This is to certify that the

dissertation entitled

The Synthesis of Polythienyls and Their Incorporation into Large Ring Macrocycles

presented by

Thungmei H. Luo

has been accepted towards fulfillment
of the requirements for

Ph. D degree in Chemistry

Eugene LeGoff
Major professor

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THE SYNTHESIS OF POLYTHIENYLS AND THEIR INCORPORATION INTO LARGE RING MACROCYCLES

By

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ABSTRACT

THE SYNTHESIS OF POLYTHIENYLS AND THEIR INCORPORATION INTO LARGE RING MACROCYCLES

By

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The synthesis of various individual unsubstituted and substituted linear polythienyls and their conversion to the macrocyclic polythienyls have been investigated. Michael addition of thiophene carboxaldehydes to Mannich base as well as vinyl sulfone gave a variety of symmetrical or unsymmetrical, substituted or unsubstituted 1,4-diones. Cyclization of 1,4-diones with Lawesson's reagent led to a series of linear polythienyls containing both odd and even numbers of thiophenes. Thus the syntheses of α-ter-, α-quater-, α-quinque-, α-sexi-, 1,12-dibromo-α-quinque-, 3',4'-dimethyl-α-quinquethienyl, and 2,5-bis-(3",4"-dimethyl-2',2"-5",2"'-terthienyl)-thiophene were accomplished.

Coupling reaction of bromothiophenes by low valent nickel provided a convenient way to prepare the even number of polythienyls: 5,5'-diformyl-2,2'-bithienyl, 1,10'-diformyl-α-quaterthienyl, α-sexithienyl, and 5,5'-bis(3",4"-dimethyl-2",2"'-bithienyl)-2,2'-bithienyl.

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Condensation of α-bi-, α-ter-, and α-quaterthienyl with benzaldehyde or anisaldehyde with Lewis acids yielded mixtures of macrocyclic oligomers.

Cyclization of linear polythienyls to the macrocyclic polythienyls, in which all the thienyl rings are connected together in a cyclic manner, were not fruitful due to the insolubility of either starting materials or products.

To My Parents

ACKNOWLEDGEMENTS

I wish to express my sincere appreciation to Professor Eugene LeGoff for his enthusiasm, encouragement and guidance throughout the course of this study.

Appreciation is extended to the departement of chemistry at Michigan State University for financial support in the form of teaching and research assistantships, and Professor Eugene LeGoff for research support at varios times during this period.

A special thanks goes to my husband, Jihmei, without his love, companionship, and encouragement this work could never have been done. Many thanks go to our family, for their love, understanding, and support over the past few years.

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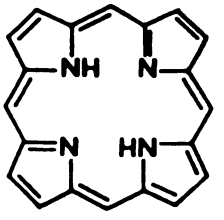
INTRODUCTION

In accord with the Hückel rule,[1] planar monocyclic conjugated systems containing 4n+2 π-electrons (n=0, 1, 2, 3, ...) are considered aromatic. This concept remains valid for polynuclear condensed systems if the Hückel number of π-electrons are located in peripheral atomic orbitals. In principle, the formation of an aromatic π-electron ensemble may occur due to the p-orbitals not only of carbon atoms but of other atoms as well. Thus, in addition to such carbocyclic compounds as benzene and naphthalene, an extensive class of heteroaromatic structure exists.

Macrocyclic systems hold great interest in the chemistry of heteroaromatic compounds. Such compounds include porphins 1, which have an aromatic π-electron system of the [18] annulene type. Like annulenes, they exhibit a diamagnetic ring current in the ^{1}H-NMR spectrum, which serves as a qualitative criterion for aromatic character. In



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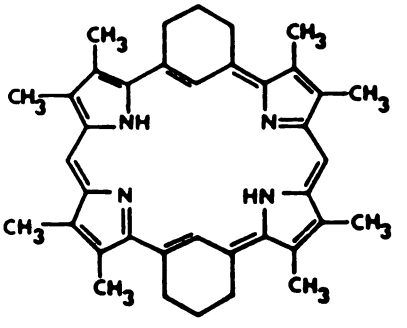

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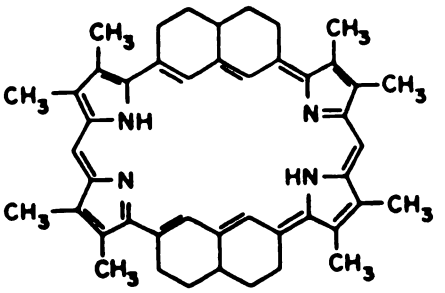

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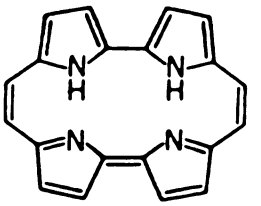

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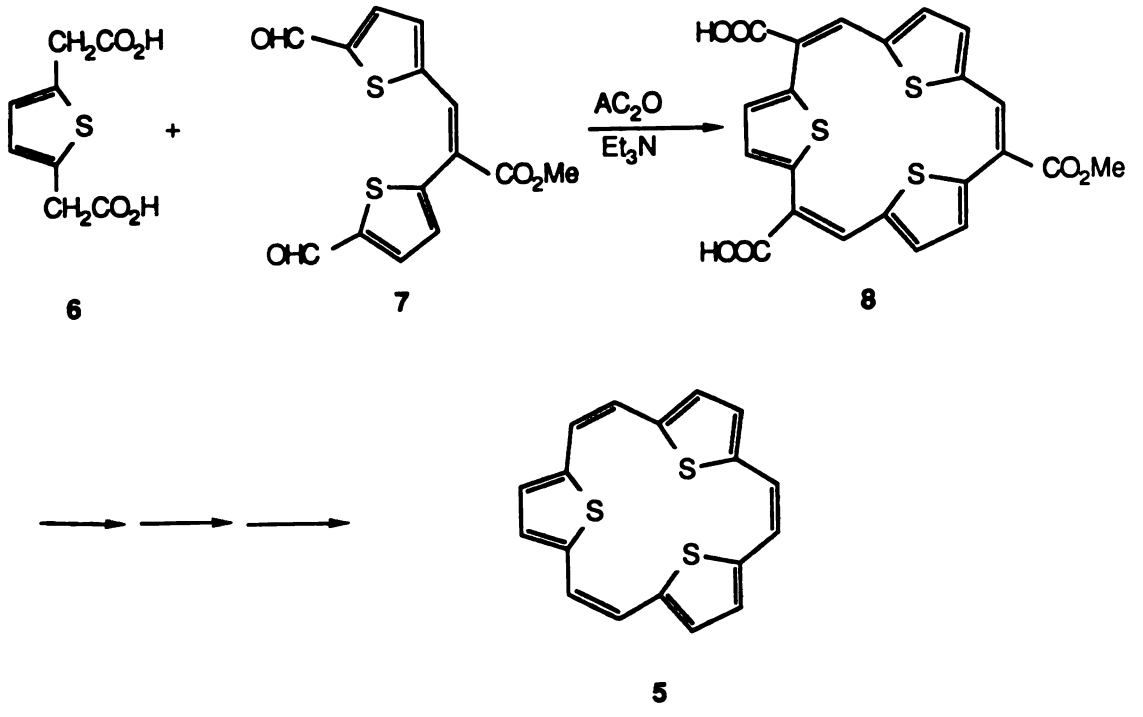
addition, several expanded porphrin molecule have been reported, such as hetero [22] annulene platyrin 2[2] and hetero [26] annulene platyrin 3.[3] Indeed, the recent synthesis of hetero [18] annulene porphycene 4[4] has caused a great deal of excitement since it is a structure isomer of porphyrin. However, though porphyrins system has been studied since the turn of the century, only a few reports has been conducted on the sulphur analogues. [18] Annulene trisulfide 5 has been synthesized by cyclocondensation of thiophene-2,5-diacetic acid 6 and methyl *cis*-α,β-bis(5-formyl-2-thienyl)-acrylate 7 under standard Perkin's reaction conditions followed by hydrolysis and decarboxylation of the product (Scheme 1).[5,6] All experimental evidence supported the fact that 5 is a nonplanar, nonaromatic system in which the aromatic thiophene subunits are bridged by olefinic vinylene groups.[5]

Scheme 1



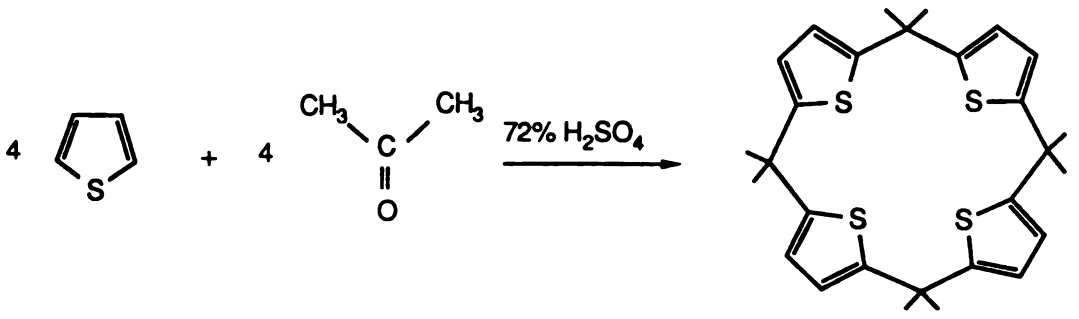
6 7 8

5

Although pyrrole and furan reacted with acetone and hydrochloric acid to generate porphyrinogen[7,8,9] and tetraoxaquaterene[10,11] respectively, initial attempts to prepare tetrathiaquaterene 9 in an analogous manner failed. However, under more vigorous reaction conditions (thiophene, acetone, and 72% sulfuric acid),[12] the residue was shown to contain the desired macrocycle 9[13] (Scheme 2).

A number of thiophene oligomers and their derivatives have recently stimulated much attraction. A great deal of the interest in this system results from their wide range of photobiological effects.[14] Most notably, they are toxic to nematodes, and this effect can be greatly enhanced by the

Scheme 2



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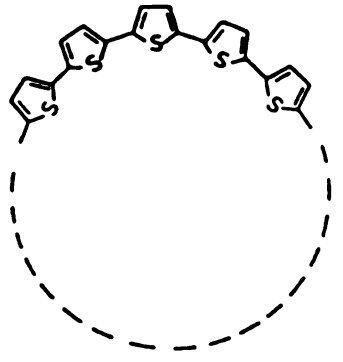
presence of ultraviolet light.[15] The most carefully scrutinized of these compound is alpha-terthienyl 10.[16] In addition, polythiophene is among the most widely studied organic materials that can be conduct electricity.[17,18] Thus, several novel macrocycles which contain the polythiophene units has been designated to make, such as 11 and 12 type cyclophanes. Apart from questions regarding



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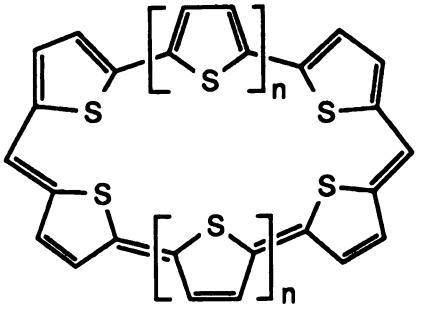

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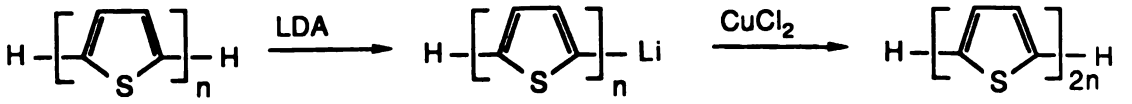
aromaticity a second point of interest here comes from the conductivity of 10 analogues.

Alpha-terthienyl 10 was isolated from Tagestes plants[19] and has now been made by many different routes. It was originally synthesized by reacting 2-iodothiophene with copper, a procedure which gives a complex mixture of products, from which the oligomers possessing 2 to 7 thiophene rings could be obtained individually in low yields after tedious purification steps.[20,21] Related reactions in which two different iodothiophenes were reacted with copper also produced complex mixtures.[22]

Even the biologically active alpha-terthienyl 10 was synthesized in good yield with reactions which did not produce any of the related oligomers, namely the cyclization of 1,4-di(2'-thienyl)-1,4-butanedione with hydrogen sulfide,[23,24] or that of 1,4-di(2'-thienyl)-1,3-butadiyne with sodium sulfide,[25,26] or a modified Wittig reaction.[27] The synthesis of the other individual alpha-thiophene had not received the same attention until 1983.

In 1983, Kagan reported three synthetic routes to the individual alpha-thiophene oligomers. The first approach involved the oxidation of the alpha-lithio derivative with cupric chloride to obtain alpha-thiophene oligomers containing an <u>even</u> nummber of thiophene rings.[28] Scheme 3 is illustrated with the synthesis of 2,2'-bithienyl 13, α-quaterthienyl 14, and α-sexithienyl 16 in 83, 85 and 73% conversion yields (but the actual yields are low) from

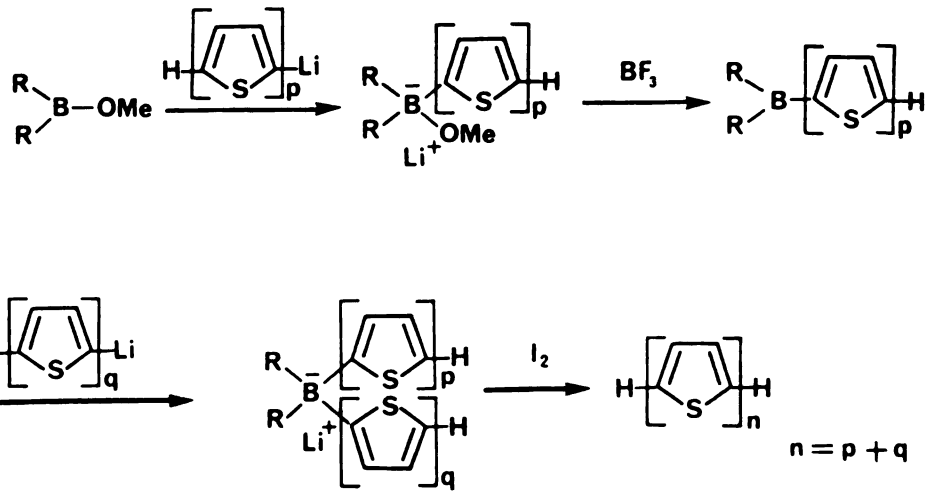
Scheme 3



thiophene, 2,2'-bithienyl 13, and α-terthienyl 10 respectively. The second approach, leading to oligomers containing from 2 to 6 thiophene units attached by their 2 and 5 positions in moderate yield, involved the iodine oxidation of a suitable complex obtained by stepwise reactions of 9-BBN with methanol, a 2-lithiothiophene, boron trifluoride etherate, and a second 2-lithiothiophene.[29] The reaction sequence is outlined in Scheme 4. The third approach provided various individual oligomers possessing either odd or even number of thiophene rings from the Glaser symmetrical coupling of thienylacetylenes (Scheme 5) or the Cadiot-Chodkiewicz unsymmetrical coupling (Scheme 6) following the cyclization of 1,3-butadiyne unit into thiophene with sodium sulfide.[30]

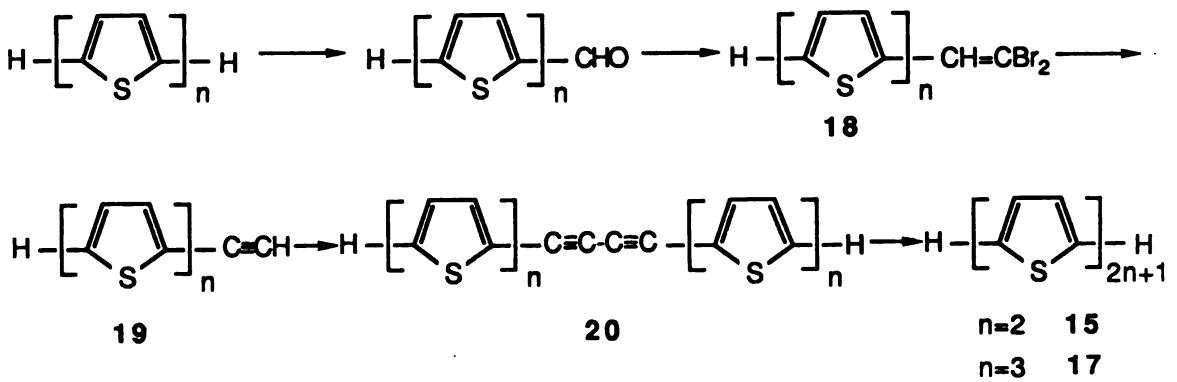
Kagan has reported the formation of α-quinquethienyl 15, α-septithienyl 17 and α-quaterthienyl 14 in moderate to excellent yield *via* the above synthetic route. However, the α-sexithienyl 16 analog was not mentioned. In addition, the yield of α-quinquethienyl 15 by the same method was not reproducible, only 21% overall yield from dibromide 18, by Tasaka and his coworkers.[17]

Scheme 4



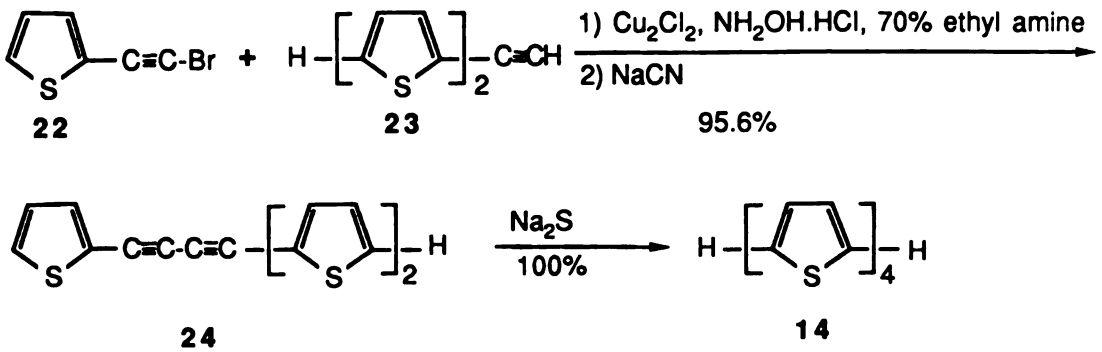
p	q	n	yield %(based on LDA)
1	1	2	80
2	2	4	48
1	3	4	50
2	3	5	55
1	4	5	53
3	3	6	45
2	4	6	59

Scheme 5



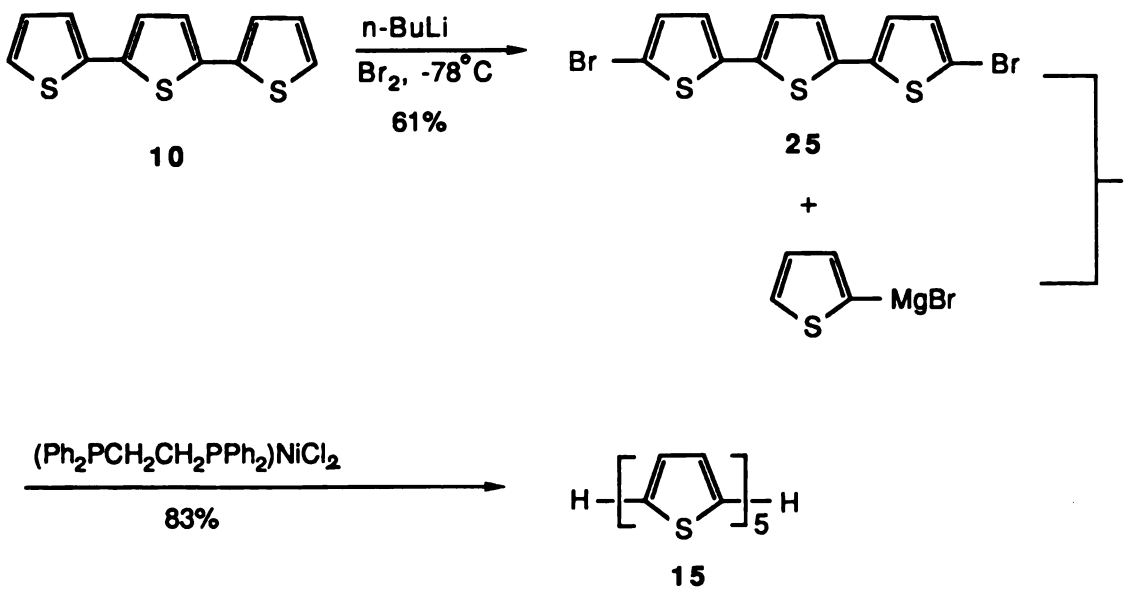
	20		
n=2	72.7%	73.5%	15
n=3	98.5%	97.5%	17

Scheme 6



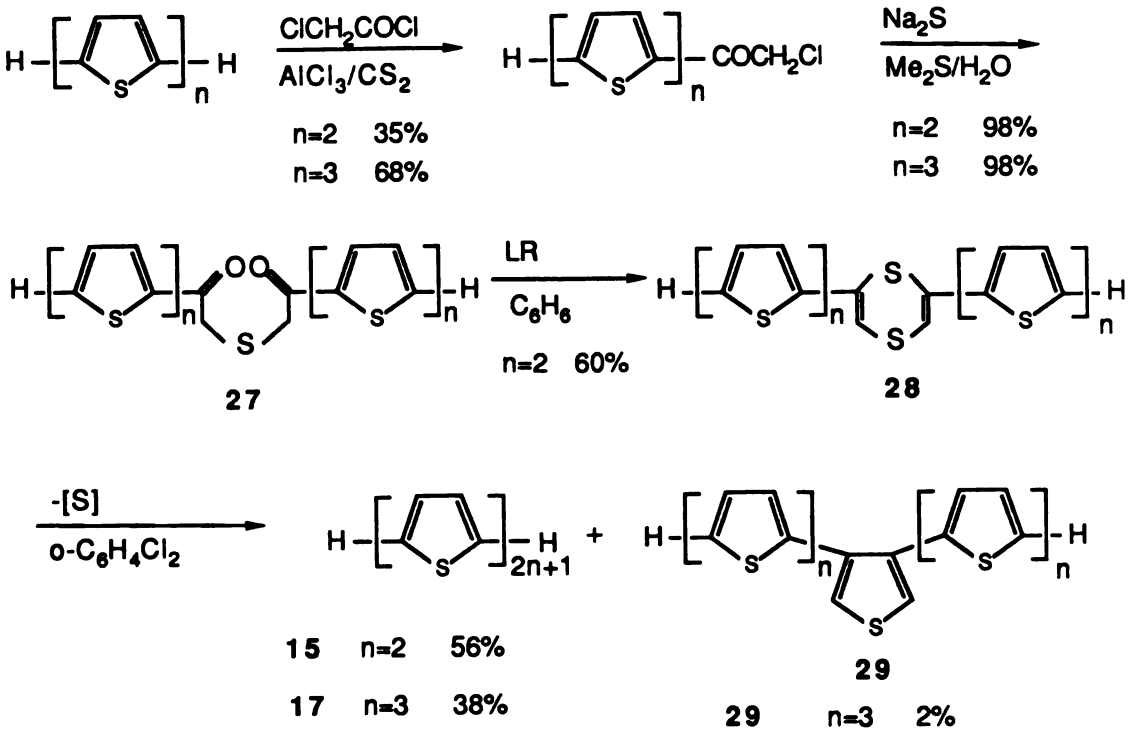
Tasaka and his coworkers also has reported the formation of α-quinquethienyl 15 in better yield *via* the coupling of thiophene-2-magnesium bromide with dibromide 25 by nickel chloride complex (Scheme 7).[17]

Scheme 7



Finally, a very recent paper reported four-steps sequence to α-quinque- 15 and α-septithienyls 17 from α-bi- 13 and α-terthiophenes 10, respectively (Scheme 8).[31]

Scheme 8



LR= Lawesson's reagent

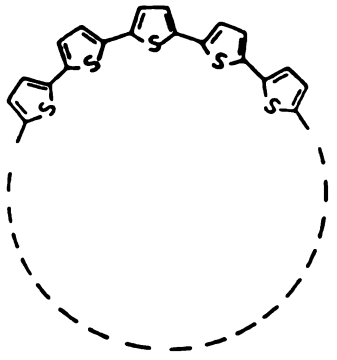
This procedure is limited to the formation of odd number of thiophene rings and the overall yields are generally quite low.

Explored in this thesis are the application of linear polythienyls in the synthesis of large ring macrocyclic polythienyls. This work is presented in two sections, describing, a) the synthesis of various unsubstituted and substituted linear polythienyls and b) the utility of the

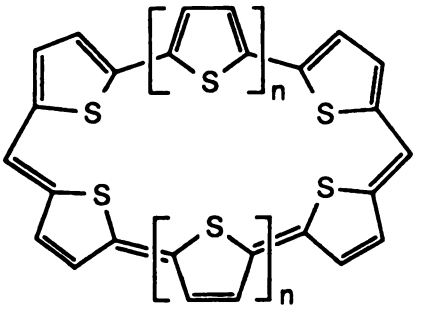
precursors in condensations leading to novel macrocyclic polythienyls.

RESULTS AND DISCUSSION

Due to their potential applications as organic conductors, molecules with large conjugated cyclic π-systems such as 11 and 12 are of great interest. As a class compound such as 11, in which all the thiophene rings are linked together in a cyclic manner, will have 4n electrons



11



12

which provides an opportunity to determine whether they exhibit localized aromaticity in the component heterocyclic nuclei or cyclic delocalization to give an antiaromatic annulene. Theoretical calculations[32] and experimental results[33,34] have shown that (4n+2) annulenes will only be aromatic up to and including [22]annulene while [26]annulene (n=6) is no longer be aromatic. However, inspection of the molecular model of 12 showed that the macrocycle is rigid

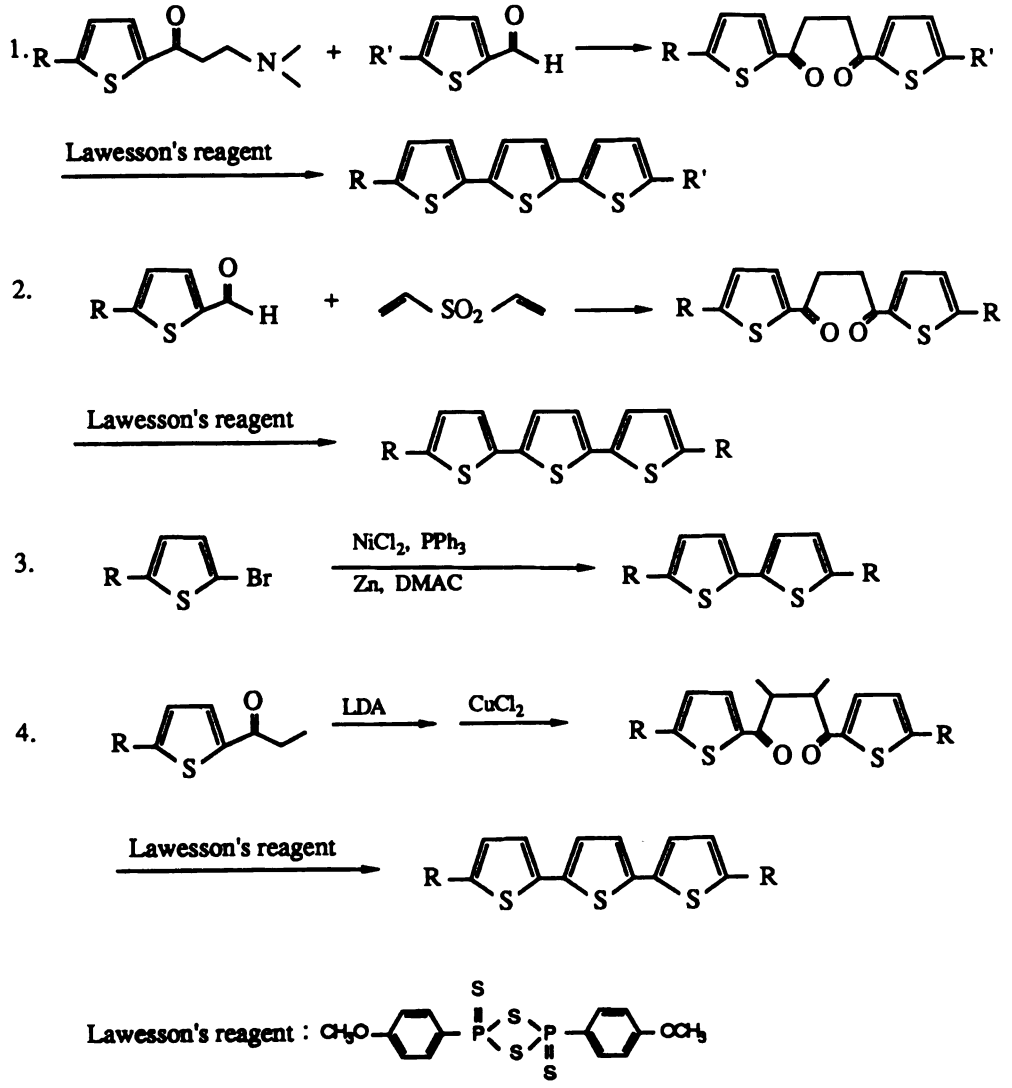
and planar. Thus it may lead to cyclic delocalization and a peripheral diamagnetic ring current.

Retroanalysis of 11 and 12 suggests the necessary of linear polythienyls. As mentioned in the introduction, the methods for the synthesis of linear polythienyls reported in literature are not very efficient. Thus, several new approaches were examined.

A. Synthesis of various unsubstituted and substituted linear polythienyls

Four different approaches to the unsubstituted and substituted linear polythienyls have been investigated. Their net transformations are summarized in Scheme 9. The first approach (eq. 1) provides various polytheniyls containing odd or even number of thiophenes resulted from the Michael addition of aldehydes to Mannich base, followed by the cyclization of resulting 1,4-diketones with Lawesson's reagents. The second approach (eq. 2), leading to polythienyls containing odd number of thiophenes, involves the Michael addition of aldehydes to vinyl sulfone, followed by the cyclization of 1,4-diketones. The third approach (eq. 3) engages the coupling reaction of bromothiophenes by nickel and reducing metals, which proves to be useful in the preparation of polythienyls containing even number of thiophenes. The fourth approach (eq. 4) provides 3',4'-dialkyl-polythienyls (i.e. 3',4'-dimethyl-2,2'-5',2"-terthienyl) from the oxidation of the lithium enolate of 2-propionythiophene with cupric chloride,

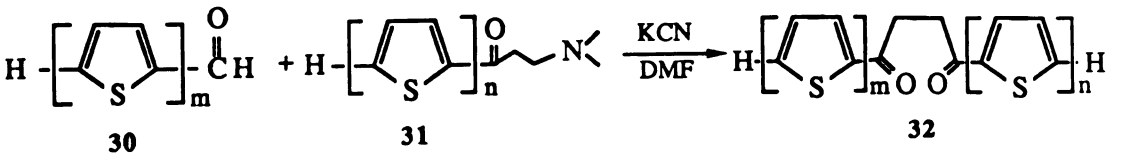
Scheme 9



followed by the ring closure reaction.

The Michael addition of aldehydes to Mannich base in the presence of cyanide as catalyst can be performed in good yields by the Stetter's procedure,[35-37] which provides a convenient method for preparing 1,4-diketones as shown in Scheme 10. In each case the necessary aldehyde 30 was synthesized from a simpler thiophene precursor, which was

Scheme 10

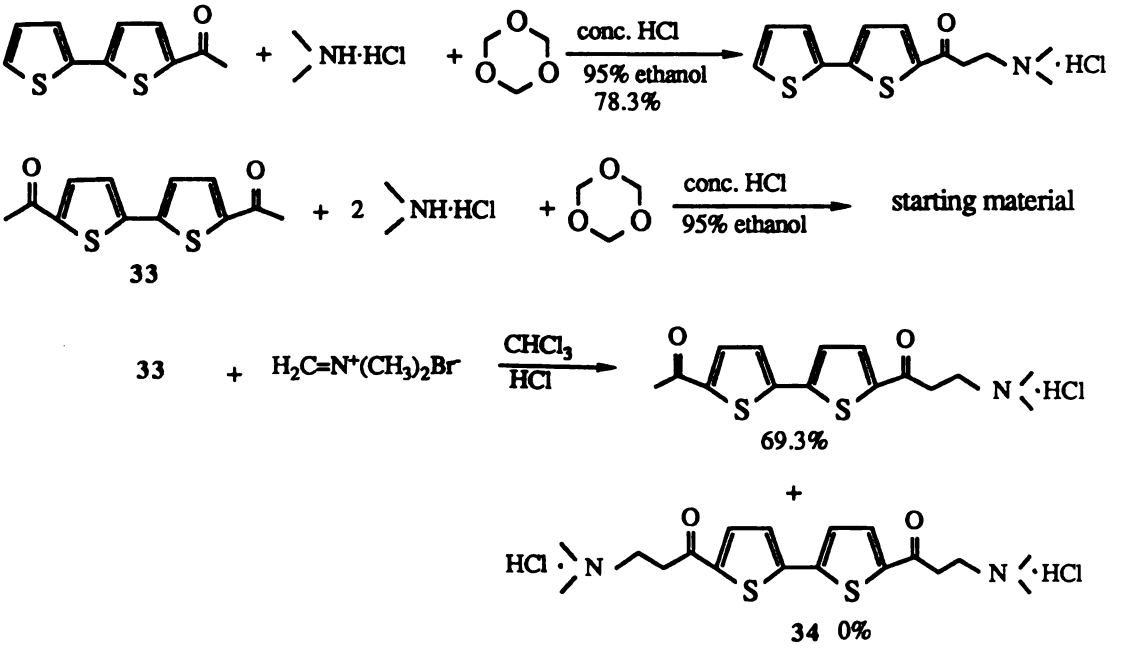


30 31 32

formylated with N-methyl-N-phenylformamide in the presence of $POCl_3$.[38] Two Mannich bases (31a, n=1; 31b, n=2) were synthesized from the reaction of 2-acetylthiophene or 2-acetylbithienyl with paraformaldehyde, dimethylamine hydrochloride and concentrated hydrochloride in ethanol solution.[39]

Attempts at nucleophilic substitution of 5,5'-diacetylbithienyl 33 with Mannich reagent under a variety of conditions failed to give the desired 34 (di-Mannichbase of bithienyl), despite the fact that a similar mononucleo-

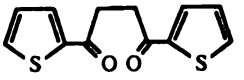
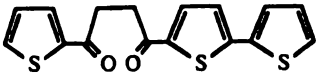
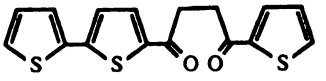
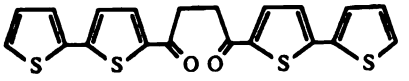
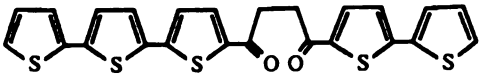
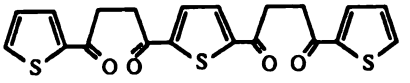
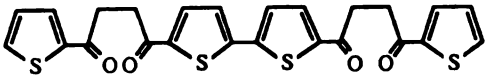
Scheme 11



philic substitution of 5-acetylbithienyl could be carried out in good yield (Scheme 11).

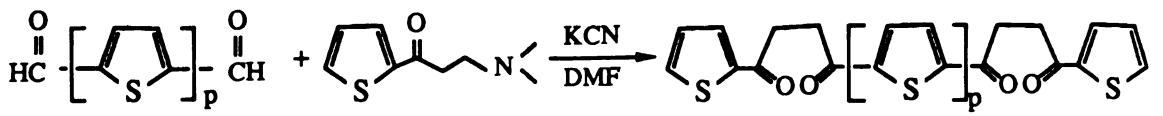
The aldehyde 30 reacted with Mannich base 31 in dry DMF in the presence of KCN at room temperature to give 1,4-diketone 32 in good yield. Table 1 (entry 1-5) lists several diketones prepared by this method. The bis-

Table 1 1,4-Diketones from Aldehyde and Mannich base

entry no.	1,4-diketone	yield(%)	m.p. (°C)
1.	 **32a** (m, n=1)	70	132-133
2.	 **32b** (m=1, n=2)	85	163.5-164.5
3.	 **32b** (m=2, n=1)	93	"
4.	 **32c** (m=2, n=2)	87	225-226
5.	 **32d** (m=3, n=2)	95	227.5-229.5
6.	 **36a** (p=1)	69	186-187.5
7.	 **36b** (p=2)	69	256-257

aldehyde 35 was also allowed to react with 3-dimethylamino-1-(2-thienyl)-propanone 31a to give bis-1,4-diketone 36 in good yield as indicated by entries 6-7 in Table 1 (Scheme 12).

Scheme 12

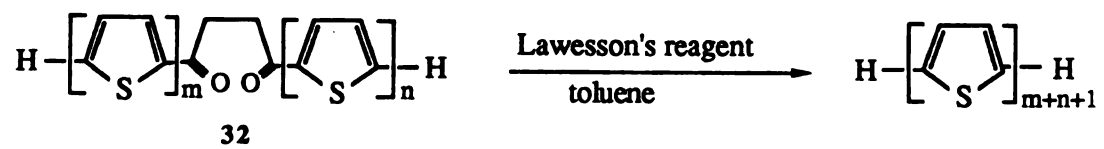


35 31a 36

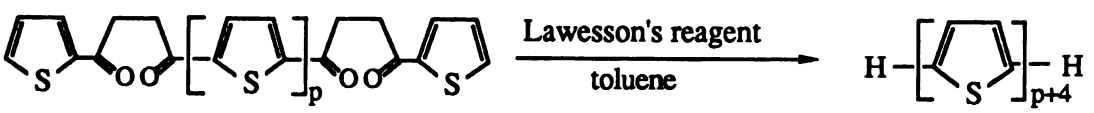
All the structures of diketones were confirmed by their spectra. The ^{1}H-NMR spectrum of methylene protons appeared at δ 3.37-3.40 and thienyl protons at δ 7.05-7.90. Low solubility of 32d prevented us from obtaining its NMR spectrum. The IR absorptions in the range of 1637-1650 cm^{-1} were obtained for the α,β-unsaturated ketones.

These 1,4-diketones readily give the polythienyls upon treatment with Lawesson's reagent in toluene (Scheme 13).[40] Oligomers possessing three, four, five, and six thiophene

Scheme 13



32



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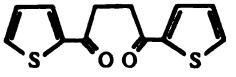
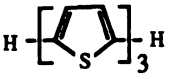
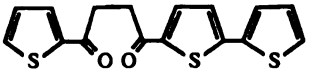
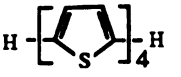
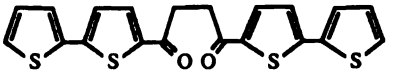
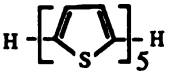
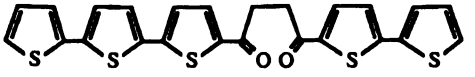
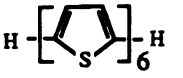
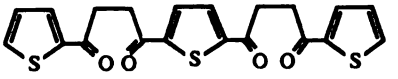
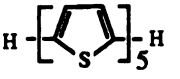
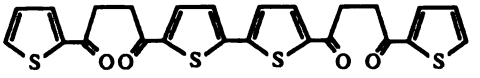
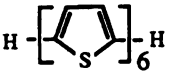
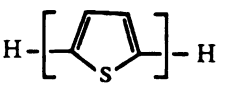
rings were prepared in this manner in excellent yields (Table 2). Their color and UV spectrum data are summarized

Table 2 Polythienyls by Ring closure of 1,4-Diketones

entry no.	1,4-diketone	polythienyl	yield(%)
1.	 **32a**	 **10**	85
2.	 **32b**	 **14**	93
3.	 **32c**	 **15**	94
4.	 **32d**	 **16**	86
5.	 **36a**	 **15**	91
6.	 **36b**	 **16**	91

in Table 3. The color apparently deepens upon going from α-bithienyl to α-sexithienyl. This is the result of the fact that an increas of the number of thienyl rings in the molecule shifts the position of the main maximum to longer wave length.

Table 3 Color and UV Spectrum Data (the highest λ_{max} value) of α-Polythienyls

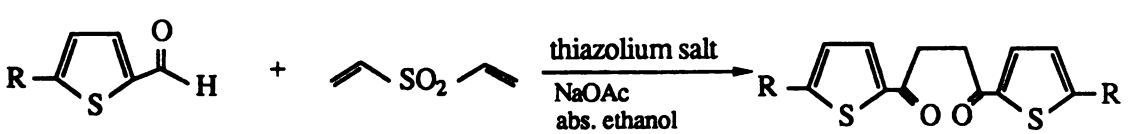


n	2	3	4	5	6
color	colorless	pale yellow	orange yellow	orange	red
$\lambda_{max}^{CHCl_3}$ (nm)	307	364	392	416	434

Individual α-polythienyls can be synthesized in greatly improved yields over the traditional methods by constructing a 1,4-diketone properly substituted with thienyl groups and treating it with Lawesson's reagent. The procedure is versatile enough to allow the synthesis of oligomers having either an odd or an even number of repeating units.

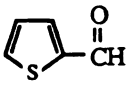
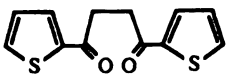
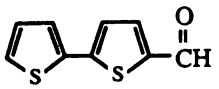
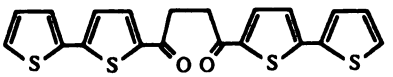
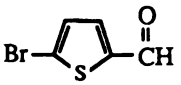
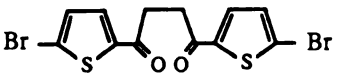
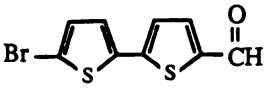
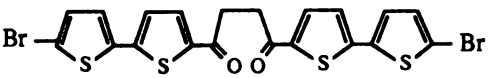
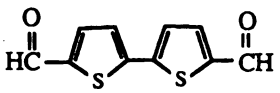
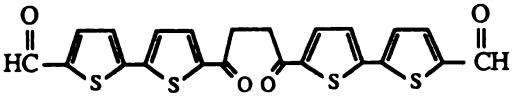
The thiazolium salt catalyzed addition of divinyl sulfone to thienyl aldehydes provides another route to make 1,4-diketones (Scheme 14). This procedure is an extension of the Michael-Stetter addition described by Stetter, which have been useful in the preparation of several symmetrical 1,4-diketones.[41, 42] The divinyl sulfone was added dropwise

Scheme 14



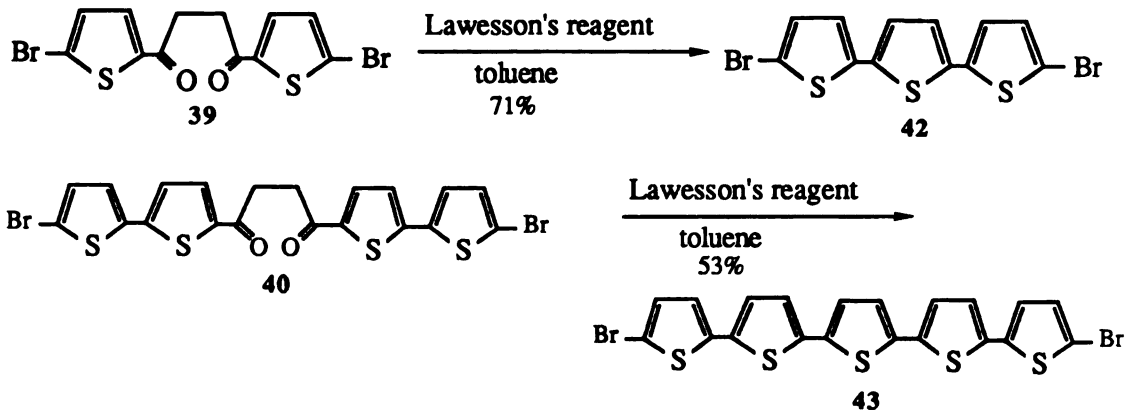
to a hot solution of thienyl aldehyde, thiazolium salt and sodium acetate in ethanol. After the mixture was stirred overnight, the desired 1,4-diketone was collected in fair to good yields (Table 4). The yields of these reactions herein described are not better than that of aldehydes with Mannich base as described in Scheme 10. However, it is a one-step facile reaction for the synthesis of 5,5'-disubstituted-1,4-diketones, which are precursors of 5,5"-disubstituted-polythienyls.

Table 4 1,4-Diketones from Aldehyde and Divinyl Sulfone

aldehyde	1,4-diketone	yield	m.p. (°C)
 **30a**	 **32a**	48	132-133
 **30b**	 **32c**	65	225-226
 **37**	 **39**	20	175-176
 **38**	 **40**	45	225(dec.)
 **35b**	 **41**	43	255(dec.)

These 1,4-diketones (except 41) readily give the polythienyls upon treatment with Lawesson's reagent in dry toluene under reflux temperature in good yields.[40] The cyclization of 32a and 32c to the corresponding polythienyls, α-ter- and α-quiquethienyl has been described earlier (see Table 2). Scheme 15 summarizes the results of 5,5'-dibromo-1,4-diketones to 5,5"-dibromopolythienyls.

Scheme 15

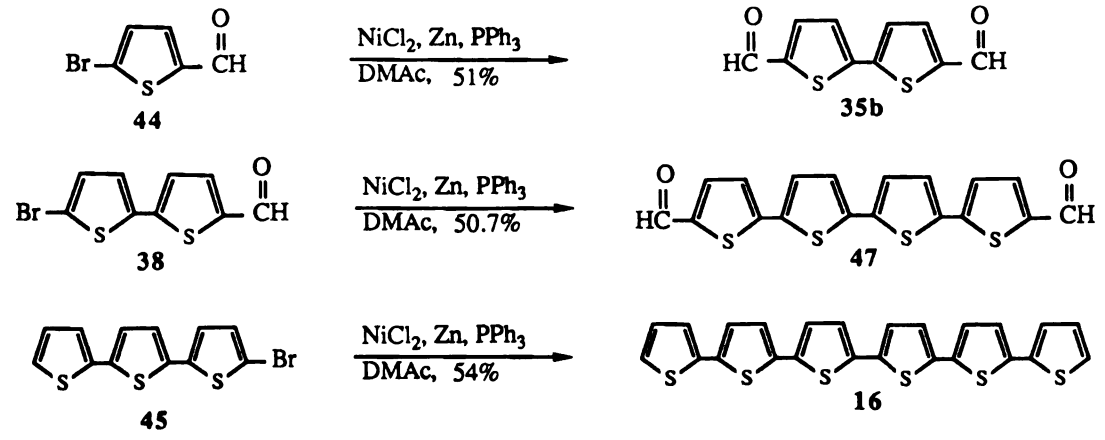


In conclusion, a simple method is available for the synthesis of unsubstituted and disubstituted linear α-polythienyls, where individual members may be obtained in good yield. However, the method herein described is limited to the synthesis of α-polythienyls with an odd number of thiophene units.

A recent report of the facile coupling reaction of chloroarenes by nickel and reducing metals to give the corresponding biaryls[43] prompted a similar study with 5'-

bromo-α-polythienyls to yield the α-polythienyls having even number of thiophene units. Only three reactions of mono-bromothienyls are summarized in Scheme 16, the further study

Scheme 16



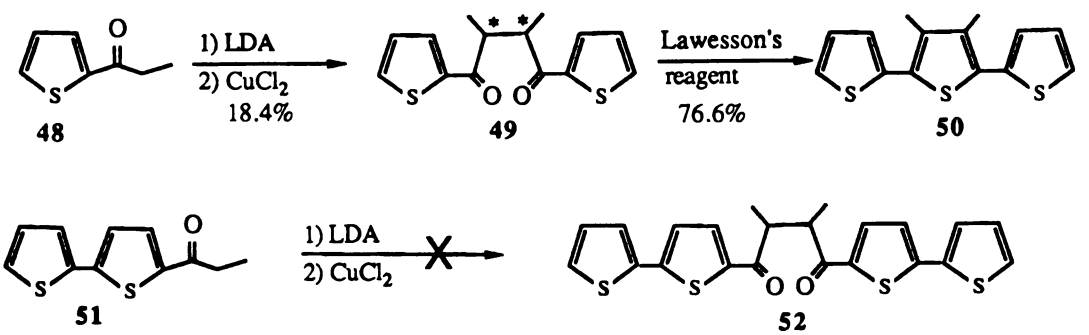
will be discussed in later section. Both of 38 and 45 (44 is commercial available) were synthesized by bromination of a simpler thiophene precursors with pyridinium perbromide in chloroform. The nickel catalyst was generated in situ from anhydrous nickel chloride, triphenylphosphine, and excess zinc in a dry, dipolar aprotic solvent DMAC(N,N-dimethylacetamide) at 60-80°C under Ar atmosphere. To zero-valent nickel reagent was added neat(or solid) bromothienyls. The mixture was heated at 80°C for 16 hrs. Work up of the resulting mixture gave the desire polythienyls in good yield.

The generality of the reactions for making the higher polythienyls is severely limited by practical considerations

of solubility, which decreases rapidly as the oligomers increases. To avoid the solubility problem, the synthesis of polythenienyls substituted in 3- and 4-posi-tions have been investigated.

The introduction of methyl substituents into the 3'- and 4' positions of the α-terthienyl can be achieved by Kagan's procedure,[44] which involves oxidation of the lithium enolate of 2-propylthiophene **48** with cupric chloride followed by cyclization of 1,4-diketone **49** with Lawesson's reagent (Scheme 17).

Scheme 17



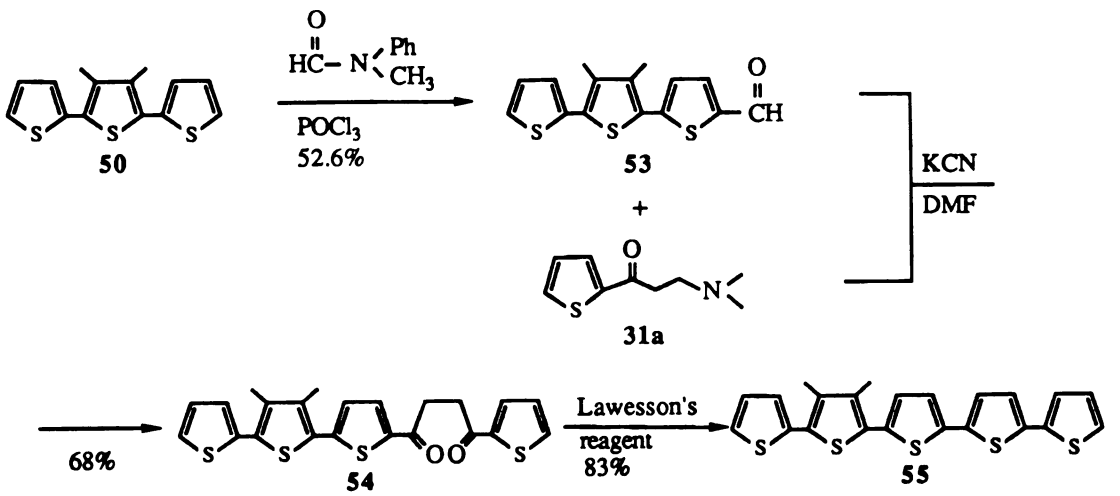
Two diastereomers of 1,4-bis-(2-thienyl)-2,3-dimethyl-1,4-butanedione **49** were separated by flash column chromatography, and identified by their ^{1}H-NMR (δ 1.33(3H, d), 3.75(1H, m), 7.12(1H, dd), 7.60(1H, dd), 7.79(1H, dd) and 1.18(3H, d), 3.77(1H, m), 7.16(1H, dd), 7.69(1H, dd), 7.84(1H, dd)).

Further extension of Kagan's method was not realized since attempts to make **52** from 5-propionyl-2,2'-bithienyl **51**

under similar condition resulted in the recovery of starting material (Scheme 17).

Formylation of 50 to 5-formyl-3',4'-dimethyl-2,2'-5,2"-terthienyl 53 followed by Michael addition[34] with Mannich base 31a provided 1,4-diketone 54. The usual cyclization of 1,4-diketone 54 with LR(Lawesson's reagent)[40] to 55 was accomplished in excellent yields (Scheme 18). The structure of orange-yellow solid 55 was obvious from its

Scheme 18

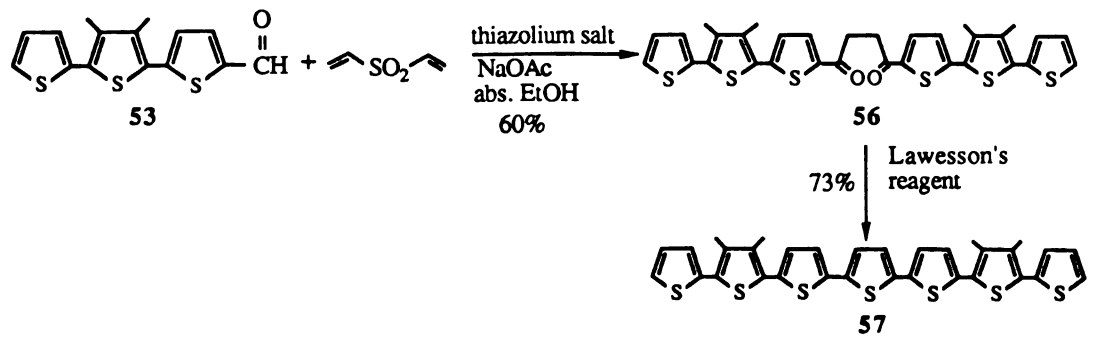


spectra. The ^{1}H-NMR spectrum contained two three-proton singlets at δ 2.24 and 2.27 for the methyl groups and ten-proton multiplet at δ 6.94-7.26 for the thienyl protons. The mass spectrum of 55 showed a strong molecular ion peak at *m/e* 440. A long wavelength absorption of UV spectrum is at 400 nm.

The 1,4-bis-(3',4'-dimethyl-2,,2'-5',2"-terthienyl)-

1,4-butanedione **56** was prepared from readily available aldehyde **53**, by Michael addition with divinyl sulfone (Scheme 19).[41] The 1,4-dione **56** then readily gave 2,5-bis-(3",4"-dimethyl-2',2"-5,2"'-terthienyl)-thiophene **57** upon usual treatment with Lawesson's reagent in toluene. The ^{1}H-NMR spectrum of orange solid **57** showed two three-proton

Scheme 19

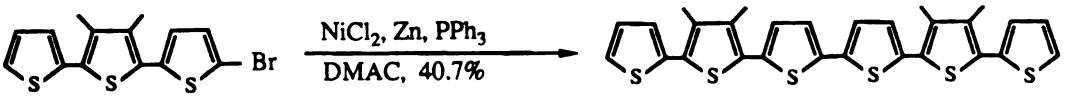


53 56 57

singlets at δ 2.29 and 2.32 for the methyl groups and six-proton multiplet at δ 7.02-7.31 for the thienyl protons. The mass spectrum of **57** showed a strong molecular ion peak at *m/e* 632. A long wavelength absorption of UV spectrum is at 428 nm.

The coupling reaction of bromothiophenes by nickel and reducing metals[43] could also be applied to the reaction of 5-bromo-3'-4'-dimethyl-2,2'-5',2"-terthienyl **58** to give 5,5'-bis-(3",4"-dimethyl-2",2"'-bithienyl)-2,2'-bithienyl **59** in modest yield (Scheme 20).

Scheme 20



58 59

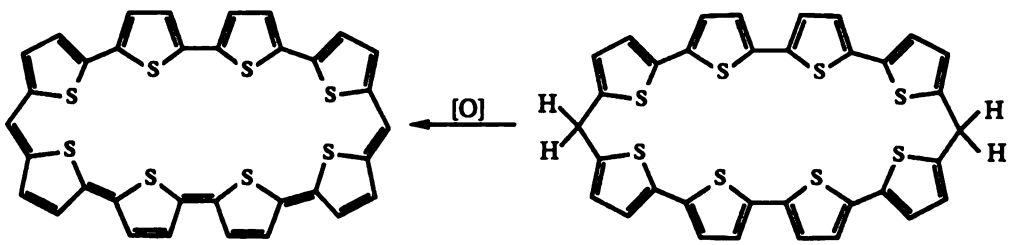
The structure of 59 was confirmed by its spectral. The ^{1}H-NMR spectrum showed two three-proton singlets at δ 2.30 and 2.33 for the methyl groups and five-proton multiplet at δ 7.03-7.31 for the thienyl protons. The mass spectrum of 59 showed a strong molecular ion peak at *m/e* 550. A long wavelength absorption of UV spectrum is at 409 nm.

B. Synthesis of novel macrocyclic polythienyls

I. Synthesis of 12 type macrocyclic polythienyls

Retroanalysis of 12c suggests that compound 61c is a possibly potential precursor to 12c, since oxidation of 61c might afford the octathio[34]annulene 12c (Scheme 21). In

Scheme 21

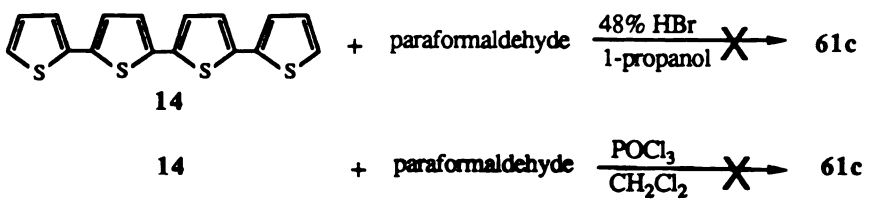


12c 61c

the case of porphyrins the carbon bridges have traditionally been linked by the acid catalyzed condensation of pyrroles.[44,45] Similar strategy was applied to attempt the

synthesis of the compound 61c by cyclization of α-quaterthienyl 14 with paraformaldehyde. First attemp was conducted using 48% HBr as a catalyst, which resulted in the recovery of starting material. The second attempt using the

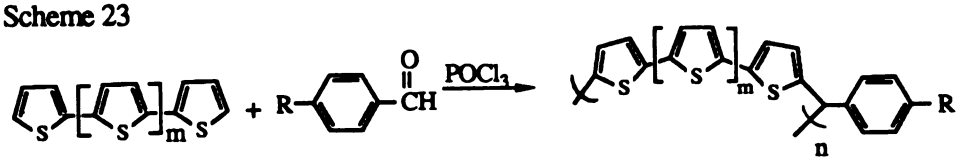
Scheme 22



the Lewis acid, $POCl_3$, as a catalyst, gave unidentifible products.

Nevertheless, it was found later that condenstation of a less reactive aldehyde (benzaldehyde, anisaldehyde) using a Lewis acid ($POCl_3$, Et_2AlCl, $EtAlCl_2$) with the polythienyl (10, 13, or 14) in methylene chloride at room temperture allowed the successful synthesis of the symmetrical macrocyclic polythienyls 64 (Scheme 23). Evident supporting of the cyclic form of 64 comes from their ^1H and ^{13}C NMR

Scheme 23



m=0 13
m=1 10
m=2 14

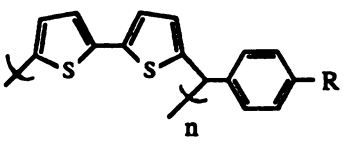
62 R=H
63 R=OCH_3

64a m=0, R=H
64b m=0, R=OCH_3
64c m=0, R=H
64d m=0, R=OCH_3
64e m=0, R=H
64f m=1, R=OCH_3

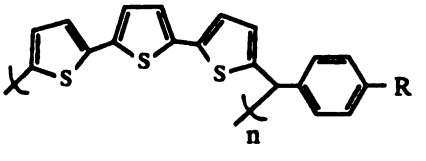
spectra. Table 5 and 6 summarize the ^{1}H and ^{13}C spectra data for the compound 64. The ^{1}H-NMR spectrum of 64 generally showed a singlet at δ 5.68-5.80 for the bridgehead protons, while in the case of anisaldehyde products, a singlet at δ 3.77, 3.70, and 3.80 (methoxyl proton) was observed. The ^{13}C-NMR spectra displayed 9 peaks for 64a,

Table 5 ^{1}H-NMR Spectra of 64

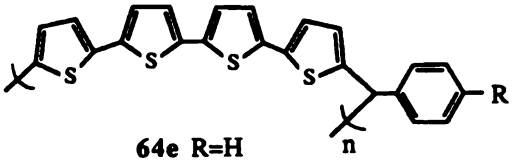
compound	bridgehead	-OCH_3	thienyl proton	phenyl proton
64a	5.80		6.50(d, 2H) 7.00(d, 2H)	7.38(s, 5H)
64b	5.66	3.77	6.64(d, 2H) 6.90(d, 2H)	6.82(d, 2H) 7.24(d, 2H)
64c	5.70		6.71(bs, 2H) 6.95(m, 4H))	7.35(s, 5H)
64d	5.68	3.70	6.70(bs, 2H) 6.95(m, 4H)	6.86(d, 2H) 7.24(d, 2H)
64e	5.75		6.73(bs, 2H) 6.97(m, 6H)	7.34(s, 5H)
64f	5.71	3.80	6.75(bs, 2H) 6.99(m, 6H)	6.87(d, 2H) 7.26(d, 2H)



64a R=H
64b R=OCH_3



64c R=H
64d R=OCH_3



64e R=H
64f R=OCH_3

Table 6 ^{13}C-NMR spectra of 28 64

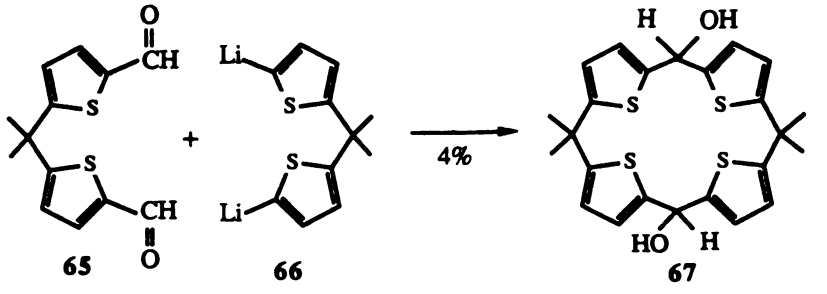
compound	bridge C	-OCH_3	thienyl	phenyl
64a	47.73(d)		122.8(d), 126.8(d) 136.8(s), 146.5(s)	127.3(d), 128.3(d) 128.6(d), 142.7(s)
64b	47.00(d)	55.2(q)	122.6(d), 126.4(d) 136.9(s), 147.3(s)	113.9(d), 129.4(d) 134.8(s), 158.8(s)
64c	47.90(d)		123.0(d), 124.1(d) 126.9(d), 136.1(s) 136.6(s), 146.5(s)	127.4(d), 128.3(d) 128.6(d), 142.7(s)
64d	47.09(d)	55.2(q)	123.0(d), 123.9(d) 126.7(d), 136.0(s) 136.5(s), 146.9(s)	114.1(d), 129.3(d) 135.5(s), 158.7(s)
64e	47.90(d)		123.1(d), 124.1(d) 126.9(d), 135.7(s) 136.2(s), 136.6(s) 146.5(s)	127.4(d), 128.3(d) 128.6(d), 142.7(d)
64f	47.20(d)	55.3(q)	123.2(d), 124.1(d) 126.8(d), 135.7(s) 136.3(s), 136.5(s) 147.0(s)	114.1(d), 129.4(d) 135.0(s), 159.0(s)

10 peaks for 64b, 11 peaks for 64c, 12 peaks for 64d, 12 peaks for 64e, and 13 peaks for 64f, corresponding to the symmetrical, cyclic structure. However, the mass spectrum (field desorption technique) showed a set of signals (i.e. 64a *m/e* 764, 1016, 1272, 1526; 64b *m/e* 568, 853, 1136, 1421, 1706) which indicated possibly a mixture of cyclic products correspounding to n equals, 2, 3, 4, 5....etc. Attempts to separate the mixtures using TLC or column chromatography failed to obtain single pure product.

Ahmed and Meth-Cohn first prepared thiaporphyrinogen 67 by the high-dilution interaction of diformyldithienyl-

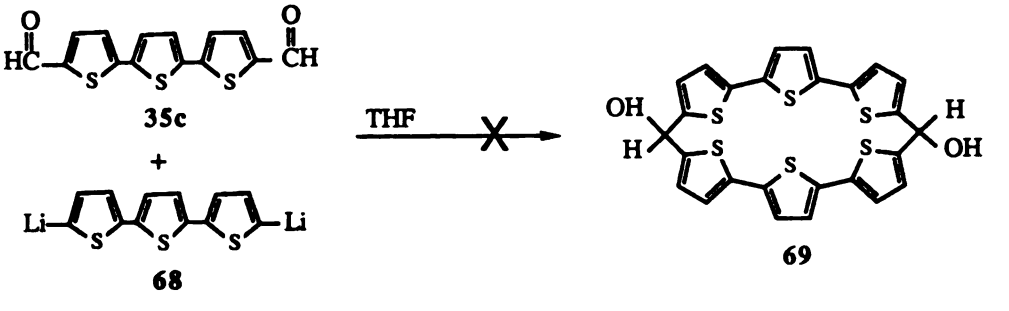
propane 65 and the corresponding dilithio compound 66 in low yield (Scheme 24).[13] However, our attempts to cyclize di-

Scheme 24



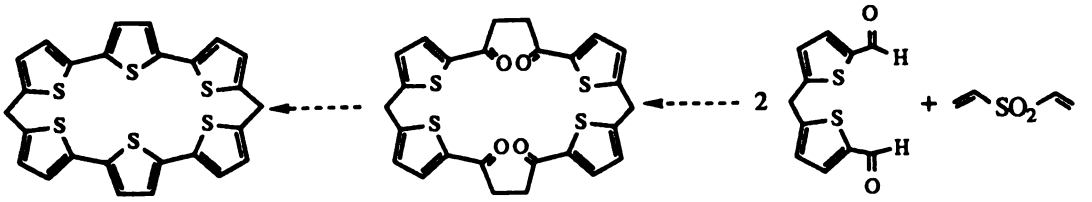
formyl-α-terthienyl 35c with the correspounding dilithio compound 68 (prepared by lithiation of α-terthienyl)[46] resulted in the recovery of starting material (Scheme 25). The lack of any reaction may be a result of the low solubility of 35c in THF solvent.

Scheme 25



Retroanalysis of 61b suggests the following synthetic pathway (Scheme 26). It involes an intermolecular catalyzed addition of dialdehydes to the activated double bond. The

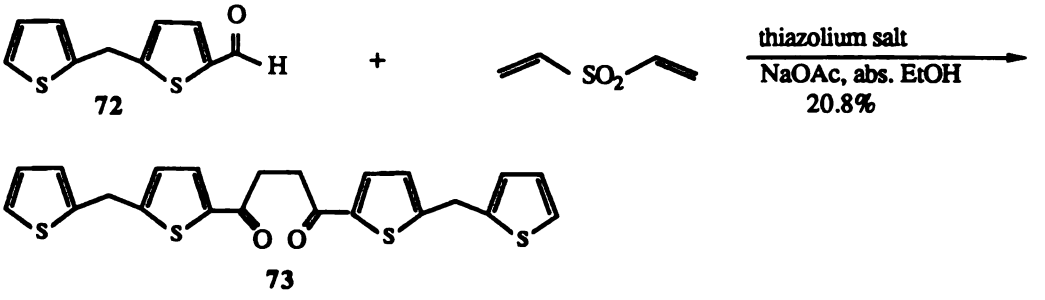
Scheme 26



61b 71 70

Michael addition of 72[13] to vinyl sulfone was accomplished to give 73 in 20.8% yield (Scheme 27). However, attempts to

Scheme 27



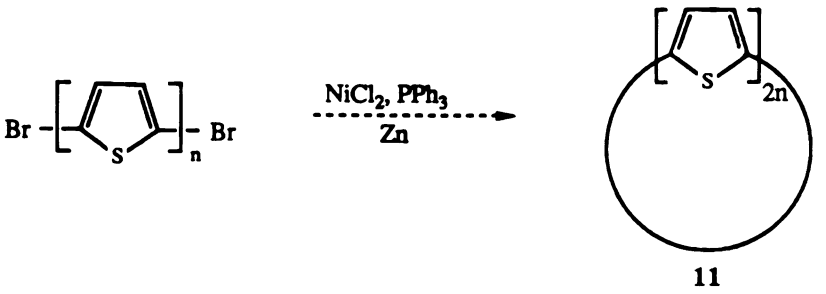
72 73

cyclize 70[13] with vinyl sulfone under same condition failed to provide the desired macrocyclic molecule 71.

II. Attempts to synthesis 11 type macrocyclic polythienyls

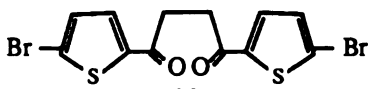
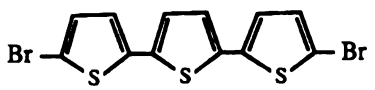
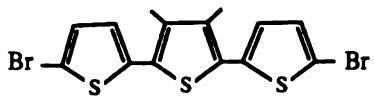
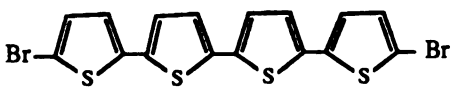
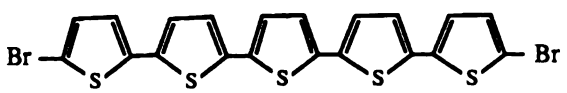
An efficient coupling reaction for the synthesis of linear polythienyls from simpler bromothiophenes (*vide supra*, Scheme 16, 20) led us to attempt the synthesis of the interesting macrocyclic polythienyls 11 from the correspounding bromothiophenes (Scheme 28). Table 7 summarizes the

Scheme 28



11

Table 7 Coupling of Various Polythienyl Dibromide

entry no.	polythienyl dibromides	products
1.	 39	off white powder
2.	 42	dark red powder
3.	 74	red powder
4.	 75	no reaction
5.	 43	no reaction

result of the attempted cyclization reactions. The reactions of 39, 42, and 74 under standard conditions yielded insoluble, unidentifiable products. For example,

only UV spectral could be taken of the reddish product obtained from the coupling reaction of 74 (entry 3). The spectrum showed a long wavelength absorption at 430 nm, which is longer than that of 5,5'-bis(3".4"-dimethyl-2"-2"'-bithienyl)-2.2'-bithienyl 59. This is consistent with the view that it possesses more thienyl units than 59. Unfortunately, due to the insolubility of the product, no other evidence (i.e. NMR, Mass spectra) could be obtained which would prove their cyclic or linear structure as well as the number of thienyl units.

The reaction of 75, 43 (entry 4, 5) resulted only in the recovery of starting material due to the insoluble nature of both compounds in the solvents tested, such as DMAC and N,N-dimethylbenzamide. In order to overcome the solubility problem, the use of ultrasonic irradiation was also applied to the system. However, no product other than starting material could be detected.

The difficulty encountered in these reactions came mainly from the low solubility, either starting material or products.

C. Conclusions

It has been demonstrated that various individual unsubstituted and substituted linear polythienyls (including both even and odd numbers of thienyl units) can be efficiently prepared 1) by constructing a 1,4-diketone properly substituted with thiophene groups followed by

treating it with Lawesson's reagent and 2) by coupling of a simpler bromothiophene using low valent nickel. Some of the new 3,4-disubstituted polythienyls (i.e. 55, 57, and 59) from these reactions could be useful as candidates in the testing of their biological properties[16] or conductivity[17,18]. Finally, attempted synthesis of macrocyclic polythienyls was severely limited by practical consideration of solubility which decreases rapidly as the molecular weight of the oligomers increases.

EXPERIMENTAL

General Methods

NMR spectra (^{1}H and ^{13}C) were recorded on a Bruker WM 250 MHz spectrometer using $CDCl_3$ as solvent and $(CH_3)_4Si$ as the internal reference. Mass spectra were obtained on a Finnigan 4000 instrument at 70ev. Some very nonvolatile materials were measured on JEOL HX110 HF spectrometer using field desorption (FD) technique at Michigan State University Mass Spectrometry Facility. High resolution mass were measured on JEOL HX110 high resolution mass spectrometer by Mr. Ernest Oliver. Electronic absorption spectra were measured on a Shimatzu 160 spectrophotometer using 1 cm matched quartz cells. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Some high melting (>300^{o}C) materials were determined with an electro-thermal melting point apparatus (Fisher Scientific) and are uncorrected. Infrared spectra were measured on a Perkin-Elmer 599 spectrophotometer as a Nujol mull for solids. Elemental analysis were performed by Galbraith Laboratories, Incorporated. Dry ethyl ether, toluene and tetrahydrofuran (THF) were obtained by distillation from potassium benzophenone. Flash column chromatography refers to the method of Still, Kahn and Mitra[47] using Merck silica gel (0.040-0,063 mm).

5-Formyl-2,2'-bithienyl (30a)

Formylation of 2,2'-bithienyl according to Uhlenbroek and Bijloo[35] furnished 30a in 80% yield, m. p. 57-58°C (lit[35] 53°C); ^{1}H-NMR: δ 7.00(1H, dd, J=5.0, 3.8Hz), 7.18(1H, d, J=4Hz), 7.29(2H, m), 7.59(1H, d, J=3.8Hz), 9.8 (1H, s); MS: *m/e* (rel. intensity) 196(M^++2, 7), 195(M^++1, 15), 194(M^+, 84), 193(100), 165(11), 121(50); IR: cm^{-1} 2725, 1650.

5-Formyl-2,2'-5',2"-terthienyl (30b)

According to the general procedure of Uhlenbroek and Bijloo[35], a mixture of α-terthienyl 10 (1 g, 4 mmole), N-methylformanilide (600 mg, 4.4 mmole) and phosphorus oxychloride (681 mg, 4.4 mmole) was heated on steam bath for 20 min. Then the reaction mixture was decomposed by adding an excess of an aqueous solution of sodium acetate with stirring on steam bath for 20 min. Recrystallization of the resulting golden yellow solid from methanol afforded 880 mg (79.1%) of 30b, m.p. 131-133°C (lit[48] 130-132°C); ^{1}H-NMR: δ 7.05(1H, dd, J=3.7, 4.2Hz), 7.13(1H, d, J=3.9Hz), 7.27(4H, m), 7.67(1H, d, J=3.9Hz), 9.86(1H, s); MS: *m/e* (rel. intensity) 278(M^++2, 14), 277(M^++1, 21), 276(M^+, 100), 275 (46), 247(11), 203(23); IR: cm^{-1} 2720, 1650.

3-Dimethylamino-1-(2-thienyl)-propanone (31a)

According to the procedure of Wynberg[34], a mixture of 2-acetylthiophene (31.5 g, 0.25 mmole), paraformaldehyde (9 g, 0.3 mmole), dimethyl amino·HCl (24.5 g, 0.3 mmole) and conc. HCl (1.25 ml) in 95% ethanol (30 ml) was heated under

reflux for 16 hrs. The resulting ppt was filtered to give 46.1 g (84.2 %) of product after cooled, m.p. 181-183°C (lit[34] 179-181°C). The Mannich base hydrochloride (2.5 g) was made alkaline (in water) using ammonia solution and extracted with ethyl ether. The combined ethyl ether layed was washed with saturated aqueous $NaHCO_3$ and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave 1.85 g of free Mannich base which was used at once in the Michael-Stetter reaction.

3-Dimethylamino-1-(2-2'-bithienyl)-propanone (31b)

A mixture of 5-acetyl-2-2'-bithenyl (3 g, 14.42 mmole), paraformaldehyde (951 mg, 31.72 mmole), dimethyl amino HCl (2.59 g, 31.72 mmole) and conc. HCl (0.1 ml) in 95% ethanol (30 ml) was heated under reflux for 16 hrs. The resulting ppt was filtered to give 3.4 g (78.3 %) of Mannich base hydrochloride after cooled, m.p. 221-222°C.

A suspension of Mannich base hydrochloride (2 g, 6.64 mmole), ethyl ether (150 ml) and water (300 ml) was made alkaline using ammonia solution which form two layers. The ethyl ether layer was washed with sat. aqueous $NaHCO_3$ and dried over anhydrous $MgSO_4$. Evaporation of the solvent and recrystallization of the residue from 95% EtOH gave 1.62 g (92%) of free Mannich base, m.p. 78-79°C; ^{1}H-NMR: δ 2.29(6H, s), 2.77(2H, t, J=7.2Hz), 3.06(2H, t, J=7.2Hz), 7.05(1H, dd, J=3.8, 5.0Hz), 7.17(1H, d, J=4Hz), 7.30(2H, m), 7.62(1H, d, J=4Hz); MS: *m/e* (rel. intensity) 267(M^++2, 2), 266(M^++1, 3), 265(M^+, 21), 220(74), 193(83), 179(9), 165(7), 121(48),

58(100).

1-(2-Thienyl)-4-(5-2,2'-bithienyl)-1,4-butanedione (32b)

A solution of 5-formyl-2-2'-bithenyl 30a (3.08 g, 15.89 mmole) in dry DMF(10 ml) under N_2 was added dropwise over a 10 min period to a suspension of KCN (516 mg, 7.93 mmole) in dry DMF (4ml). After the mixture had been stirred for 15 min, the free Mannich base 3-dimethylamino-1-(2-thienyl)-propanone 31a (1.1 g, 6 mmole) in dry DMF (10 ml) was addedd over a 30 min period and the resulting dark brown solution was stirred overnight. To the crude mixture was added 20 ml water. The tan precipitate was filtered from the reaction mixture, thoroughly washed with ethyl ether and recrystallization from acetone to give 3.82 g (93.5%) of 1,4-butanedione 32b, m.p. 163.5-164.5°C; ^{1}H-NMR: δ 3.38(4H, m),7.05(1H, dd, J=5, 3.8Hz), 7.15(1H, dd, J=3.8, 5Hz), 7.19 (1H, d, J=4Hz), 7.32(2H, m), 7.64(1H, dd, J=1, 5Hz), 7.71 (1H, d, J=4Hz), 7.82(1H, dd, J=1, 3.7Hz); ^{13}C-NMR: δ 32.79, 33.27, 124.22, 125.64, 126.49, 128.13, 128.21, 132.10, 132.98, 133.65, 191.02, 191.36; MS: *m/e* (rel. intensity) 334 (M^++2,3), 333(M^++1, 4), 332(M^+, 25), 221(82), 193(100), 165 (10), 121(53), 111(50); IR: cm^{-1} 1650.

Anal. Calcd. for $C_{16}H_{12}O_2S_3$:C, 57.80; H, 3.64

Found :C, 57.59; H, 3.82

1,4-Bis-(5-2,2'-bithienyl)-1,4-butanedione (32c)

Method A: A solution of 5-formyl-2-2'-bithenyl 30a (1.3 g, 6.68 mmole) in dry DMF (5 ml) under N_2 was added dropwise

over a 10 min period to a suspension of KCN (208 mg, 3.19 mmole) in dry DMF (2ml). After the mixture had been stirred for 15 min, the free Mannich base 3-dimethyl-amino-1-(2-2'-bithienyl)-propanone 31b (1.4 g, 5.28 mmole) in dry DMF (24 ml) was addedd over a 30 min period and the resulting dark brown solution was stirred overnight. To the crude mixture was added water. The light yellow precipitate was filtered from the reaction mixture, thoroughly washed with ethyl ether and recrystallization from dioxane to give 1.9 g (86.9%) of 1,4-butanedione 32c, m.p. 225-226°C; ^{1}H-NMR: δ 3.37(4H, s), 7.06(1H, dd, J=3.8, 5.0Hz), 7.20(1H, d, J=4Hz), 7.30(2H, m), 7.71(1H, d, J=4Hz), MS: *m/e*(rel. intensity) 416(M^++2, 5), 415(M^++1, 6), 414(M^+, 26), 249(1), 221(100), 193(83), 179(1), 165(9), 121(40); IR: cm^{-1} 1650.

Anal. Calcd. for $C_{20}H_{14}O_2S_4$:C, 57.94; H, 3.40

Found :C, 57.41; H, 3.48

Method B: Divinyl sulfone (31 mg, 0.26 mmole) was added dropwise to a hot stirred solution of 5-formyl-2,2'-bithenyl 30a (100 mg,0.52 mmole), thiazolium salt (13.9 mg, 0.052 mmole) and sodium acetate (8 mg, 0.1mmole) in abs. ethanol (2 ml). After the mixture was refluxed for 2 hrs under Ar, the tan precipitate was filtered from the reaction mixture and recrystallized from chloroform to give 70 mg (65%) of 32c, m.p. 225-226°C.

1-(5-2,2'-bithienyl)-4-(5-2,2'-5',2"-terthienyl)-1,4-butanedione (32d)

A solution of 5-formyl-2,2'-5',2"-terthienyl 30b (730 mg, 2.65 mmole) in dry DMF (14 ml) under N_2 was added

dropwise over a 15 min period to a suspension of KCN (86 mg, 1.32 mmole) in dry DMF (4ml). After the mixture had been stirred for 15 min, the free Mannich base 3-dimethylamino-1-(2-2'-bithienyl)-propanone 31b (500 mg, 1.89 mmole) in dry DMF (10 ml) was addedd over 1 hr. The resulting dark brown solution was stirred overnight. To the crude mixture was added water. The precipitate was filtered from the reaction mixture, thoroughly washed with ethyl ether and recrystallization from dioxane to give 800 mg (85.3%) of 1,4-butanedione 32d as a reddish-brown solid, m.p. 227.5-229.5°C; MS: *m/e* (rel. intensity) 496(M^+, 13), 330(23), 247 (12), 203(58), 193(51), 165(16), 121(73) ; IR: cm^{-1} 1650.

Anal. Calcd. for $C_{24}H_{16}O_2S_5$:C, 58.04; H, 3.25

Found :C, 57.83; H, 3.44

5,5'-Diformyl-2,2'-bithienyl (35b)

According to the general procedure of Uhlenbroek and Bijloo[35], bithienyl (2.1 g, 12.7 mmole) was added to a mixture of N-methylformanilide (8.6 mg, 63.5 mmole) and phosphorus oxychloride (9.75 mg, 63.5 mmole). The temperature rose gradually to 60°C. After the exothermic reaction had ceased the mixture was warmed for 2 hrs on the steam bath. Then the reation mixture was decomposed by adding an excess of an aqueous solution of sodium acetate with stirring and cooling. After standing for 1 hr at room temperature the precipitate was filtered from the reaction mixture, and recrystallized from CH_2Cl_2/MeOH to give 1.03 (36.5%) of 35b, m.p. 216-217°C (lit[49] 217-218°C); ^{1}H-NMR: δ

7.42(2H, d, J=4Hz), 7.73(2H, d, J=4Hz), 9.91(2H, s); MS: *m/e* (rel. inrensity) 224 (M^++2, 11), 223(M^++1, 21), 222(M^+, 100), 221(86), 193(15), 149(52), 121(64), 108(10); IR: cm^{-1} 2720, 1650.

5,5'-Diformyl-2,2'-5',2"-terthienyl (35c)

A mixture of α-terthienyl 10 (300 mg, 1.2 mmole), N-methylformanilide (812 mg, 6 mmole) and phosphorus oxychloride (921 mg, 6 mmole) was heated at 100°C on steam bath for 1.5 hrs. Then the reation mixture was decomposed by adding an excess of an excess of an aqueous solution of sodium acetate on steam bath for 20 min with stirring. The precipitate was filtered from the reaction mixture after cooling, and recrystallized from benzene to give 230 mg (63%) of 35c, m.p. 218-220°C (lit[48] 215-218°C); ^{1}H-NMR: δ 7.28-7.35(2H, m), 7.68(1H, d, J=4Hz), 7.69(1H, d, J=4Hz, 9.88(1H, s); MS: *m/e* (rel. inrensity) 306(M^++2, 12), 305(M^++1, 17), 304(M^+, 86), 275(7), 247(2), 43(100), 108(10); IR: cm^{-1} 2720, 1650.

2,2'-Bis[4-(2-thienyl)-1,4-butanedione]-thiophene (36a)

A solution of 2,5-diformylthiophene 35a (200 mg, 1.429 mmole) in dry DMF (6 ml) under N_2 was added dropwise over a 10 min period to a suspension of KCN (91 mg, 1.5 mmole) in dry DMF (6ml). After the mixture had been stirred for 15 min, the free Mannich base 3-dimethylamino-1-(2-thienyl)-propanone 31a (437 mg, 2.38 mmole) in dry DMF (6 ml) was added over a 30 min period. The reaction mixture was stirred

overnight. To the crude mixture was added water. The tan precipitate was filtered from the reaction mixture, thoroughly washed with ethyl ether and recrystallization from dioxane to give 340 mg (68%) of 1,4-butanedione **36a** as white crystals, m.p. 186-187.5°C; ^{1}H-NMR: δ 3.40(8H, s), 7.15 (2H, dd, J=3.8, 4.9Hz), 7.65(1H, dd, J=1.1, 4.9Hz), 7.80(2H, s), 7.81(2H, dd, J=1.1, 3.8Hz), MS: *m/e* (rel. intensity) 416(M^+, 0.35), 277(9), 221(1), 167(5), 111(100); IR: cm^{-1} 1650.

Anal. Calcd. for $C_{20}H_{16}O_4S_3$:C, 57.67; H, 3.87
Found :C, 57.69; H, 4.13

5,5'-Bis[4-(2-thienyl)-1,4-butanedione]-2,2'-bithienyl (36b)

A solution of 5,5'-diformyl-2,2'-bithienyl **35b** (444 mg, 2 mmole) in dry DMF (60 ml) under Ar was added dropwise over a 10 min period to a suspension of KCN (130 mg, 2 mmole) in dry DMF (2ml). After the mixture had been stirred for 15 min, the free Mannich base 3-dimethylamino-1-(2-thienyl)-propanone **31a** (581 mg, 3.17 mmole) in dry DMF (5 ml) was addedd over a 30 min period and the reaction mixture was stirred overnight. To the crude mixture was added water. The yellow-orange precipitate was filtered from the reaction mixture, thoroughly washed with ethyl ether and recrystallized from dioxane to give 540 mg (68.4%) of 1,4-butanedione **36b**, m.p. 255.5-256.5°C; ^{1}H-NMR: δ 3.38(4H, t, J=4.8Hz), 3.40 (4H, t, J=4.8Hz), 7.19-7.82(10H, m); MS: *m/e* (rel. intensity) 498(M^+, 4), 387(14), 359(10), 220(9), 111(100); high resolution mass calcd. for $C_{24}H_{18}O_4S_4$ 498.0084; found

498.0078; IR: cm^{-1} 1650.

Anal. Calcd. for $C_{24}H_{18}O_4S_4$:C, 57.81; H, 3.64

Found :C, 57.85; H, 4.60[50]

5-Bromo-5'-formyl-2,2'-bithenyl (38)

A mixture of 5-formyl-2,2'-bithenyl (1 g, 5.15 mmole), and pyridine hydrobromide (1.65 g, 5.15 mmole) in $CHCl_3$ (100 ml) was stirred for 2 hrs at room temperature. The reaction mixture was washed with sat. $NaHCO_3$ solution, dried over anhydrous $MgSO_4$ and concentrated in *vacuo*. Recrystallization the residue from petrolium ether (50^oC-110^oC) gave 1.10 g (78.5%) of 38 as a greenish solid, m.p. 144.5-145.5°C; ^1H-NMR: δ 6.98(1H, d, J=3.8Hz), 7.05(1H, d, J=3.8Hz), 7.12(1H, d, J=3.8Hz), 7.60(1H, d, J=3.8Hz); MS: *m/e* (rel. intensity) 274(M^++2, 98), 272(M^+, 100), 245(8), 243(7), 199(18), 197(1), 121(34); IR: cm^{-1} 1655.

1,4-Bis-(2-bromo-5-thienyl)-1,4-butanedione (39)

Divinyl sulfone (295 mg, 2.5 mmole) was added dropwise to a hot stirred solution of 2-bromo-5-formylthiophene (955 mg, 5 mmole), thiazolium salt (134.9 mg, 270 mmole) and sodium acetate (82 mg, 1 mmole) in abs. ethanol (5 ml). After the mixture was refluxed for 4 hrs under Ar, it was poured into water, and the resulting mixture was extracted with $CHCl_3$. The organic layer was washed with water several times, dried over anhydrous $MgSO_4$ and concentrated. Recrystallization the residue from abs. EtOH gave 195 mg (19.2%) of 39 as a light yellow solid, m.p. 175-176°C; ^1H-

NMR: δ 3.20(2H, s), 7.04(1H, d, J=4Hz), 7.46(1H, d, J=4Hz); ^{13}C-NMR: δ 32.42, 122.86, 131.30, 132.25, 145.05, 190.14; MS: *m/e* (rel. intensity) 410(M^++4, 6), 408(M^++2, 16), 406(M^+, 6), 217(16), 190(32), 189(100), 161(11), 117(16), 82(63); IR: cm^{-1} 1650.

1,4-Bis-(5-bromo-5'-2,2'-bithienyl)-1,4-butanedione (40)

Divinyl sulfone (88.6 mg, 0.75 mmole) was added dropwise to a hot stirred solution of 5-bromo-5'-formyl-2,2'-bithenyl 38 (408 mg, 1.5 mmole), thiazolium salt (41 mg, 0.15 mmole) and sodium acetate (25 mg, 0.31 mmole) in abs. ethanol (20 ml). After the mixture was refluxed for 4.5 hrs under Ar, the yellow precipitate was filtered from the reaction mixture to give 190 mg (44.4%) of 40, m.p. 225°C (dec.); ^{1}H-NMR: δ 3.28(2H, s), 7.55(1H, d, J=4Hz), 7.66(1H, d, J=4Hz) 7.85(1H, d, J=4Hz), 7.92(1H, d, J=4Hz); MS: *m/e* (rel. intensity) 574(M^++4, 13), 572(M^++2, 15), 570(M^+, 7), 301(92), 299(100), 273(82), 271(79), 245(11), 243(11), 201(35), 199(27); IR: cm^{-1} 1649.

1,4-Bis-(5-formyl-5'-2,2'-bithienyl)-1,4-butanedione (41)

Divinyl sulfone (88.5 mg, 0.75 mmole) was added dropwise to a hot stirred solution of 5,5'-diformyl-2,2'-bithenyl 35b (333 mg, 1.5 mmole), thiazolium salt (40 mg, 0.15 mmole) and sodium acetate (25 mg, 0.31mmole) in abs. ethanol (80 ml). After the mixture was refluxed for 17 hrs under Ar, the orange precipitate was filtered from the reaction mixture to give 150 mg (43%) of 41, m.p.

255°C(dec.); ^{1}H-NMR: δ 3.34(2H, s), 7.32(1H, d, J=4Hz), 7.33(1H, d, J=4Hz) 7.65(1H, d, J=4Hz), 7.70(1H, d, J=4Hz), 9.85(1H, s); MS: *m/e* (rel. intensity) 470(M^+, 3), 442(3), 414(trace), 221(100), 149(36), 121(20); IR: cm^{-1} 2720, 1655, 1625.

α-Quaterthienyl (14)

A mixture of the 1,4-butanedione **32b** (3 g, 9.36 mmole) and Lawesson's reagent (2.19 g, 5.42 mmole) in dry toluene (180 ml) was refluxed under Ar for 1 hr. The yellow-orange precipitate was filtered from the reaction mixture and recrystallized from 95% ethanol to give 2.77 g (93%) of **14**, m.p. 212-213°C (lit[30] 211-212°C); MS: *m/e* (rel. intensity) 334(M^++2, 1), 333(M^++1, 3), 332(M^+, 100), 165(8).

α-Quinquethienyl (15)

Method A: A mixture of the 1,4-butanedione **32c** (500 mg, 1.2 mmole) and Lawesson's reagent (293 g, 0.73 mmole) in dry toluene (100 ml) was refluxed under Ar for 4.5 hrs. The red precipitate was filtered from the reaction mixture and thoroughly washed with ethanol to give 468 mg (94%) of **15**, m.p. 256-257°C (lit[30] 256-258°C); MS: *m/e* (rel. intensity) 414(M^++2, 18), 413(M^++1, 18), 412(M^+, 82).

Method B: A mixture of the bis(1,4-butanedione) **36a** (100 mg, 0.24 mmole) and Lawesson's reagent (116 g, 0.288 mmole) in dry toluene (20 ml) was refluxed under Ar for 1 hr. The precipitate was filtered from the reaction mixture and thoroughly washed with ethanol to give 90 mg (91%) of **15**,

m.p. 256.5-257.5°C.

α-Sexithienyl (16)

Method A: A mixture of the 1,4-butanedione **32d** (200 mg, 0.4 mmole) and Lawesson's reagent (97 g, 0.24 mmole) in dry toluene (200 ml) was refluxed under Ar for 24 hrs. The orange precipitate was filtered from the reaction mixture and thoroughly washed with ethanol to give 169 mg (85.5%) of **16**, m.p. 302-303°C (lit[28] 304-305°C); MS: *m/e* (rel. intensity) 496(M^++2, 28), 495(M^++1, 28), 494(M^+, 100), 247(63).

Method B A mixture of the bis(1,4-butanedione) **36b** (227 mg, 0.46 mmole) and Lawesson's reagent (221 g, 0.56 mmole) in dry toluene (200 ml) was refluxed under Ar for overnight. The orange precipitate was filtered from the reaction mixture and thoroughly washed with ethanol to give 207 mg (91%) of **16**, m.p. 307-308°C.

5,5"-Dibromo-2,2',5',2"-terthienyl (42)

A mixture of the 1,4-butanedione **39** (100 mg, 0.246 mmole) and Lawesson's reagent (60 mg, 0.148 mmole) in dry toluene (20 ml) was refluxed under Ar for 20 min. The reaction mixture was subjected to flash column chromatography (slica gel, CH_2Cl_2/petrolem ether (35-60°C) 1:1) to furnish a greenish-yellow solid. Recrystallization of the crude product from abs. EtOH gave 70 mg (70.4%) of **42**, m.p. 160-161°C (lit[51] 160-161°C); MS: *m/e* (rel. intensity) 408(M^++4, 46), 406(M^++2, 100), 404(M^+, 46),

325(5) 283(17), 281(17), 246(4).

1,12-Dibromo-α-quinquethienyl (43)

A mixture of the 1,4-butanedione 40 (100 mg, 0.175 mmole) and Lawesson's reagent (43 mg, 0.05 mmole) in dry toluene (100 ml) was refluxed under Ar overnight. The orange precipitate was filtered from the reaction mixture to give 53 mg (53.3%) of 43, m.p. 289-291°C . This compound is too insoluble to obtain NMR spectra; MS: *m/e* (rel. intensity) 572(M^++4, 70), 570(M^++2, 100), 568(M^+, 38), 492(6), 490(6), 489(2), 447(18), 445(14), 285(16); high resolution mass cacld. for $C_{20}H_{10}S_5Br_2$ 567.7763; found 567.7749.

5-Bromo-2,2'-5',2"-terthienyl (45)

A mixture of α-terthienyl (500 mg, 2 mmole), and pyridinium perbromide (644 mg, 2 mmole) in $CHCl_3$ (100 ml) was stirred for 2 hrs at 0°C. The reaction mixture was washed with sat. $NaHCO_3$ solution, dried over anhydrous $MgSO_4$ and concentrated in *vacuo*. Recrystallization of the residue from abs. EtOH gave 400 mg (61.3%) of 45 as a greenish solid, m.p. 133-134.5°C; ^{1}H-NMR: δ 6.8-7.2(m) ; MS: *m/e* (rel. intensity) 328(M^++2, 57), 326(M^+, 62), 247(20), 203(68).

Coupling of 44 to 5,5'-diformyl-2,2'-bithienyl (35b)

A 50-ml round-bottomed, two-necked flask was charged with $NiCl_2$ (130 mg, 1 mmole), triphenylphosphine (2 g, 7.6

mmole), and Zn dust (1 g, 15 mmole). A rubber serum cap was placed over one neck of the flask and a stopcock adapter in the other. The flask was evacuated and flushed with Ar several times. Dry DMAC (N,N-dimethylacetamide) (10 ml) was added via syringe through the serum cap. The reaction flask was then placed in an oil bath at 80°C and stirred magnetically. After the red-brown catalyst had formed, a Ar-purged solution of 5-bromo-2-thiophene-carboxaldehyde 44 (1.9 g, 10 mmole) in DMAC (2 ml) was added via syringe to the reaction mixture. The reaction was conducted at 80°C for overnight. The precipitate was filtered and washed with water. The solid was dissolved in methylene chloride and the solution was filtered to remove Zn. Evaporation of the solvent gave 586 mg (52.8%) of 35b, m.p. 214-215°C (lit[49] 217-218°C).

Coupling of 38 to 1,10'-diformyl-α-quaterthienyl (47)

A 25-ml round-bottomed, three-necked flask was charged with $NiCl_2$ (6 mg, 0.046 mmole), triphenylphosphine (74 mg, 0.281 mmole), and Zn dust (76 mg, 1.163 mmole). A rubber serum cap was placed over middle neck of the flask, stopcock adapter in the other and one bent tube charged with 38 (50 mg, 0.184 mmole) was placed over another neck. The flask was evacuated and flushed with Ar several times. Dry DMAC (1 ml) was added via syringe through the serum cap. The reaction flask was then placed in an oil bath at 80°C and stirred magnetically. After the red-brown catalyst had formed, the 38 in the bent tube was poured into the rection

mixture and maintained at 80°C for overnight. The precipitate was filtered and washed with $CHCl_3$. The solid was then tri-turated with 10% HCl to remove Zn, followed by washing with water and dried to give 18mg (50.7%) of 47 as a orange solid, m.p. 200°C (dec); MS: *m/e* (rel. intensity) 386(M^+, 34), 358 (3), 193(9), 183(15), 44(100).

Coupling of 45 to -sexithienyl (16)

A 25-ml round-bottomed, three-necked flask was charged with $NiCl_2$ (4 mg, 0.03 mmole), triphenylphosphine (59 g, 0.225 mmole), and Zn dust (29 mg, 0.45 mmole). A rubber serum cap was placed over middle neck of the flask, stopcock adepter in the other and one bent tube charged with 45 (97.8 mg, 0.3 mmole) was placed over another neck. The flask was evacuated and filled with Ar several times. Dry DMAC (1 ml) was added via syringe through the serum cap. The reaction flask was then placed in an oil bath at 80°C and stirred magnetically. After the red-brown catalyst had formed, the 45 in the bent tube was poured into the rection mixture The reaction was conducted at 80°C for overnight. The precipitate was collected from the reation mixture, washed with $CHCl_3$. The precipitate was triturated with 10% HCl to remove Zn and filtered. The solid was washed with water and dried to give 40 mg (54%) of 16 as a red solid, m.p. 302-304°C (lit[28] 304-305°C).

1,4-Bis-(2-thienyl)-2,3-dimethyl-1,4-butanedione (49)

n-Butyllithium (0.12 mOle, 2.5 M in hexane) was added

dropwise to a stirred solution of diisopropylamine (12.12 g, 0.12 mole) in dry THF (30 ml) at -78°C under Ar. After 15 min, 2-propionylthiophene (15.12 g, 0.108 mole) was added dropwise at the same temperature. The mixture was stirred for 30 min, and anhydrous $CuCl_2$ (16.128 g, 0.12 mole) in dry DMF (60 ml) was added in one portion. The dark solution stirred for an additional 10 min at -78°C and warmed up to room temp. and stirred overnight. After addition of 150 ml of 3% HCl, the mixture was extracted with CH_2Cl_2 three times. The combined organic layer was washed sucessively with 3% HCl, water, dried over anhydrous $MgSO_4$ and concentrated. The residue was flash column chromatographed over silica gel, using ethyl acetate-hexane (1:4) as eluent, after recrystallization from abs. EtOH to give 1.85 g (12.3%) of one diastereomer of 49, m.p. 94-95.5°C; ^{1}H-NMR: δ 1.33(3H, d, J=6.9Hz), 3.75(1H, m), 7.12(1H, dd, J=3.8, 5.0Hz), 7.60 (1H, dd, J=1.1, 5.0Hz), 7,79(1H, dd, J=1.1, 3.8Hz); MS: *m/e* (rel. intensity) 278(M^+, 6); high resolution mass calcd. for $C_{14}H_{14}O_2S_2$ 278.0432; found 278.0429; IR: cm^{-1} 1650. further elution furnished 0.92 g (6.1%) of another diasteromer of 49, m.p. 123-125°C; ^{1}H-NMR: δ 1.18(3H, d, J=6.3Hz), 3.77(1H, m), 7.16(1H, dd, J=3.8, 5.0Hz), 7.69(1H, dd, J=1.1, 5.0Hz), 7,84 (1H, dd, J=1.1, 3.8Hz).

3',4'-Dimethyl-2,2'-5',2"-terthienyl (50)

A mixture of the 1,4-butanedione 49 (300 mg, 1.079 mmole) and Lawesson's reagent (262 mg, 0.65 mmole) in dry toluene (2 ml) was refluxed under Ar for 15 min. The

reaction mixture was subjected to flash column chromatography (slica gel, CH_2Cl_2/petrolem ether (35-60°C) 1:1). to furnish a tan solid. Recrystallization of the crude product from MeOH gave 228 mg (76.6%) of 50 as a white solid m.p. 126-128°C (lit[38] 128°C); ^{1}H-NMR: δ 2.3(3H, s), 7.07(1H, dd, J=3.6, 5.0HZ), 7.13(1H, dd, J=3.6, 1.0Hz), 7.31(1H, dd, J=1.0, 5.0Hz); ^{13}C-NMR: δ 14.30, 125.30, 125.94, 127.42, 129.50, 135.15, 136.35; MS: *m/e* (rel. intensity) 278(M^++2, 16), 277(M^++1, 20), 276(M^+, 100).

5-Formyl-3',4'-dimethyl-2,2'-5',2"-terthienyl (53)

A mixture of α-terthienyl 50 (552 mg, 2 mmole), N-methylformanilide (298 mg, 2.2 mmole) and phosphorus oxychloride (338 mg, 2.2 mmole) was heated on steam bath for 10 min. Then the reaction mixture was decomposed by adding an excess of an aqueous solution of sodium acetate with stirring on steam bath for 20 min. The mixture was extracted with CH_2Cl_2. The combined organic fractions were dried over anhydrous $MgSO_4$ and concentrated in *vacuo*. The residue was flash column chromatographed (silica del, $CHCl_3$) to give 170 mg (30.8%) of 50, 320 mg (52.6%) of the title compound 53, m.p. 115-116.5°C (95% EtOH); ^{1}H-NMR: δ 2.29(3H, s), 2.35(3H, s), 7.07(1H, dd, J=3.7, 5.0Hz), 7.15(1H, dd, J=1.1, 3.6Hz), 7.21(1H, d. J=4.0Hz), 7.32(1H, dd, J=1.1, 5.0Hz), 7.68(1H, d, J=4.0Hz), 9.85(1H, s); MS: *m/e* (rel. intensity) 306(M^++2, 10), 305(M^++1, 15), 304(M^+, 100); IR: cm^{-1} 2725, 1650. Further elution furnished 28 mg (4.2%) of 5,5'-formyl-3',4'-dimethyl-2,2'-5',2"-terthienyl m.p. 199-201°C (95% EtOH);

^{1}H-NMR: δ 2.32(3H, s), 7.20(1H, d. J=4.0Hz), 7.67 (1H, d, J=4.0Hz), 9.83(1H, s); MS: *m/e* (rel. intensity) 334 (M^++2, 12), 333(M^++1, 19), 332(M^+, 100).

1-(2-Thienyl)-4-(3',4'-dimethyl-2,2'-5',2"-terthienyl)-1,4-butanedione (54)

A solution of 5-formyl-3',4'-dimethyl-2,2'-5',2"-terthienyl 53 (400 mg, 1.316 mmole) in dry DMF (7 ml) under Ar was added dropwise over a 10 min period to a suspension of KCN (43 mg, 0.66 mmole) in dry DMF (1.5ml). After the mixture had been stirred for 15 min, the free Mannich base 3-dimethylamino-1-(2-thienyl)-propanone 31a (50 mg, 0.274 mmole) in dry DMF (5 ml) was addedd over a 30 min period and the reaction mixture was stirred overnight. To the crude mixture was added water. The orange precipitate was filtered from the reaction mixture, thoroughly washed with ethyl ether and recrystallized from dioxane/H_2O to give 340 mg (58.5%) of 1,4-butanedione 54, m.p. 156-158°C; ^{1}H-NMR: δ 2.25(s, 3H), 2.30(s, 3H),3.33(4H, t, J=4.8Hz), 7.02(1H, dd, J=3.8, 5.0Hz), 7.09(2H, m), 7.27(1H, d, J=4.8Hz), 7.58(1H, d, J=4.8Hz), 7.70(1H, d, J=4Hz), 7.76(1H, d, J=4Hz); MS: *m/e* (rel. intensity) 442(M^+, 64); high resolution mass calcd. for $C_{22}H_{18}O_2S_4$ 442.0186; found 442.0200; IR: cm^{-1} 1650.

3',4'-Dimethyl-α-quinquethienyl (55)

A mixture of 1,4-butanedione 55 (300 mg, 0.68 mmole) and Lawesson's reagent (165 mg, 0.408 mmole) in dry toluene (5 ml) was refluxed under Ar for 20 min. The reaction mixture was subjected to flash column chromatography (slica

gel, CH_2Cl_2/petrolem ether (35-60°C) 1:1) to furnish a solid. Recrystallization of the crude product from dioxane/H_2O gave 250 mg (83.6%) of 55 as a orange-yellow solid, m.p. 135-136.5°C; ^{1}H-NMR: δ 2.23(3H, s), 6.92-7.24(10H, m); MS: *m/e* (rel. intensity) 442(M^++2, 17), 441(M^++1, 20), 440(M^+, 100); high resolution mass calcd. for $C_{22}H_{16}S_5$ 439.9853; found 439.9818.

1,4-Bis-(3',4'-dimethyl-2,2'-5',2"-terthienyl)-1,4-butanedione (56)

Divinyl sulfone (78 mg, 0.658 mmole) was added dropwise to a hot stirred solution of 5'-formyl-3',4'-dimethyl-2,2'-5',2"-terthienyl 53 (400 mg, 1.315 mmole), thiazolium salt (35 mg, 0.132 mmole) and sodium acetate (22 mg, 0.263mmole) in abs. ethanol (20 ml). After the mixture was refluxed under Ar for overnight, the orange-yellow precipitate was filtered from the reaction mixture and recrystallized from dioxane/H_2O to give 250 mg (60%) of 56, m.p. 205-206°C; ^{1}H-NMR: δ 2.25(3H,s), 2.31(3H, s), 3.33(2H, s), 7.02(1H, dd, J=3.7, 5.0Hz), 7.10(2H, m), 7.27(1H, dd, J=1.0, 5.0Hz), 7.70(1H, d, J=4Hz); MS: *m/e* (rel. intensity) 635(M^++1, 8), 634(M^+, 13), 331(100), 167(21), 113(13), 55(172); high resolution mass calcd. for $C_{32}H_{26}S_6O_2$ 634.0246; found 634.0225; IR: cm^{-1} 1650.

2,5-Bis-(3",4"-dimethyl-2',2"-5",2'"-terthienyl)-thiophene (57)

A mixture of 1,4-butanedione 56 (30 mg, 0.047 mmole) and Lawesson's reagent (12 mg, 0.028 mmole) in dry toluene (2 ml) was refluxed under Ar for 2 hrs. The precipitate was

collected to give 15 mg (50.5%) of 55 as a orange solid, m.p. 205-207°C; ^{1}H-NMR: δ 2.29(3H, s), 2.32(3H, s), 7.02-7.31(6H, m); MS: *m/e* (rel. intensity) 634(M^++2, 22), 633(M^++1, 37), 632(M^+, 87); high resolution mass calcd. for $C_{32}H_{24}S_7$ 631.9912; found 631.9953.

5-Bromo-3',4'-dimethyl-2,2'-5'-2"-terthienyl (58) and 5,5-dibromo-3',4'-dimethyl-2,2'-5'-2"-terthienyl (74)

A mixture of 3',4'-dimethyl-2,2'-5',2"-terthienyl 50 (500 mg, 1.81 mmole) and N-bomosuccinimide (332 mg, 1.81 mmole) in CCl_4 (50 ml) was stirred for 3 hrs at 0°C. The succinimide formed was removed by filtration. After removal of solvent, the residue was flash column chromat-graphed using hexanes as eluent to give 437 mg (68.2%) of title compound 58 (Rf=0.86) as a pale yellow solid, m.p. 79-81°C; ^{1}H-NMR: δ 2.25(3H, s), 2.28(3H, s), 6.85(1H, d, J=3.9 Hz), 7.00(1H, d, J=3.9Hz), 7.05(1H, dd, J=3.6, 5.1 Hz), 7.12 (1H, dd, J=3.6, 1.2Hz), 7.30(1H, dd, J=1.2, 5.1Hz); MS: *m/e* (rel. intensity) 356(M^++2, 58), 354(M^+, 100). Further elution furnished 100 mg (12.8%) of 5,5-dibromo-3',4'-dimethyl-2,2'-5',2"-terthienyl 74 , m.p. 128-129°C(abs. EtOH), ^{1}H-NMR: δ 2.19(3H, s), 6.79(1H, d, J=3.8Hz), 6.95(1H, d, J= 3.8Hz); MS: *m/e* (rel. intensity) 432(M^++, 17).

Coupling of 58 to 5,5'-bis(3",4"-dimethyl-2",2'"-bithenyl)-2,2'-bithienyl (59)

A 25-ml round-bottomed, three-necked flask was charged with $NiCl_2$ (7 mg, 0.056 mmole), triphenylphosphine (110 g, 0.423 mmole), and Zn dust (110 mg, 1.692 mmole). A rubber

serum cap was placed over middle neck of the flask, stopcock adapter in the other and one bent tube charged with 58 (95 mg, 0.208 mmole) was placed over another neck. The flask was evacuated and flushed with Ar several times. Dry DMAC (1 ml) was added via syringe through the serum cap. The reaction flask was then placed in an oil bath at 80°C and stirred magnetically. After the red-brown catalyst had formed, the 58 in the bent tube was poured into the rection mixture and maintained at 80°C for overnight. The precipitate was filtered and washed with $CHCl_3$. The solid was then triturated with 10% HCl to remove Zn followed by washing with water and dried to give 30mg (40.7%) of 59 as a egg yellow solid, m.p. 245-247°C; ^{1}H-NMR: δ 2.30(3H, s), 2.33(3H, s), 7.03-7.31(5H, m); MS: *m/e* (rel. intensity) 552(M^++2, 172), 551(M^++1, 41), 550(M^+, 100), 275(13); high resolution mass calcd. for $C_{28}H_{22}S_6$ 550.0042; found 550.0017.

Cyclization of 13 with 62 (64a)

Phosphorus oxychloride (277 mg, 1.80 mmole) was added to a solution of bithenyl 13 (150 mg, 0.9 mmole) and benzaldehyde 62 (1.9g, 18 mmole) in CH_2Cl_2 (80 ml) at 25°C and stirred for 42 hrs. Evaporation of the solvent to one-third and flash column chromatography of the reaction mixture using $CHCl_3$ as eluent gave 176 mg of 64a as a deep-green solid, m.p. 80°C (dec.); ^{1}H-NMR: δ 5.8(1H, m), 6.5(2H, m), 7.0(2H, m), 7.38(5H, sb); ^{13}C-NMR: δ 47.73(d), 122.8(d), 126.8(d), 127.3(d), 128.3(d), 128.5(d), 136.8(s), 142.7(s),

146.5(s); MS(FD)[52]: *m/e* (rel. intensity) 1526(8), 1525(10), 1272(28), 1182(75), 1016(45), 928(100), 764(7).

Cyclization of 13 with 63 (64b)

Phosphorus oxychloride (1 g, 6.6 mmole) was added to a solution of bithienyl 13 (500 mg, 3.0 mmole) and anisaldehyde 63 (8.16g, 60 mmole) in CH_2Cl_2 (150 ml) at 25°C and stirred for 28 hrs. Evaporation of the solvent to one-third and flash column chromatography of the reaction mixture using $CHCl_3$ as eluent gave 145 mg of 64b as a green solid, m.p. 124°C (dec.); ^{1}H-NMR: δ 3.77(3H, s), 5.661H, m), 6.64(2H, m), 6.84(2H, d), 6.90(2H, m), 7.24(2H, d); ^{13}C-NMR: δ 47.0(d), 55.2(q), 113.9(d), 122.6(d), 126.4(d), 129.4(d), 134.8(s), 136.9(s), 147.3(s), 158.8.5(s); MS(FD)[52]: *m/e* (rel. intensity) 1706(86), 1421(21), 1136(55), 853(48), 710(100), 568(90), 372(85).

Cyclization of 10 with 62 (64c)

Phosphorus oxychloride (123 mg, 0.8 mmole) was added to a solution of α-terthenyl 10 (100 mg, 0.4 mmole) and benzaldehyde 62 (848 mg, 8 mmole) in CH_2Cl_2 (40 ml) at 25°C and stirred for 24 hrs. Evaporation of the solvent to half and flash column chromatography of the reaction mixture using $CHCl_3$ as eluent gave 135 mg of 64c as a yellow-greenish solid, m.p. 140°C (dec.); ^{1}H-NMR: δ 5.70(1H, bs), 6.71(2H, bs), 6.95(4H, m), 7.35(5H, sb); ^{13}C-NMR: δ 47.9(d), 123.0(d), 124.1(d), 126.9(d), 127.4(d), 128.3(d), 128.6(d), 136.1(s), 136.6(s), 142.7(s), 146.5(s); MS(FD)[52]: *m/e* (rel.

intensity) 1009(100), 672(15).

Cyclization of 13 with 63 (64d)

Phosphorus oxychloride (123 mg, 0.8 mmole) was added to a solution of α-terthienyl 10 (100 mg, 0.4 mmole) and anisaldehyde 63 (1g, 8 mmole) in CH_2Cl_2 (40 ml) at 25°C and stirred for 68 hrs. Evaporation of the solvent to half and flash column chromatography of the reaction mixture using $CHCl_3$ as eluent gave 60 mg of 64d as a yellowlish-green solid, m.p. 115°C (dec.); ^{1}H-NMR: δ 3.7(3H, s), 5.68(1H, bs), 6.70(2H, bs), 6.86(2H, d), 6.95(4H, m), 7.24(2H, d); ^{13}C-NMR: δ 47.09(d), 55.2(q), 114.1(d), 123.0(d), 123.9(d), 126.7(d), 129.3(d), 135.5(s), 136.0(s), 136.5(s), 146.9(s), 158.7(s); MS(FD)[52]: *m/e* (rel. intensity) 1099(18), 979 (100), 732(5).

Cyclization of 14 with 62 (64e)

Phosphorus oxychloride (808 mg, 5.26 mmole) was added to a solution of α-quaterthienyl 14 (810 mg, 2.45 mmole) and benzaldehyde 62 (5 ml) in CH_2Cl_2 (400 ml) at 25°C and refluxed for 48 hrs. Evaporation of the solvent to half and double flash column chromatography of the reaction mixture using $CHCl_3$ as eluent gave 405 mg of 64e as a greenish-yellow solid, m.p. 145°C (dec.); ^{1}H-NMR: δ 5.75(1H, bs), 6.73(2H, bs), 6.97(6H, m), 7.34(5H, sb); ^{13}C-NMR: δ 47.9(d), 123.1(d), 124.1(d), 126.9(d), 127.4(d), 128.3(d), 128.6(d), 135.7(s), 136.2(s), 136.6(s), 142.7(s), 146.5(s); MS(FD)[52]: *m/e* (rel. intensity) 1675(38), 1586(80), 1420(55), 1256(87),

1186(100), 838(70), 418(45).

Cyclization of 14 with 63 (64f)

Phosphorus oxychloride (205 mg, 1.33 mmole) was added to a solution of α-quaterthenyl 14 (200 mg, 0.6 mmole) and anisaldehyde 63 (1.638g, 12 mmole) in CH_2Cl_2 (180 ml) at 25°C and refluxed for 7 days. Evaporation of the solvent to half and double flash column chromatography of the reaction mixture using $CHCl_3$ as eluent gave 90 mg of 64f as a greenish-yellow solid, m.p. 140°C (dec.); ^{1}H-NMR: δ 3.80(3H, s), 5.71(1H, bs), 6.76(2H, bs), 6.99(6H, m), 6.87(2H, d), 7.26(2H, d); ^{13}C-NMR: δ 47.2(d), 55.3(q), 114.1(d), 123.2(d), 124.1(d), 126.8(d), 129.4(d), 135.0(s), 135.7(s), 136.3(s), 136.5(s), 147.0(s), 159.0(s); MS(FD)[52]: *m/e* (rel. intensity) 1796(20), 1677(39), 1346(100), 1226(85), 898(25), 449(30).

1,4-Bis(2,2-dithienylmethane)-1,4-diketone (73)

Divinyl sulfone (90 mg, 0.758 mmole) was added dropwise to a hot stirred solution of 5-formyl-2,2'-dithienylmethane 72 (316 mg, 1.52 mmole), thiazolium salt (41 mg, 0.152 mmole) and sodium acetate (24 mg, 0.304mmole) in abs. ethanol (15 ml). After the mixture was refluxed under Ar for overnight, the precipitate was filtered from the reaction mixture and recrystallized from dioxane/H_2O to give 250 mg (60%) of 73, m.p. 160°C(dec.); ^{1}H-NMR: δ 3.28(2H, s), 4.34(2H, s), 6.87-6.94(3H, m), 7.17(1H, dd, J=0.9, 5.0Hz), 7.62(1H, d, J=3.8Hz); MS: *m/e* (rel.

intensity) 442(M^+, 5), 263(37), 207(100), 135(14), 79(27); IR: cm^{-1} 1650.

1,10-Dibromo-α-quaterthienyl (75)

A suspension of α-quaterthienyl (100 mg, 0.303 mmole), and pyridinium perbromide (194 mg, 0.606 mmole) in $CHCl_3$ (30 ml) was refluxed for 3 hrs. The precipitate was filtered from the reaction mixture and recrystallized from toluene to give 400 mg (61.3%) of 75 as a golden yellow solid, m.p. 261-263°C (lit[20] 251°C); MS: *m/e* (rel. intensity) 490(M^++4, 52), 488(M^++2, 100), 486(M^+, 39), 410(3), 409(3), 408(3), 407(2), 365(23), 363(22).

APPENDIX

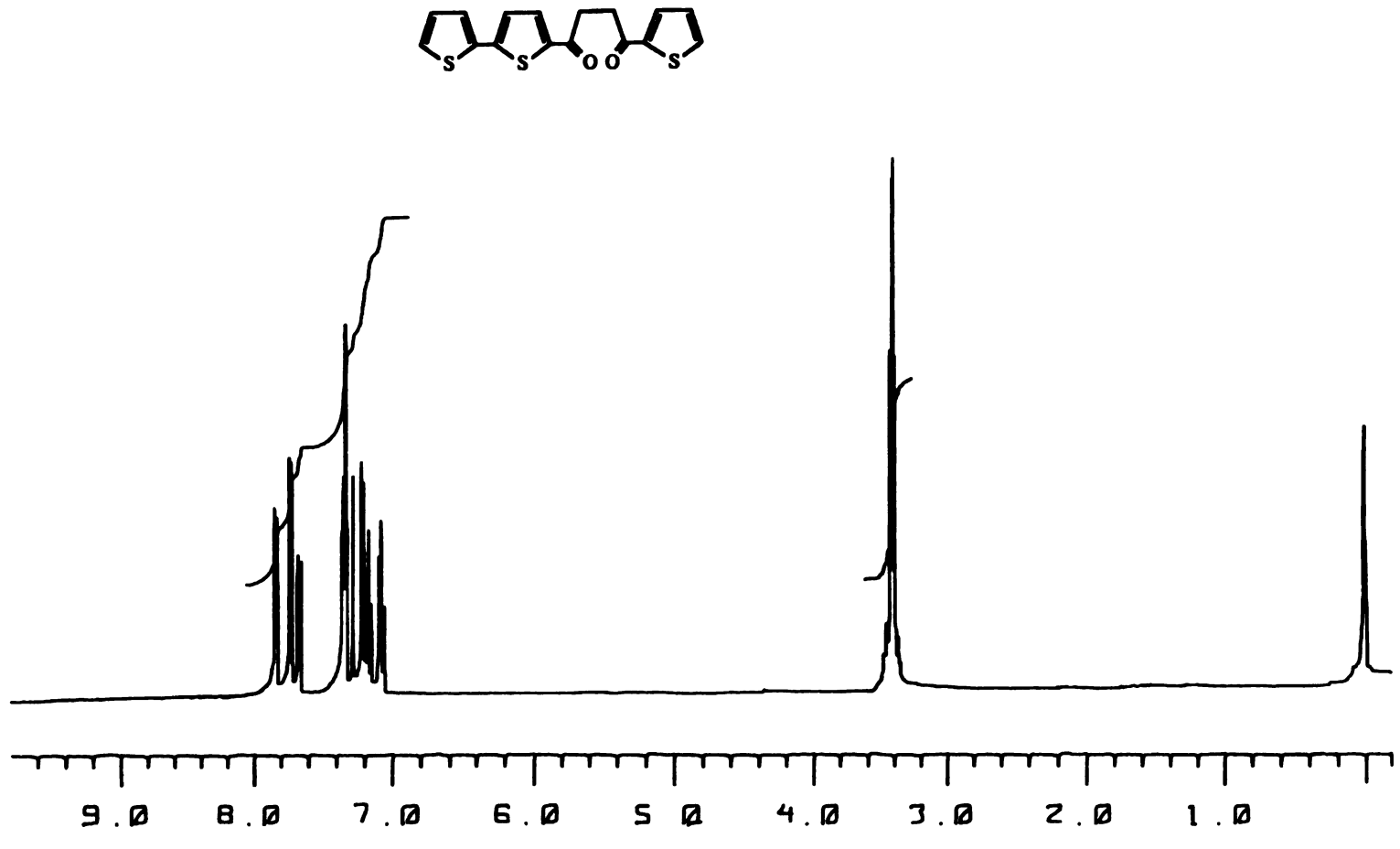


Figure 1. 250 MHz ^{1}H NMR spectrum of 1-(2-Thienyl)-4-(5-2,2'-bithienyl)-1,4-butanedione (32b).

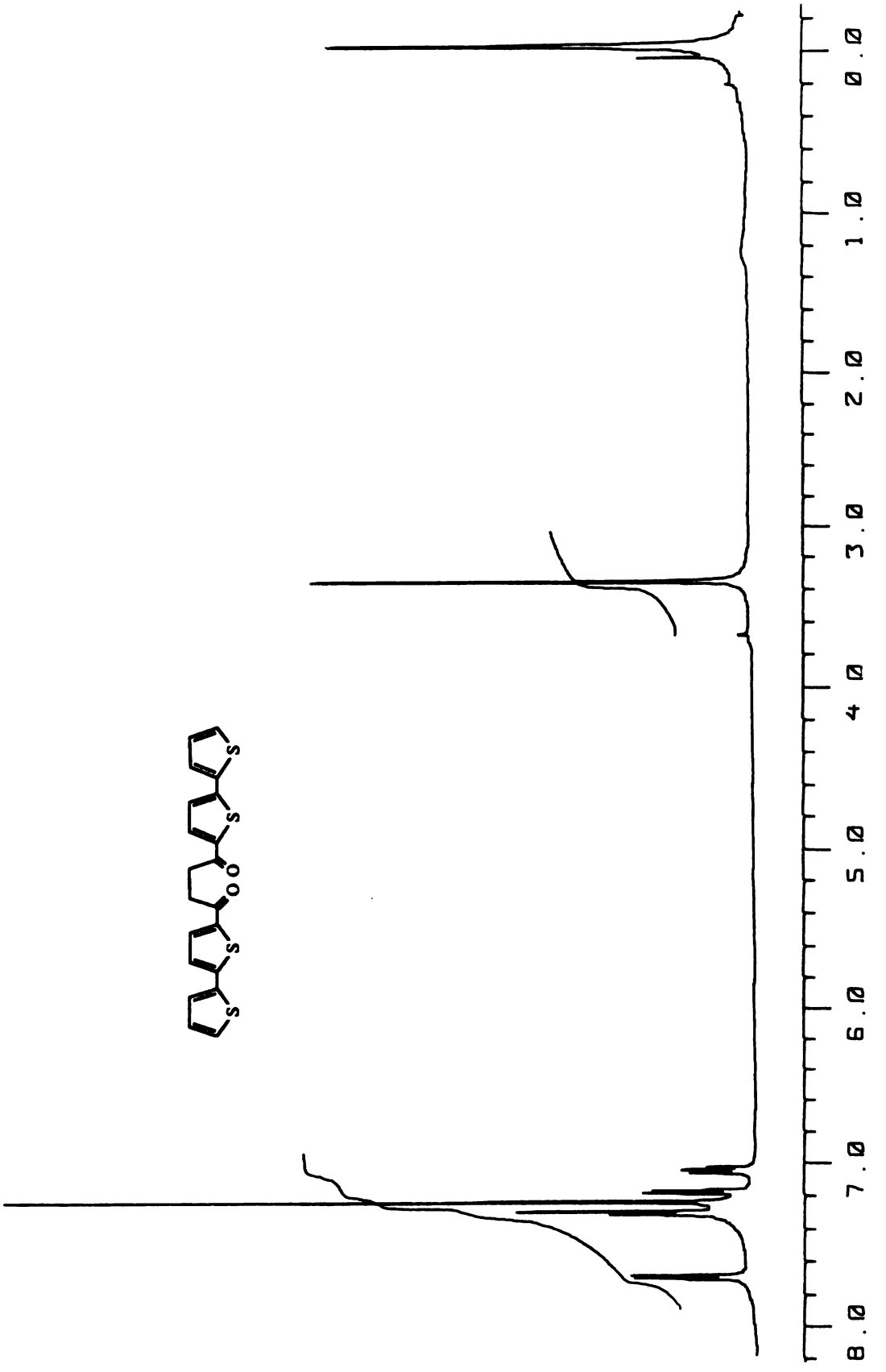


Figure 2. 250 MHz ^{1}H NMR spectrum of 1,4-Bis-(5-2,2'-bithienyl)-1,4-butanedione (32c)

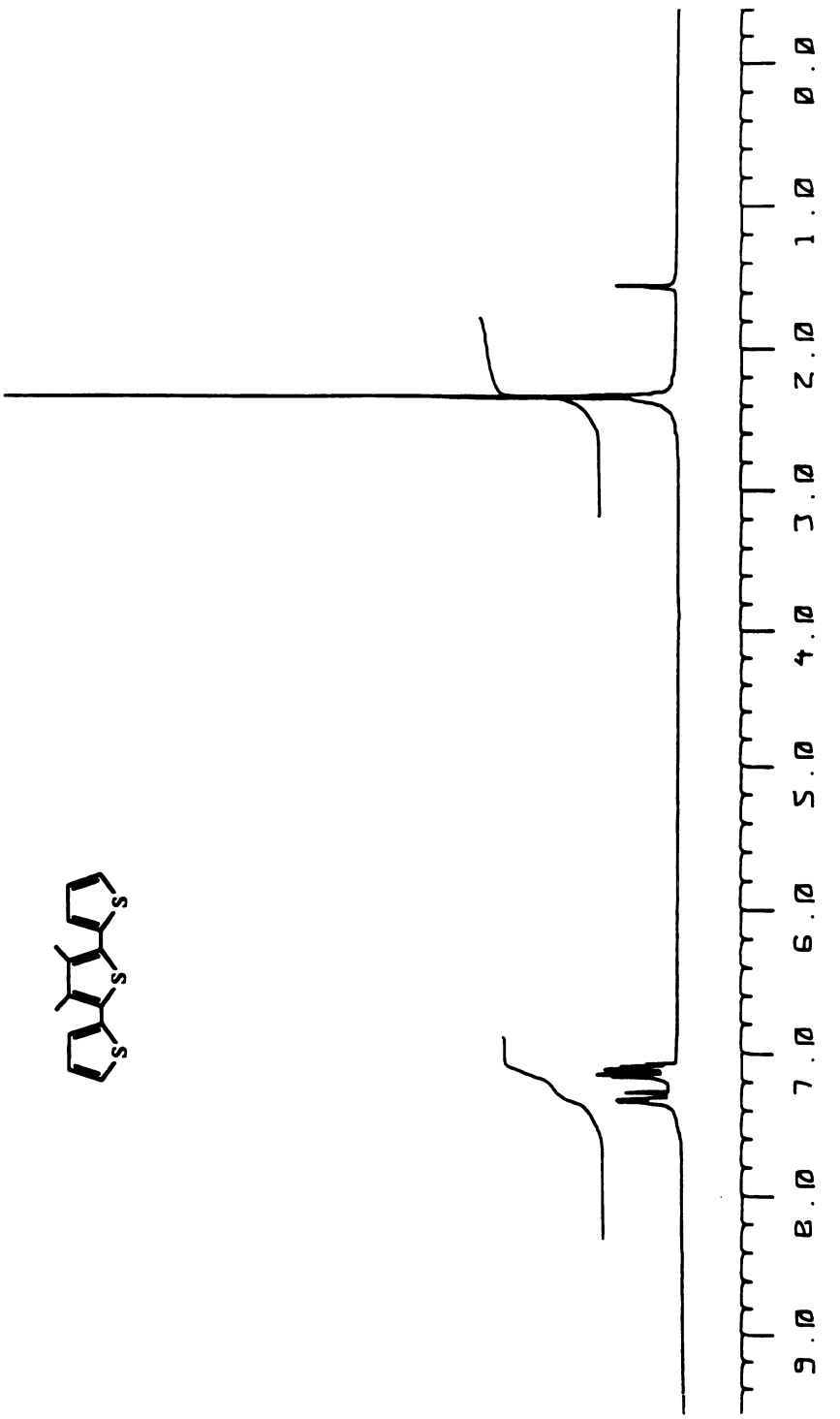


Figure 3. 250 MHz ^{1}H NMR spectrum of 3',4'-Dimethyl-2,2'-5',2"-terthienyl (50)

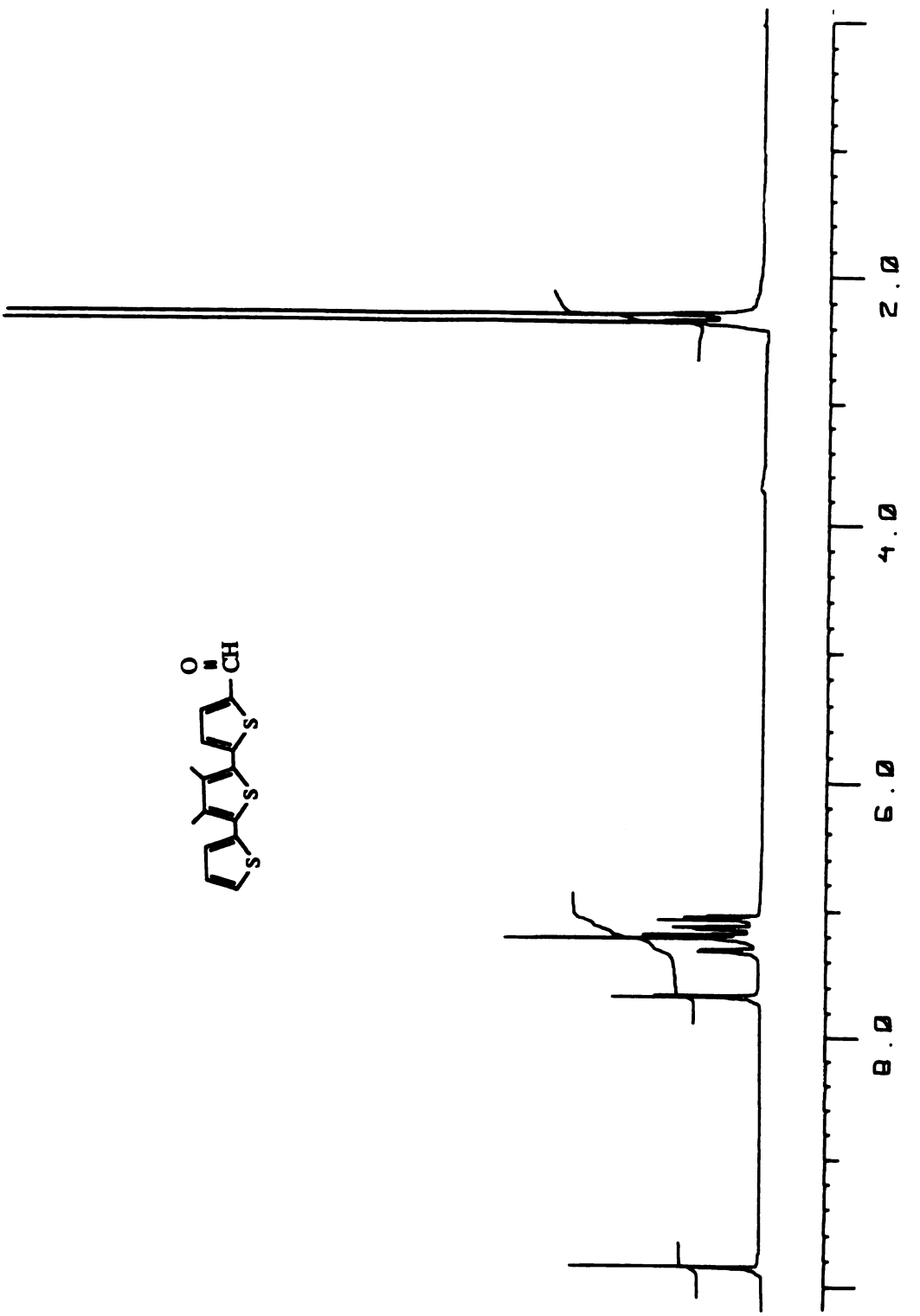


Figure 4. 250 MHz ^{1}H NMR spectrum of 5-Formyl-3',4'-dimethyl-2,2'-5',2"-terthienyl (53)

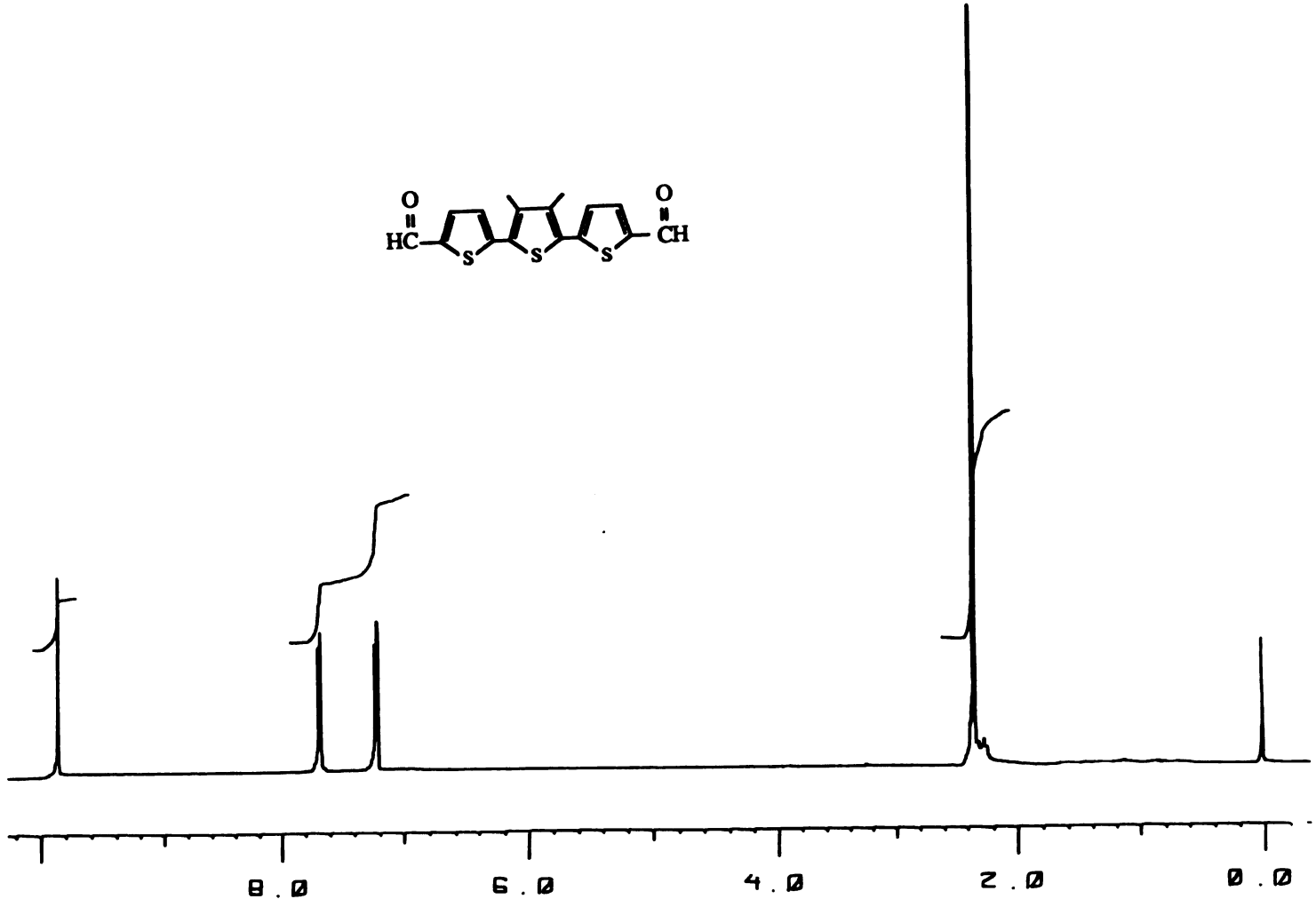


Figure 5. 250 MHz ^{1}H NMR spectrum of 5,5'-Diformyl-3',4'-dimethyl-2,2'-5',2"-terthienyl

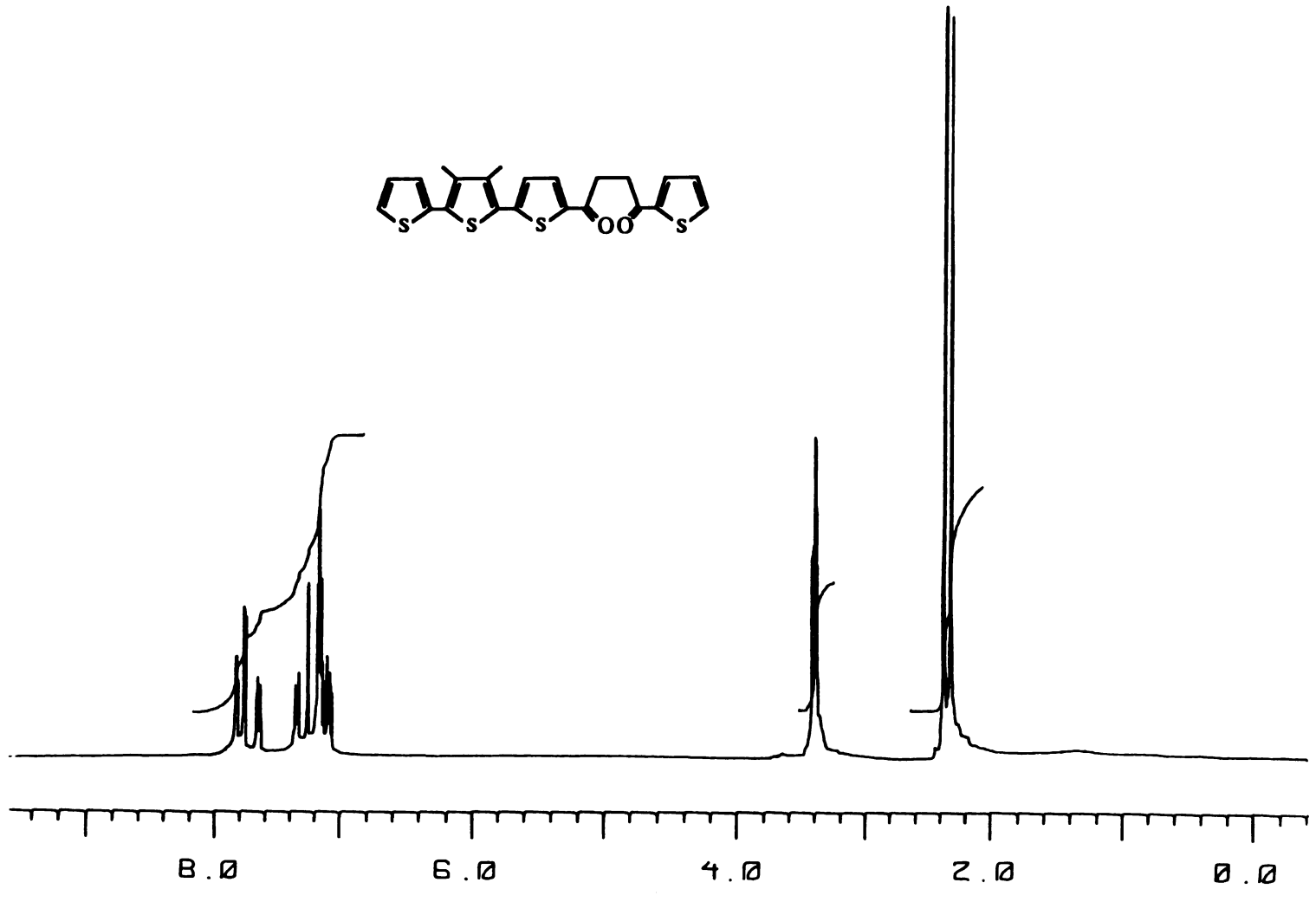


Figure 6. 250 MHz ^{1}H NMR spectrum of 1-(2-Thienyl)-4-(3',4'-dimethyl-2,2'-5',2"-terthienyl)-1,4-butanedione (54)

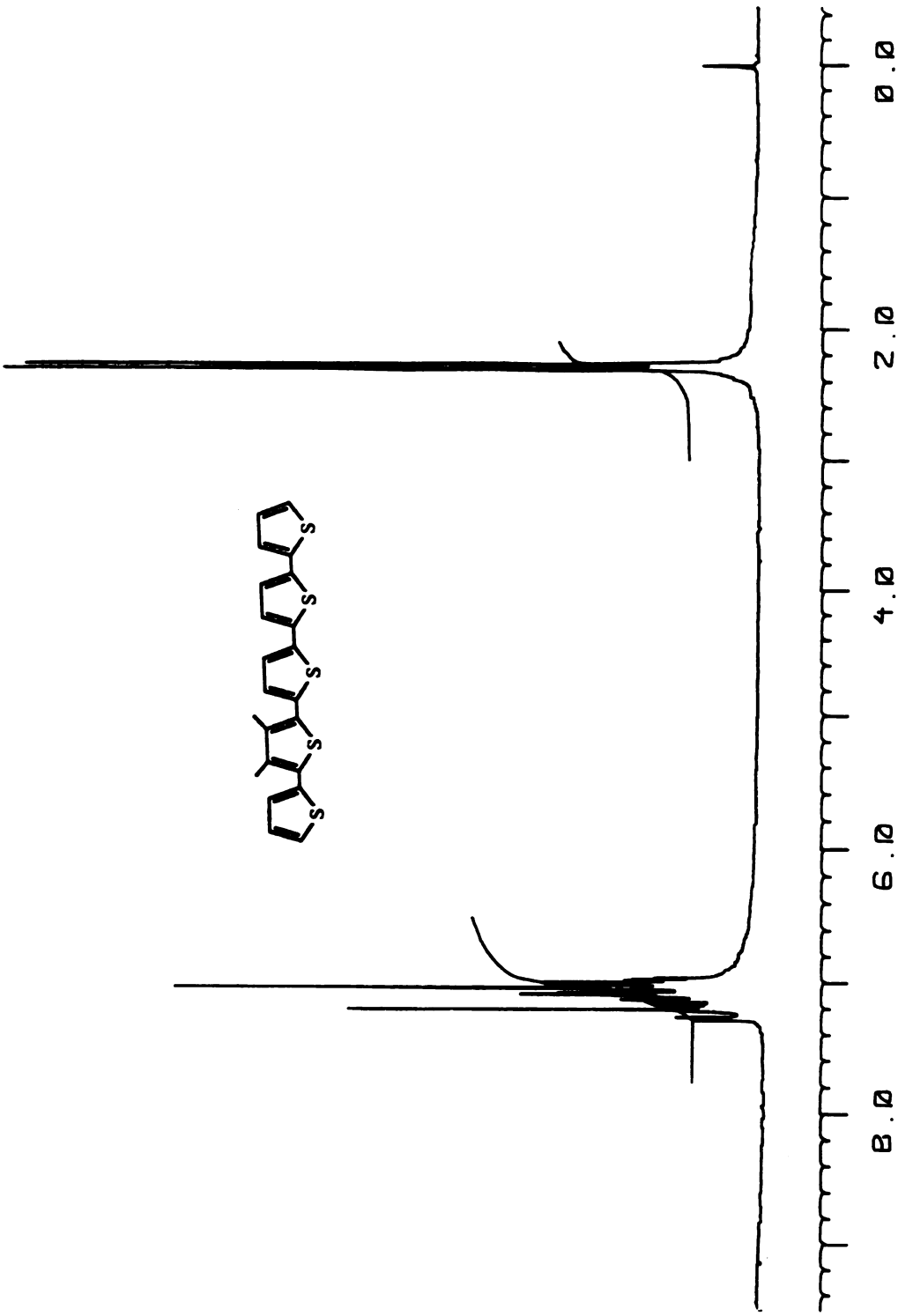


Figure 7. 250 MHz ^{1}H NMR spectrum of 3',4'-Dimethyl-α-quinquethienyl (55)

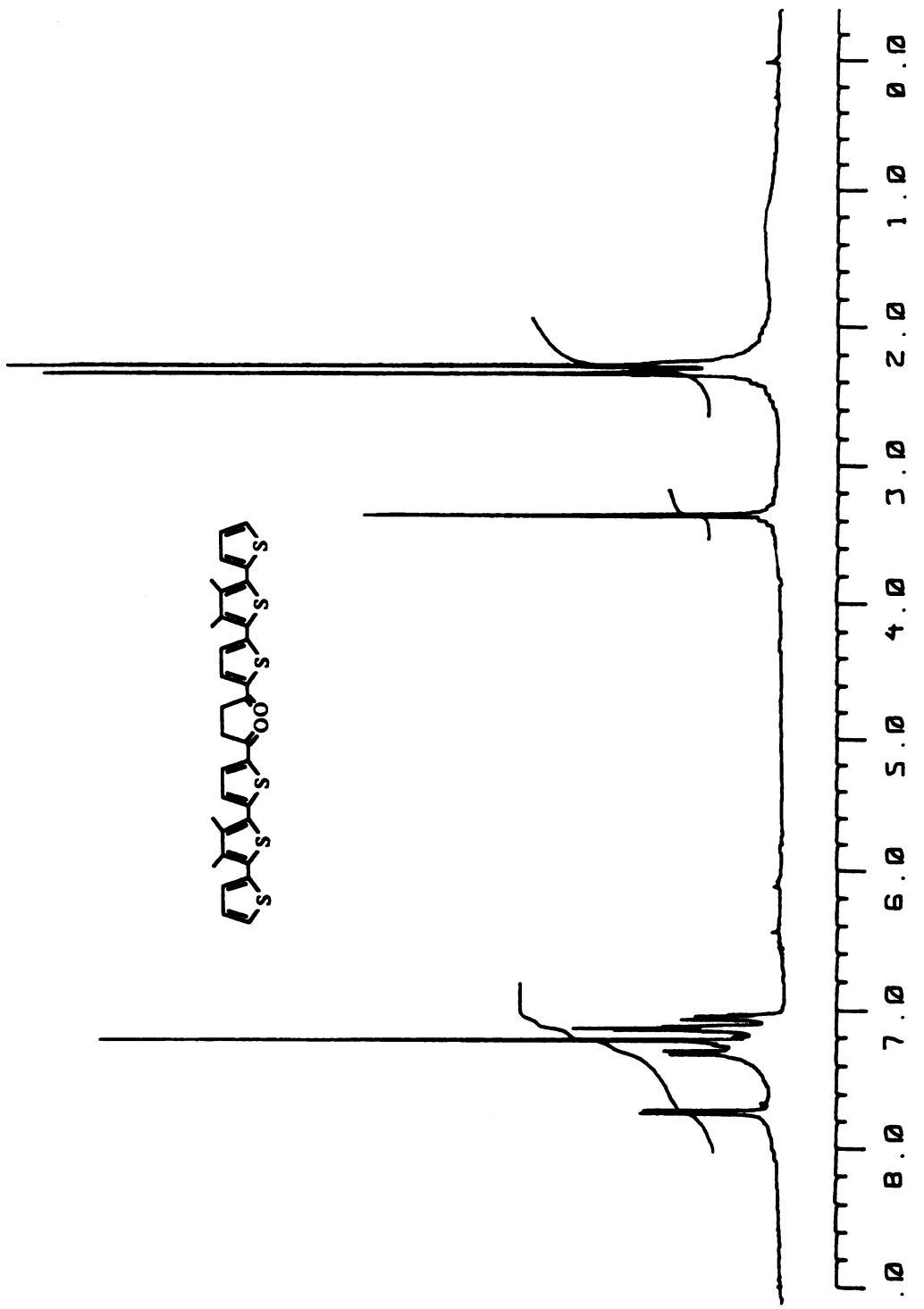


Figure 8. 250 MHz ^{1}H NMR spectrum of 1,4-Bis-(3',4'-dimethyl-2,2'-5',2"-terthienyl)- 1,4-butanedione (56)

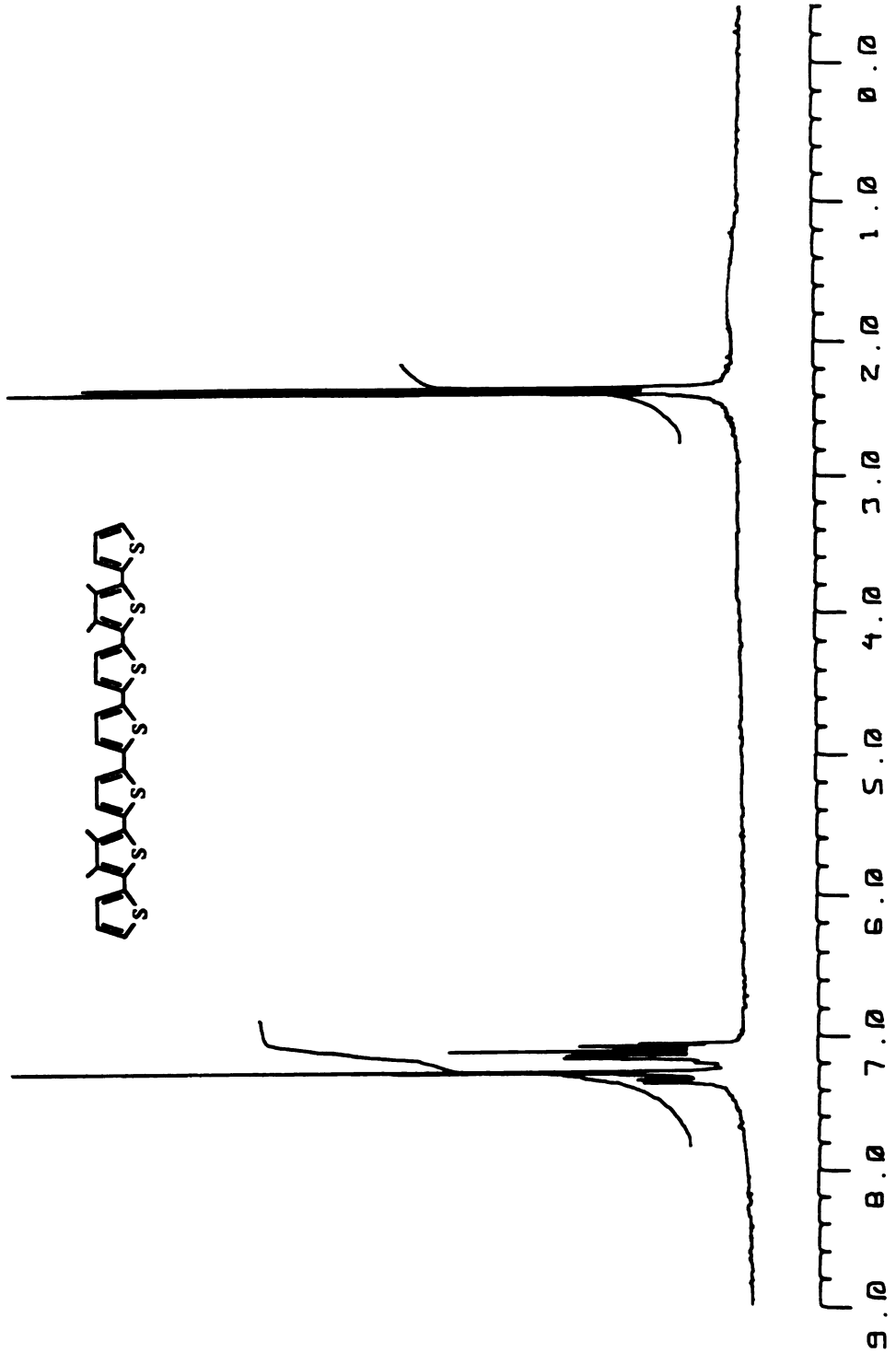


Figure 9. 250 MHz ^{1}H NMR spectrum of 2,5-Bis-(3",4"-dimethyl-2',2"-5",2'"-terthienyl)thiophene (57)

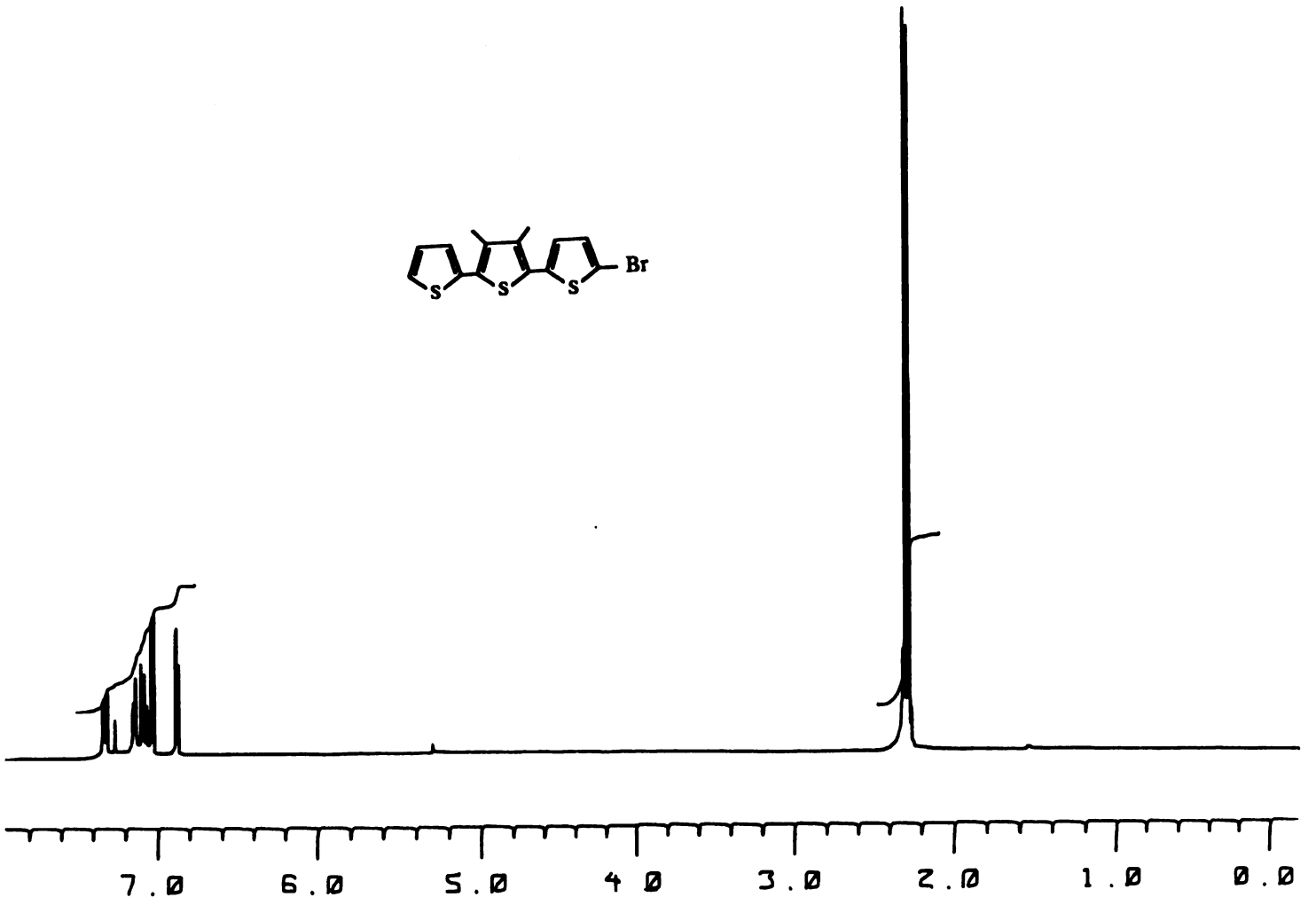


Figure 10. 250 MHz ^{1}H NMR spectrum of 5-Bromo-3',4'-dimethyl-2,2'-5'-2"-terthienyl (58)

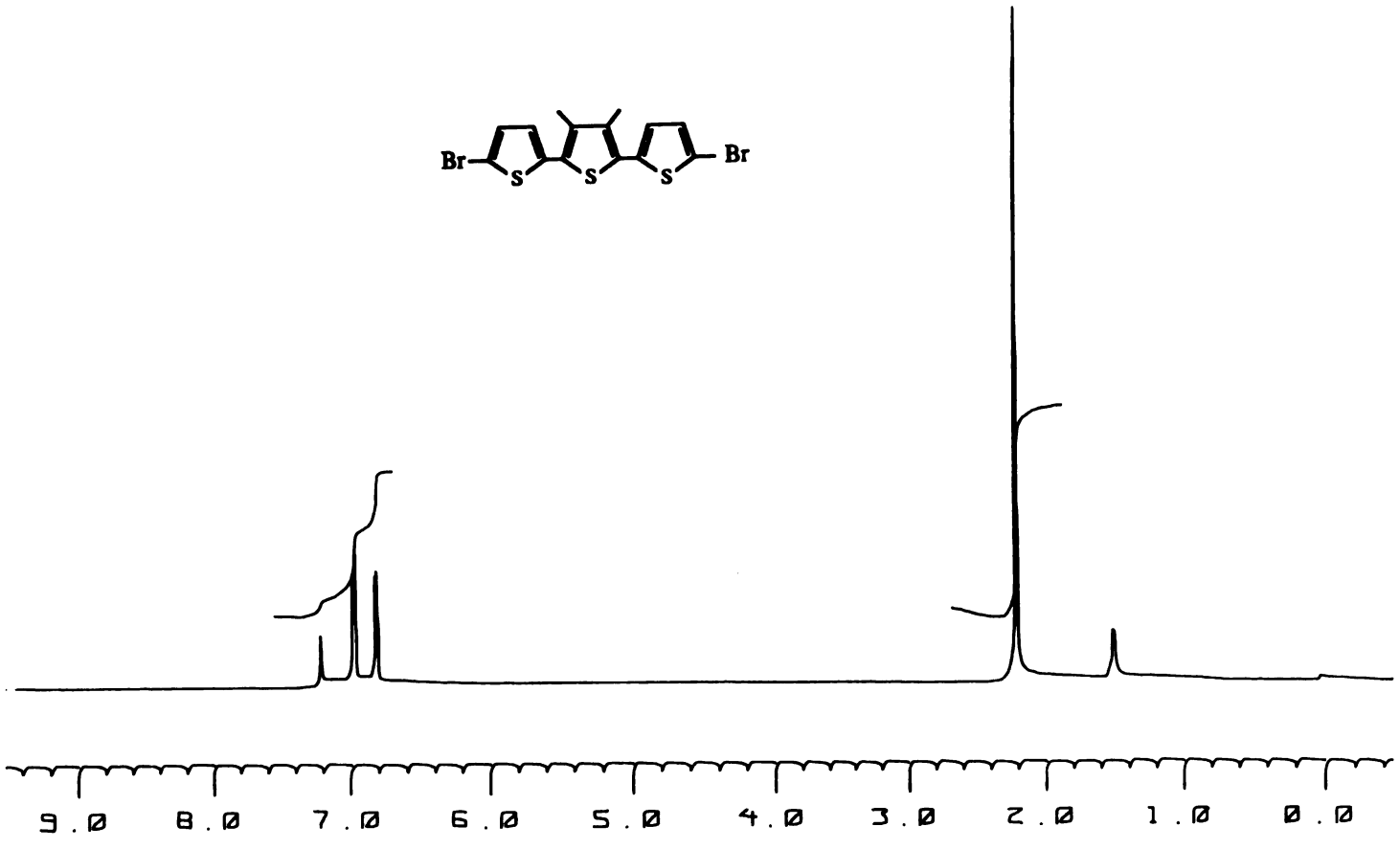


Figure 11. 250 MHz ^{1}H NMR spectrum of 5,5-dibromo-3',4'-dimethyl-2,2'-5'-2"-terthienyl (74)

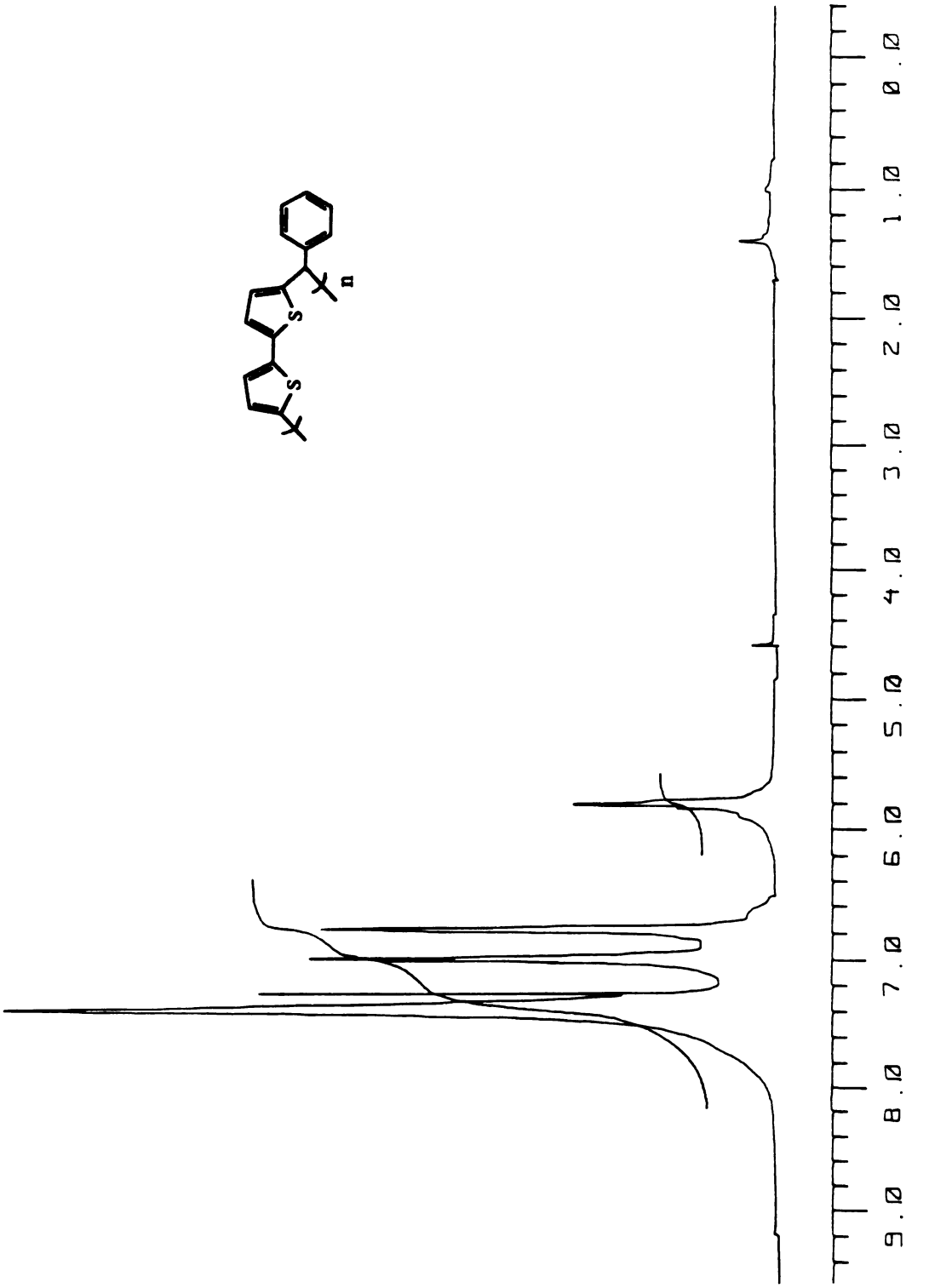


Figure 12. 250 MHz ^{1}H NMR spectrum of (64a)

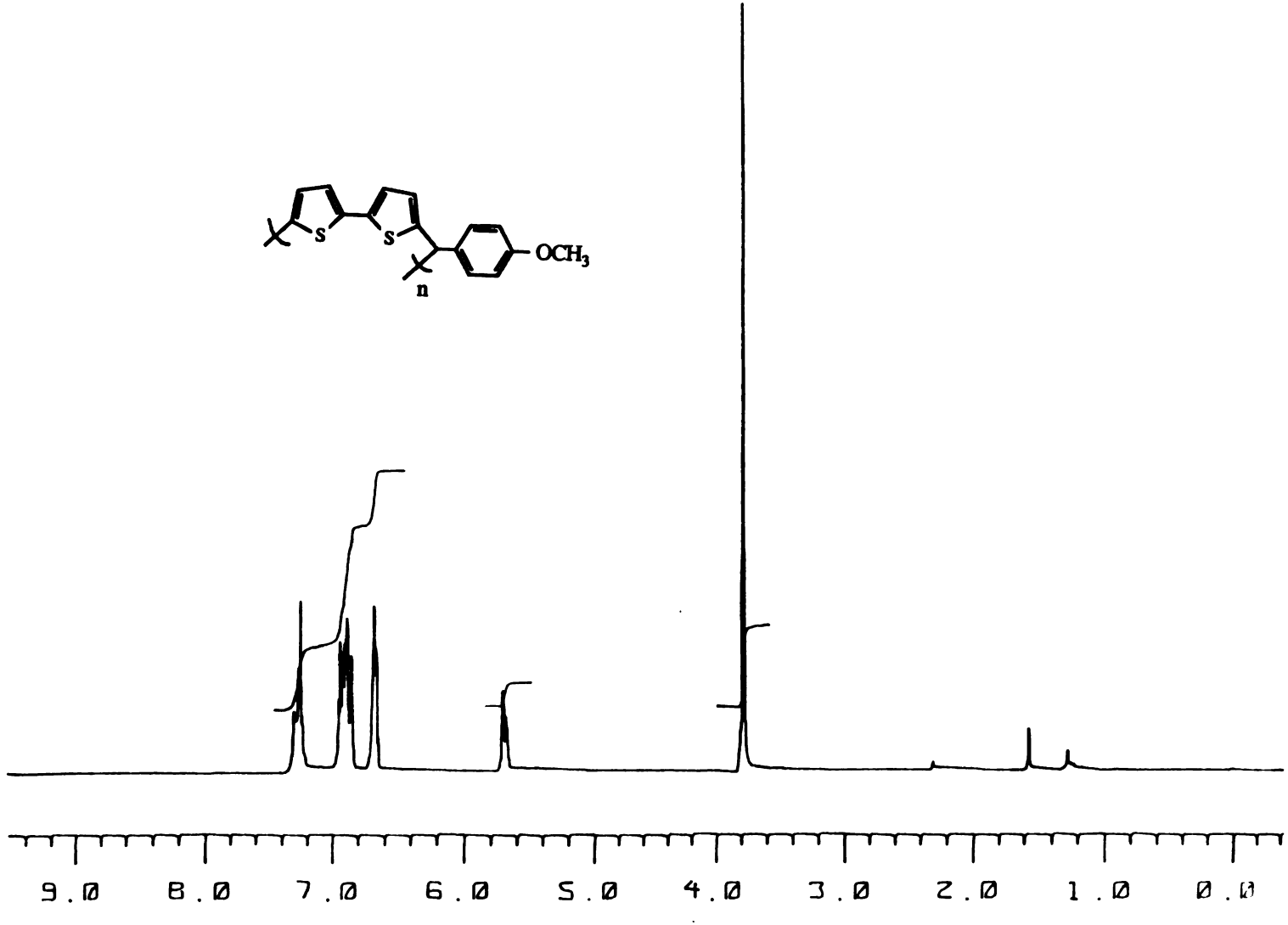


Figure 13. 250 MHz ^{1}H NMR spectrum of (64b)

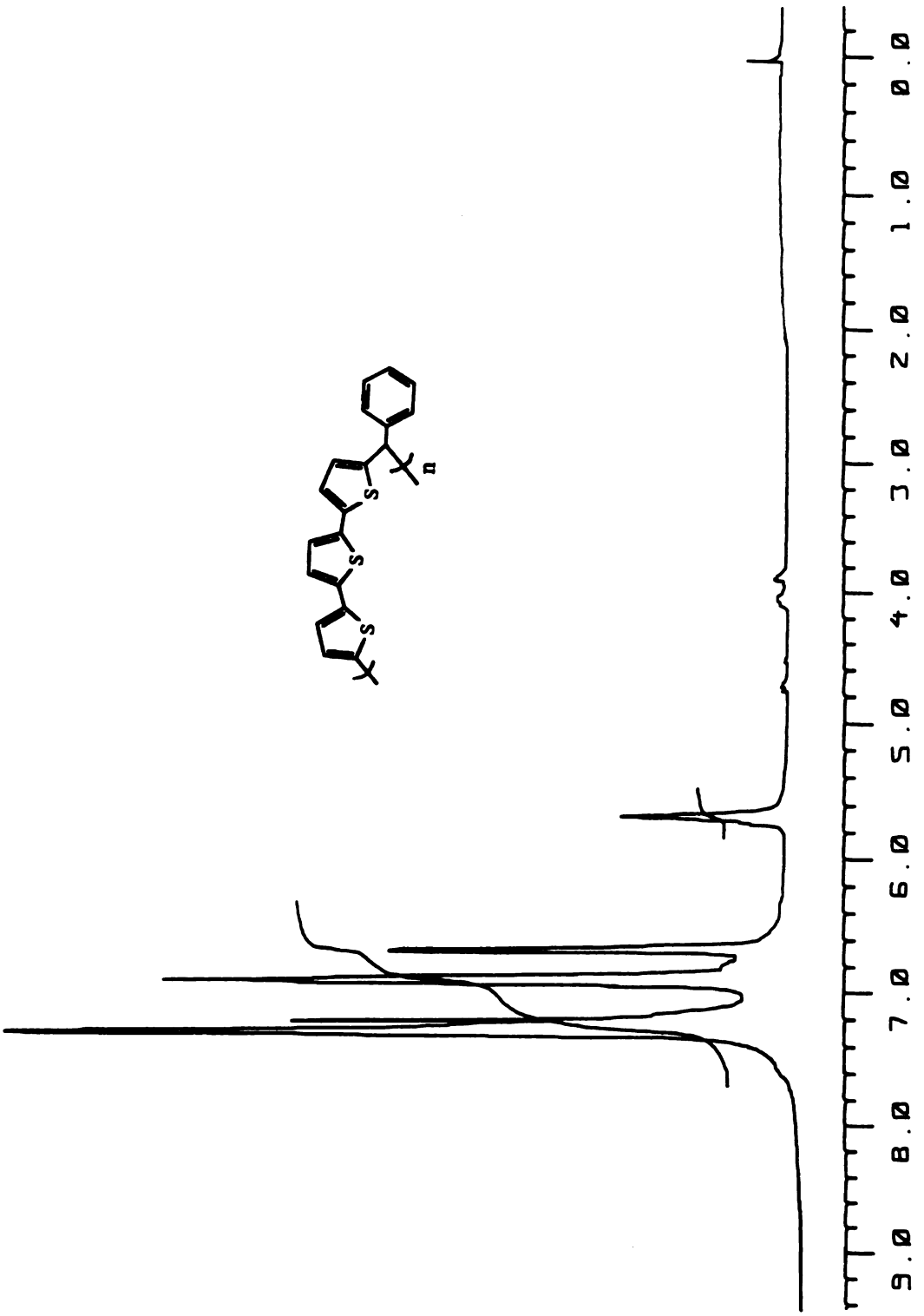


Figure 14. 250 MHz ^{1}H NMR spectrum of (64c)

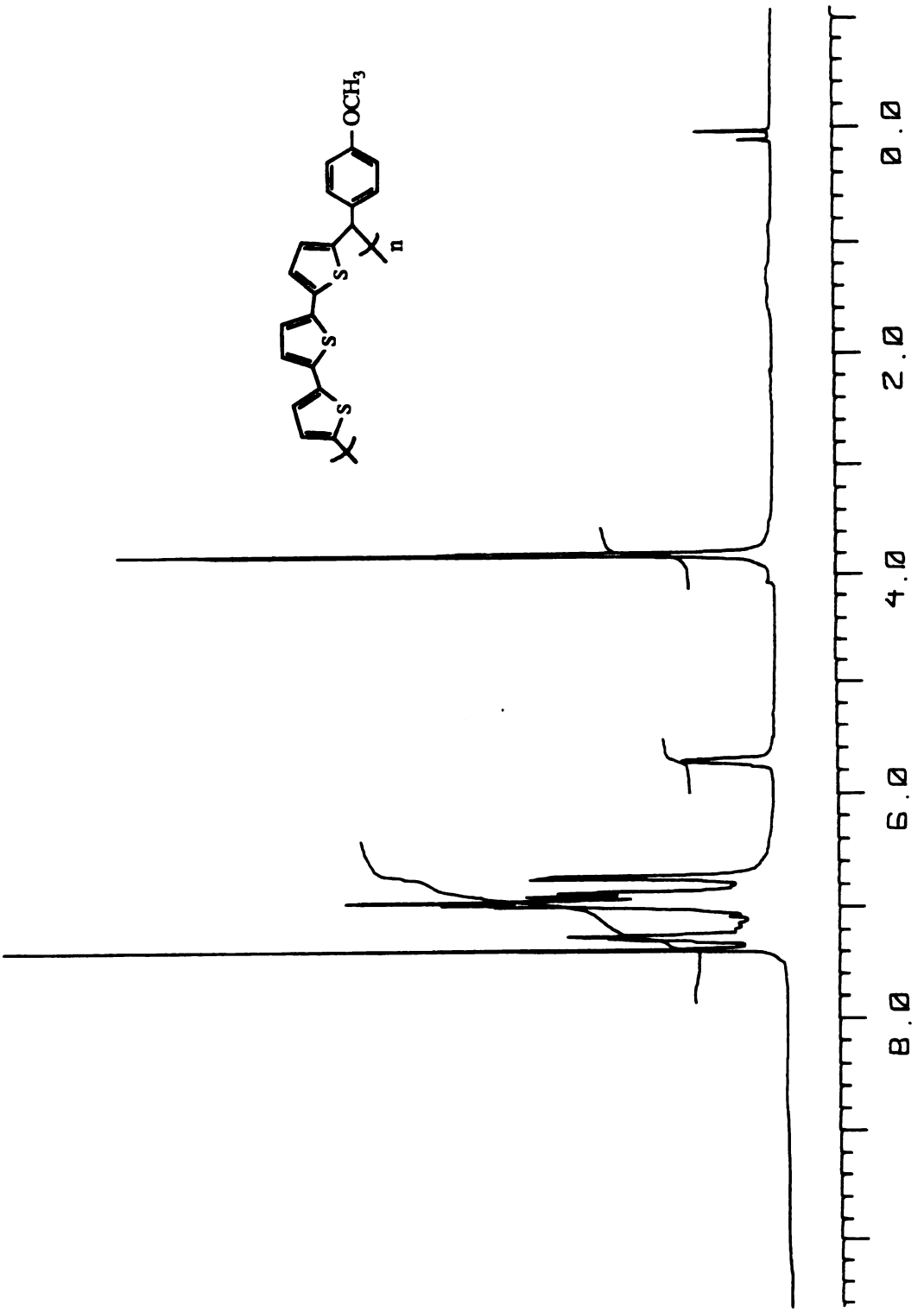


Figure 15. 250 MHz ^{1}H NMR spectrum of (64d)

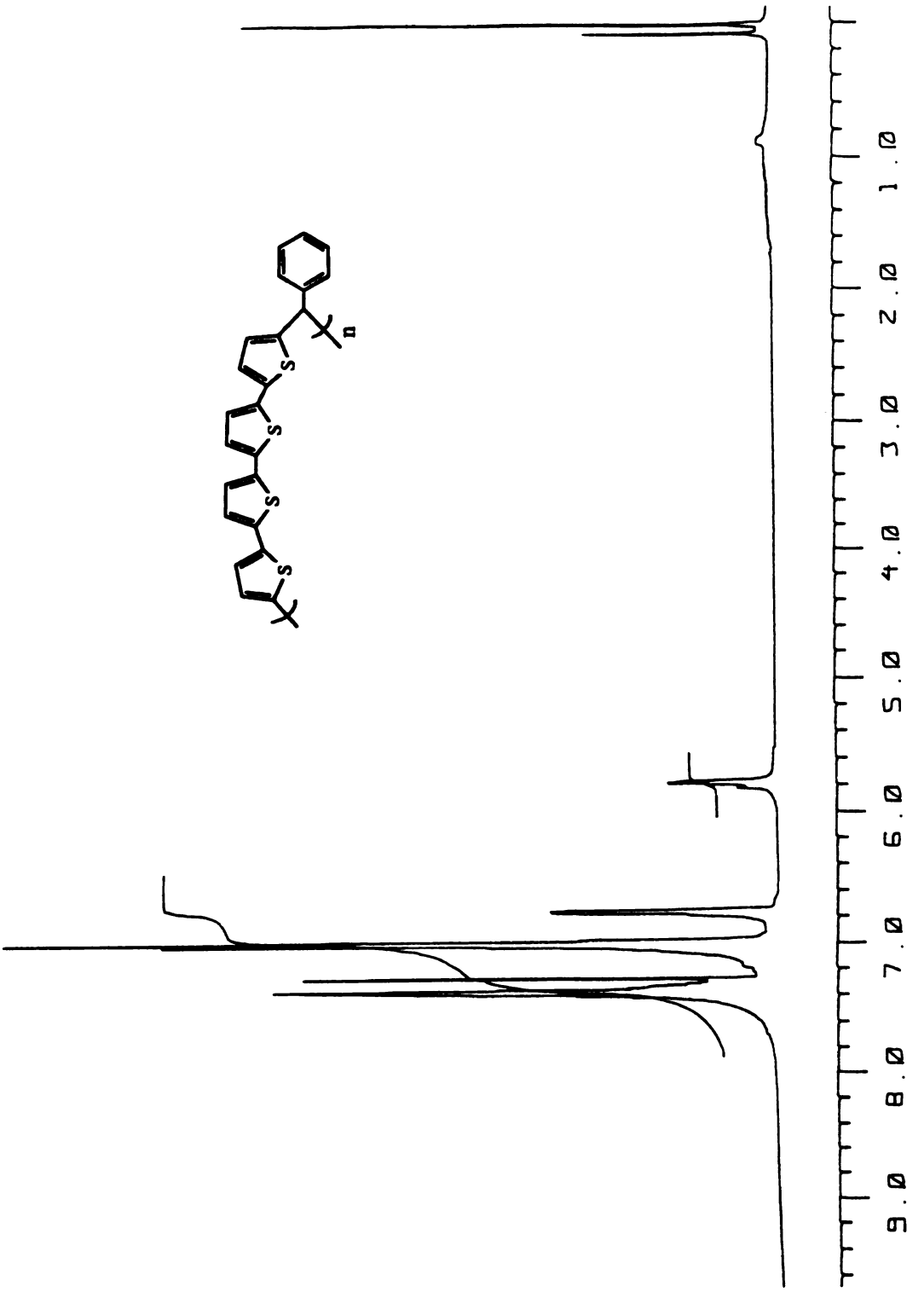


Figure 16. 250 MHz ^{1}H NMR spectrum of (64e)

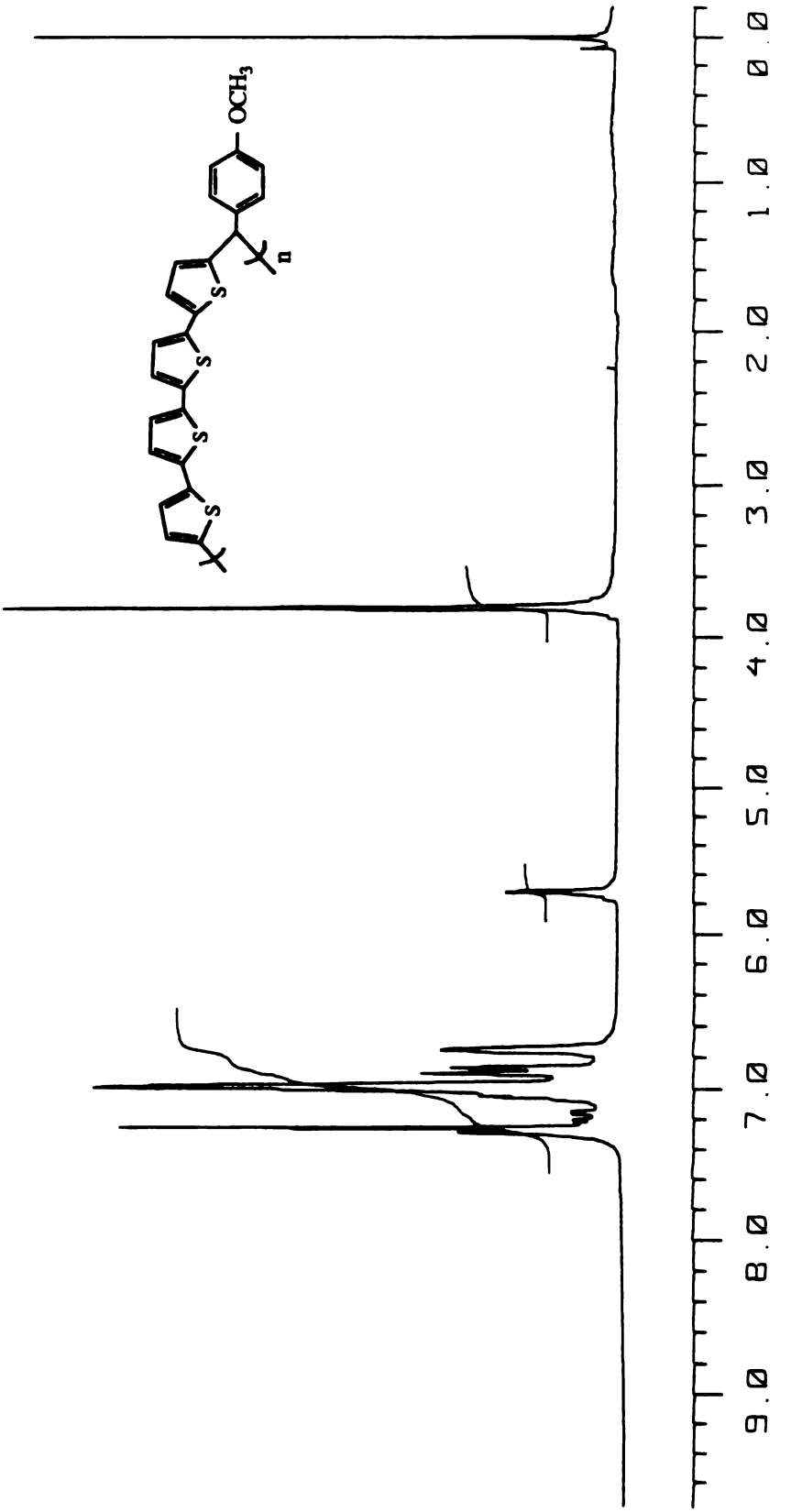


Figure 17. 250 MHz ^{1}H NMR spectrum of (64f)

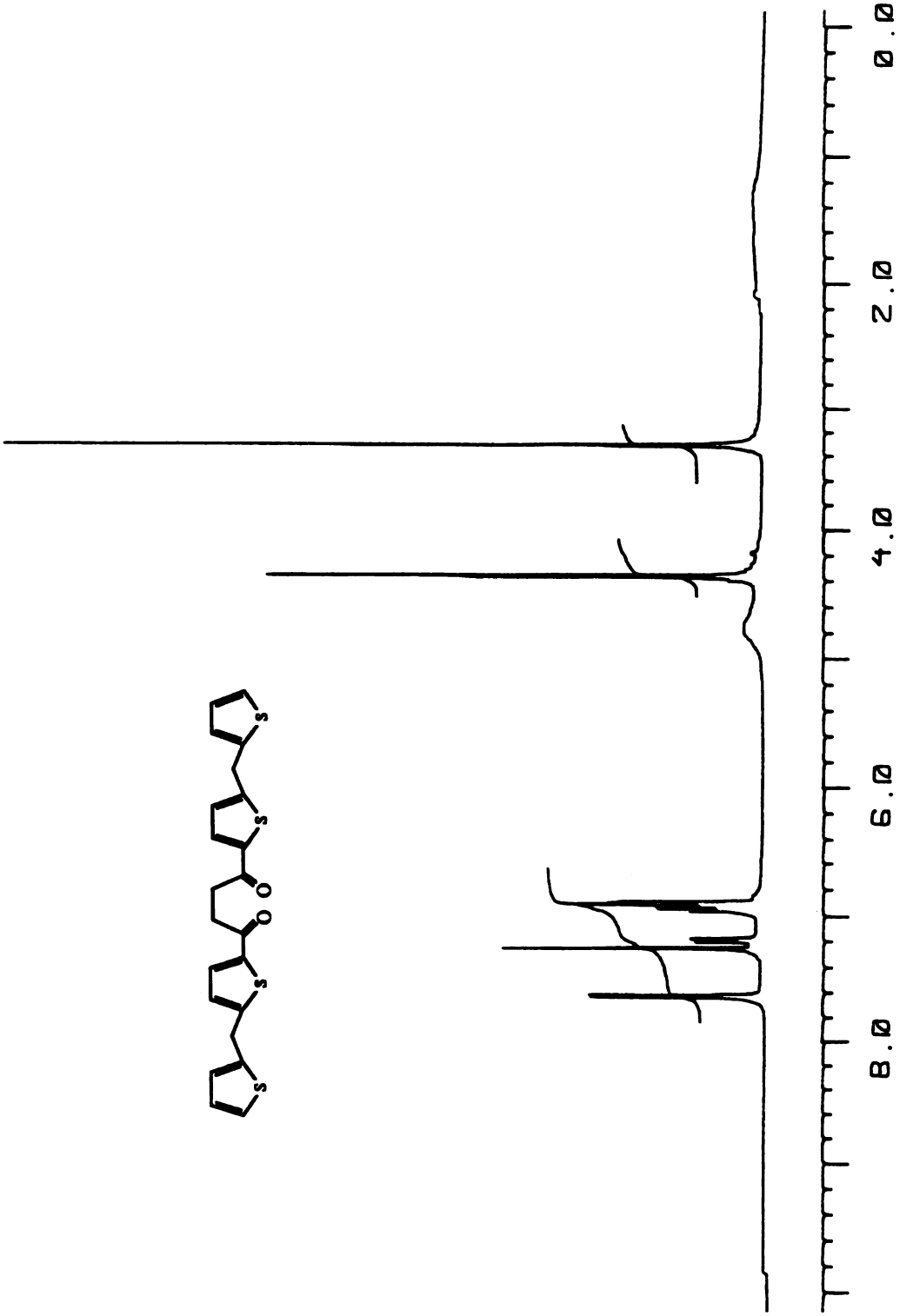


Figure 18. 250 MHz ^{1}H NMR spectrum of 1,4-bis(2,2-dithienylmethane)-1,4-diketone (73)

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BIBLIOGRAPHY

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50. The NMR spectra indicate an impurity of dioxane. *Anal.* Cacld. for $C_{24}H_{18}O_4S_4$ 0.5 dioxane C, 57.32; H, 4.46.

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