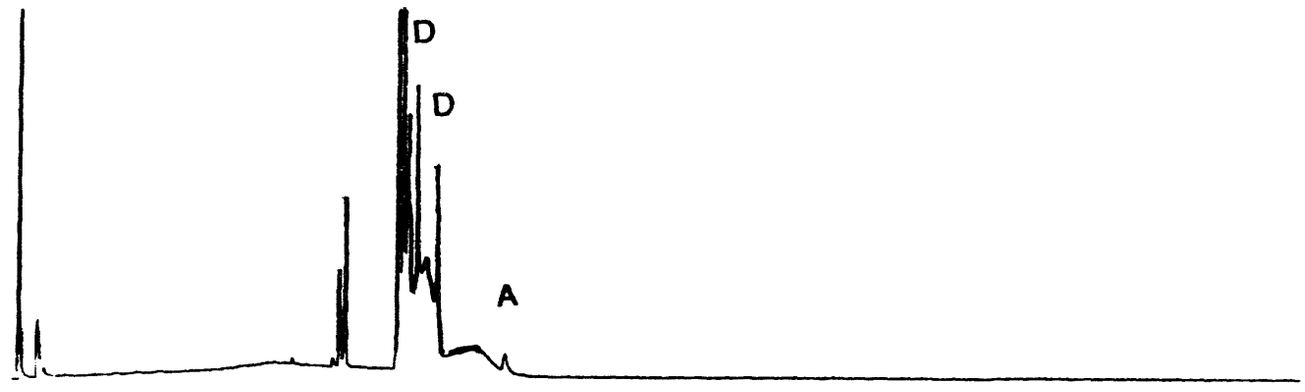


Figure A-28. Gas chromatograph of dimers **33a** and **33b** and acyclic dimer **34a** (DB-1, 135°C, 10°C/min, 200°C, 10 min, 10°C/min, 250°C, 10 min; Injector temperature = 150°C, A: acyclic dimer; D: dimer).

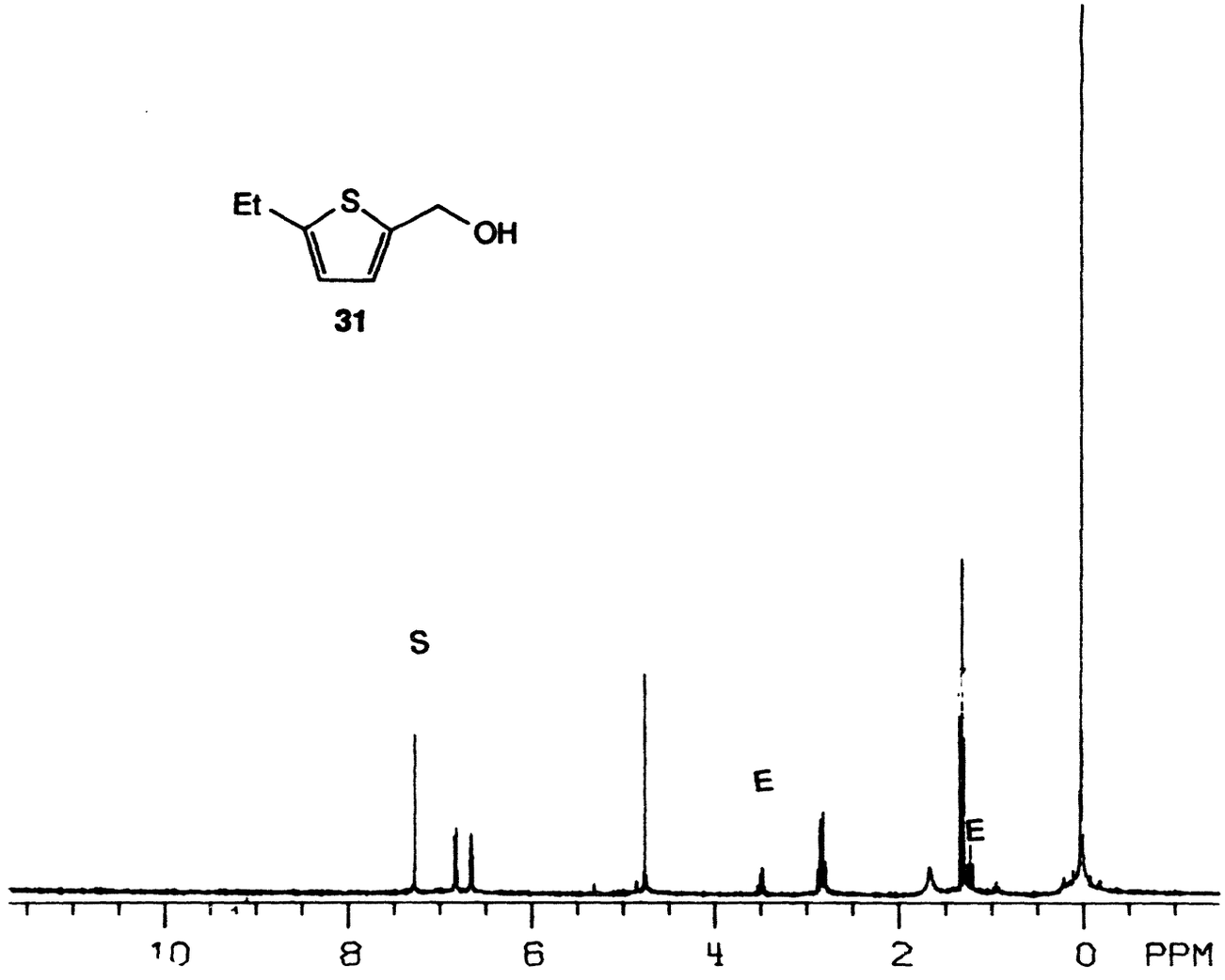


Figure A-29. ^1H NMR spectrum (300 MHz, $CDCl_3$) of 5-ethyl-2-thiophenemethanol (**31**) (S: chloroform, E: ether).

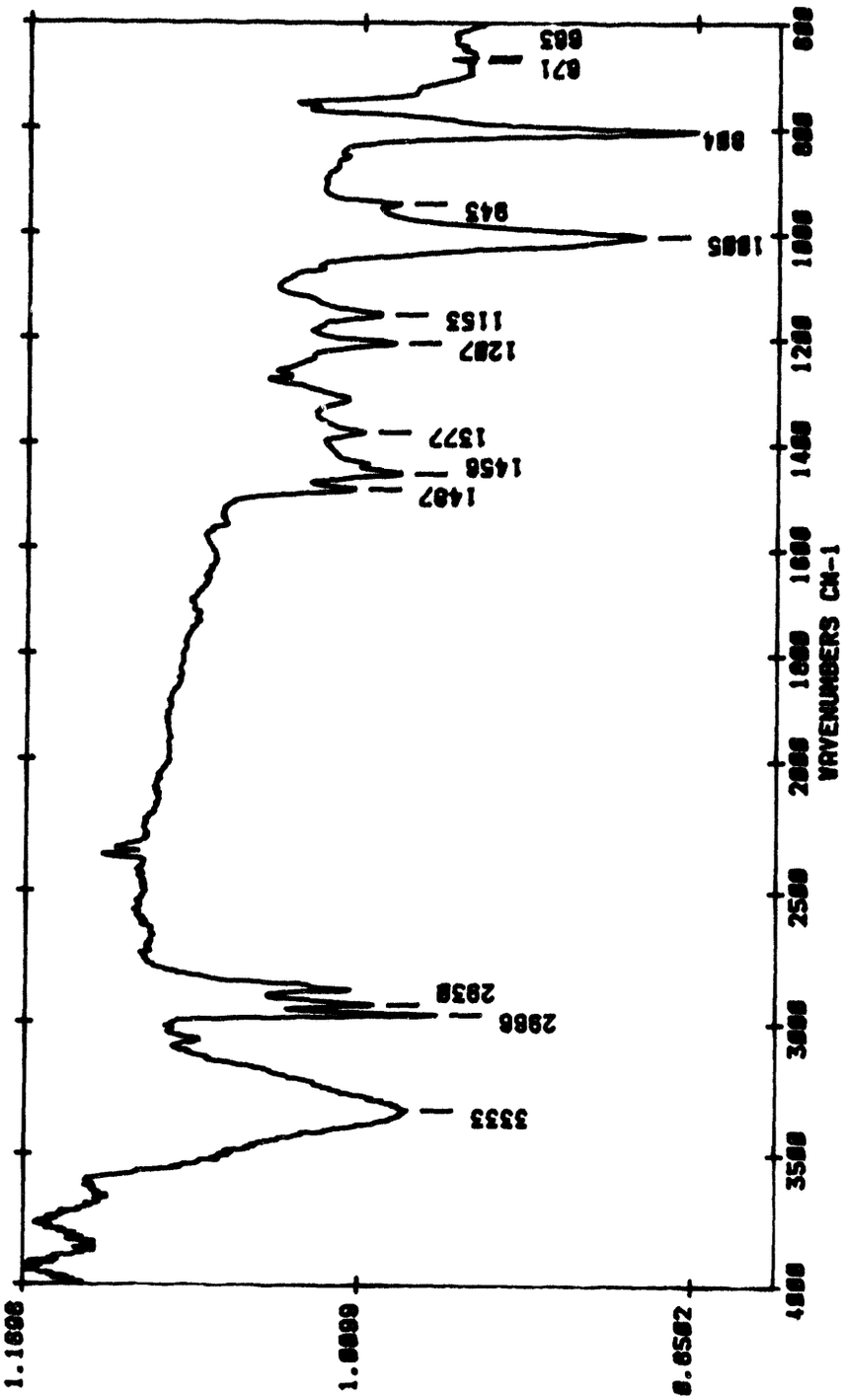


Figure A-30. IR (thin film) spectrum of 5-ethyl-2-thiophenemethanol (31).

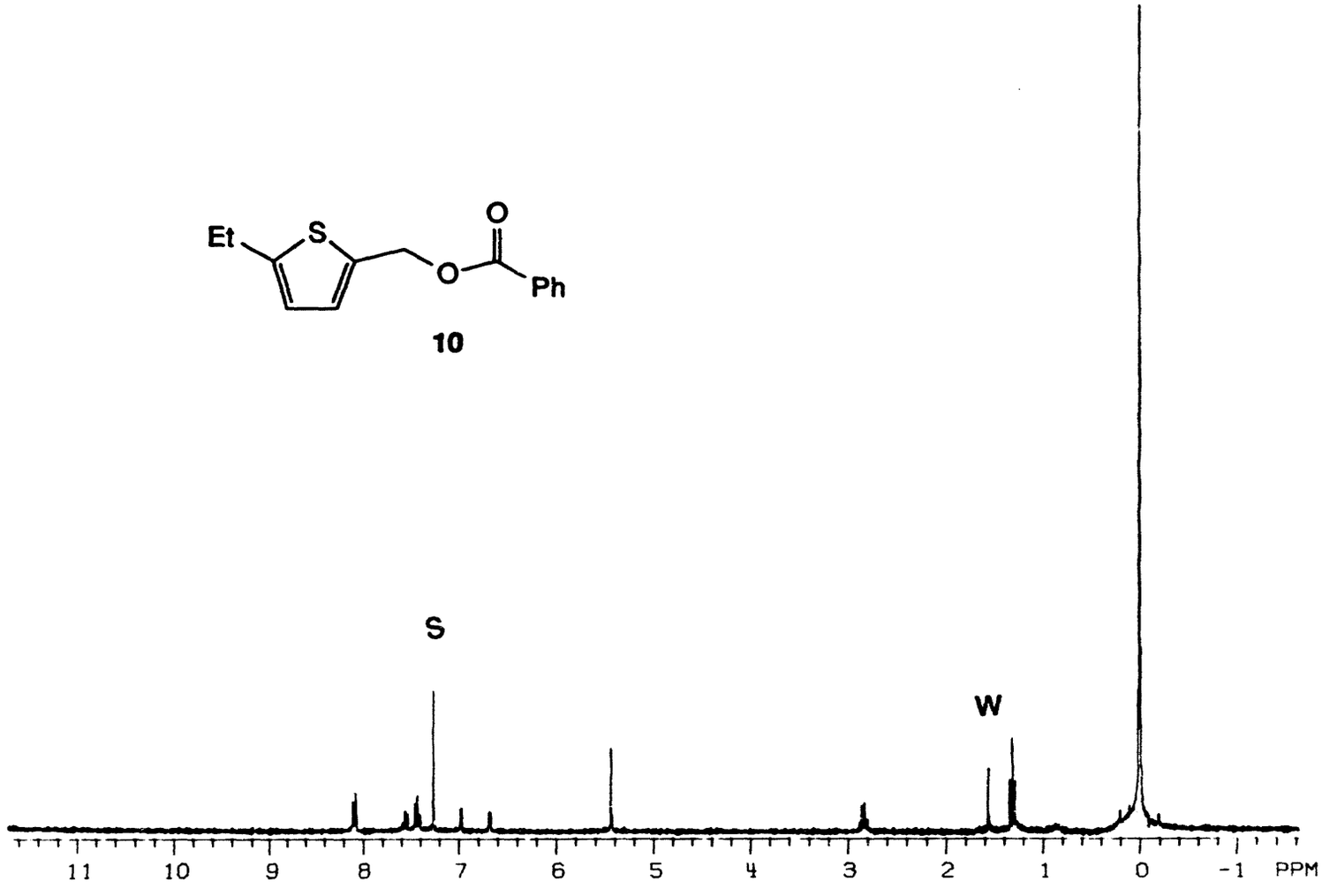


Figure A-31. ^1H NMR spectrum (300 MHz, $CDCl_3$) of 5-ethyl-2-thiophenemethyl benzoate (**10**) (S: chloroform, W: H_2O).

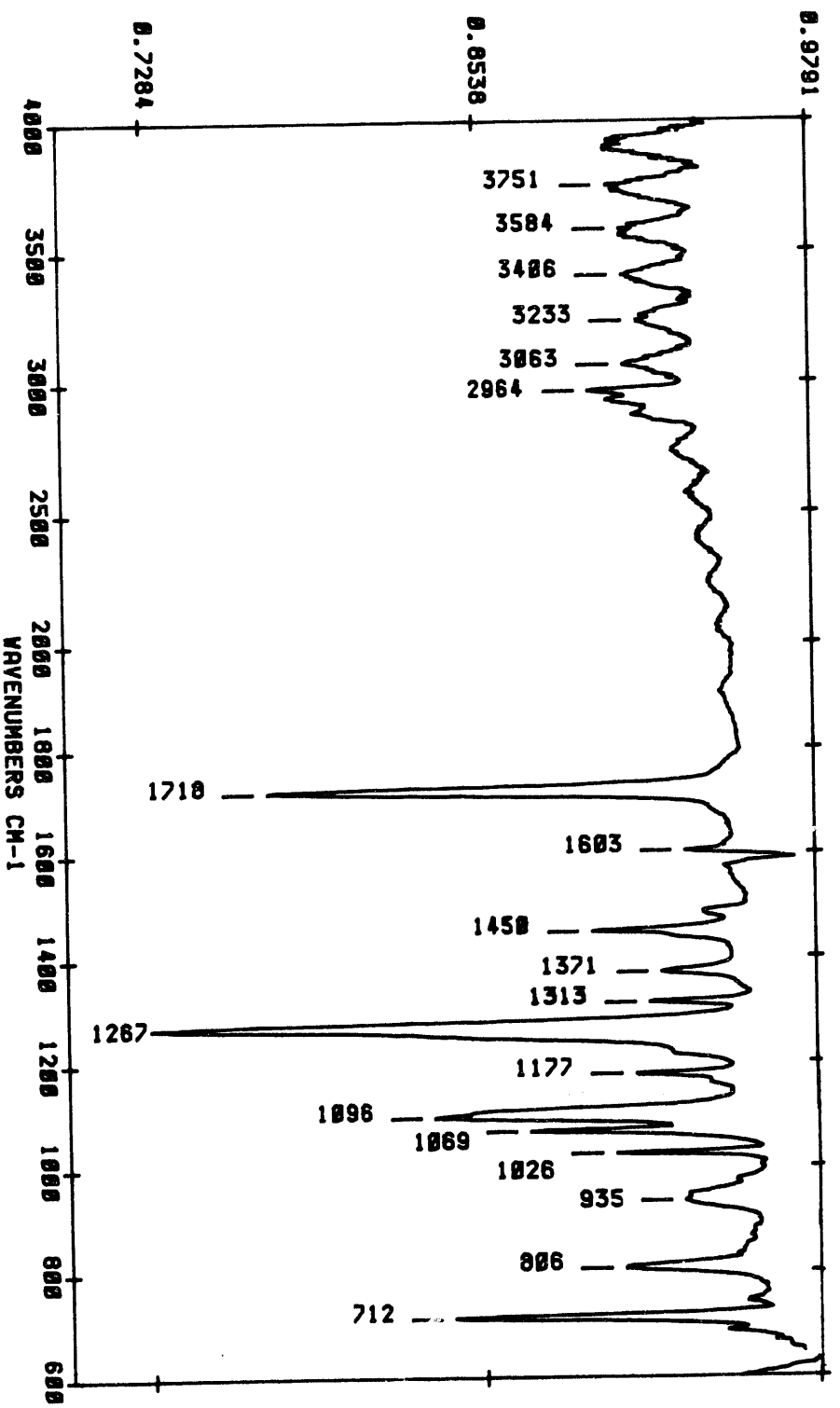


Figure A-32. IR (thin film) spectrum of 5-ethyl-2-thiophenemethyl benzoate (10).

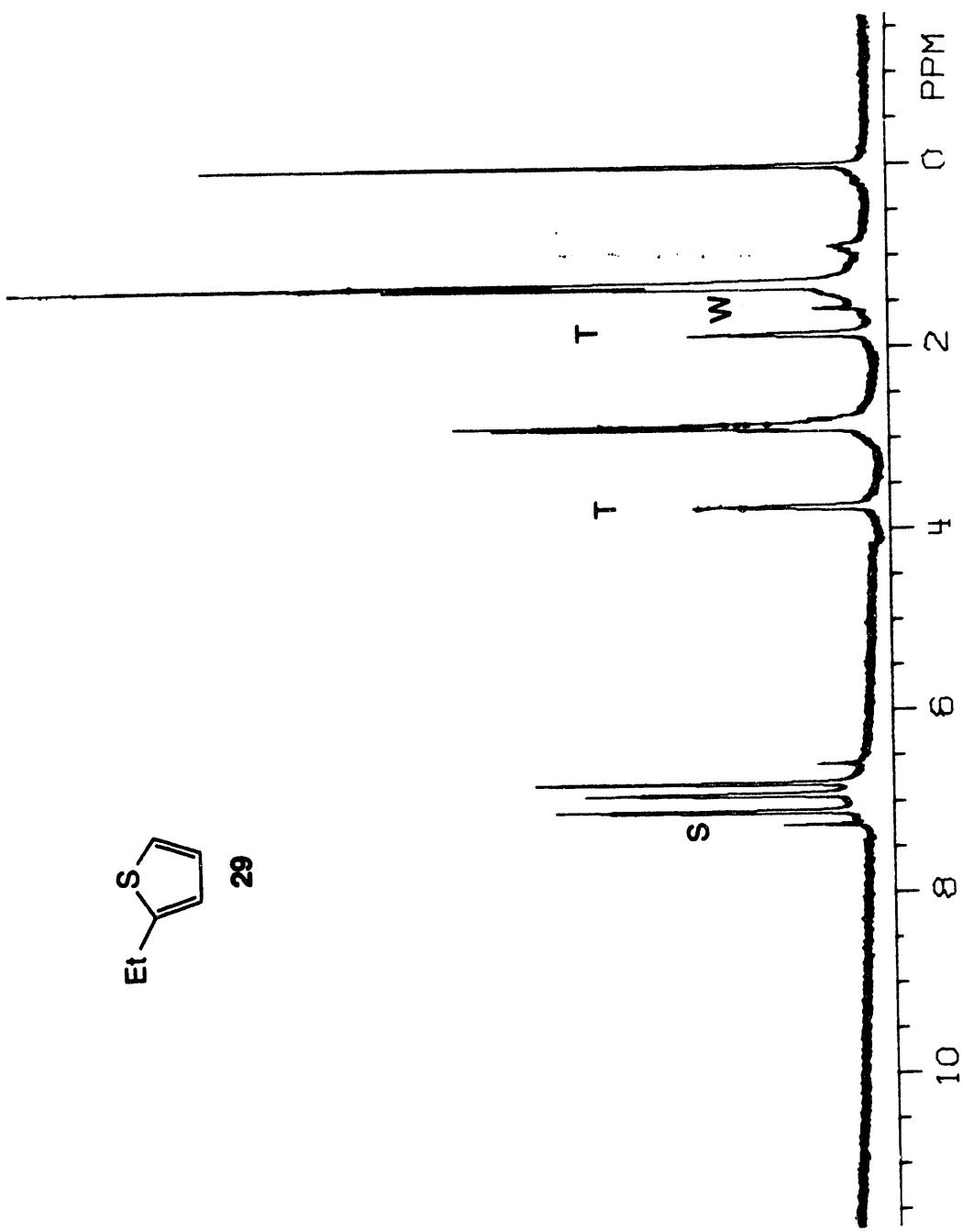


Figure A-33. ^1H NMR spectrum (300 MHz, $CDCl_3$) of 2-ethylthiophene (**29**) (S: chloroform, W: H_2O, T: tetrahydrofuran).

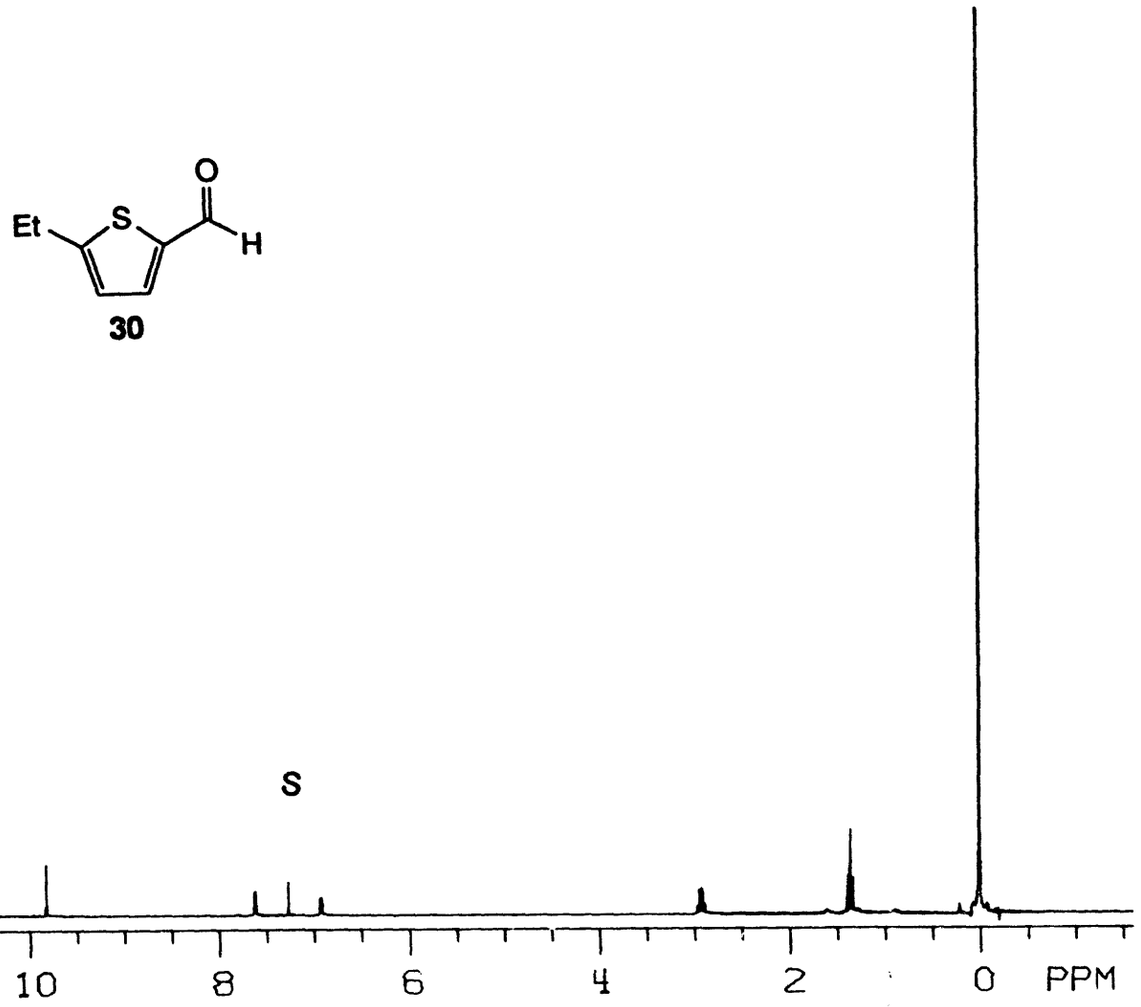


Figure A-34. ^1H NMR spectrum (300 MHz, $CDCl_3$) of 5-ethyl-2-thiophenecarboxaldehyde (**30**) (S: chloroform).

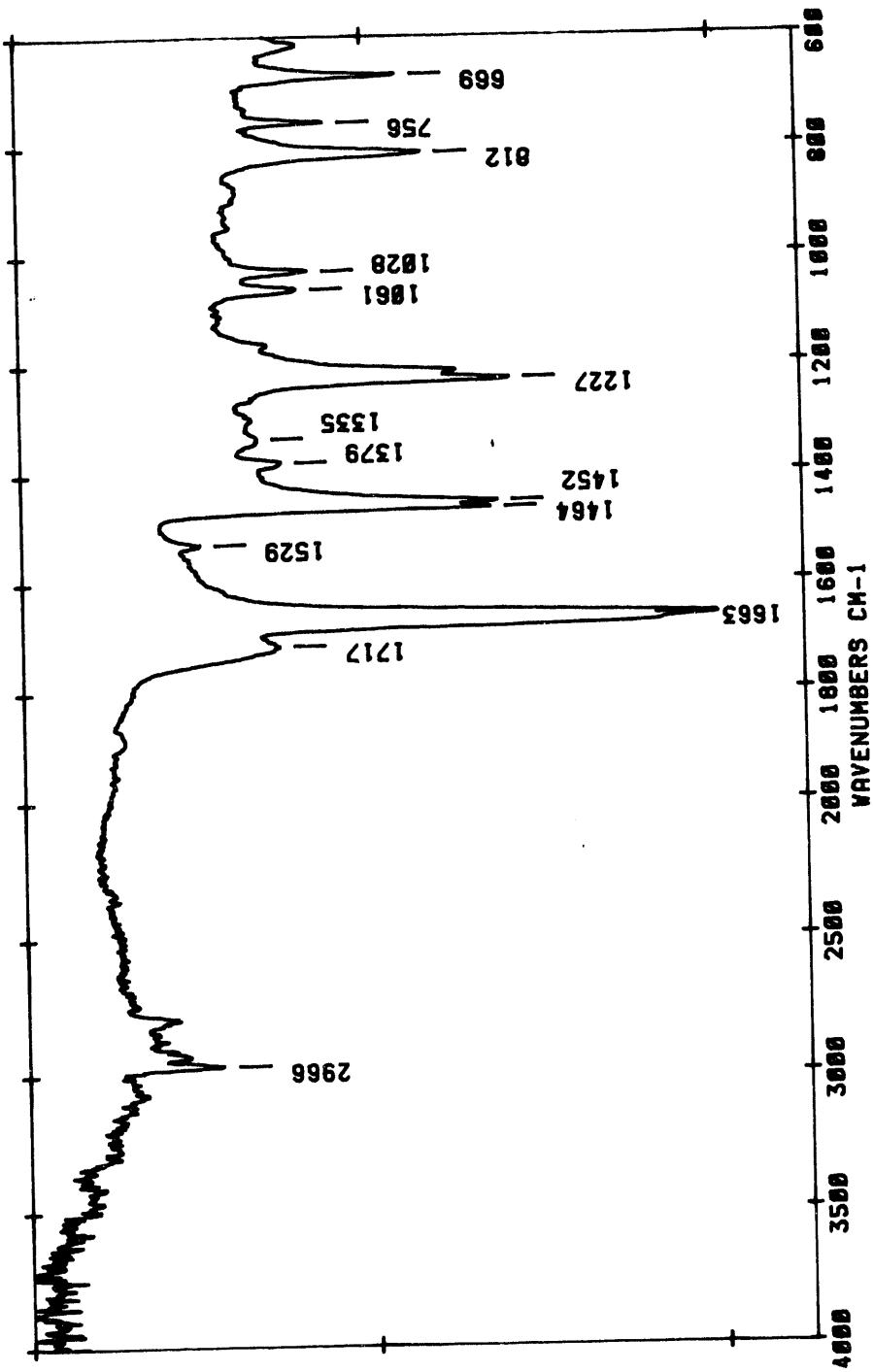


Figure A-35. IR (thin film) spectrum of 5-ethyl-2-thiophenecarboxaldehyde (30).

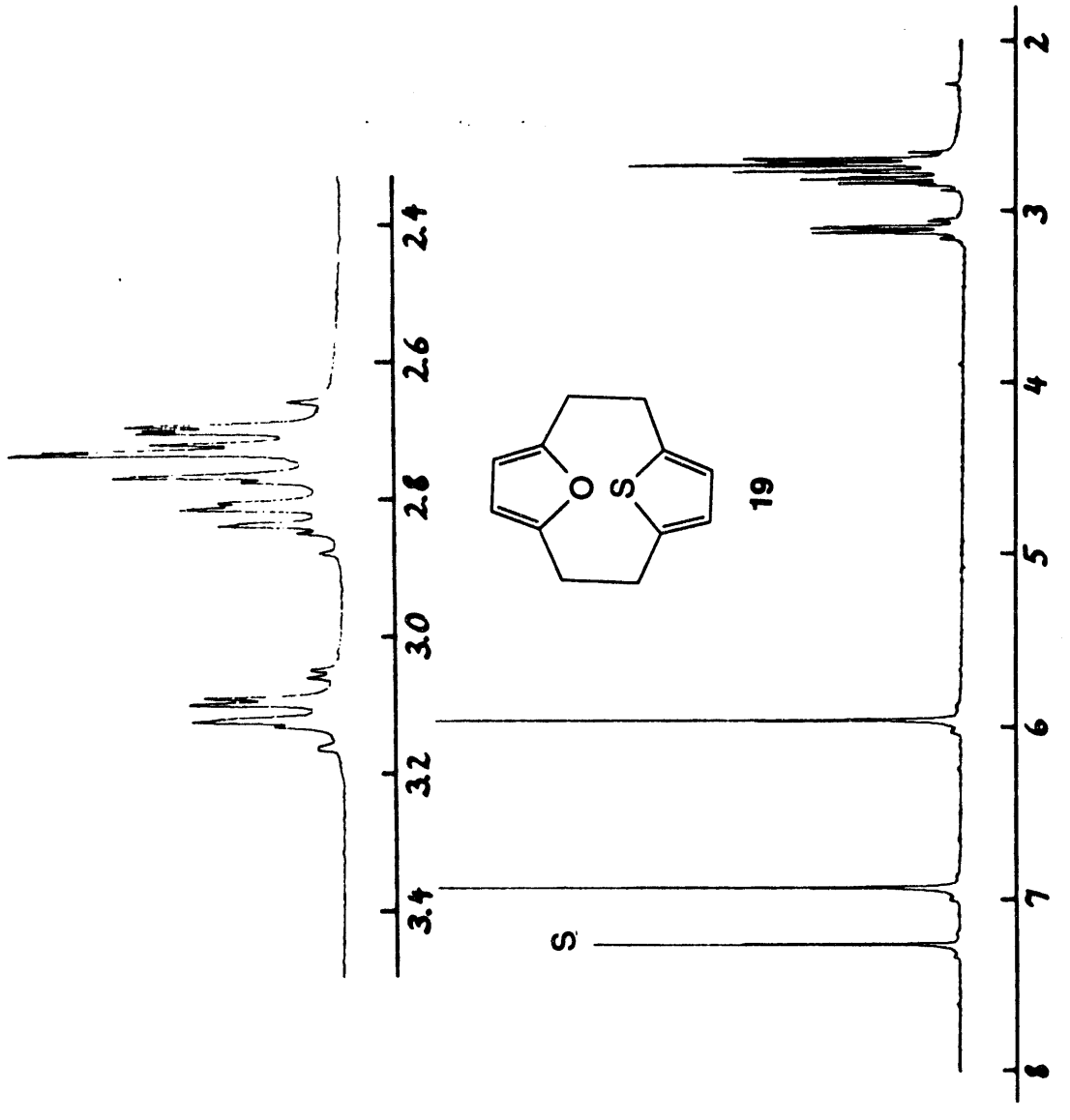


Figure A-36. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of OS-dimer **19** (S: chloroform).

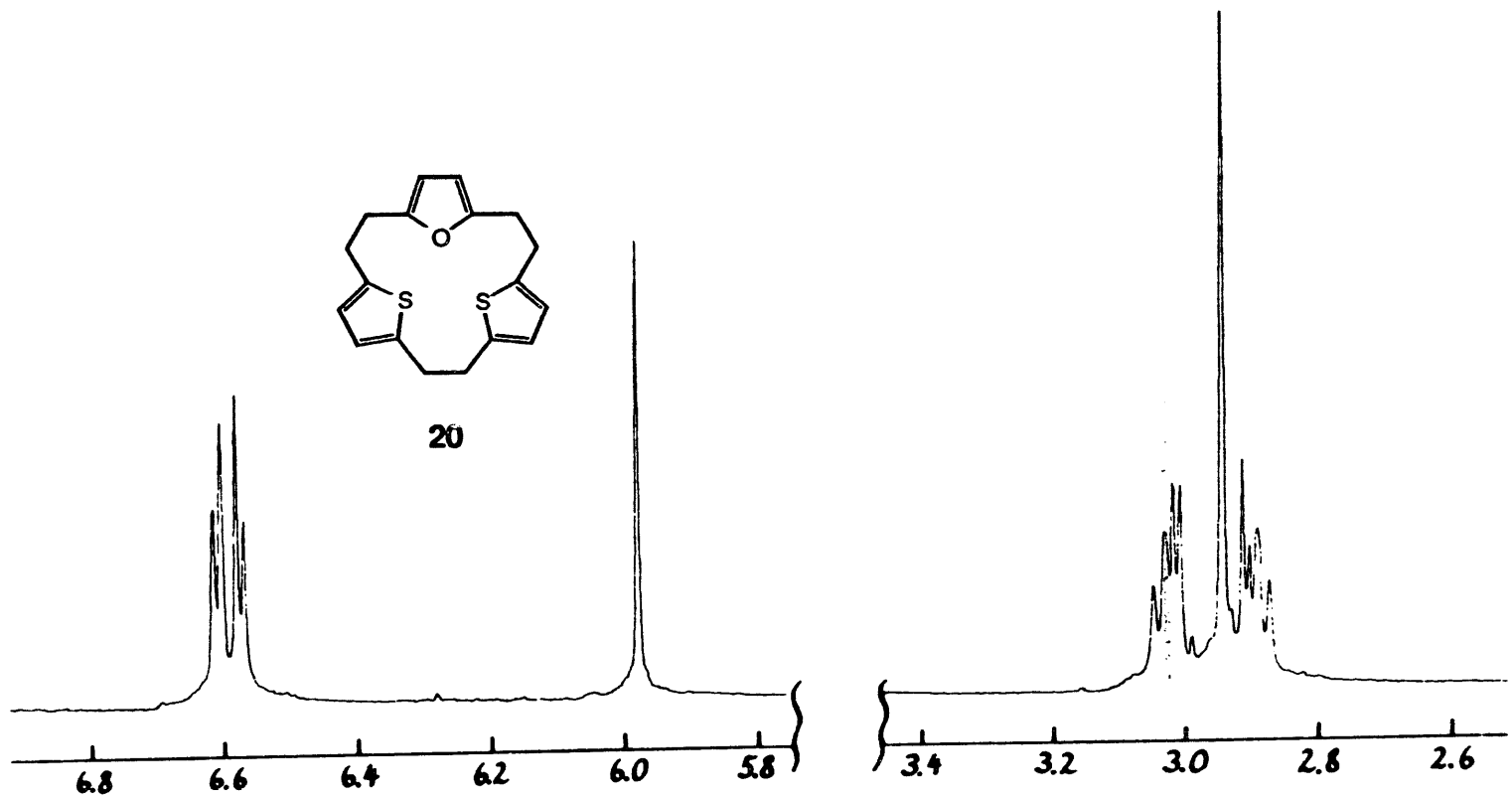


Figure A-37. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of OSS-trimer **20**.

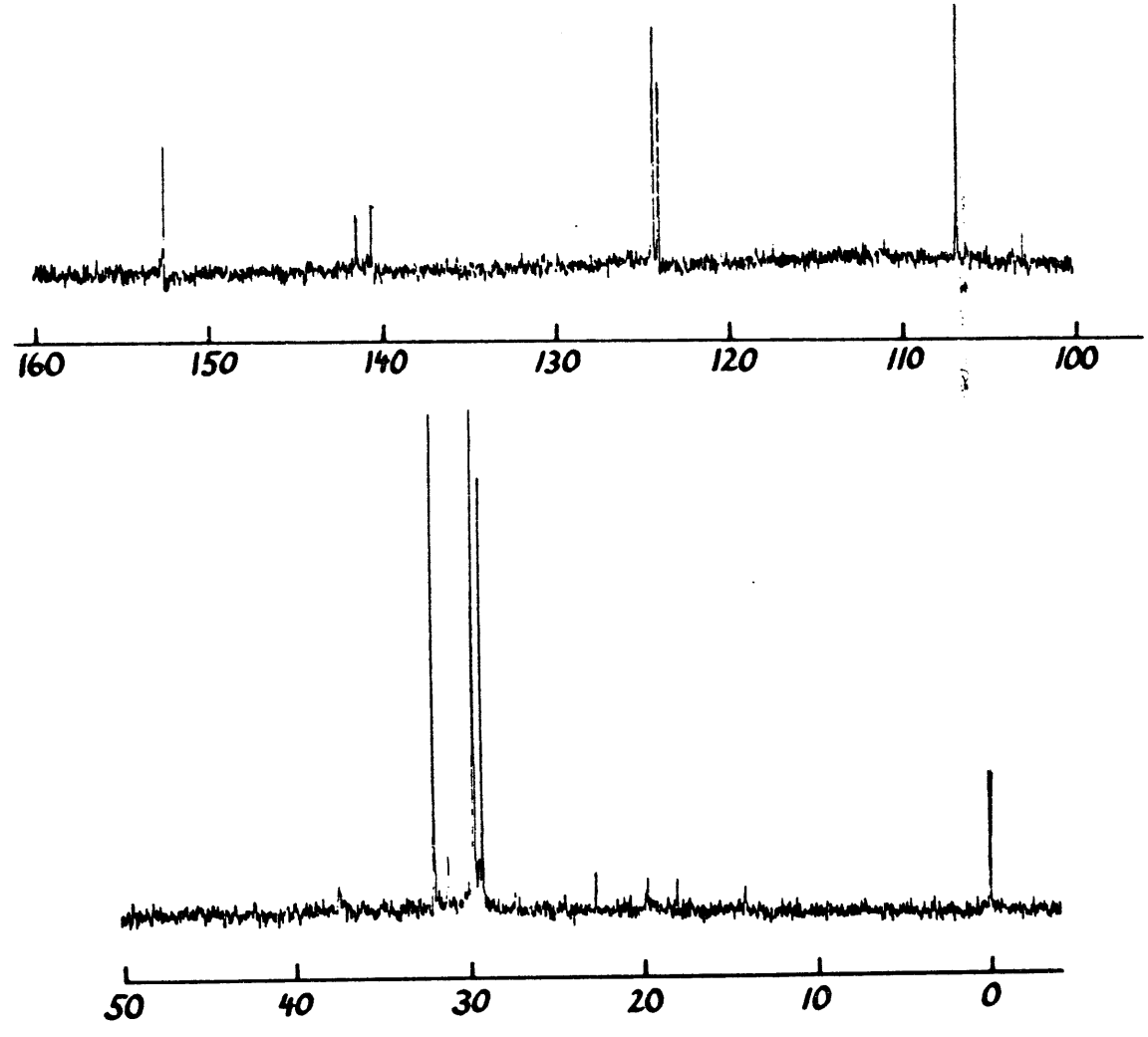


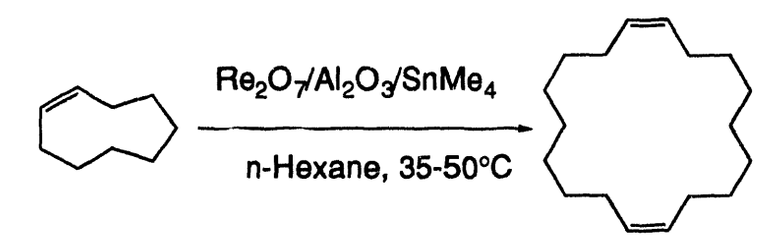
Figure A-38. ^{13}C spectrum (75.5 MHz, $CDCl_3$) of OSS-trimer **20**.

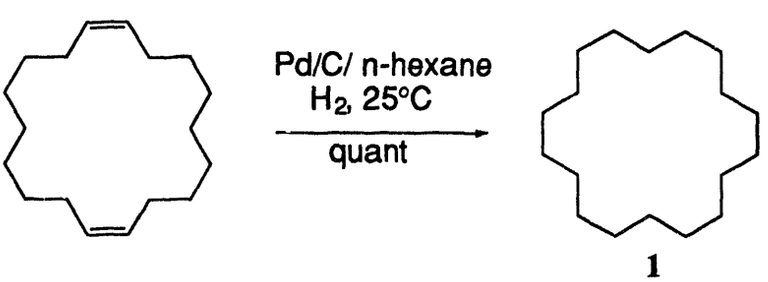
PAPER 2. A CONVENIENT SYNTHESIS OF CYCLOOCTADECANE

INTRODUCTION

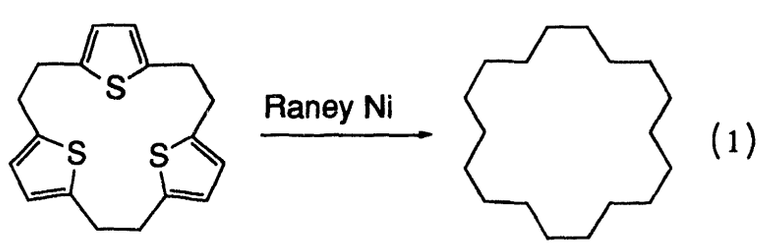
Cyclooctadecane (**1**) has been used in a number of physical and mechanistic studies[1-3] and as a synthetic intermediate.[4] It was first prepared in 1928 by Clemmensen reduction of 1,10-cyclooctadacadione which was prepared by decomposition of a metallic salt of sebacic acid[5] and it has since been prepared by several lengthy, multi-step routes.[6,7] Recently, compound **1** was prepared by a sequence involving the metathesis of cyclononene.[8]

We now wish to report that cyclooctadecane (**1**) can be prepared conveniently by the Raney nickel reduction of [2,2,2](2,5)thiophenophane (**2**).





1

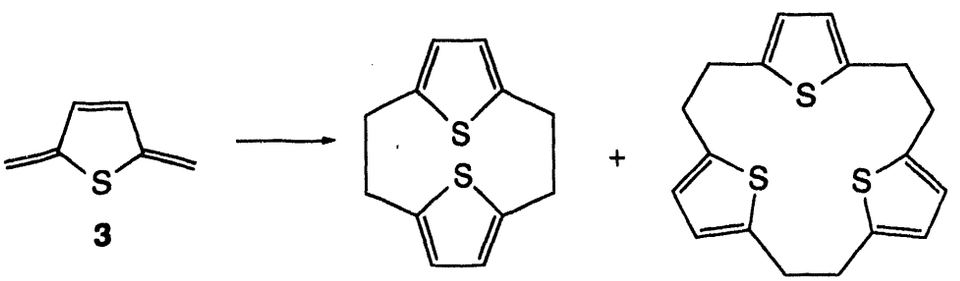


(1)

2 **1**

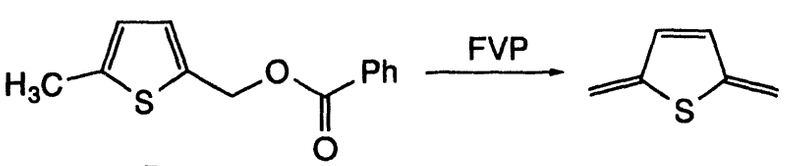
RESULTS AND DISCUSSION

[2.2.2](2,5)Thiophenophane (**2**) has been produced by the oligomerization of 2,5-dimethylene-2,5-dihydrothiophene (**3**) which was prepared by a Hofmann reaction[9] or by fluoride-ion induced 1,6-elimination from the appropriate trimethylsilyl-trimethylammonium ion.[10] In both cases dimer **4** was also produced.



3 **4** **2**

We have found that 2,5-dimethylene-2,5-dihydrothiophene (**3**) can be prepared in high yield by flash vacuum pyrolysis of 5-methyl-2-thiophenemethyl benzoate (**5**).[11] We have studied the oligomerization of 1:1 carbon disulfide-deuterochloroform solution of various concentrations of **3** at various temperatures and have concluded



5 **3**

that a fair yield of trimer **2** is obtained by oligomerization of a 0.1 M solution of **3** at 35°C.[12] Pure trimer **3** can be obtained from the product mixture by flash chromatography.

Reduction of **3** with an excess of Raney nickel[13-16] gives a yield of 75% cyclooctadecane (**1**), eq. (1).

EXPERIMENTAL SECTION

The pyrolysis apparatus has been previously described.[17] ^1H NMR spectrum was obtained on a Nicolet NT-300 spectrometer. ^{13}C NMR spectra were obtained from VXR-300 spectrometers. Chemical shifts are reported in parts per million (δ) from chloroform ($CDCl_3$). Gas chromatographic analysis was performed on a Hewlett-Packard model 5840A gas chromatography equipped with a 30 meter DB-1 capillary column and a flame ionization detector. GC-MS analysis was performed on a Finnigan 4000 GC/MS with Incos data system. Raney Nickel was purchased from Aldrich.

5-Methyl-2-thiophenemethyl benzoate (5)

A solution of 11.8 g (0.0935 mol) of 5-methyl-2-thiophenecarboxaldehyde in 50 mL of ether was reduced and esterified by the procedure reported[11] to yield 18.7 g (0.080 mol) of 5-methyl-2-thiophenemethyl benzoate (**5**) (95%): b.p. 87-89°C (0.05 mmHg); ^1H NMR ($CDCl_3$, 300MHz) δ 8.15-8.02 (m, 2H), 7.55-7.38 (m, 3H), 6.95 (m, 1H), 6.50 (m, 1H), 5.40 (s, 2H), 2.38 (s, 3H).

Pyrolysis of 5-methyl-2-thiophenemethyl benzoate (5)

A 0.6210 g (0.0027 mol) of **5** was pyrolyzed at 640°C in the normal manner[17]. Upon completion, 20 mL of 1:1 mixture of carbon disulfide (CS_2) and deuterochloroform[18] ($CDCl_3$) was distilled through the side arm to the trap, which resulted in a 0.1 M solution of monomer **3** After allowing the pyrolysate to stand at room temperature for ca. 48 h, [2,2](2,5)thiophenophane (dimer **4**), and [2,2,2](2,5) thiophenophane (trimer **2** , 60%) were formed. Pure trimer (39.8 mg, 0.00012 mol)

was separated from dimer by flash column (silica gel) using 1:150 ethyl acetate and hexane as eluent.

Desulfurization of Trimer (2) with Raney Nickel

A solution of 33.2 mg (0.0001 mol) of thiophene trimer **2** in 25 mL of absolute ethanol was stirred under argon. Excess Raney-Ni (1.2 g) in absolute ethanol was added to the flask. The reaction was allowed to reflux (78°C) for ca. 18 h. Upon completion, Raney nickel was filtered off and 25 mL of pentane and 50 mL of saturated sodium chloride was added to the reaction mixture. The aqueous layer was extracted with pentane (2x10 mL). The combined organic layers was washed by saturated sodium chloride. After drying and concentrating, 24 mg of a light oil was recovered. GC analysis of this product showed the presence of cyclooctadecane (**1**) as the major component (75-80%, 0.000076 mol) retention time 13 min on DB-1 column. GC-MS analysis shows this single peak has mass 252.3. ^{1}H NMR of **1** ($CDCl_3$, 300 MHz) (see appendix, Figure **A-1**): δ 1.3 (s , 36H). [lit[2] ($CDCl_3$) δ 1.3]. ^{13}C NMR of **1** ($CDCl_3$, 75.5 MHz) (see appendix, Figure **A-2**): δ 27.5. [lit[2] ($CDCl_3$, 75.5 MHz) δ 27.53]. GC/MS m/e (relative intensity) (see appendix, Figure **A-3, 4**): 252.3 (M^+, 19), 224.2 (1) 167.1 (1), 153.12 (2), 139.09 (3), 125.07 (8), 111.05 (15), 97.03 (29), 83.06 (38), 69.02 (41), 55.03 (75), 41.00 (100). [lit[8] GC/MS 252 (M^+,25), 55 (100)].

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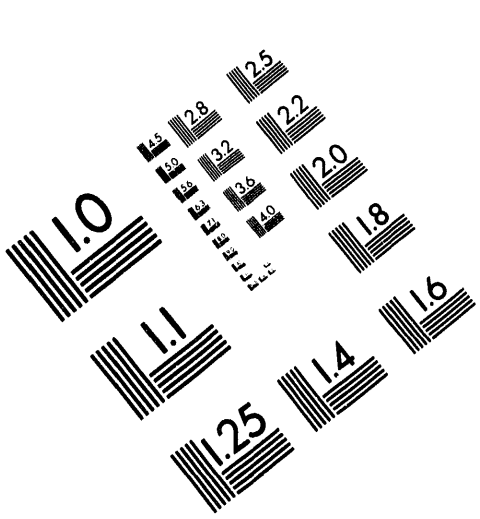

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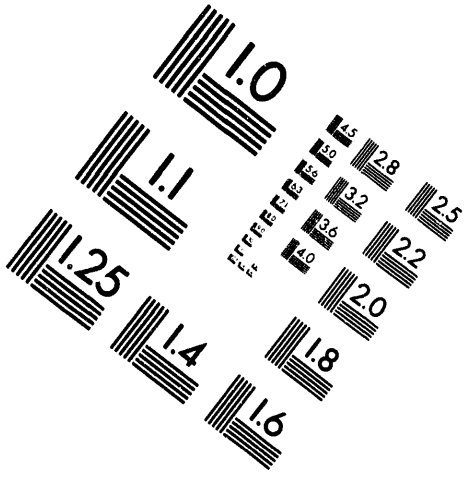

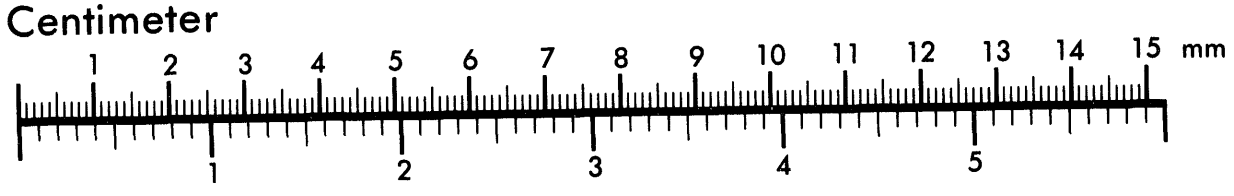

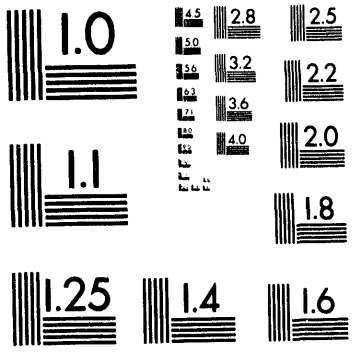

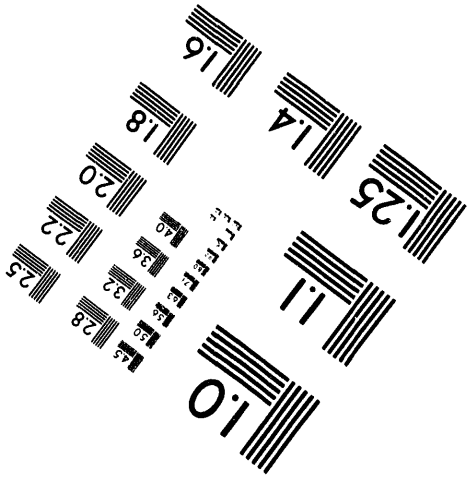

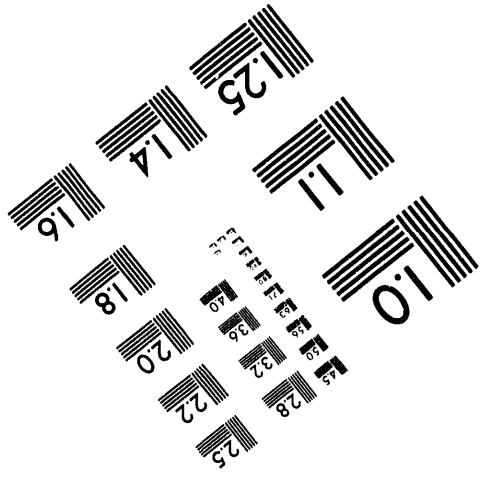

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19. $CDCl_3$ was used as the solvent because the purity of monomer (**3**) has determined by ^1H NMR spectroscopy.

APPENDIX

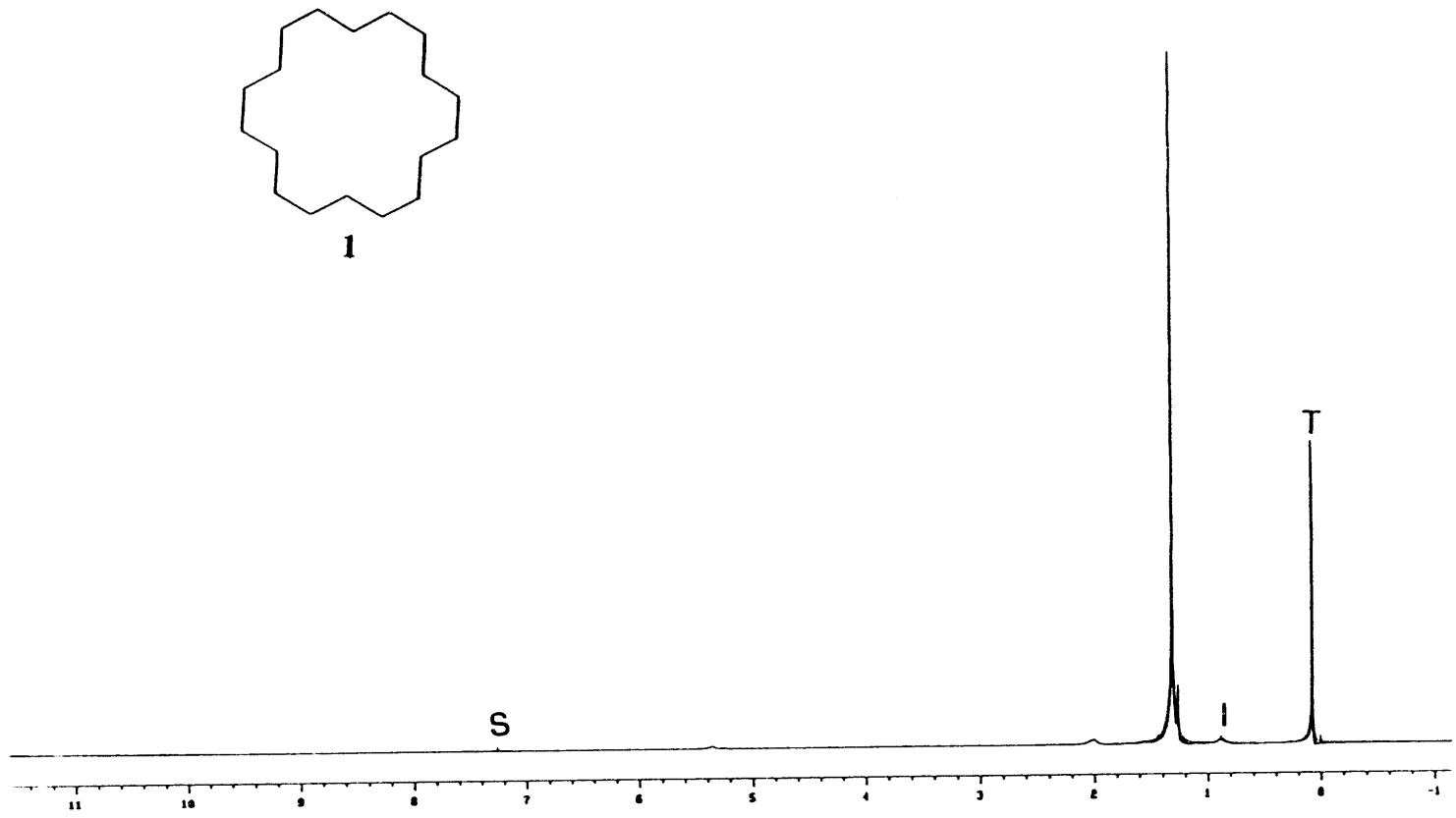

Figure A-1. ^1H NMR spectrum (300 MHz, $CDCl_3$) of cyclooctadecane (**1**) (I: material from pentane, the solvent for extraction, S: chloroform, T: TMS).

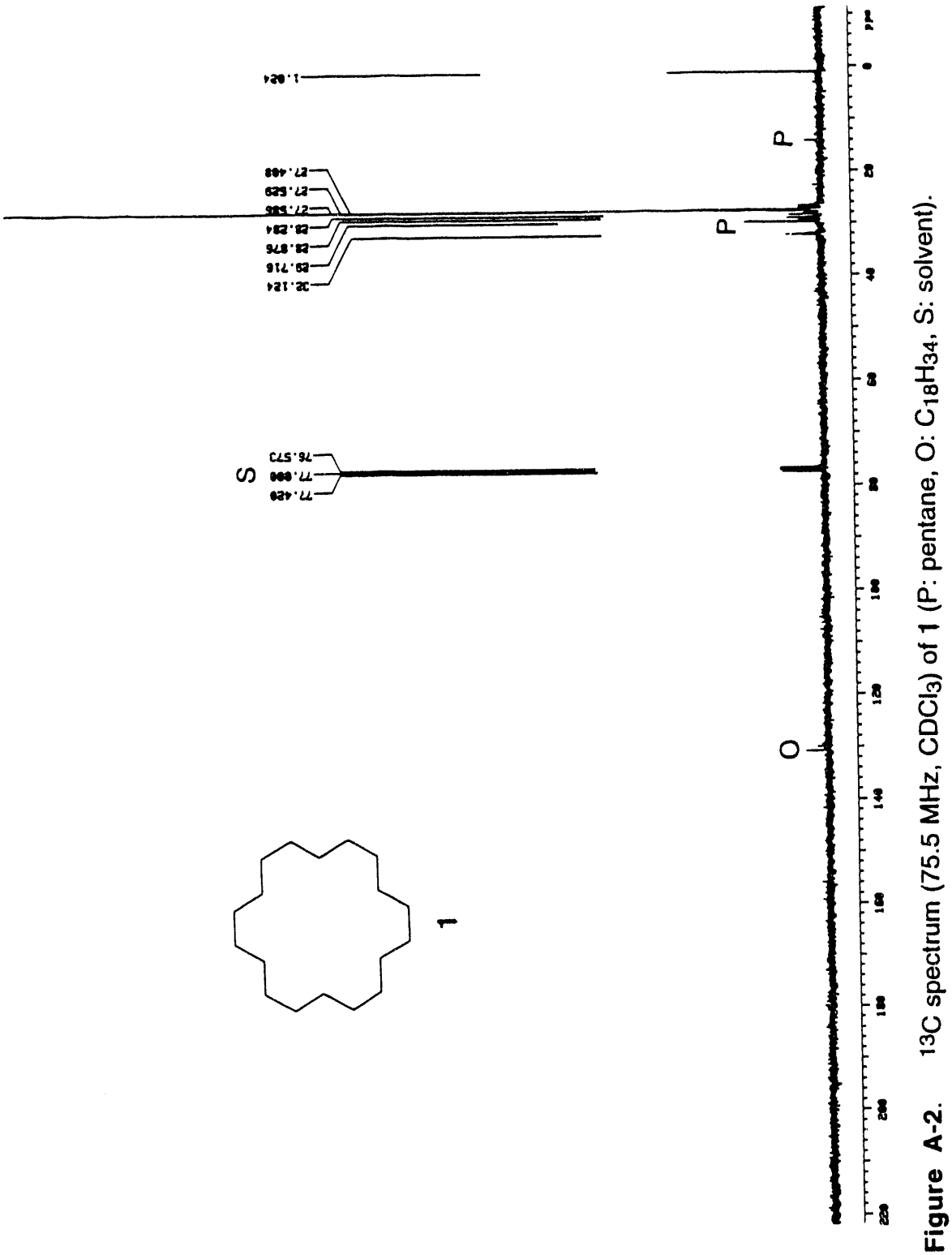

Figure A-2. ^{13}C spectrum (75.5 MHz, $CDCl_3$) of **1** (P: pentane, O: $C_{18}H_{34}$, S: solvent).

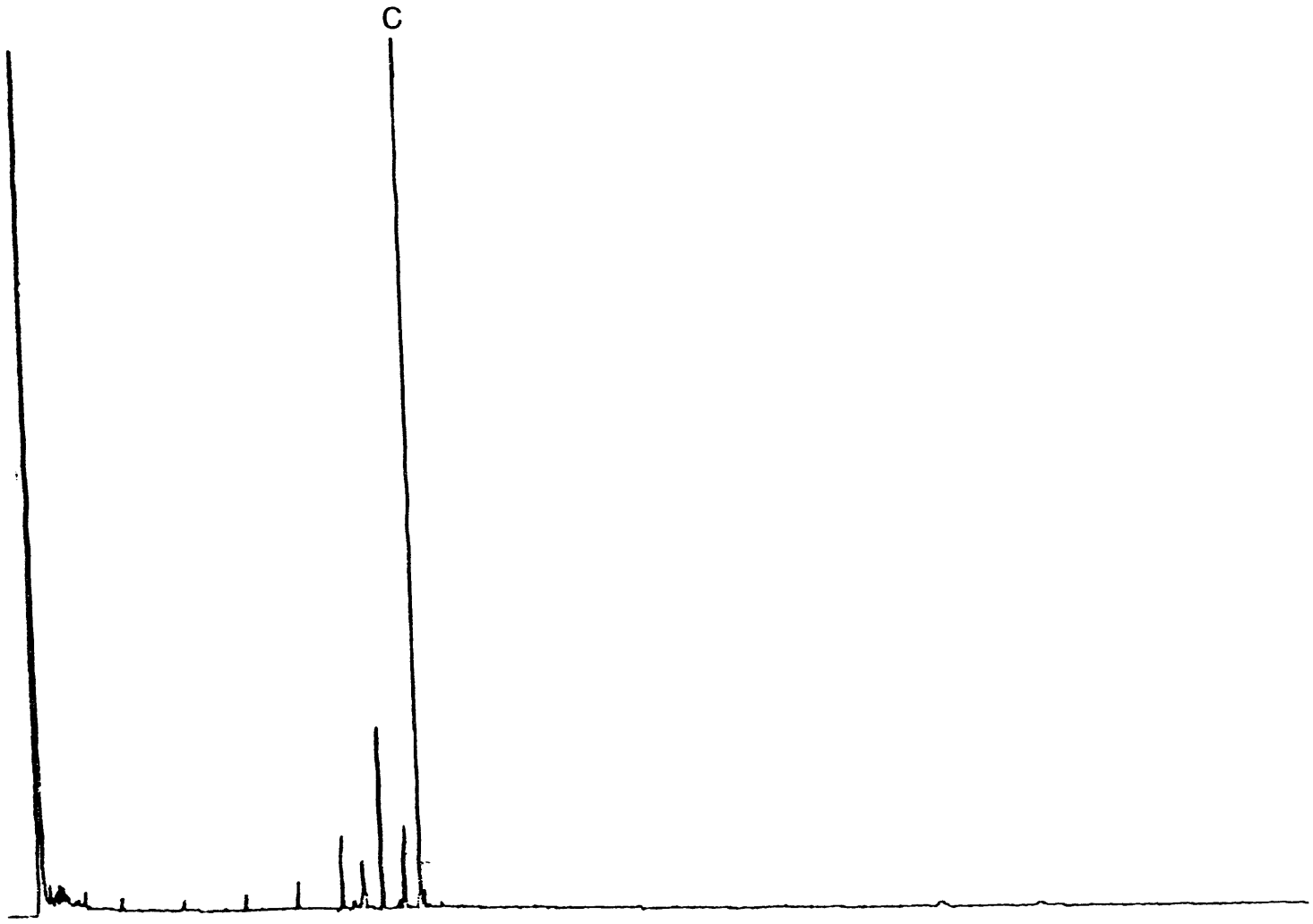

Figure A-3. Gas chromatograph (DB-1, temperature program 100°C, 5 min, 10°C/min, 200°C, 20 min) of the desulfurization product (C: cyclooctadecane).

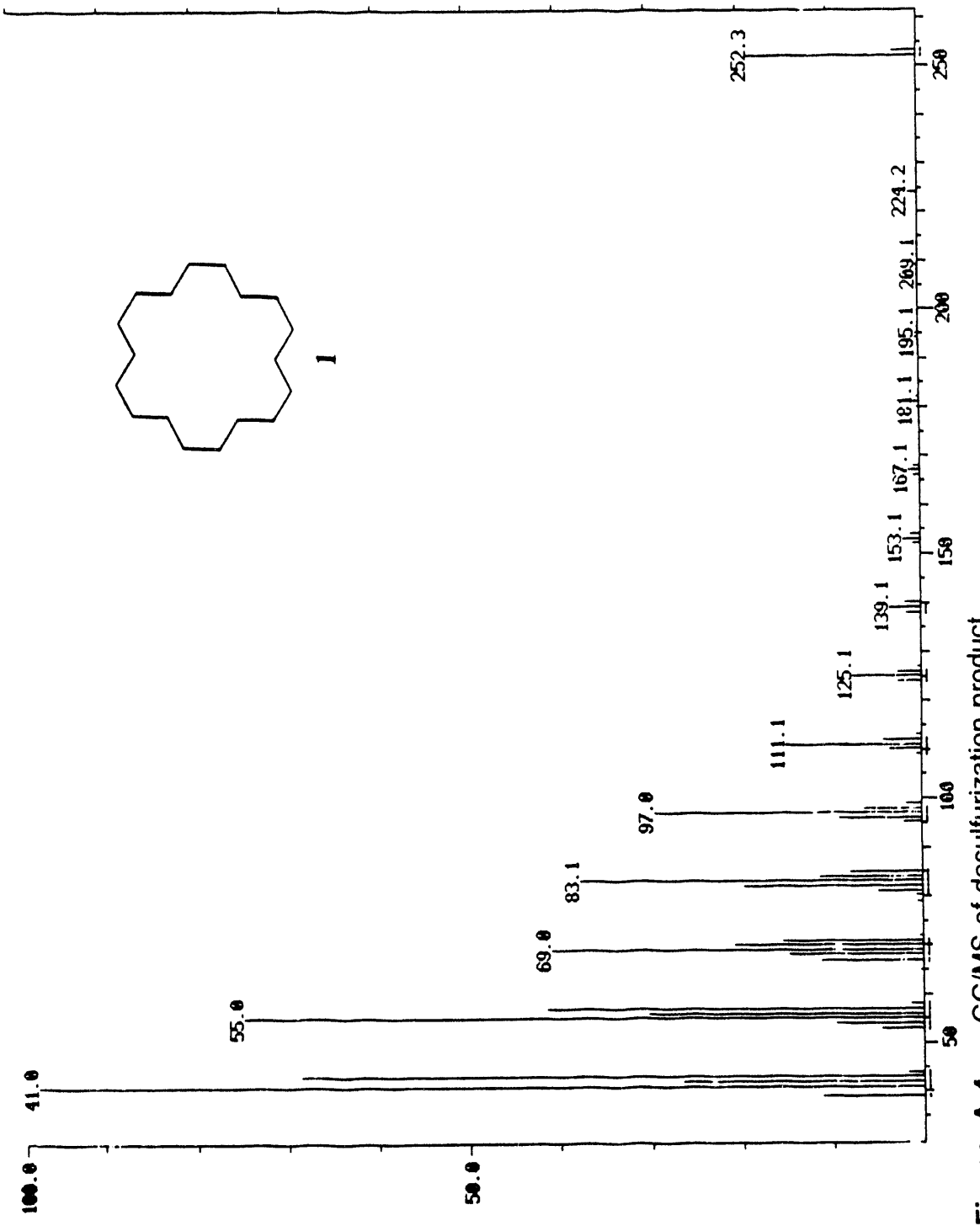

Figure A-4. GC/MS of desulfurization product.

GENERAL SUMMARY

Effects of α-substitution on the termini of the reactive diene unit of 2,5-dimethylene-2,5-dihydrothiophene revealed a non-concerted mechanism for thiophene-based *p*-quinodimethanes. Formation of 19-oxa-20,21-dithiatetracyclo[14.2.1.1^{3,6}.1^{9,12}]heneicosa-4,6,10,12,16,18-hexaene (OSS-Trimer **20**) from the trapping experiment also provides evidence that oligomerization of 2,5-dimethylene-2,5-dihydrothiophene proceeds via a diradical mechanism.

In paper 2, we found that cyclooctadecane can be conveniently prepared by the Raney Nickel reduction of [2.2.2](2,5)thiophenophane.

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