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SYNTHESIS OF LINEAR α-POLYFURANS
AND
SYNTHETIC APPROACHES TO POLYFURAN MACROCYCLES

presented by

Wai-Yee Leung

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of the requirements for

Ph.D degree in Chemistry

Eugene E. Galloff
Major professor

Date 1 August 1988

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SYNTHESIS OF LINEAR α-POLYFURANS

AND

SYNTHETIC APPROACHES TO POLYFURAN MACROCYCLES

By

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DOCTOR OF PHILOSOPHY

Department of Chemistry

1988

ABSTRACT

SYNTHESIS OF LINEAR α-POLYFURANS AND SYNTHETIC APPROACHES TO POLYFURAN MACROCYCLES

By

Wai-Yee Leung

The synthesis and the chemical properties of α-polyfurans are described. The conversion of α-terfuran **12** to the [26]annulene hexoxide **9** and macrocyclic α-polyfuran **10** has been investigated.

The 1,4-diketone precursors to α-polyfurans were prepared in the following ways: 1) Michael addition of aldehydes to Mannich bases, 2) Michael addition of aldehydes to vinyl sulfone and 3) nucleophilic addition of organolithium compounds to N,N,N',N'-tetramethylsuccinamide **19**. Cyclization of the 1,4-diketones by acid catalyst gave the α-polyfurans in fair yields. The α-polyfurans showed electrophilic and nucleophilic properties from which various monosubstituted and disubstituted derivatives can be obtained.

Condensation of the open-chain furan compound **55a** with benzaldehyde or **55b** with anisaldehyde in the presence of Lewis acid yielded a mixture of macrocyclic oligomers **42c** or **42d**. Oxidation of **42c** or **42d** to the 26 π-electron annulene hexoxide **9** was not successful.

Due to the solubility problem of the oligomeric intermediate which decreased rapidly as the molecular weight

increases, the synthesis of the macrocyclic α-polyfuran **10** from the simple precursors was also not successful.

To my wife, Ching-ying
for her love, support and understanding.

ACKNOWLEDGEMENTS

The author is greatly indebted to Professor Eugene LeGoff for his patience, guidance and encouragement during the course of research.

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INTRODUCTION

At an early stage in organic chemistry the characteristic differences in physical properties and chemical reactivity bewteen benzenoid hydrocarbons and their acyclic analogues led Kekule[1] to make his fundamental studies on the structure of benzene. Since that time, the theory of "aromatic character" has attracted the interest of organic chemists to an ever increasing degree. Alongside the benzenoid compounds numerous non-benzenoid heterocyclic and carbocyclic systems with very similar properties have appeared, which have robbed the classical aromatic substance, benzene, of its special position and have necessitated a wider and deeper definition of the concept of "aromatic character".

The theory of "aromatic character" has thereby undergone manifold changes. The empirical generalization of the "aromatic sextet"[2] was followed by Huckel's rule,[3] which was based upon quantum mechanical considerations. According to this rule, it predicts that those fully conjugated, planar, monocyclic polyolefins with [4n+2] π-electrons, where n is an integer, will have properties similar to those of benzene whereas those with [4n] π-electrons will not possess any aromatic stability. A shortcoming of this HMO theory is that it also predicts a sizable resonance energy for

cyclobutadiene and cyclooctatetraene even though this is not the case as proved experimentally [Figure 1].

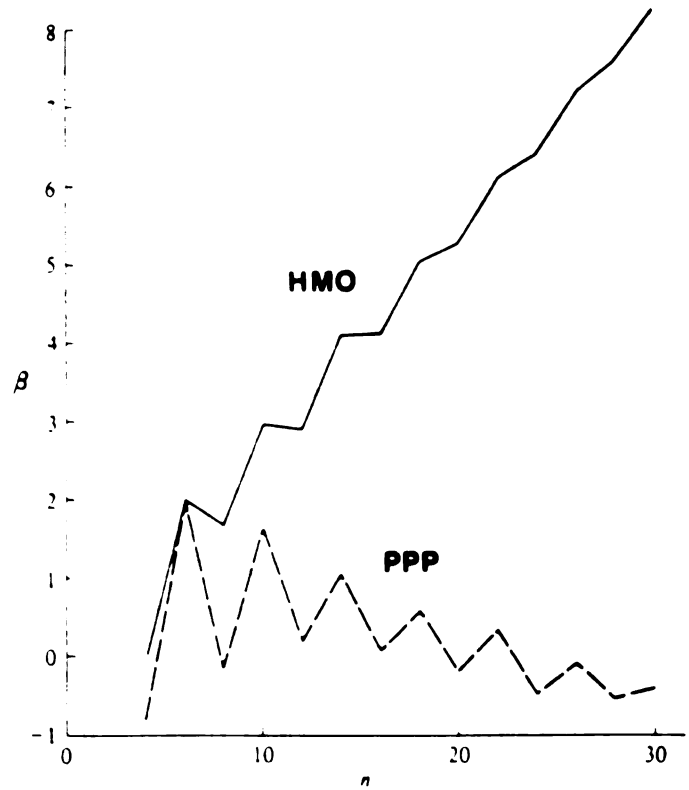


Figure 1. The delocalization energy (in β) calculated by the HMO and Pople-Pariser-Parr approximations for monocyclic conjugated systems.

To solve the quantitative discrepancies bewteen the theoretical and experimental results from the HMO method, Dewar[4] derived the resonance energy by using the Pople-Pariser-Par (PPP) approximation. From this calculation,

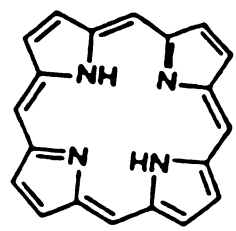
the [4n] system now have negative resonance energy and localized double bond whereas the [4n+2] system possesses positive resonance energy and is delocalized [Figure 1]. It also indicates that the Huckel's rule should break down at higher value of n, with the onset of bond alternation[5] and zero resonance energy, and it has been predicted that the limit should lie bewteen [22] and [26]annulenes.[4]

In order to provide an experimental test of these predictions, Sondheimer and his collaborators began, in 1965, to investigate the preparation of a number of annulenes. Using the proton NMR as the diagnostic test for aromaticity, it was found that [14],[6] [18][7] and [22][8] annulenes were diatropic while [24]annulene[9] was paratropic. The [26] and [28]annulenes have not been synthesised and although [30]annulene[10] has been prepared, its NMR spectrum was not studied. A monodehydro[26]annulene[11] has been synthesized and this compound did show a diamagnetic ring current. However, a tridehydro[26]annulene[12] has also been synthesized which showed no ring current effect. So there is still some argument as to whether or not a 26 π-electron system is aromatic. A problem associated with these large ring monocyclic compounds is their conformational mobility which might not give any diatropic effect if the molecules are in a non-planar conformation.

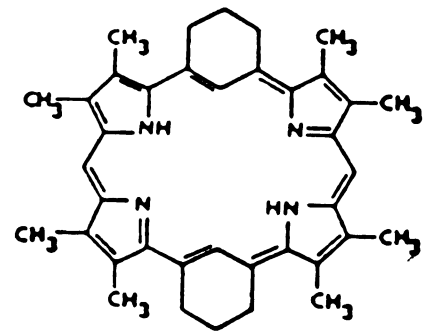
An ideal molecule for aromatic study should have a rigid and planar framework. This can be achieved if pairs of internal hydrogen atoms in the annulenes are replaced by

heteroatoms. In this case, the peripheral conjugation is not perturbed significantly and again systems containing [4n+2] peripheral π-electrons exhibit aromaticity. Perhaps the best known example for this class is the porphrin molecule **1**. Porphyrins are stable 18 π-electron systems and aromatic in character. The expansion of the porphyrin macrocycle to [22] and [26]platyrins, **2**[13] and **3**[14], by formally inserting three and five carbons atoms between the pyrrolic rings has been reported from this laboratory. Both **2** and **3** showed significant diamagnetic ring current in an applied magnetic field. Besides nitrogen, the use of oxygen as the bridging atom has also been studied. The [18]annulene trioxide **4**[15] and the [18]annulene dioxide **5**[16] have proved to be aromatic while the [24]annulene tetraoxide **6**[17] was anti-aromatic. Macrocycles **7** and **8** that contained furan and pyrrole rings have been synthesized[18] and also found to be diatropic.

Because the literature contains so few 26 or more π-electron systems, a study of their synthesis would provide a better understanding of the concept of aromaticity. The compounds of interest in the present study are the [26]annulene hexoxide **9** and cyclic α-polyfuran **10**. While the furan ring imposes the rigidity to the carbon framework, molecular model of **9** reveals that the compound can adapt a planar conformation without much steric and angle strain, hence this might lead to cyclic delocalization and a peripheral diamagnetic ring current. For the class of compounds such as **10**, they might provide some insight as to



1



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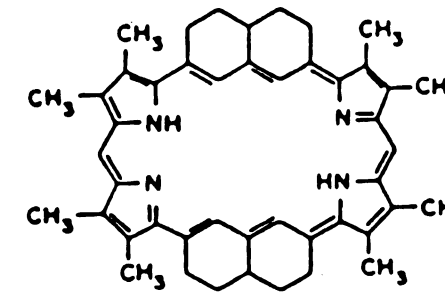

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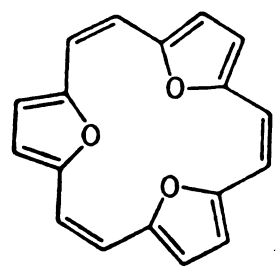

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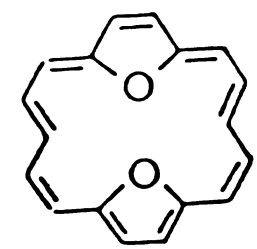

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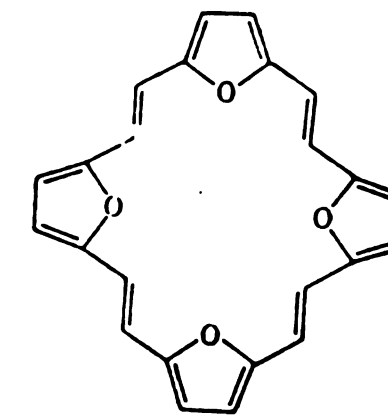

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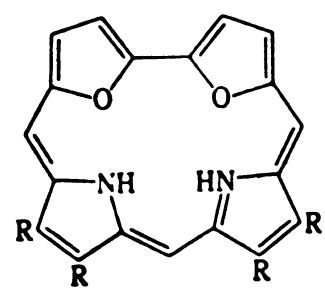
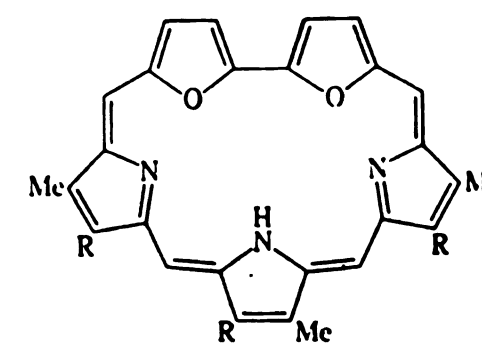
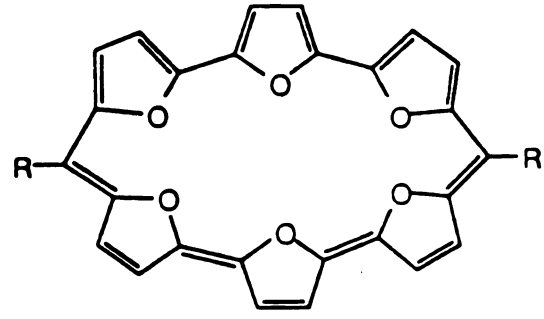


7 R=Me, Et



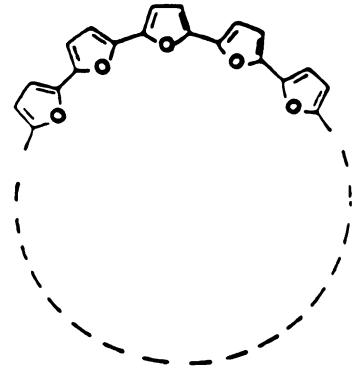
8 R=Me, Et

what stage (if at all) a [4n] π-electron system will cease to be paratropic.



R = H, alkyl or aryl

9



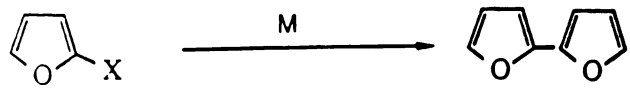
10

A closer look at **9** shows that it consists of the α-terfuran structural unit while **10** actually is the cyclic form of linear α-polyfuran, so a logical synthetic approach to **9** and **10** would come from the linear α-polyfuran.

Unlike its heavy congener, the α-polythienyls, that has been studied in great detail due to their bioactivities and physicochemical properties,[19,20] the linear α-polyfuran only received little attention in the literature. A few studies on the syntheses of α-bi, α-ter and α-quaterfurans have been reported,[21] but α-quinque, α-sexi and α-septifurans are still unknown.

The α-bifuran **11** was basically prepared from the oxidative coupling of the furylmetallic compound in the presence of catalytic or stiochiometric amount of transition

metal salt [Scheme 1].

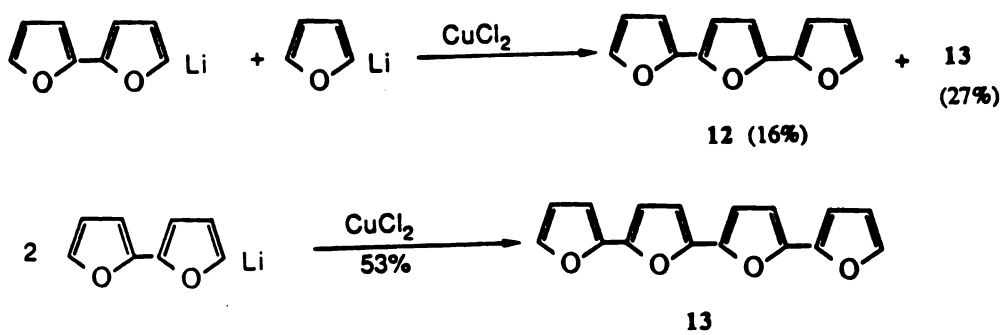


11

X	M	11(%)	Ref
HgOAc	Cu, $PdCl_2$	86	21a
HgCl	$[ClRh(CO)_2]_2$, LiCl	70	21b
Li	$CuCl_2$	85	21c
MgI	$CoCl_2$	30	21d

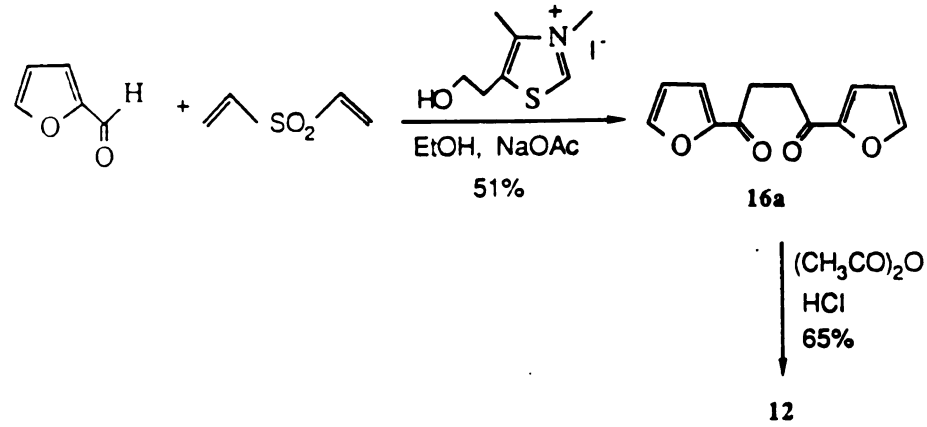
Scheme 1

The extension of this oxidation coupling reaction by copper(II) chloride has led to the synthesis of α-terfuran 12 and α-quaterfuran 13[21c] [Scheme 2].



Scheme 2

Recently, Descotes[21f] reported the addition of vinyl sulfone to furfural in the presence of a thiazolium salt to give the 1,4-diketone **16a** which undergo dehydrative cyclization to α-terfuran **12** in 33% overall yield [Scheme 3].



Scheme 3

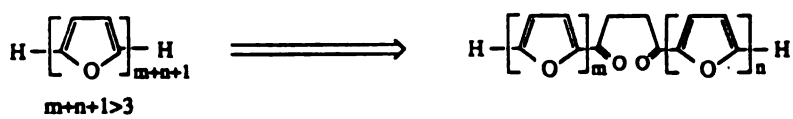
Because of such little and scattered studies, the potential of α-polyfurans as an organic conductor remains totally unexplored.

There are two goals in this work. Firstly, the synthesis of the linear α-polyfurans and the study of some of their chemistry. Secondly, the incorporation of the linear α-polyfurans into large ring macrocycles which may ultimately lead to **9** and **10**.

RESULTS AND DISCUSSION

A. Synthesis of linear α-polyfurans

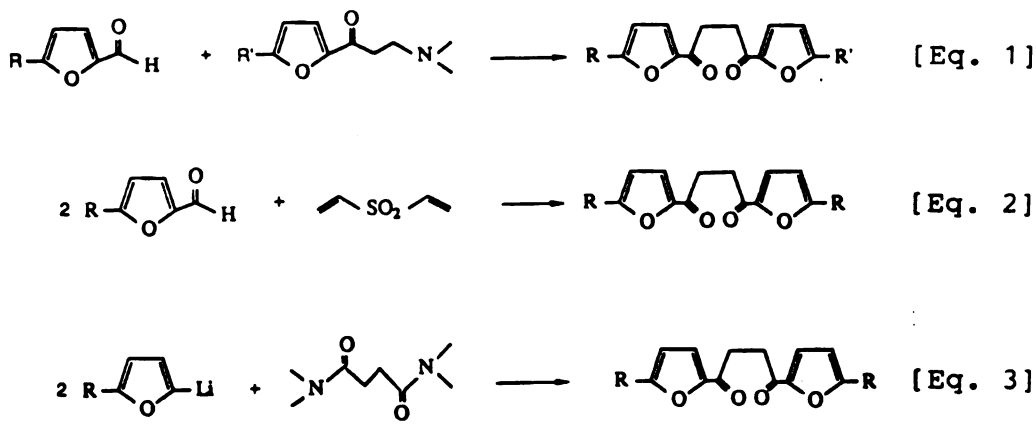
In this study, the synthetic approach to the linear α-polyfurans is based on the dehydrative cyclization of the 1,4-dicarbonyl compounds [Scheme 4]. We believe this is the general approach to both odd and even number of α-polyfurans. Furthermore, the presence of many dehydration methods[22] that might effect this cyclization also makes this approach more attractive. So the problem remaining is the preparation of the symmetrical (m=n) and unsymmetrical (m≠n) 1,4-butanedione precursors.



Scheme 4

Although there is a large number of synthetic methods for the 1,4-diketones in the literature,[23] only three different approaches that are suitable in the present study have been investigated. Their net transformations are summarized in Scheme 5. The first approach provides the 1,4-diketones from the Michael addition of aldehydes to the Mannich bases [Eq.1].

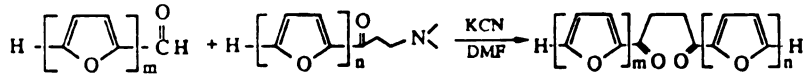
The second approach involves the Michael addition of aldehydes to vinyl sulfone [Eq. 2]. The third approach to the 1,4-diketones comes from the reaction of the organolithium compounds with the N,N,N',N'-tetramethylsuccinamide [Eq. 3]. One obvious point can be made immediately from these different synthetic pathways, namely the first approach may provide access to both symmetrical (R=R') and unsymmetrical (R≠R') 1,4-dicarbonyl compounds while both the second and third approaches give convenient entry to the symmetrical 1,4-diketones.



Scheme 5

The Michael addition of aldehydes to α,β-unsaturated ketones or Mannich bases in the presence of cyanide as catalyst has been utilized by Stetter for the general synthesis of 1,4-diketones.[24] Indeed, we have already used this method as an efficient way to the synthesis of

α-polythienyls with excellent yields.[25] So an extension of this method to the preparation of α-polyfurans via the 1,4-diketones is worth studying.



14a m=1
14b m=2
14c m=3
14d m=4

15a n=1
15b n=2

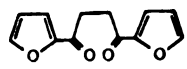
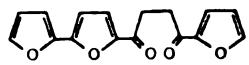
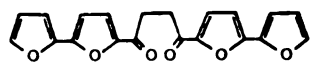
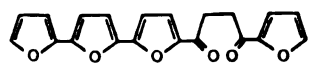
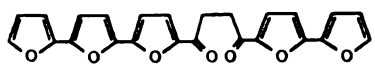
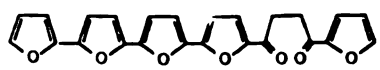
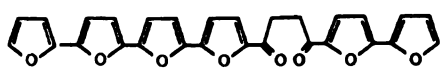
16a m=n=1 (9%)
16b m=2, n=1 (63%)
16c m=n=2 (68%)
16d m=3, n=1 (59%)
16e m=3, n=2 (53%)
16f m=4, n=1 (40%)
16g m=4 , n=2 (51%)

Scheme 6

The furfural **14a** reacted with the 3-dimethylamino-1-(2-furyl)-propanone **15a** in dry DMF in the presence of KCN at room temperature gave the 1,4-diketone **16a** in disappointing low yield (9%). Surprisingly, this Mannich base **15a** reacted with other aldehydes **14b-14d** to give the corresponding 1,4-diketones (**16b, 16d, 16f**) in fair to good yields [Scheme 6]. The 1,4-diketone compounds (**16c, 16e, 16g**) were also obtained in comparable yields when the Mannich base was changed to 3-dimethylamino-1-(5-2,2'-bifuryl)-propanone **15b** [Scheme 6]. The structures and the melting points of the 1,4-diketones were shown in Table 1.

The reason for the low yield of the reaction bewteen furfural **14a** and the Mannich base **15a** is unclear. Stetter

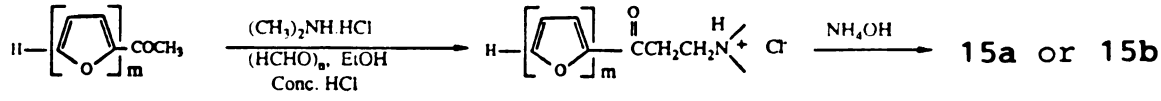
Table 1 1,4-Diketones from Aldehyde and Mannich base

1,4-diketone	m.p. (°C)
 **16a**	130-131
 **16b**	98-99
 **16c**	151-152
 **16d**	137-139
 **16e**	150-152
 **16f**	168-169 (dec)
 **16g**	165 (dec)

has mentioned this reaction in a review paper[24a] but the yield was not reported.

The Mannich bases, **15a** and **15b**, used in here were synthesized from the reaction of 2-acetylfuran **17a** or 5-acetyl-2,2'-bifuran **17b** with paraformaldehyde, dimethylamine hydrochloride and concentrated hydrochloric acid in ethanol solution [Scheme 7]. An attempt to prepare the Mannich base from 5-acetyl-2,2':5',2''-terfuran **17c** failed.

Only **17c** was recovered quantitatively after the reaction. The necessary aldehydes, **14b-14d**, were synthesized from the Vilsmeier reaction of the corresponding α-polyfurans (*Vide infra*).



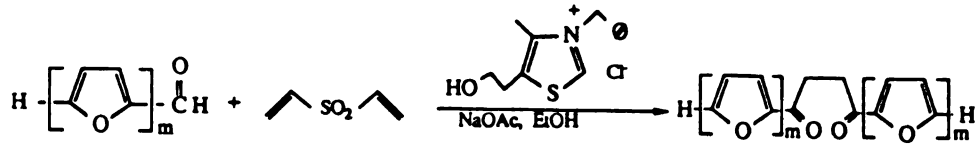
17a m=1
17b m=2
17c m=3

18a m=1 (68%)
18b m=2 (45%)

Scheme 7

At first, we anticipate to prepare both symmetrical and unsymmetrical 1,4-diketones from this cyanide catalyzed Michael addition reaction. But the low yield of **16a** and the failure to prepare the Mannich base from **17c** prompted us to make the symmetrical 1,4-diketones by other means.

One solution to the symmetrical 1,4-diketones came from the thiazolium salt catalyzed addition of aldehydes to vinyl sulfone [Scheme 8], a reaction that was also well studied by Stetter.[26] This reaction is mechanistically parallel to the cyanide catalyzed 1,4-diketone synthesis except in this



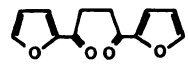
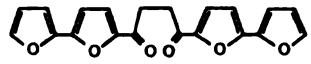
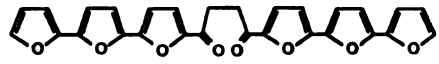
14a m=1
14b m=2
14c m=3
14d m=4

16a m=1
16c m=2
16h m=3
16i m=4

Scheme 8

case, the thiazolium salt exerts the catalytic effect in the presence of a base. In this reaction, the vinyl sulfone was added dropwise to a hot ethanolic solution containing the aldehyde, thiazolium salt (3-benzyl-5-(2-hydroxyethyl)-4-methyl-thiazolium chloride) and sodium acetate. After the mixture was refluxed overnight or 24h, the desired 1,4-diketones can be isolated in fair to good yields [Table 2]. The side product polysulfone can be separated easily by simple filtration. This reaction did not work when applied to 5-bromofurfural, thus limited access to 5,5'-disubstituted 1,4-diketone.

Table 2. 1,4-Diketones from aldehydes and vinyl sulfone

1,4-diketone	yield (%)	m.p. (°C)
 **16a**	66	130-131
 **16c**	50	151-152
 **16h**	63	208-210
 **16l**	28	242-245 (dec)

Unlike the above two methods which led to the 1,4-diketones from the furan derivatives, the second way to the symmetrical

1,4-diketones derived directly from the heteroaromatic nucleus. At the beginning, we were interested in the synthesis of 1,4-diketones from the Lewis acid catalyzed reaction bewteen succinyl chloride or fumaryl chloride with furan. Due to the acid sensitive nature of furan, the Lewis acid employed was alkylaluminum chloride which can also function as proton scavenger. Unfortunately, this study gave fruitless results under various reaction conditions (-78°C up to room temperature in dichloromethane or ether as solvent). Only in one case could a small amount of ethyl 3-furoyl-propionate be isolated from the reaction in ether bewteen furan and succinyl chloride in the presence of ethylaluminum dichloride.

Our attention was then drawn to a report published in 1973 which disclosed the synthesis of 1,4- and 1,5-diketones from the reaction of N,N,N',N'-tetramethyldiamides with organolithium reagents at -78°C.[27] The results of this study are shown in Table 3. In view of these results, the prospect

Table 3. Yields of products from the reaction

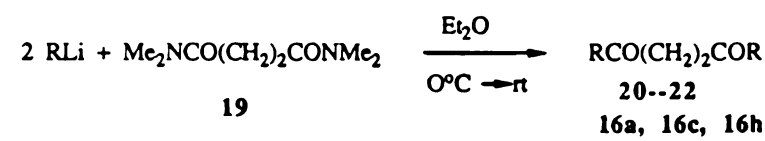
$$2\ RLi + Me_2NCO(CH_2)_nCONMe_2 \xrightarrow{-78^\circ C} RCO(CH_2)_nCOR$$

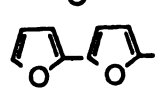
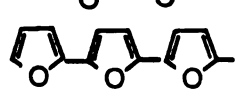
R	n	Yield(%)	Solvent	Time(h)
Phenyl	2	4	Ether	24
6-Bromo-2-pyridyl	2	71	Ether	3
2-Pyridyl	2	20	Ether	3-4
2-Thienyl[a]	2	33	THF	24
Phenyl	3	50	Ether	24
6-Bromo-2-pyridyl	3	76	Ether	3
2-Pyridyl	3	20	Ether	3-4
2-Thienyl[a]	3	24	THF	24
n-Butyl	3	19	Ether	2

[a] Run with 4 equiv of 2-thienyllithium

of this method for 1,4-diketone synthesis did not look promising as we can see that the yields of the 1,5-diketones were generally higher than those of 1,4-diketones. In the case of phenyllithium, only a 4% yield of 1,4-diphenylbutanedione was formed in the reaction with N,N,N',N'-tetramethylsuccinamide **19**. Furthermore, it was reported that n-butyllithium gave a very complex mixture with the diamide **19**. However, when this reaction was performed by adding the diamide **19** in one portion to the organolithium reagent at $0^{o}C$ and then stirring at room temperature for a further 24h,

Table 4. Yields of 1,4-diketones from the reaction



R	Time(h)	Product	Yield(%)
n-Butyl	24	**20**	20
 [a]	24	**21**	47
	24 (36)[b]	**22**	22 (25)[b]
	24	**16a**	50
	24	**16c**	61
	24	**16h**	49

[a] Added as etheral PhLi.LiBr Solution. [b] Reaction at room temperature for 36h with 25% yield.

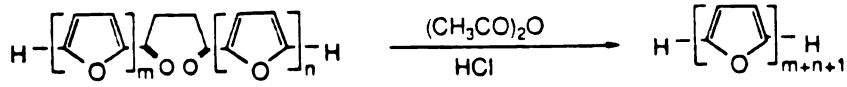
the yield of 1,4-diphenylbutanedione **21** was increased

approximately twelve times to 47% while n-butyllithium gave 5,8-dodecanedione **20** in a 20% yield [Table 4]. Similarly, both 2-furyllithium and 2-thienyllithium gave the corresponding 1,4-diketones in 50% and 22% yields respectively [Table 4]. For the case of 2-thienyllithium, using excess lithium reagent or longer reaction time did not improve the yield. This yield was somewhat lower than the result from the literature which has 33% optimal yield when the reaction was done in THF at -78^{o}C [Table 3]. The extension of this reaction to the organolithium reagents derived from α-bifuran **11** and α-terfuran **12** also gave the symmetrical 1,4-diketones **16c** and **16d** in modest yields [Table 4].

In summary, three different approaches are available for the synthesis of 1,4-diketone precursors to α-polyfurans. While the Mannich base method is good for the synthesis of unsymmetrical 1,4-diketones, the other two methods (vinyl sulfone and diamide) are complement to it for the preparation of symmetrical 1,4-butanediones.

All the structures of the 1,4-diketones were confirmed by their spectra (see Experimental). For the unsymmetrical 1,4-diketones such as **16b, 16d, 16f** and **16g,** their ^{13}C NMR spectra clearly showed two distinct signals for the two carbonyl carbons or two α-methylene carbons or both. The IR absorptions in the range of 1640-1670 cm^{-1} were obtained for the 1,4-diketones.

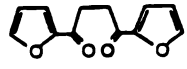
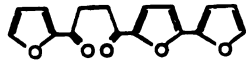
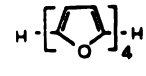
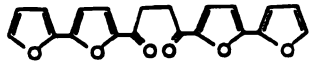
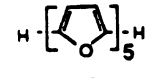
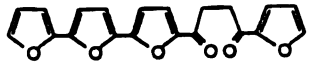
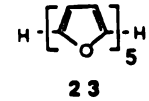
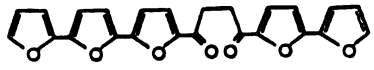
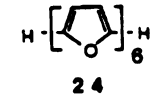
With the 1,4-diketones in hand, the time has come to study their ring closure to α-polyfurans. It was found that



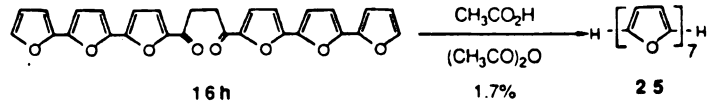
Scheme 9

most of these 1,4-diketones readily gave the α-polyfurans upon treatment with acetic anhydride in the presence of a catalytic amount of concentrated hydrochloric acid [Scheme 9]. Oligomers possessing three, four, five and six furan rings were prepared in this manner in fair yields [Table 5].

Table 5. Polyfurans by ring closure of 1,4-diketones

1,4-diketone	Polyfurans	Yield(%)
 16a	 12	63
 16b	 13	42
 16c	 23	40
 16d	 23	44
 16e	 24	20

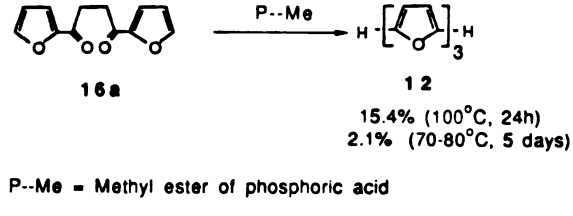
However, the diketone **16h** resisted the dehydration under the same condition or gave unidentified products under other dehydration conditions (DMSO, polyphosphoric ester, P_2O_5, HMPA and p-TsOH in $CHCl_3$). But the α-septifuran **25** was obtained in very small yield when a solution of the diketone **16h** in acetic acid and acetic anhydride was refluxed for 48h [Scheme 10].



Scheme 10

Due to their limited amount available or low solubility, the dehydration of **16f, 16g** and **16i** was not studied.

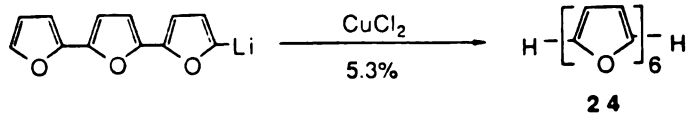
Attempts have been made to improve the yield by doing the dehydration under neutral condition, but this resulted in very poor yields [Scheme 11].



Scheme 11

Besides the dehydration of 1,4-diketone **16e**, the

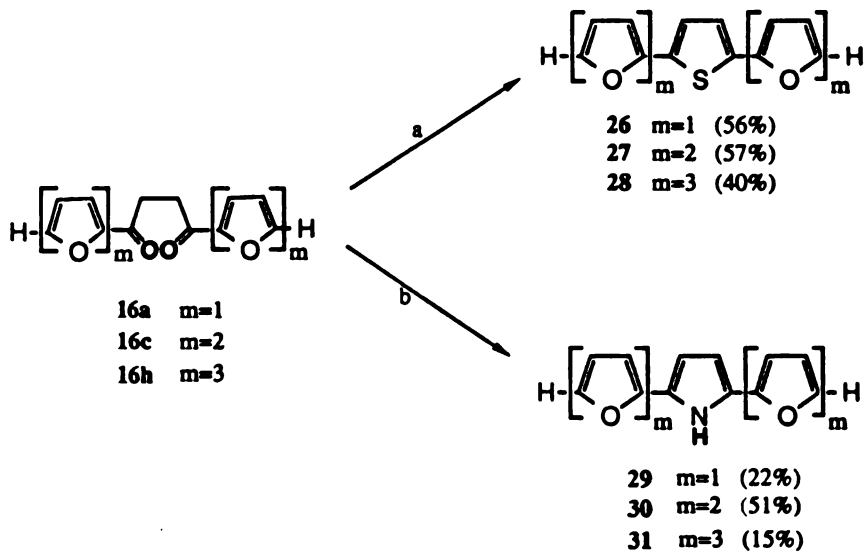
α-sexifuran **24** can also be prepared from the oxidative coupling of α-terfuryllithium by anhydrous copper(II) chloride but only in a 5.3% yield [Scheme 12].



24

Scheme 12

We have completed the syntheses of α-polyfurans from the 1,4-diketones and also proved that this is a general approach to both the odd and even number of α-polyfurans. In addition to α-polyfurans, this 1,4-diketone synthesis is also useful in providing a facile route to the mixed α-polyaryls. To demonstrate this point, we have prepared



16a m=1
16c m=2
16h m=3

26 m=1 (56%)
27 m=2 (57%)
28 m=3 (40%)

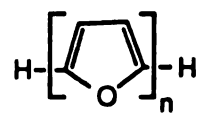
29 m=1 (22%)
30 m=2 (51%)
31 m=3 (15%)

Scheme 13: a) Lawesson's reagent, toluene; b) NH_4OAc, CH_3CO_2H, $(CH_3CO)_2O$

several linear mixed α-furylthiophenes **26-28** and α-furylpyrroles **29-31** from three symmetrical 1,4-diketones [Scheme 13]. While there were some difficulties in synthesis the α-septifuran **25**, its mixed counterparts **28** and **31** can be easily prepared in high yields.

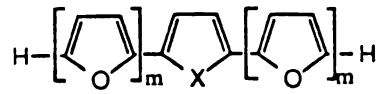
A study and comparison of the UV spectrum data of α-polyfurans [Table 6] and α-polyaryls [Table 7] reveals some interesting points. For the linear α-polyfurans, the data showed a decreasing incremental bathochromic shift of the longest wavelength absorption as the molecule increases in length. In fact the bathochromic shift observed on going from α-sexifuran **24** to α-septifuran **25** is only 5 nm and this indicates that there might exist a limit to the conjugation bewteen the furans rings in the vicinity of six or seven furan rings. When one of the furan rings in α-polyfuran is replaced by a pyrrole ring, the longest wavelength absorption of the resulting α-furylpyrroles remains nearly the same as its counterparts from α-polyfurans. However, when the furan

Table 6 UV spectrum data (the highest λ_{max} value) of α-polyfurans



n	3	4	5	6	7
$\lambda_{max}^{CHCl_3}$ (nm)	350	390	415	436	441

Table 7 UV spectrum data (the highest λ_{max} value) of α-polyaryls

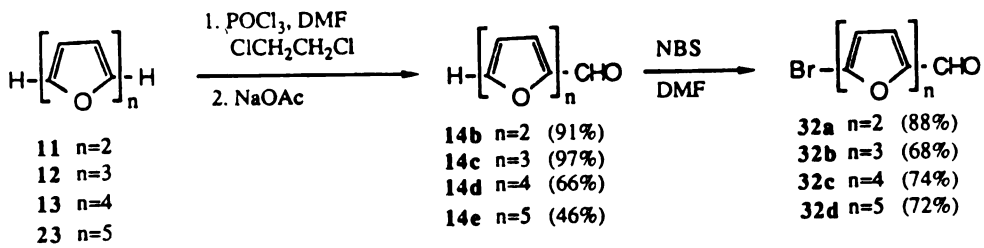


m		1	2	3
$\lambda_{max}^{CHCl_3}$ (nm)	X=NH	345	411	441
	X=S	369	432	464

ring is replaced by the thiophene ring, the highest λ_{max} of the α-furylthiophenes shifts to longer wavelength by about 20 nm compares to its counterparts from α-polyfurans and α-furylpyrroles. Such phenomenon is in agreement with the general observation that the thiophene compounds are usually absorbed at longer wavelength than structurally similar furan and pyrrole compounds, possibly due to the thiophene is more aromatic in character or the participation of the low lying d-orbitals in bond interaction.

Although the syntheses of α-polyfurans (up to α-quaterfuran) have been reported,[21] their chemistry has not been well studied.[21c, 21d, 21e, 28] So we undertook to study the chemistry of the α-polyfurans for two reasons. Firstly, the studies would enrich our understanding of the properties of this type of compounds. Secondly, the results from these studies might be useful to accomplish our second goal, i.e. the synthesis of the polyfuran macrocycles **9** and **10**.

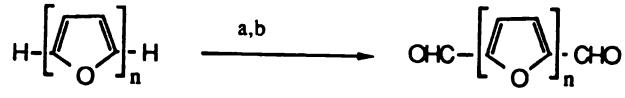
The α-polyfurans (**11-13** and **23**) were easily formylated by the Vilsmeier-Haack method to give the corresponding 5-formyl derivatives, **14b-14e**, in good to excellent yields [Scheme 14]. These monoaldehydes (**14b-14d**) have been used to synthesiz the 1,4-diketones either by reacting with Mannich bases or vinyl sulfone (*Vide supra*). Treatment of these monoaldehydes (**14b-14e**) with N-bromosuccinimide (NBS) in dimethylformamide (DMF) gave the corresponding bromoaldehydes, **32a-32d**, in good yields [Scheme 14]. However, the use of pyrindine hydrobromide as brominating agent in chloroform only led to the destruction of the aldehydes.



Scheme 14

When the α-bifuran **11** and α-terfuran **12** were treated with more than 2 equivalents of Vilsmeier reagent ($POCl_3$, DMF), only the corresponding monosubstitution products, **14b** and **14c**, were isolated, no dialdehyde compounds were detected. This was consistent with a report[21e] in which the Gattermann reaction of α-bifuran **11** gave only the monoaldehyde **14b**

even when a large excess of the reagent (HCN, HCl) was employed. It would appear from this evidence that the deactivating effect of an electrophilic group (in this instance CHO) is transferred through the extended conjugated system of α-bifuran and α-terfuran, thereby inhibiting the introduction of second formyl group to the remaining α position. This trend of deactivation is expected to carry on to other α-polyfurans. But we were surprised to find that treating the α-quaterfuran **13** and α-quinquefuran **23** with excess Vilsmeier reagent gave the corresponding dialdehydes **33c** and **33d** exclusively in modest yields [Scheme 15]. These results might reflect that the furan rings in larger α-polyfurans behave more like an individual unit than an extended conjugated system, thus diminishes the deactivating effect of the first formyl group.

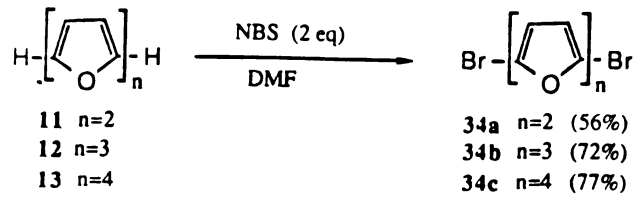


13 n=4
23 n=5

33c n=4 (65%)
33d n=5 (57%)

Scheme 15: a) Excess Vilsmeyer reagent; b) NaOAc

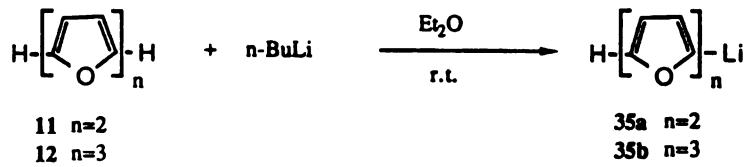
The dibromides, **34a-34c**, were readily obtained by brominating the corresponding α-polyfurans, **11-13**, with NBS in DMF in fair to good yields [Scheme 16]. These dibromides are slowly decomposed at room temperature but stable for a long time if kept at $0^{o}C$.



Scheme 16

The preparation of the ketone derivatives from α-bifuran and α-terfuran by acylation with acetic anhydride in the presence of an acid (H_3PO_4) or a Lewis acid catalyst (BF_3.OEt) led only to the decomposition of the starting material. Fortunately,the successful synthesis of 1,4-diketones from organolithium reagent and N,N,N',N'-tetramethyldiamide **19** provides an alternative route to make the ketone compounds.

Based on competition experiments, Kauffmann et al.[21c] has found that the acidity of α-hydrogen from the α-polyfurans against n-butyllithium decreases in the following sequence: α-terfuran > α-bifuran > furan. So while the 2-furyllithium in ether was usually prepared by refluxing a solution of furan and n-butyllithium for 4 hours,[29] the corresponding

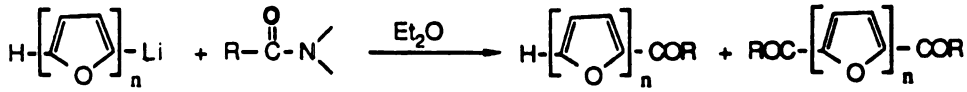


Scheme 17

α-lithiated compounds, **35a** and **35b**, from α-bifuran **11** and α-terfuran **12** were easily obtained by stirring a solution of α-polyfuran and n-butyllithium at room temperature for 2 hours [Scheme 17].

These organolithium compounds, **35a** and **35b**, readily reacted with various N,N-dimethylamides to give the ketones together with a small amount of diketones. The results are summarized in Table 8. The yields of the ketones from α-bifuran are generally better than those from α-terfuran, a

Table 8 Yields of monoketone and diketone from the reaction



35a n=2
35b n=3

17b - 17c
36a - 36d

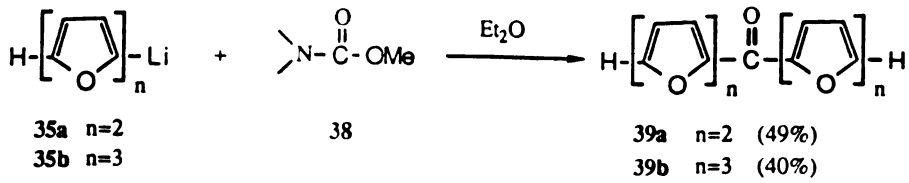
37a - 37f

n	R	Product		Yield (%)	
		Monoketone	Diketone	17 or 36	: 37
2	CH_3	17b	37a	60	: 1
3	CH_3	17c	37b	47	: 6
2	C_6H_5	36a	37c	59	: 6
3	C_6H_5	36b	37d	42	: 6
2	p-$MeOC_6H_4$	36c	37e	56	: 6
3	p-$MeOC_6H_4$	36d	37f	46	: 5

result that is presumably due to steric effect. The ketone compound **17b**, prepared in this manner, has been used to make the Mannich base **15b** for 1,4-diketone synthesis (*Vide supra*).

Besides the amides, the methyl N,N-dimethylcarbamate **38**

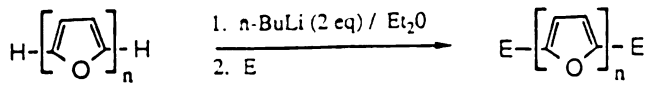
also reacted with the organolithium compounds to give the symmetrical ketones, **39a** and **39b** in modest yields [Scheme 18].

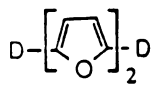
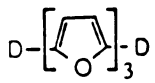
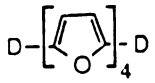
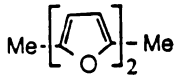
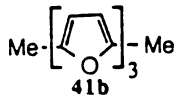
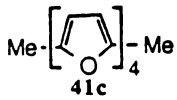
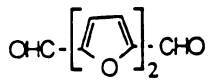
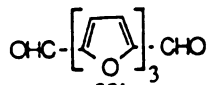
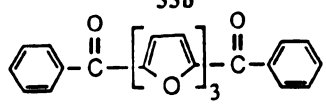


Scheme 18

The formation of the diketones from the above nucleophilic reactions suggests that treating the α-polyfurans with 2 molar equivalents of n-butyllithium under the same condition could generate the dianion. This is shown to be the case by trapping the dianion with D_2O or methyl iodide [Table 9]. In all cases (entries 1-6), only the disubstituted products **(40-41)** were formed and this is supported by their ^1H and ^{13}C NMR spectra (see Experimental). For example, their ^1H NMR spectra showed the absence of the α-hydrogen signal around 7.4-7.5 ppm and ^{13}C NMR spectra of the deuterated derivatives **(40a-40c)** showed triplet for the free α-carbon while the free α-carbon was shifted downfield by 10 ppm in the dimethyl compounds **(41a-41c)**. The exclusive formation of dimethyl compound **41a** from α-bifuran **11** in ether is contrast to a

Table 9 Yields of disubstituted products from the reaction



Entry	n	E	Product	Yield (%)
1	2	D_2O	 **40a**	65
2	3	D_2O	 **40b**	75
3	4	D_2O	 **40c**	17
4	2	MeI	 **41a**	48
5	3	MeI	 **41b**	81
6	4	MeI	 **41c**	9
7	2	DMF	 **33a**	9
8	3	DMF	 **33b**	39
9	3	$C_6H_5CON(Me)_2$	 **37d**	30

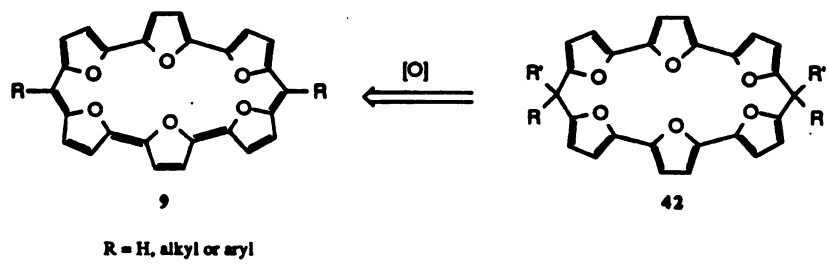
report[28a] that treating the bifuran 11 with two molar equivalents of n-butyllithium in THF gave a mixture of starting material, methyl and dimethyl derivatives in 76% total

yield. The poor yields of the disubstituted products, **40c** and **41c**, from α-quaterfuran may be due to the decomposition of the starting material during the dianion formation because substantial amount of insoluble black solid was observed during work-up. The reason for this decomposition is not clear. Although the yield of the dialdehyde **33a** is disappointing, the reaction bewteen the dianions from α-bifuran and α-terfuran with DMF (entries 7 and 8) provides a way to synthesiz the dialdehydes, **33a** and **33b**, which cannot be obtained from the corresponding α-polyfurans with excess Vilsmeier reagent. Finally, the dianion from α-terfuran also reacted with N,N-dimethylbenzamide to give the diketone **37d** in 30% yield (entry 9).

B. Synthesis of novel macrocyclic α-polyfurans

I. Studies towards the synthesis of [26]annulene hexoxide 9

Retrosynthetic analysis of **9** suggests that compound **42** is a potential precursor since oxidation of **42** (R'=H) might afford the [26]annulene hexoxide **9** [Scheme 19]. Consequently,

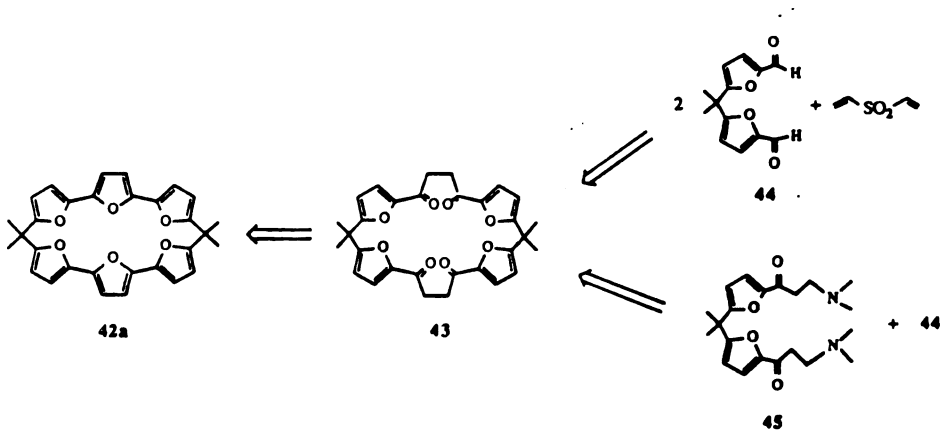


Scheme 19

efforts have been made to construct the ring compound **42.**

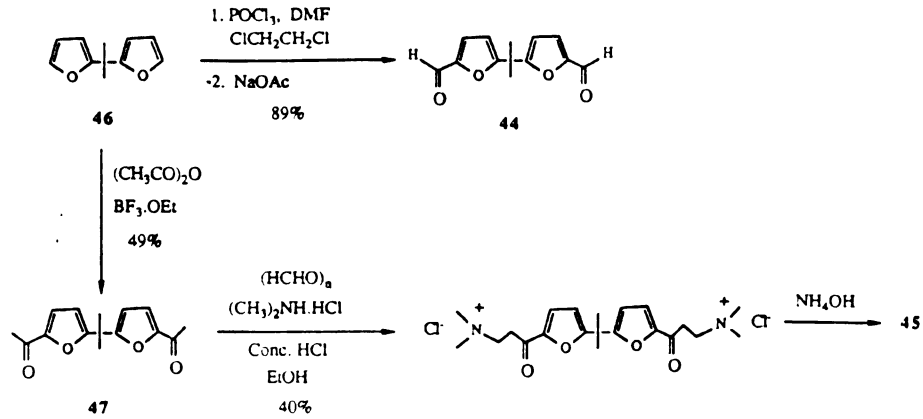
At the beginning, a model compound **42a** ($R=R'=CH_3$) is made so as to test the feasibility of various synthetic approaches to the macrocyclic ring structure.

The first retrosynthetic analysis of **42a** suggests it may come from the dehydrative cyclization of the tetraketone **43** which in turn may involve an intermolecular catalyzed addition of the dialdehyde **44** to vinyl sulfone or the bis-Mannich base **45** [Scheme 20].



Scheme 20

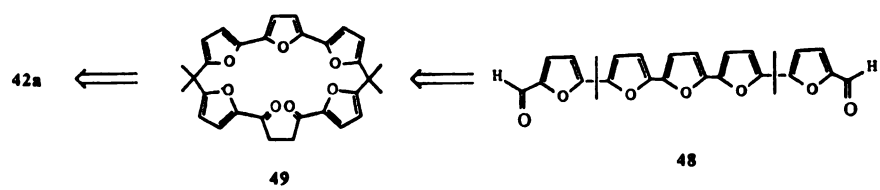
The dialdehyde 44 was readily obtained in excellent yield by treating the 2,2-difurylpropane 46[30] **with Vilsmeier reagent ($POCl_3$, DMF) [Scheme 21]. The desired bis-Mannich base 45 was prepared from the diketone compound 47 which in turn was synthesized by reacting 46 with acetic anhydride in the presence of a catalytic amount of boron trifluoride etherate [Scheme 21].**



Scheme 21

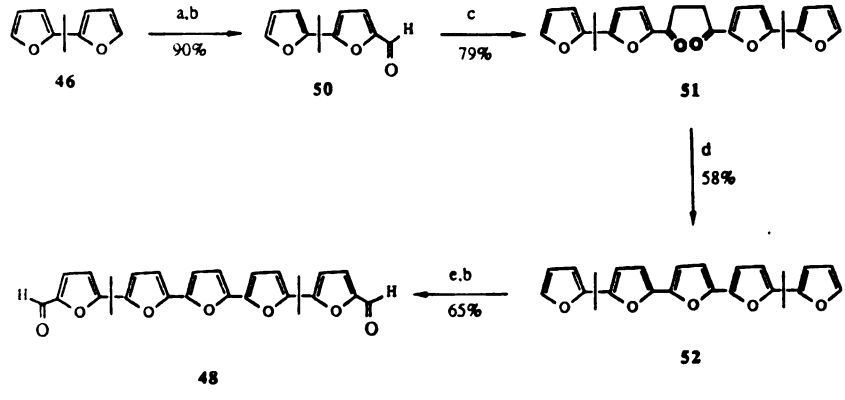
Unfortunately, the dialdehyde **44** gave rise to a plethora of unidentified products upon treatment with the vinyl sulfone. The dialdehyde **44** was the only detectable compound in minute amount after its reaction with the bis-Mannich base **45.**

Our second synthetic approach to **42a** is based on the intramolecular catalyzed addition of the dialdehyde **48** to the vinyl sulfone [Scheme 22]. Since the dialdehyde **48** consists all but two carbon atoms of the macrocyclic framework, it was anticipated that **48** is more readily to form the cyclic 1,4-diketone **49** with vinyl sulfone.



Scheme 22

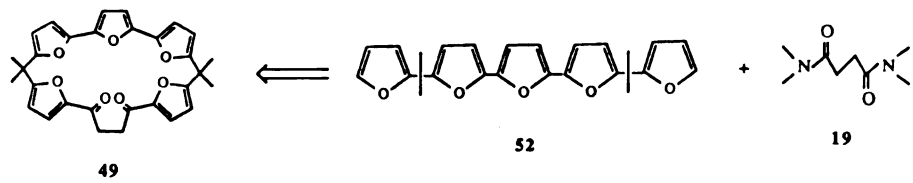
The preparation of the dialdehyde **48** is shown in Scheme 23. Vilsmeier-Haack reaction of **46** gave the aldehyde **50** in excellent yield. The thiazolium salt catalyzed addition of **50** to vinyl sulfone gave the 1,4-diketone **51** which in turn was dehydrated with acetic anhydride to give the furan compound **52**. Treatment of **52** with 2 molar equivalents of Vilsmeier reagent gave the desired dialdehyde **48**.



Scheme 23: a) DMF, $POCl_3$, $ClCH_2CH_2Cl$; b) NaOAc; c) Vinyl sulfone, thiazolium salt, NaOAc, EtOH; d) $(CH_3CO)_2O$, HCl; e) Excess Vilmeyer reagent

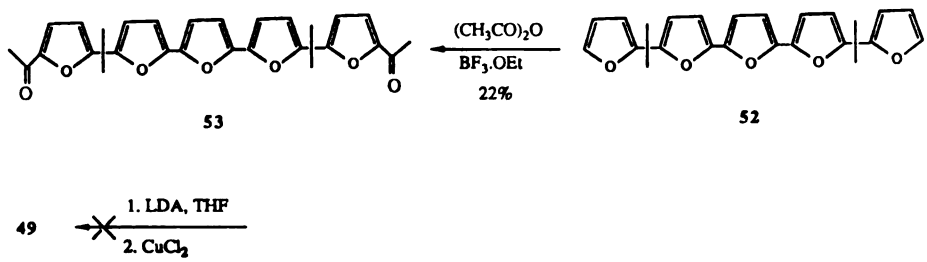
Like **44**, the dialdehyde **48** only gave a complex mixture of unidentified products when reacted with the vinyl sulfone.

The formation of 1,4-diketone from organolithium and diamide **19** prompts us to study the synthesis of **49** from the furan compound **52** [Scheme 24]. However, under the conditions (n-BuLi or LDA in ether) studied, the cyclic diketone **49** was not detected.



Scheme 24

There is a report of the synthesis of 1,4-diketones by oxidative coupling of ketone enolates with anhydrous copper(II) chloride.[23d] The application of this synthetic methodology to the cyclic 1,4-diketone **49** from the diketone compound **53** is very attractive [Scheme 25]. Unlike the previous synthetic approaches to **49** that involves formation of two carbon-carbon bonds, the present approach needs to form only one carbon-carbon bond because the diketone **53** has all the carbon atoms of the macrocyclic 1,4-diketone **49**.



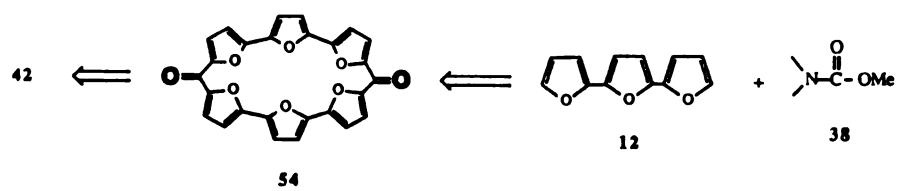
Scheme 25

The diketone **53** was obtained by the Lewis acid catalyzed

reaction of **52** with acetic anhydride. But to our disappointment, the dienolate, generated by treating **53** with LDA, gave a plethora of unidentified products upon treatment with copper(II) chloride.

In view of the above results, the 1,4-diketone synthesis is an ineffective approach to the macrocycle **42**. Therefore, other ways have to be devised for making **42**.

It has been demonstrated that α-terfuran **12** gave dianion efficiently by treating with 2 molar equivalents of n-BuLi and also the monolithiated derivative **35b** of α-terfuran **12** reacted with carbamate **38** to give the symmetrical ketone **39b** in modest yield (*Vide supra*). Retrosynthetic analysis of **42** suggests the symmetrical and cyclic diketone **54** as a possible precursor which may obtain from α-terfuran **12** and carbamate **38** [Scheme 26].

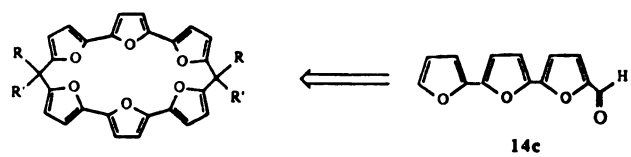


Scheme 26

The dianion from **12** did react with **38** and give a reddish brown solid as major product together with small amount of **12** and **39b**. Unfortunately, the solid was insoluble in any

solvent system and was assumed to be a linear polymeric ketone because its IR spectrum showed carbonyl group absorption. However, the mass spectrum of the solid did not give any additional information as no peak greater than m/e 250 was observed.

Another retrosynthetic analysis suggests **42** might come from the self cyclization of 5''-formyl-2,2':5',2''-terfuran **14c** [Scheme 27].



R' = OH

42

14c

Scheme 27

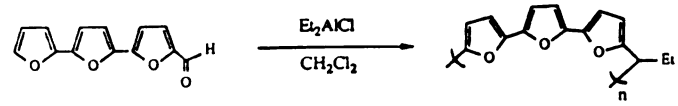
Efforts to accomplish this cyclization in ethanol or benzene with various protonic acids (concentrated HCl, gaseous HCl, p-TsOH and CF_3CO_2H) were all in vain. For each case, either the starting material or intractable material was obtained. We think these reaction conditions may be too harsh so that the product hydrolyzed or decomposed rapidly after its formation. So this cyclization reaction has been studied under mild condition by employing a Lewis acid in aprotic solvent.

The use of some common Lewis acids such as BF_3.OEt,

$SnCl_4$, $MgBr_2$.OEt and $POCl_3$ in dichloromethane did not cyclize the aldehyde **14c**. In both BF_3.OEt and $SnCl_4$ cases, addition of the Lewis acid to the dichloromethane solution of **14c** resulted in the formation of a quantitative amount of red precipitate. Quenching the solution with saturated NH_4Cl solution and usual work-up gave back **14c** near quantitatively. A similar situation occurred with $MgBr_2$.OEt except a yellow precipitate in this case. These results indicated the Lewis acids may form an insoluble complex with **14c**, thereby inhibited the cyclization. Although there was no precipitation from $POCl_3$ as Lewis acid, no reaction occurred as **14c** was recovered quantitatively.

Attention was then turned to the alkylaluminum chloride reagents for the cyclization of **14c**. The alkylaluminum chloride reagents have an advantage over other Lewis acids because the alkyl group can function as proton scavenger so that any side reaction caused by the presence of adventitious protons can be avoided. This is particularly true in this work as the furan nucleus is extremely sensitive to acidic medium.

We were delighted to find that the diethylaluminum chloride (Et_2AlCl) in dichloromethane caused the aldehyde **14c** to cyclize [Scheme 28]. The cyclization reaction did not go to completion but this gave us no problem as the cyclized product **42b** can be easily separated from the starting material by flash column chromatography. Evidence for the cyclization comes from the ^1H and ^{13}C NMR spectra of



14c 42b

Scheme 28

the product **42b**. Besides indicating the absence of the α-hydrogen at 7.40-7.50 ppm for the cyclic structure of **42b**, the ^{1}H NMR spectrum [Figure 2] also showed that there was an ethyl group transferred from the Lewis acid so that the bridging carbon has an ethyl group instead of the hydroxyl group. Such an alkyl group transfer from the alkylaluminum chloride reagent is known.[31] The centrosymmetrical formulation for **42b** is also indicated by the presence of 9 peaks in its ^{13}C NMR spectrum [Figure 3]. However, the EI mass spectrum of **42b** at 20 eV showed that the compound is the cyclic trimer (n=3) with parent ion at m/e 720. But by comparison to other cyclization study below, we believe **42b** is a mixture of cyclic oligomers (n=2, 3, 4...etc) and diastereomers with the cyclic trimer (n=3) as the major product.

Attempts to avoid the ethyl group transfer from the Lewis acid by using ethylaluminum dichloride ($EtAlCl_2$) were not

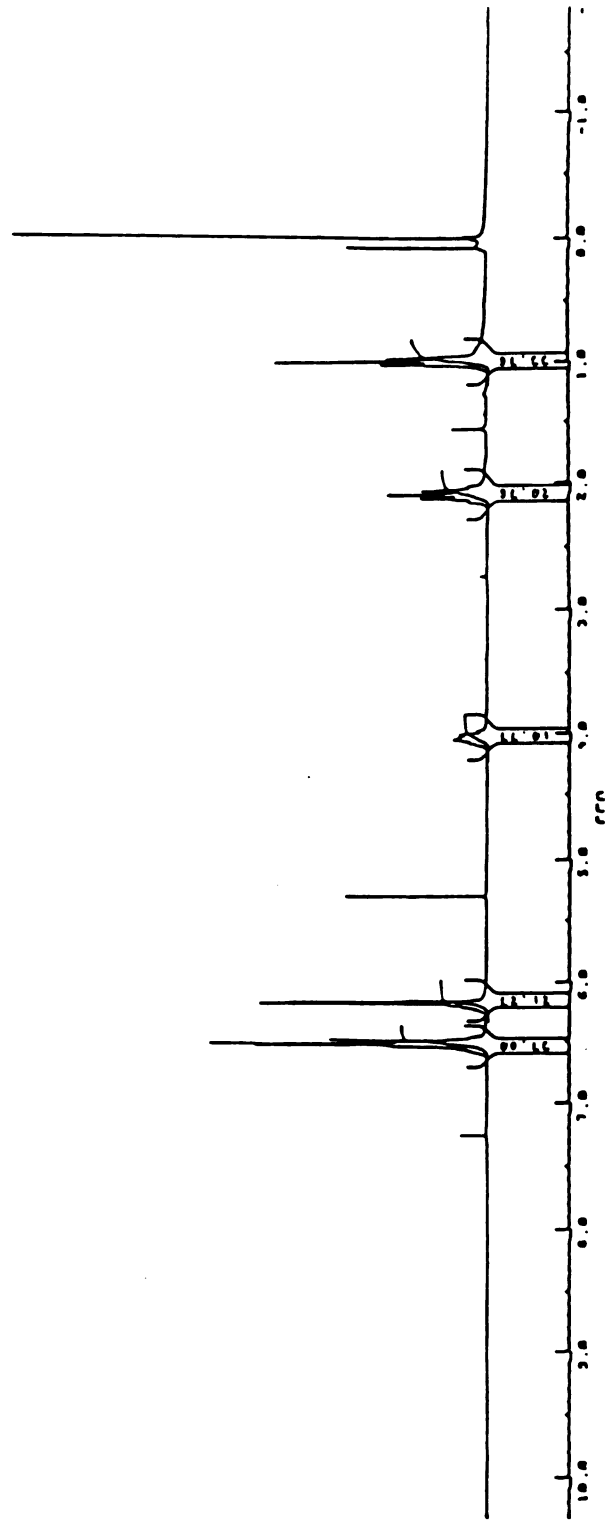


Figure 2. 250 MHz ^{1}H NMR spectrum of **42b**.

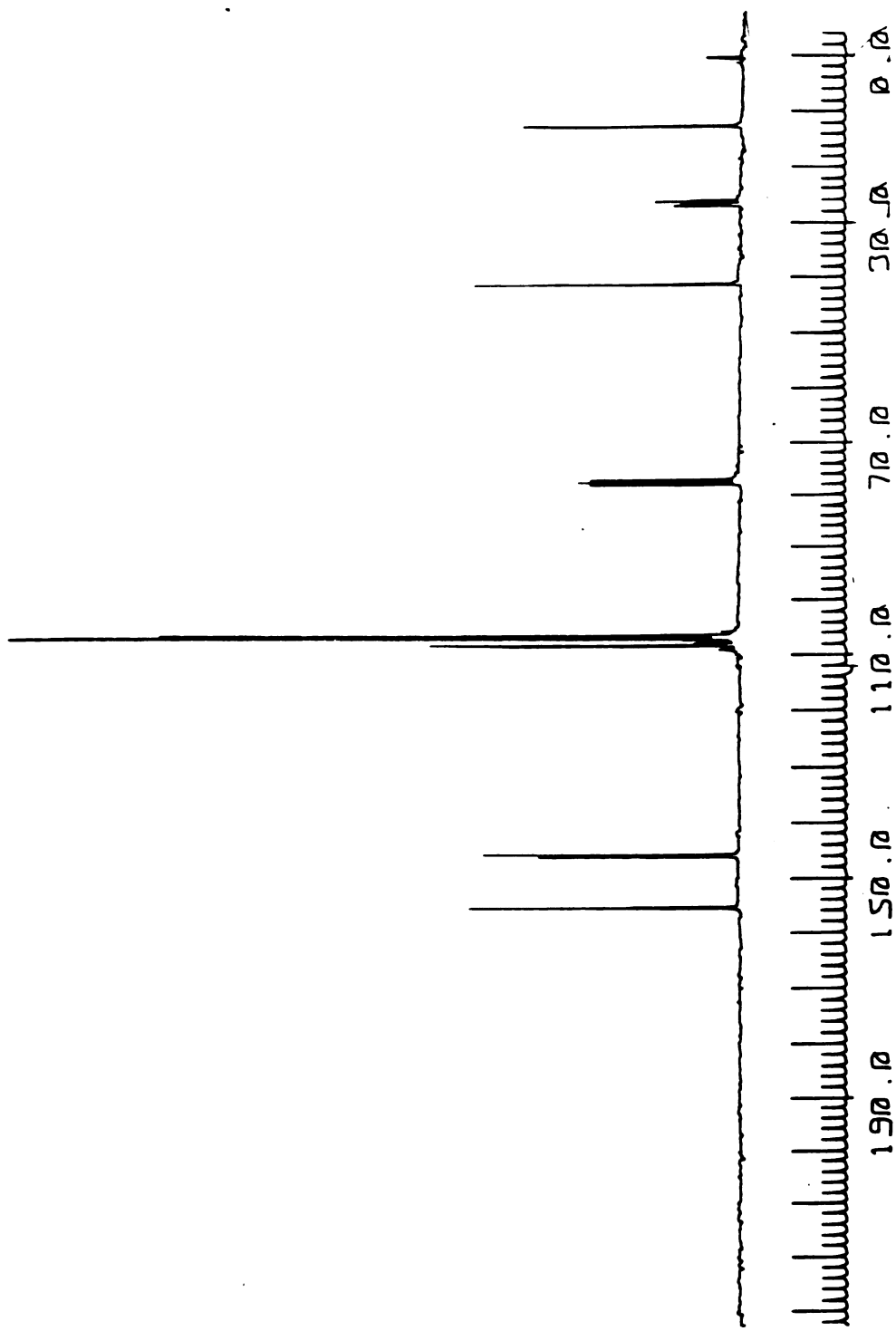
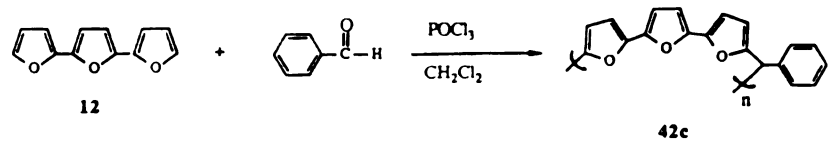


Figure 3. 62.9 MHz ^{13}C NMR spectrum **42b.**

successful as no cyclization occurred even though the temperature of the reaction was raised to 60°C. This may possibly due to the greater acidity of $EtAlCl_2$ which deactivate the α position through the extended conjugated system of **14c**.



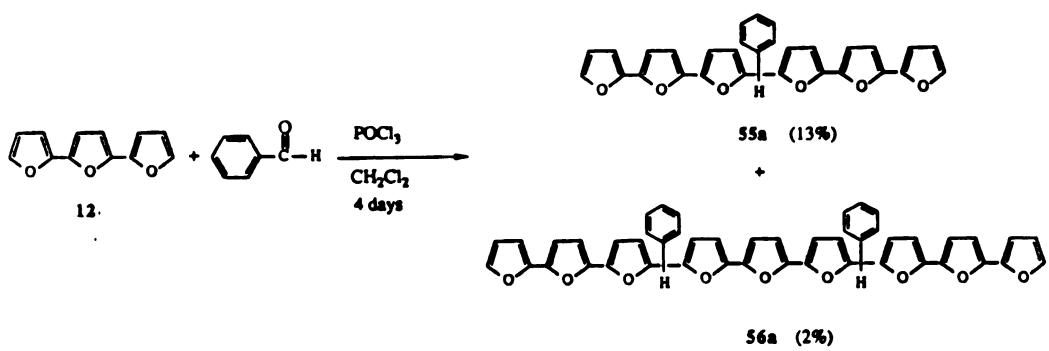
12 42c

Scheme 29

Finally, it was found that the condensation of benzaldehyde with α-terfuran **12** in dichloromethane ($1x10^{-2}$ M) at room temperature by using $POCl_3$ as Lewis acid allowed the successful synthesis of the symmetrical macrocyclic polyfuran **42c** after 24 hours [Scheme 29]. Evidence supported the cyclic form of **42c** comes from its ^1H and ^{13}C NMR spectra (see Appendix, Figures A20 and A21). However, the EI mass spectrum of **42c** showed the parent peak at m/e 864 which came from the cyclic trimer (n=3) and the field desorption (FD) mass spectrum indicated **42c** was actually a mixture of cyclic oligomers (n=2, 3, 4...etc). These mass spectrum results suggested the desired cyclic dimer (n=2) existed but in very small amount. Attempts to separate the mixture of cyclic oligomers using chromatography or recrystallization failed to

give any single, pure product.

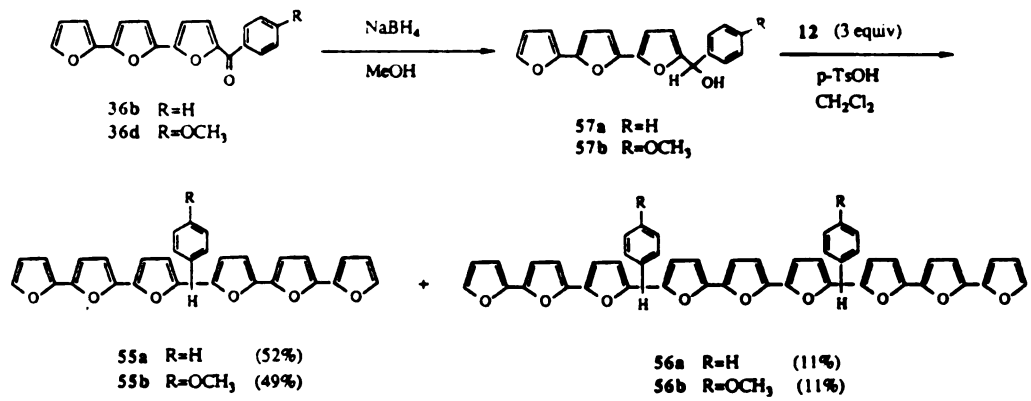
To avoid the formation of higher cyclic oligomers, the reaction was done under more dilute condition. At the concentration of $1x10^{-3}$ M, the solution gave back the starting materials after 24 hours. When the solution was allowed to stir for 4 days, in addition to some starting material and cyclized products, two linear, open-chain compounds were detected and identified as **55a** and **56a** [Scheme 30]. The formation of these linear compounds **55a** and **56a** from the reaction suggests their cyclization could give the cyclized products and this provides us a practical solution to the desired cyclic dimer (n=2) without the contamination of any odd number of cyclic oligomers by studying the cyclization of **55a**.



Scheme 30

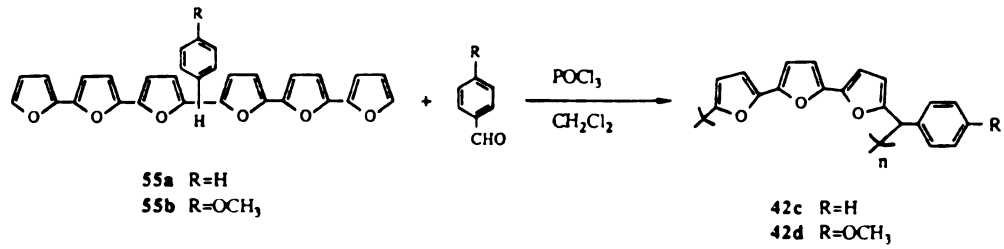
An efficient synthesis of **55a** and its methoxy derivative **55b** was shown in Scheme 31. Reduction of the ketones, **36b**

and **36d**, with sodium borohydride in methanol gave the corresponding alcohols **57a** and **57b** in quantitative yields respectively. Without purification, the alcohol **57a** or **57b** was treated with excess α-terfuran **12** in the presence of catalytic amount of p-toluenesulfonic acid to give the open-chain compound **55a** or **55b** together with small amount of linear compound **56a** or **56b**. Compound **55a** or **55b** was readily separated from its high analogy **56a** or **56b** by column chromatography.



Scheme 31

The cyclization of 55a with benzaldehyde in dichloromethane was completed after the solution was stirred at room temperature for 9 days [Scheme 32]. A comparison of the ^{1}H and ^{13}C NMR spectra of 55a and 42c revealed cyclization had occurred. The ^{1}H NMR spectrum [Figure 4] of 55a displayed the



Scheme 32

free α-hydrogens (5''-H) at 7.39 ppm. The protons from the benzene ring were shown by the peak at 7.33 ppm. The peaks at 6.44 ppm were assigned to the β-hydrogens (4''-H) next to the α-hydrogens. The doublet at 6.11 ppm is due to the β-hydrogen (3-H) from the furan rings nearest to the benzene ring. The rest of β-hydrogens (4-H, 3'-H, 4'-H and 3''-H) are appeared at 6.55 ppm. The singlet at 5.54 ppm is due to the bridging hydrogen. The ^{13}C NMR spectrum [Figure 6] of **55a** displayed the characteristic free α-carbon signal at 141.90 ppm. The spectrum also showed a total of 15 peaks due to the combined carbons from the benzene and furan rings. When **55a** cyclized to **42c**, the ^{1}H NMR spectum [Figure 5] of **42c** showed the disappearance of the peak from the α-hydrogens and the β-hydrogens (4''-H) signal coalesced with other β-hydrogens at 6.55 ppm. The peaks from the benzene hydrogens, bridging hydrogen and β-hydrogens (3-H) remained intact.

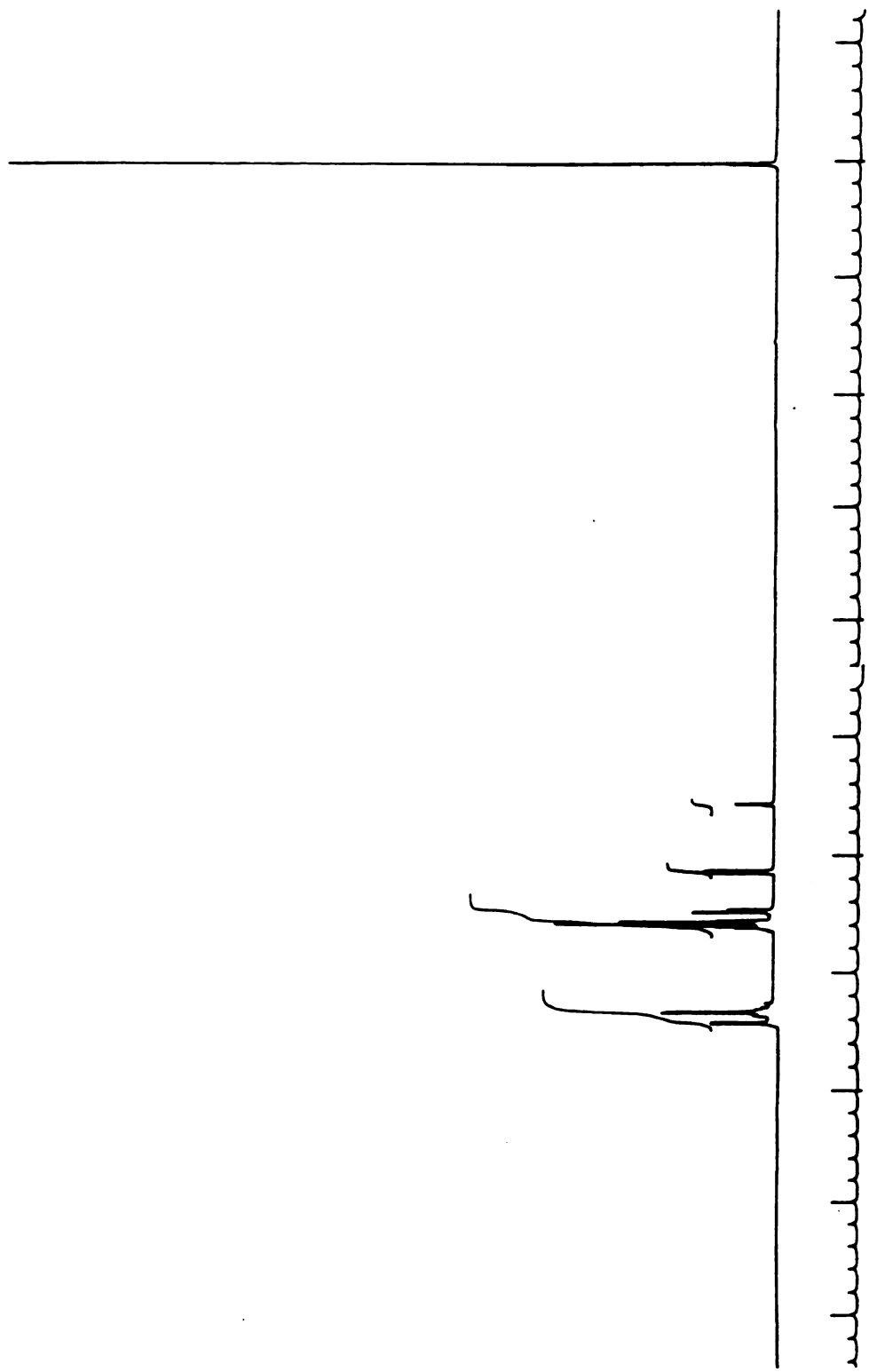


Figure 4. 250 MHz ^{1}H NMR spectrum of phenylbis(5-2,2':5',2''-terfuryl)methane **55a**.

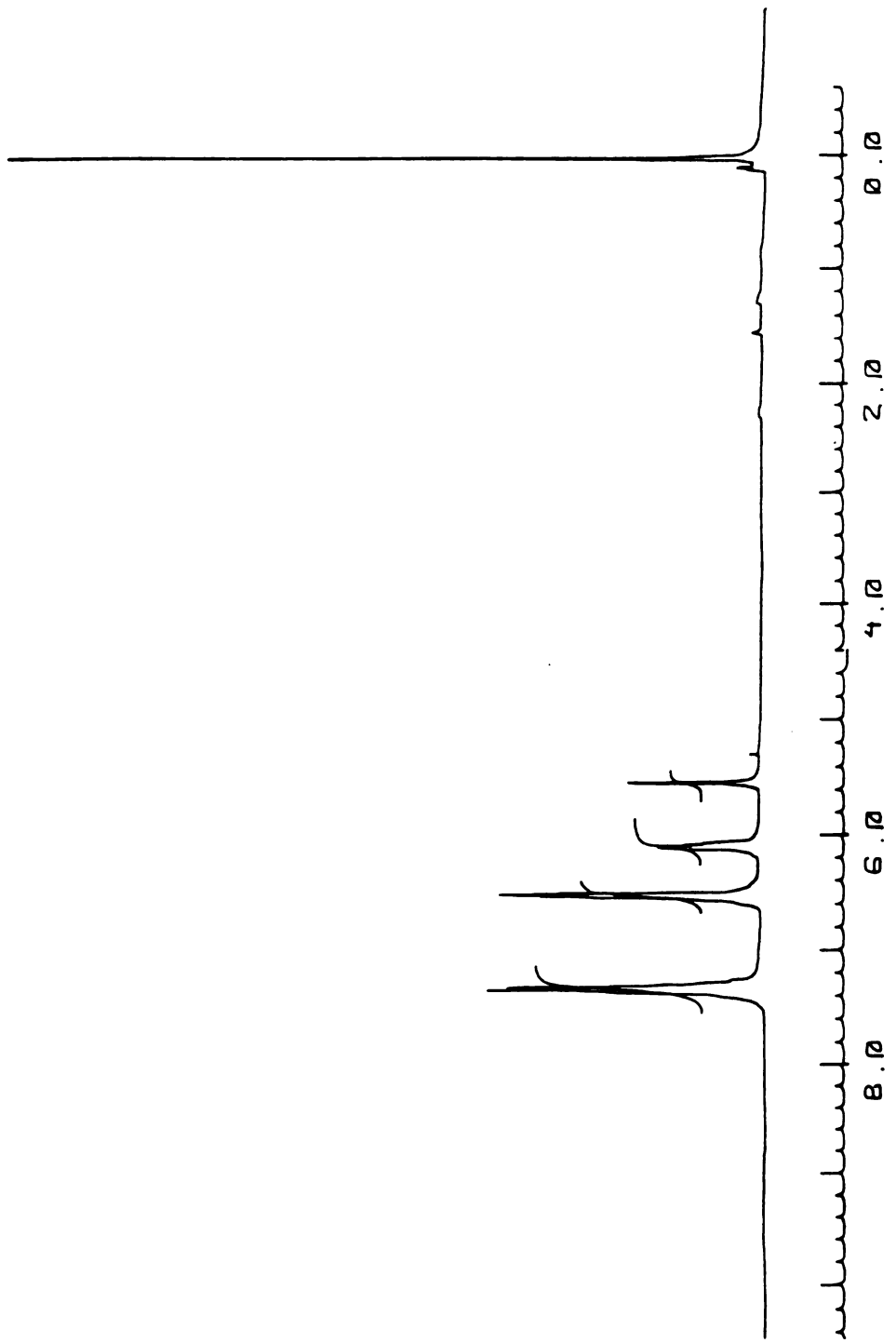


Figure 5. 250 MHz ^{1}H NMR spectrum of **42c.**

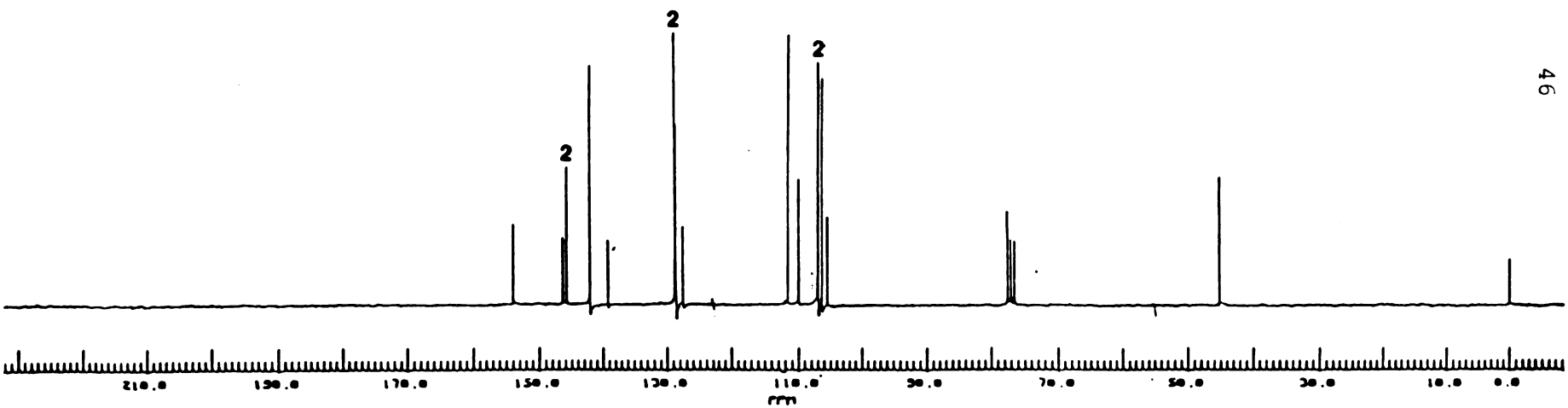


Figure 6. 62.9 MHz ^{13}C NMR spectrum of phenylbis(5-2,2':5',2''-terfuryl)methane 55a.

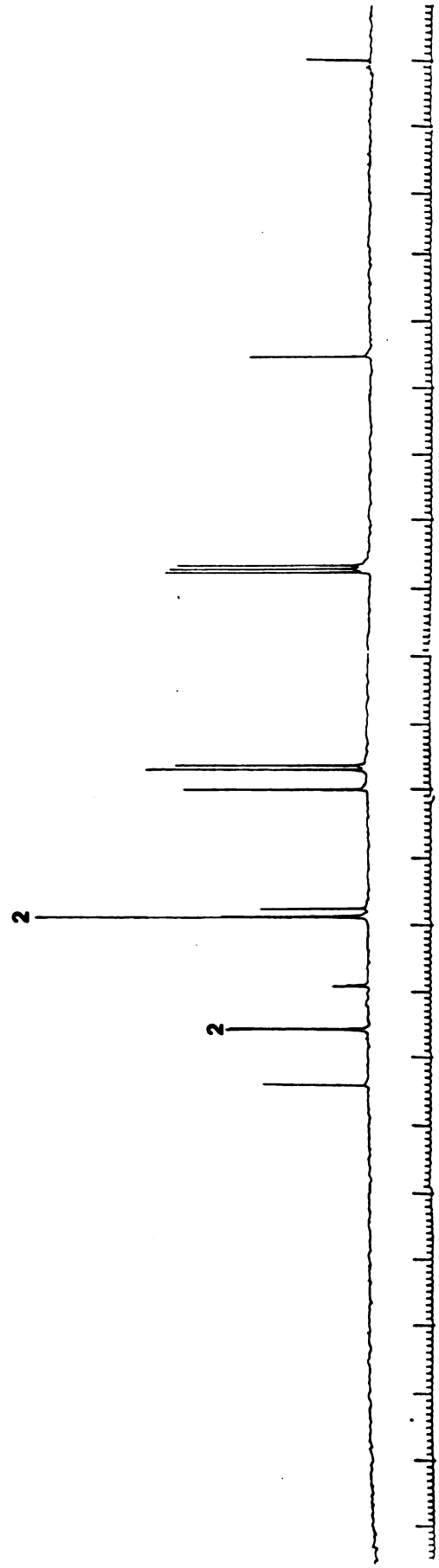


Figure 7. 62.9 MHz ^{13}C NMR spectrum 42c.

The disappearance of the free α-carbon's peak and the presence of only 11 peaks in the ^{13}C NMR spectrum [Figure 7] of **42c** also demonstrated its centrosymmetrical structure.

The EI mass spectrum of **42c** showed the parent ion of the desired cyclic dimer (n=2) at m/e 576. But the fast atom bombardment (FAB) mass spectrum showed **42c** was still a mixture of cyclic dimer (n=2) and tetramer (n=4). The cyclic tetramer arises from the cyclic dimerization of the linear compound **55a**.

In a similar manner, the methoxy derivative **55b** also underwent cyclization with 4-methoxybenzaldehyde to give **42d** after the solution was stirred for 18 days [Scheme 32]. Evidence of cyclization also comes from the comparison of the ^{1}H and ^{13}C NMR spectra of **55b** and **42d**. The ^{1}H NMR spectrum [Figure 8] of **55b** looked like that of **55a** with two exceptions. The proton from the benzene ring now appears as two doublets (J=8.7 Hz), one at 6.85 ppm while the other at 7.20 ppm. The peak at 3.75 ppm was assigned to the methoxy protons. The linear open-chain structure of **55b** is also indicated by the free α-carbon peak at 141.86 ppm and the presence of 14 peaks due to the aromatic carbons in its ^{13}C NMR spectrum [Figure 10]. However, the disappearance of the free α-hydrogen's and α-carbon's signals as well as the simplicity of the ^{1}H [Figure 9] and ^{13}C NMR (12 peaks) [Figure 11] spectra of **42d** proved it has a cyclic, symmetrical structure. The EI mass spectrum of **42d** showed the parent ion of the cyclic dimer (n=2) at m/e 636. Again, the FAB mass

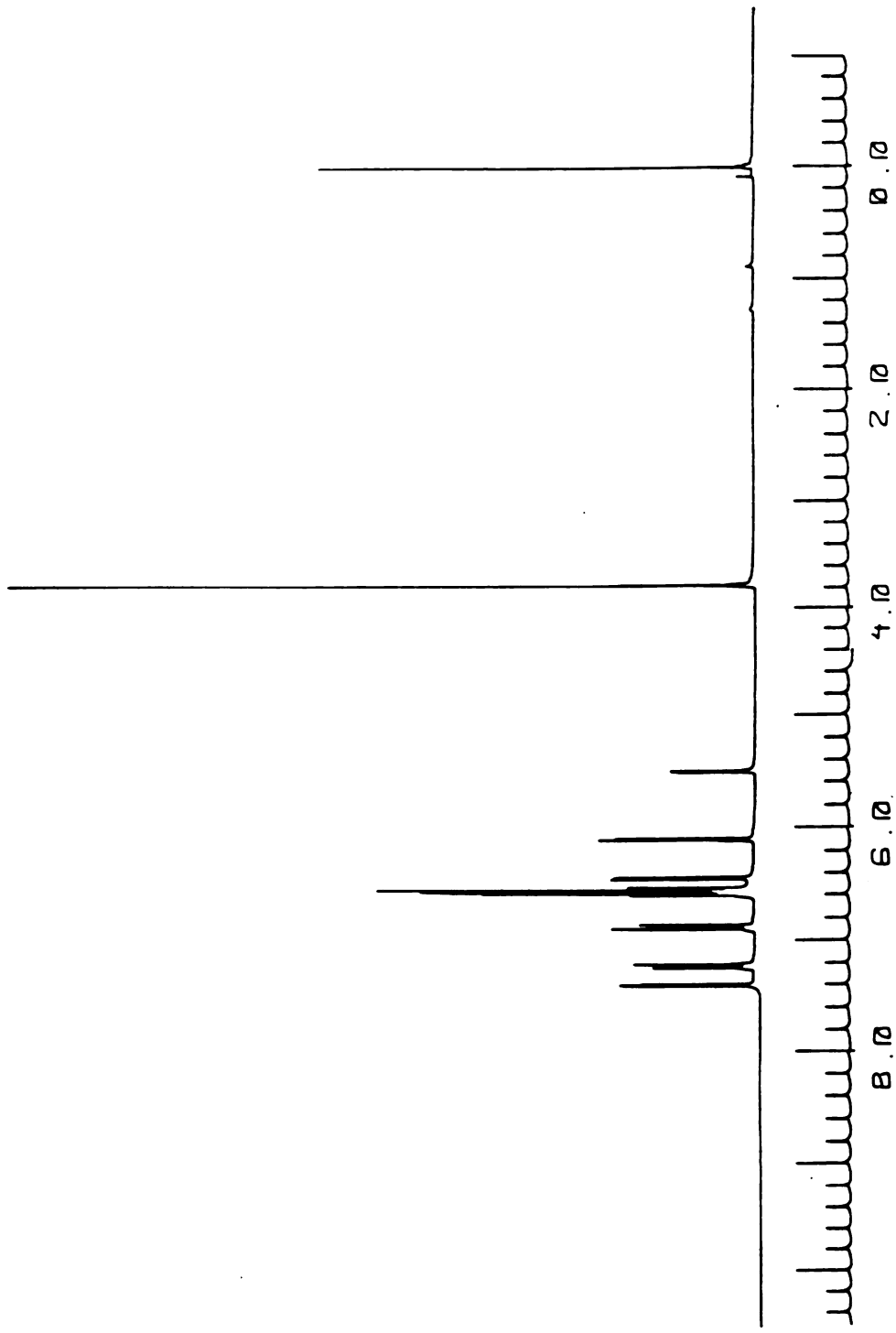


Figure 8. 250 MHz ^{1}H NMR spectrum of 4-methoxyphenyl-bis(5-2,2':5',2''-terfuryl)methane 55b.

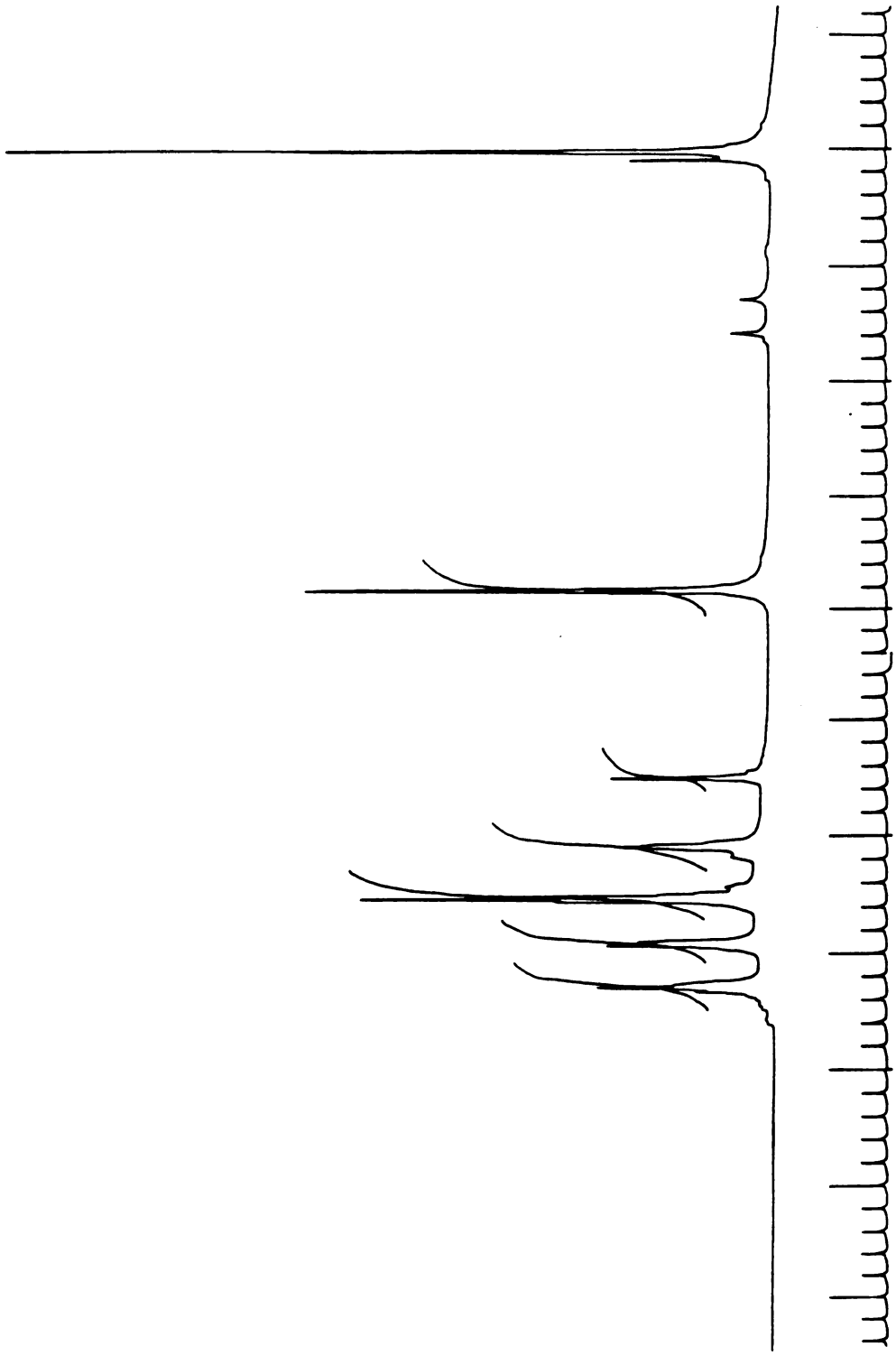


Figure 9. 250 MHz ^{1}H NMR spectrum of **42d**.

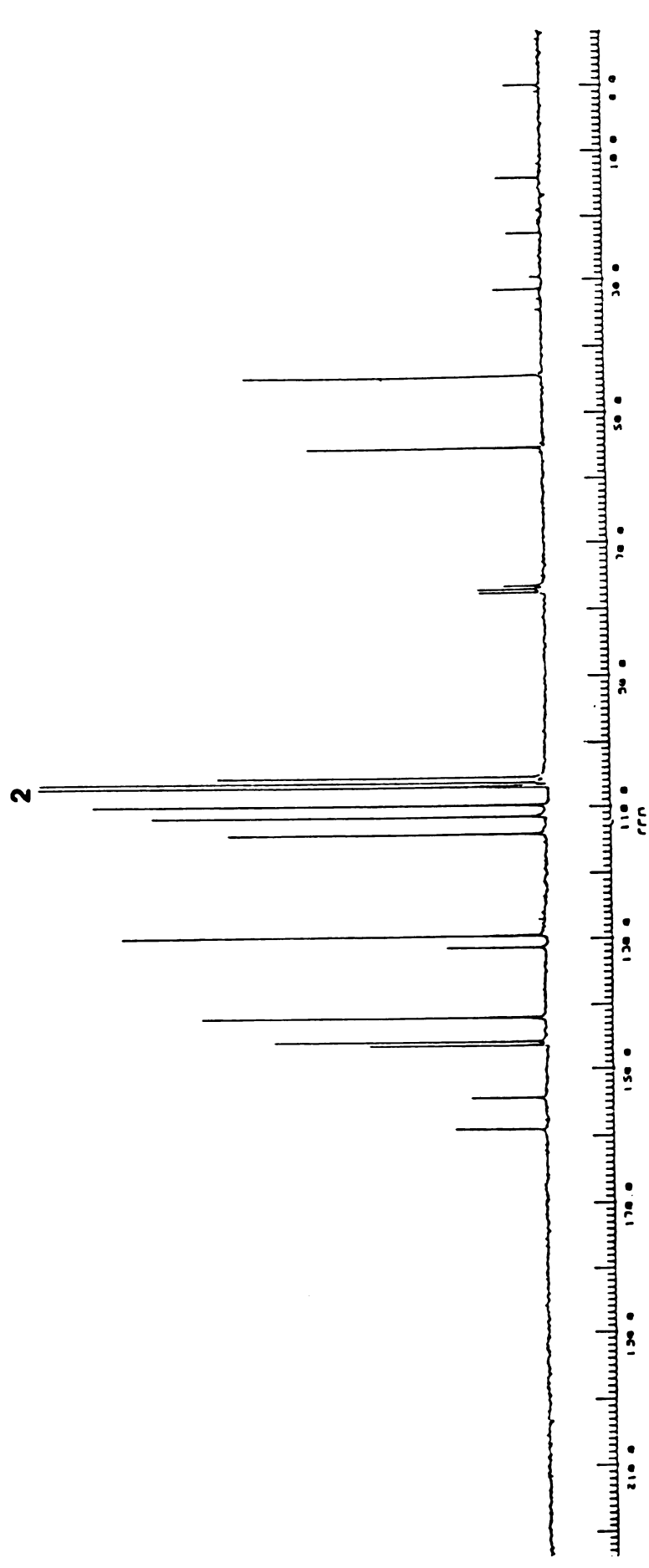


Figure 10. 62.9 MHz ^{13}C NMR spectrum of 4-methoxyphenyl-bis(5-2,2':5',2''-terfuryl)methane **55b**.

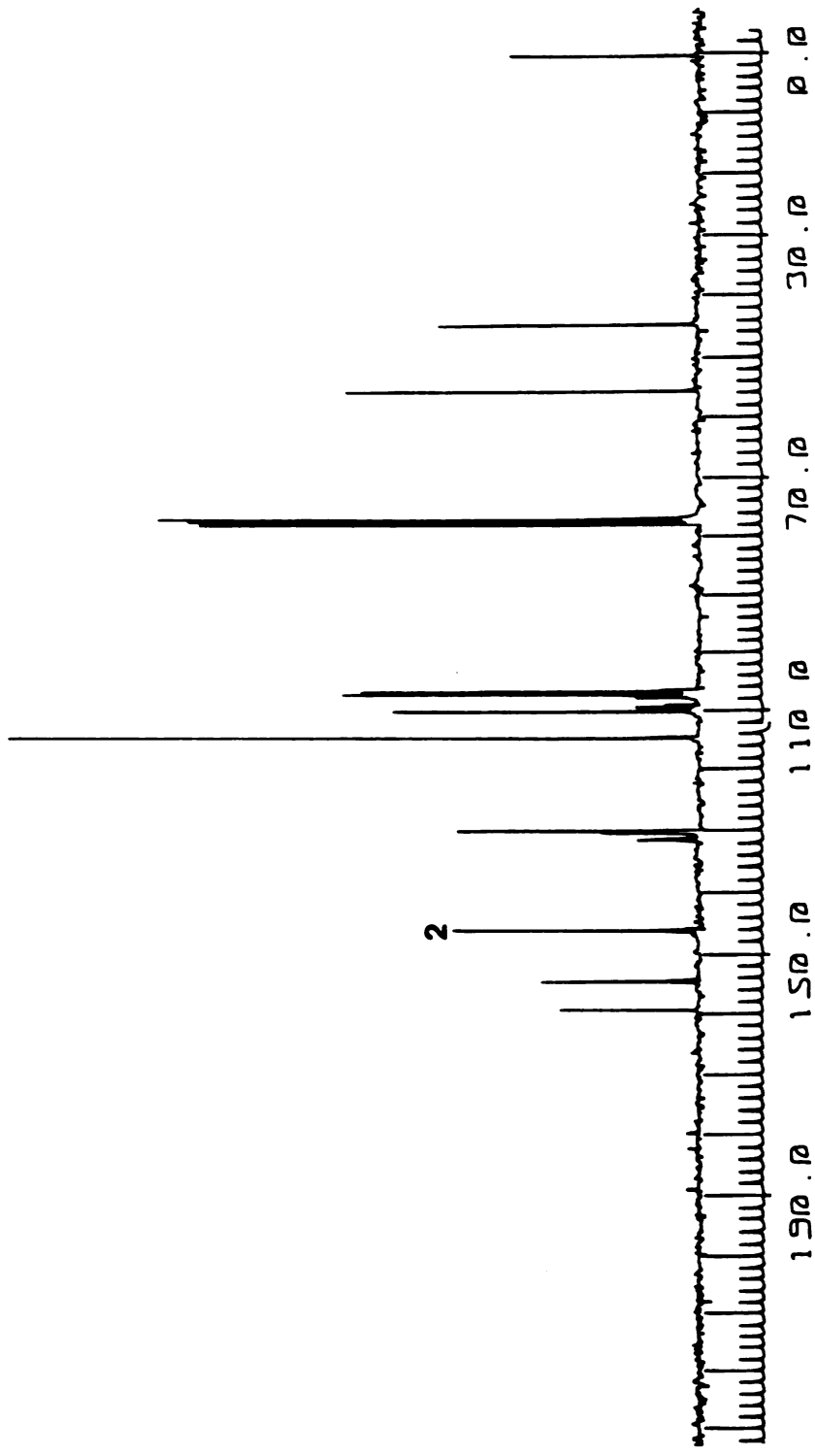
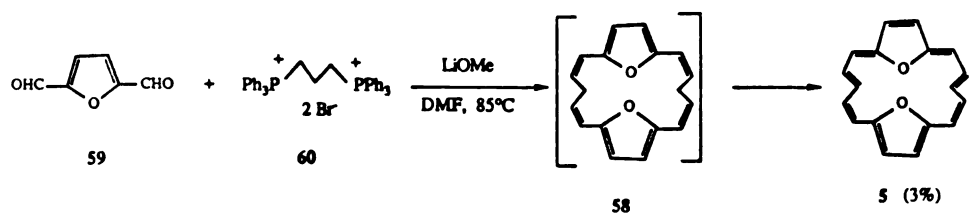


Figure 11. 62.9 MHz ^{13}C NMR spectrum of **42d**.

spectrum indicates **42d** is still a mixture of cyclic dimer (n=2) and tetramer (n=4).

Although **42c** and **42d** are a mixture of cyclic dimer and tetramer, their oxidation to the [26]annulene hexoxide **9** is still worth studying.

Ogawa et al.[16] reported an "one pot synthesis" of [18]annulene dioxide **5** via the thermal dehydrogenation of the cycloolefin **58** from the double Wittig reaction of 2,5-furandialdehyde **59** with trimethylenebis(triphenylphosphonium) bromide **60** in DMF at 85°C under high dilution condition [Scheme 33].



Scheme 33

This thermal dehydrogenation caught our attention because we envisioned that the cyclic dimer from 42c or 42d was looked like an expanded system of 58 by inserting a double bond on each side of the sp^3 carbons and then confined each pair of double bond by an oxygen bridge.

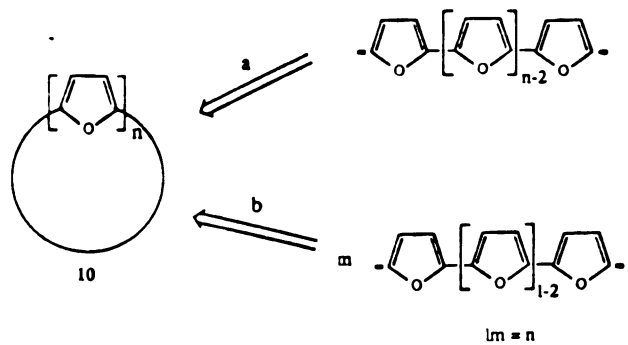
Using UV-vis spectrum to monitor the reaction, we found

that no reaction occurred when a solution of **42d** in DMF was heated at 85°C for 2 days. Neither did the dehydrogenation occur when the solution was heated at 100°C. However, when the temperature was raised to 120°C and the solution was heated at this temperature for 3 days, longer wavelength absorption was detected and the compound was later isolated and identified as 5,5''-bis(4-methoxybenzoyl)-terfuran **37f**. This result indicated the cyclic product **42d** broke apart at 120°C to give **37f**, possibly via a hydroperoxide intermediate.

Compound **42c** could not be oxidized to the 26 π-electron annulene with any of the following reagents: 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), benzoyl peroxide, azabisisobutyronitrile (AIBN) or lithium diisopropylamine (LDA) then oxygen. The products obtained from these reactions were unidentified by 250 MHz ^{1}H NMR analysis. Attempt to introduce a bromine atom onto one of the methine hydrogens of **42c** and then elimination to **9** was also unsuccessful.

II. Studies towards the synthesis of cyclic α-polyfuran **10**

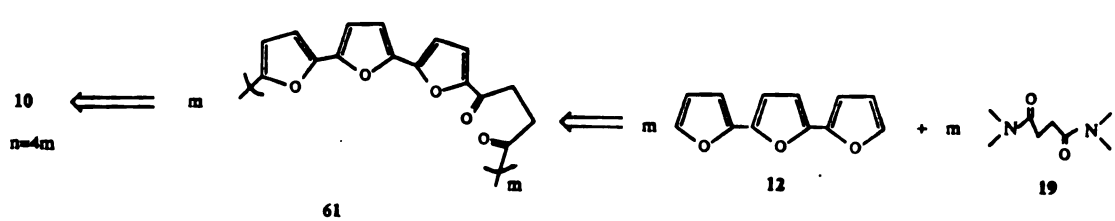
The first synthetic approach to the cyclic α-polyfuran **10** is based on either the intramolecular or intermolecular oxidative coupling of the dianion from linear α-polyfuran [Scheme 34]. However, the insolubility of the larger linear α-polyfurans in etheral solvents prevents the study of intramolecular cyclization to **10** (path a). Consequently, only the intermolecular oxidative coupling of the dianion has been investigated (path b).



Scheme 34

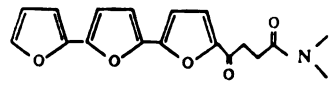
The dianion (l=3), generated from the α-terfuran **12** with 2 molar equivalents of n-BuLi and then treated with anhydrous copper(II) chloride , gave an insoluble, unidentified substance as the major product together with some starting material and α-sexifuran **24**. Vacuum sublimation of the unidentified product gave nothing even when the pot temperature reached 300°C.

Another retrosynthetic analysis of **10** suggests the macrocyclic 1,4-diketone **61** as a possible precursor. This compound might be obtained from α-terfuran **12** and the diamide **19** [Scheme 35].



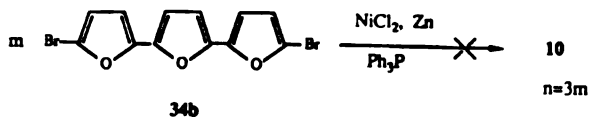
Scheme 35

The reaction bewteen the dianion of **12** and the diamide **19** gave a multitude of products, including a significant amount of a reddish brown solid and some starting material, ketone compound **39b** and an amide **62.** Due to its insolubility in any solvent system, the identification of the solid was not possible and the solid was assumed to be a polymeric substance.



62

Finally, a recent report of the facile coupling reaction of aryl chlorides by nickel and reducing metals to the corresponding biaryls[32] led us to attempt the synthesis of **10** from the dibromide **34b** [Scheme 36]. Unfortunately, the



34b

Scheme 36

reaction of **34b** with the nickel(0) triphenylphosphine complex which was generated <u>in situ</u> from nickel(II) chloride, triphenylphosphine and zinc metal yielded unidentified products.

CONCLUSIONS

It has been demonstrated that the linear α-polyfurans can be obtained in fair yields from the dehydrative cyclization of 1,4-diketones. Besides, this 1,4-diketone approach also provided a convenient entry to the mixed α-polyaryls (**26-31**). The α-polyfurans exhibit electrophilic and nucleophilic properties which give rise to various monosubstituted and disubstituted derivatives. However, the use of the α-polyfurans as the candidates for conductivity study still remains to be explored.

Several unsuccessful attempts have been carried out to oxidize compound **42c** or **42d** to the annulene hexoxide **9**. The failure of this last oxidation step might in part due to the instability of the product **9**. Theoretical calculation[4] has predicted that there would be little or no resonance energy for annulenes having 22 π-electrons or more. Of course, more experimental results have to be obtained to support this theory.

Finally, the attempts to the synthesis of macrocyclic α-polyfuran **10** have been thwarted by the sparing solubility of the oligomeric intermediates which were build up from the simple precursors.

EXPERIMENTAL

General Methods All melting points were determined by using a Thomas-Hoover capillary melting point apparatus and are uncorrected. The NMR spectra were recorded on a Bruker WM-250 (^{1}H NMR at 250 MHz and ^{13}C NMR at 62.9 MHz) instrument in $CDCl_3$ or as noted. The internal standard used was tetramethylsilane (TMS) unless sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) is indicated. Infrared (IR) spectra were obtained from Nujol mull for solids or neat for liquids and recorded on a Perkin-Elmer 599 spectrophotometer. All ultraviolet and visible (UV-vis) spectra were recorded on a Schimatzu 160 spectrophotometer in chloroform solution by using 1 cm matched quartz cells. Mass spectra were obtained on a Finnigan 400 instrument with EI at 70 eV. High resolution mass were measured on JOEL HX110 high resolution mass spectrometer by Mr. Ernest Oliver. Microanalyses were performed by Galbraith Laboratories, Incorporated. Flash column chromatography refers to the method of Still, Kahn and Mitra[33] using Merck silica gel (0.040-0.063 mm). Dry diethyl ether, tetrahydrofuran and toluene were obtained by distillation from potassium with benzophenone as indicator. Dry methylene chloride (CH_2Cl_2) and 1,2-dichloroethane were obtained by distillation from calcium hydride. Dimethylformamide (DMF)

was dried with molecular sieve (4A) and then distilled under reduced pressure. n-Butyllithium (2.5M in hexanes), phenyllithium-lithium bromide complex (1.0M in diethyl ether), diethylaluminum chloride (1.0M in hexanes), vinyl sulfone, 3-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride and Lawesson's reagent were purchased from Aldrich Chemical Company, Inc and used as received. 2-Furyllithium [29] and 2-thienyllithium[34] were prepared according to the literature methods. All the reactions were done under an argon atmosphere unless otherwise stated.

N,N,N',N'-Tetramethylsuccinamide 19

To an ice cold solution of 40% aqueous dimethylamine (14.6 g, 129.5 mmol) was added dropwise a solution of succinyl chloride (5.0 g, 32.3 mmol) in methylene chloride (40 mL). After addition was completed, the solution was stirred at $0^{o}C$ for 4h. The organic layer was separated from the water layer, diluted with CH_2Cl_2 (60 mL) and washed with saturated $NaHCO_3$ solution. The solution was dried over anhydrous $MgSO_4$ and evaporated in vacuo to dryness to give **19** (3.6 g, 65%) as white solid. After vacuum dried for 24h, the compound was pure enough for further use: m.p. 80-82^{o}C (lit.[35] m.p. 84.5-85.5^{o}C); ^{1}H NMR: δ 2.69 (s, 4H), 3.00 (broad d, 12H); MS: m/e (rel. intensity) 172 (M^{+}, 15), 128 (100), 100 (79), 72 (93), 55 (30), 44 (40).

Methyl N,N-dimethylcarbamate 38

Methyl chloroformate (20.0 g, 0.22 mol) was added dropwise to a stirred ice-cold solution of 40% aqueous dimethylamine (55.0 g, 0.49 mol). Stirring was continued for a further 1h after the addition; the ice-bath was removed and stirring was continued for 6h. The mixture was then extracted with ether and the extract was washed with saturated NaCl solution. The solution was dried over anhydrous $MgSO_4$ and evaporated in vacuo to give a brownish liquid. The liquid was distilled to give 10.6 g (49%) of **38** as colorless liquid: b.p. 129-130°C/760 mmHg (lit.[36] b.p. 131°C/760 mmHg); ^{1}H NMR: δ 2.91 (s, 6H), 3.68 (s, 3H); MS: m/e (rel. intensity) 103 (M^+, 54), 88 (74), 72 (100), 44 (65), 42 (58), 40 (96); IR: cm^{-1} 1702.

3-Dimethylamino-1-(2-furyl)-propanone 15a

A mixture of 2-acetylfuran **17a** (10.0 g, 0.09 mol), paraformaldehyde (3.2 g, 0.11 mol), dimethylamine hydrochloride (8.9 g, 0.11 mol) and concentrated HCl (0.5 mL) in 95% ethanol (20 mL) was heated under reflux for 16h. After cooling, the white precipitate was suction filtered to give the Mannich base hydrochloride **18a** (12.6 g, 68%): m.p. 177-179°C (lit.[37] m.p. 178°C); ^{1}H NMR: (D_2O, DSS) δ 2.95 (s, 6H), 3.58 (bs, 4H), 6.78 (dd, 1H), 7.62 (d, 1H), 7.94 (d, 1H); MS: m/e (rel. intensity) 205 (M^++2, not observed), 203 (M^+, not observed), 167 (M^+-HCl, 18), 95 (25), 58 (100); IR: cm^{-1} 1660.

The Mannich base hydrochloride was treated with an aqueous ammonia solution and extracted with ether (3x50 mL). The combined organic extracts were washed with water (10 mL), then saturated NaCl solution (10 mL) and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo furnished the free Mannich base **15a** which was used immediately in the Michael-Stetter reaction. ^1H NMR of **15a**: δ 2.28 (s, 6H), 2.76 (t, 2H), 3.03 (t, 2H), 6.54 (dd, 1H), 7.22 (d, 1H), 7.60 (d, 1H).

3-Dimethylamino-1-(5-2,2'-bifuryl)-propanone 15b

A mixture of 5-acetyl-2,2'-bifuran **17b** (1.21 g, 6.88 mmol), paraformaldehyde (258.3 mg, 8.60 mmol), dimethylamine hydrochloride (0.70 g, 8.60 mmol) and concentrated HCl (0.03 mL) in 95% ethanol (5 mL) was heated under reflux for 16h. After cooling in the refrigerator overnight, the precipitate was collected to give 0.82 g (44%) of Mannich base hydrochloride **18b**: m.p. 166-168^oC; ^1H NMR: (D_2O, DSS) δ 3.02 (s, 6H), 3.58 (s, 4H), 6.68 (dd, J=3.4, 1.8 Hz, 1H), 6.79 (d, J=3.8 Hz, 1H), 6.97 (d, J=3.5 Hz, 1H), 7.55 (d, J=3.8 Hz, 1H), 7.71 (d, J=1.7 Hz, 1H); MS: m/e (rel. intensity) 269 (M^+, not observed), 233 (M^+-HCl, 20), 188 (19), 161 (12), 105 (21), 58 (100); IR: cm^{-1} 1660.

The Mannich base hydrochloride was treated with an aqueous ammonia solution and extracted with ether (3x50 mL). The combined organic extracts were washed with water (10 mL), then saturated NaCl solution (10 mL) and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo gave the free Mannich

base **15b** which was used immediately in the Michael-Stetter reaction. ^{1}H NMR of **15b**: δ 2.30 (s, 6H), 2.78 (t, 2H), 3.04 (t, 2H), 6.52 (dd, 1H), 6.68 (d, 1H), 6.84 (d, 1H), 7.25 (d, 1H), 7.51 (d, 1H); MS: m/e (rel. intensity) 233 (M^+, 3), 188 (5), 161 (3), 105 (12), 58 (100).

General procedure for 1,4-diketones 20-22 from N,N,N',N'-tetramethylsuccinamide 19

To the organolithium reagent (6.0 mmol) in dry ether (15 mL) at 0^{o}C was added the diamide **19** (0.5 g, 2.9 mmol) in one portion. The solution was then allowed to stir at room temperature for 24h. The solution was cooled in an ice bath and 10% HCl was added (15 mL). After stirring for 1h. the ether layer was separated from the water layer. The aqueous layer was extracted with $CHCl_3$ (2x20 mL). The combined organic layers were washed successively with water and brine solution. The organic phase was dried over anhydrous $MgSO_4$, filtered and the solvent was removed under reduced pressure. Yields and purification are given below.

5,8-Dodecanedione 20

Flash column chromatographed over silica gel using ether:hexane (v/v=1/1) as eluent gave 0.12 g (20%) of **20** as white solid: m.p. 48-50^{o}C (lit.[38] m.p. 53^{o}C); ^{1}H NMR: δ 0.90 (t, J=7.2 Hz, 6H), 1.32 (tq, 4H), 1.58 (tt, 4H), 2.45 (t, J=7.6 Hz, 4H), 2.68 (s, 4H); ^{13}C NMR: δ 13.74, 22.23, 25.86, 35.92, 42.48, 209.67; MS: m/e (rel. intensity) 198

(M^+, 0.5), 156 (26), 141 (53), 113 (14), 85 (99), 57 (100); IR: cm^{-1} 1670.

1,4-Diphenyl-1,4-butanedione 21

Obtained as a white solid (0.33 g, 48%) after flash column chromatographed over silica gel using CH_2Cl_2 as eluent: m.p. 139-141°C (lit.[39] m.p. 144°C); ^1H NMR: δ 3.47 (s, 4H), 7.26-7.58 (m, 6H), 8.02-8.06 (m, 4H).

1,4-Bis(2-thienyl)-1,4-butanedione 22

Obtained as a pale brownish solid (0.16 g, 22%) after flash column chromatographed over silica gel using $CHCl_3$ as eluent:m.p. 128-130°C (lit.[40] m.p. 131-132°C); ^1H NMR: δ 3.40 (s, 4H), 7.15 (dd, 2H), 7.65 (d, 2H), 7.82 (d, 2H).

1,4-Bis(2-furyl)-1,4-butanedione 16a

From vinyl sulfone: To a hot stirred solution of thiazolium salt (10.7 g, 0.04 mol) and sodium acetate (6.56 g, 0.08 mol) in absolute ethanol (400 mL) was added furfural **14a** (38.4 g, 0.4 mol) in one portion. The vinyl sulfone (23.6 g, 0.2 mol) was added dropwise to the solution. The mixture was refluxed overnight and then poured into water (500 mL). The aqueous solution was extracted with chloroform (5x100 mL) and the combined organic extracts were suction filtered to remove the polysulfone. The filtrate was washed with saturated NaCl solution and dried over $MgSO_4$. Removal of the solvent in vacuo gave the crude product which was recrystallized from

ethanol to give 28.7 g (65.8%) of 16a as colorless crystals: m.p. 130-131°C (lit.[41] m.p. 132°C); ^{1}H NMR: δ 3.30 (s, 4H), 6.52 (dd, 2H), 7.25 (d, 2H), 7.60 (d, 2H); ^{13}C NMR: δ 31.80, 112.15, 117.05, 146.31, 152.37, 187.45; MS: m/e (rel. intensity) 218 (M^+, 84), 123 (39), 95 (100).

From diamide **19:** To the 2-furyllithium (6.0 mmol) in dry ether (15 mL) at 0°C was added the diamide **19** (0.5 g, 2.9 mmol) in one portion. The solution was then allowed to stir at room temperature for 24h. The solution was cooled in an ice bath and 10% HCl was added (15 mL). After stirring for 1h, the ether layer was separated from the water layer. The aqueous layer was extracted with $CHCl_3$ (2x20 mL). The combined organic layers were washed successively with water and brine solution. The solution was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography over silica gel using $CHCl_3$ as eluent to give 0.32 g (50%) of **16a.**

1-(2-Furyl)-4-(5-2,2'-bifuryl)-1,4-butanedione 16b

A solution of aldehyde **14b** (1.40 g, 8.64 mmol) in dry DMF (4 mL) was added over a period of 15 min to a suspension of KCN (0.30 g, 4.61 mmol) in dry DMF (4 mL). After the mixture had been stirred for 15 min, the free Mannich base 3-dimethylamino-1-(2-furyl)-propanone **15a** (1.12 g, 6.71 mmol) in dry DMF (8 mL) was added over a period of 30 min. The solution was allowed to stir overnight. The solution was poured into water and extracted with chloroform. The organic

layers were washed thoroughly with water and dried over anhydrous $MgSO_4$. Evaporation of the solvent in vacuo gave the crude product which was purified by flash column chromatography over silica gel using $CHCl_3$ to afford **16b** (1.20 g, 63%). An analytical sample can be obtained by recrystallization from ethanol with charcoal decolorization to give colorless needle: m.p. 98-99°C; ^{1}H NMR: δ 3.30 (s, 4H), 6.50 (dd, J=3.6, 1.8 Hz, 1H), 6.53 (dd, J=3.6, 1.8 Hz, 1H), 6.68 (d, J=3.7 Hz, 1H), 6.84 (d, J=3.5 Hz, 1H), 7.24 (d, J=3.6 Hz, 1H), 7.30 (d, J=3.7 Hz, 1H), 7.49 (d, J=1.8 Hz, 1H), 7.60 (d, J=1.8 Hz, 1H); ^{13}C NMR: δ 31.77, 31.92, 107.14, 108.52, 111.81, 112.14, 117.08, 118.11, 143.40, 145.19, 146.31, 149.72, 150.98, 152.40, 186.83, 187.51; MS: m/e (rel. intensity) 284 (M^+, 15), 189 (100), 161 (45), 105 (91), 95 (47), 51 (52); UV-vis: λ_{max} (ϵ_M) 270 (1.35×10^4), 336 (1.60×10^4); IR: cm^{-1} 1665.

Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.60; H, 4.25
Found: C, 67.46; H, 4.37

1,4-Bis(5-2,2'-bifuryl)-1,4-butanedione 16c

From Mannich base: Using the procedure described for **16b**, the aldehyde **14b** (160 mg, 0.99 mmol) and the Mannich base **15b** (180 mg, 0.77 mmol) gave 186 mg (68%) of the 1,4-diketone **16c**. Recrystallization from ethanol with charcoal decolorization gave colorless leaflet: m.p. 151-152°C; ^{1}H NMR: δ 3.32 (s,4H), 6.51 (dd, J=3.3, 1.8 Hz, 2H), 6.67 (d, J=3.7 Hz, 2H), 6.84 (d, J=3.4 Hz, 2H), 7.30 (d, J=3.7 Hz, 2H),

7.48 (d, J=1.8 Hz, 2H); ^{13}C NMR: δ 31.95, 107.17, 108.55, 111.84, 119.16, 143.43, 145.25, 149.78, 151.07, 186.92; MS: m/e (rel. intensity) 350 (M^+, 15), 189 (100), 105 (93); UV-vis: λ_{max} (ϵ_M) 346.0 (4.03×10^4); IR: cm^{-1} 1671.

Anal. Calcd for $C_{20}H_{14}O_6$: C, 68.57; H, 4.03

Found: C, 68.40; H, 4.25

From vinyl sulfone: To a hot stirred solution of thiazolium salt (200 mg, 0.74 mmol) and sodium acetate (120 mg, 1.46 mmol) in absolute ethanol (8 mL) was added the aldehyde **14b** (1.18 g, 7.28 mmol) in one portion. The vinyl sulfone (430 mg, 3.64 mmol) was added dropwise to the solution. The mixture was refluxed overnight and then poured into water. The aqueous solution was extracted with chloroform and the combined organic extracts were suction filtered. The filtrate was washed with saturated NaCl solution and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo gave the crude product which was flash column chromatographed over silica gel using CH_2Cl_2:EtOAc (v/v=40/1) as eluent to give 640 mg (50%) of **16c**.

From diamide **19**: n-BuLi (5.2 mmol) was added to a solution of α-bifuran **11** (700 mg, 5.2 mmol) in dry ether (15 mL) at -60^oC. The solution was raised slowly to room temperature and stirred at room temperature for 2h. The solution was cooled at 0^oC and the diamide **19** (400 mg, 2.3 mmol) was added in one portion. The solution was allowed to stir at room temperature for 24h. Work-up as described before and the crude product was flash column chromatographed over silica

gel using $CHCl_3$ as eluent to give 500 mg (61%) of **16c.**

1-(2-Furyl)-4-(5-2,2':5,2''-terfuryl)-1,4-butanedione 16d

A solution of aldehyde **14c** (1.30 g, 5.70 mmol) in dry DMF (4 mL) was added over a period of 15 min to a suspension of KCN (200 mg, 3.07 mmol) in dry DMF (4 mL). After the mixture had been stirred for 15 min, the free Mannich base **15a** (133.4 mg, 4.39 mmol) in dry DMF (10 mL) was added over a period of 30 min. The solution was allowed to stir overnight. The solution was poured into water and extracted with $CHCl_3$. The combined organic layers were washed thoroughly with water and dried over anhydrous $MgSO_4$. Evaporation of the solvent in vacuo gave the crude product which was flash column chromatographed over silica gel using $CHCl_3$ as eluent to give 900 mg (59%) of **16d.** An analytical sample can be obtained by recrystallization from ethanol with charcoal decolorization to give pale brownish needle: m.p. 137-139°C; ^1H NMR: δ 3.30 (s, 4H), 6.48 (dd, J=3.4, 1.8 Hz, 1H), 6.55 (dd, J=3.4, 1.6 Hz, 1H), 6.65 (d, J=3.6 Hz, 1H), 6.68 (d, J=3.4 Hz, 1H), 6.72 (d, J=3.7 Hz, 1H), 6.88 (d, J=3.6 Hz, 1H), 7.25 (d, J=3.5 Hz, 1H), 7.31 (d, J=3.7 Hz, 1H), 7.45 (d, J=1.4 Hz, 1H), 7.59 (d, J=1.3 Hz, 1H); ^{13}C NMR: δ 31.80, 31.98, 106.46, 107.23, 107.35, 110.47, 111.58, 112.17, 117.08, 119.28, 142.48, 144.22, 145.75, 146.32, 147.31, 149.43, 151.13, 152.45, 186.74, 187.57; MS: m/e (rel. intensity) 350 (M^+, 14), 255 (21), 95 (59), 43 (100); UV-vis: λ_{max} (ϵ_M) 271.5 (2.46×10^4), 374.0 (3.21×10^4); IR: cm^{-1} 1662.

Anal. Calcd for $C_{20}H_{14}O_6$: C, 68.57; H, 4.03

Found: C, 68.06; H, 4.22

1-(5-2,2'-Bifuryl)-4-(5-2,2':5',2''-terfuryl)-1,4-butanedione 16e

Using the procedure described for **16d**, the aldehyde **14c** (228.6 mg, 1.00 mmol) and the Mannich base **15b** (186.9 mg, 0.80 mmol) gave 176 mg (53%) of the 1,4-butanedione **16e**; m.p. 150-152°C; ^{1}H NMR: δ 3.34 (s, 4H), 6.50 (m, 2H), 6.62-6.70 (m,3H), 6.75 (d, J=3.7 Hz, 1H), 6.84 (d, J=3.5 Hz, 1H), 6.89 (d, J=3.6 Hz, 1H), 7.32 (t, 2H), 7.45 (d,J=1.7 Hz, 1H), 7.49 (d, J=1.6 Hz, 1H); ^{13}C NMR: δ 31.99, 106.49, 107.20, 107.28, 107.40, 108.58, 110.52, 111.64, 111.90, 119.23, 119.37, 142.52, 143.46, 144.25, 145.78, 147.28, 149.48, 149.83, 151.13, 186.89; MS: m/e (rel. intensity) 416 (M^+, 47), 255 (100), 171 (44), 115 (41), 105 (94); UV-vis: λ_{max} (ϵ_M) 348.5 (3.34×10^4); IR; cm^{-1} 1662: Exact mass calcd for $C_{24}H_{16}O_7$: 416.0898, found 416.0912.

1-(2-Furyl)-4-(5-2,2':5',2'':5'',2'''-quaterfuryl)-1,4-butanedione 16f

A solution of aldehyde 14d (26.4 mg, 0.09 mmol) in dry DMF (1 mL) was added over a period of 5 min to a susupension of KCN (2.90 mg, 0.04 mmol) in dry DMF (0.5 mL). After the mixture had been stirred for 15 min, the free Mannich base 15a (12.0 mg, 0.07 mmol) in dry DMF (1 mL) was added over a period of 5 min. The solution was allowed to stir overnight.

The solution was poured into water and extracted with $CHCl_3$. The combined organic layers were washed thoroughly with water and dried over anhydrous $MgSO_4$. Evaporation of the solvent in vauco gave the crude product which was chromatographed over silica gel by flash technique using CH_2Cl_2:EtOAc (v/v=40/1) as eluent to give 11.9 mg (40%) of 1,4-diketone **16f**: m.p. 168-169°C (dec); ^{1}H NMR: δ 3.32 (s, 4H), 6.48 (dd, J=3.4, 1.8 Hz, 1H), 6,54 (dd, J=3.6, 1.7 Hz, 1H), 6.63-6.66 (m, 2H), 6.72-6.75 (m, 3H), 6.92 (d, J=3.6 Hz, 1H), 7.25 (d, 1H), 7.32 (d, J=3.7 Hz, 1H), 7.45 (d, J=1.3 Hz, 1H), 7.60 (d, J=1.8 Hz, 1H); ^{13}C NMR: δ 31.86, 32.01, 105.91, 107.14, 107.49, 107.58, 108.38, 110.68, 111.57, 112.23, 117.17, 119.37, 142.22, 144.43, 146.38, 146.45, 149.43, 151.16, 152.49, 186.80, 187.62; MS: m/e (rel. intensity) 416 (M^+, 59), 321 (37), 95 (100); UV-vis: λ_{max} (ϵ_M) 398.0 (5.96×10^4); IR: cm^{-1} 1647; Exact mass calcd for $C_{24}H_{16}O_7$: 416.0896, found 416.0913.

1-(5-2,2'-Bifuryl)-4-(5-2,2':5',2'':5'',2'''-quaterfuryl)-1,4-butanedione 16g

Using the procedure described for **16f**, the aldehyde **14d** (61.5 mg, 0.21 mmol) and the Mannich base **15b** (39.0 mg, 0.17 mmol) gave 40.8 mg (51%) of desired **16g**: m.p. 165-166°C (dec); ^{1}H NMR: δ 3.34 (s, 4H), 6.48-6.53 (m, 2H), 6.63-6.69 (m, 3H), 6.72-6.76 (m, 3H), 6.84 (d, J=3.4 Hz, 1H), 6.92 (d, J=3.6 Hz, 1H), 7.31 (d, J=3.8 Hz, 1H), 7.33 (d, J=3.7 Hz, 1H), 7.44 (d, J=1.4 Hz, 1H), 7.49 (d, J=1.2 Hz, 1H); ^{13}C NMR: δ 32.01, 105.91, 107.14, 107.23, 107.52, 107.58, 108.38, 108.61,

110.70, 111.58, 111.91, 119.26, 119.41, 142.23, 143.49, 144.43, 144.84, 145.31, 146.05, 146.46, 147.02, 149.46, 151,19, 186.89, 187,01; MS: m/e (rel. intensity) 482 (M^+, 18), 321 (30), 294 (20), 161 (46), 149 (82), 105 (70), 57 (100); UV-vis: λ_{max} (ϵ_M) 348.5 (1.63×10^4), 397.5 (2.09×10^4); IR: cm^{-1} 1670.

1,4-Bis(5-2,2':5',2''-terfuryl)-1,4-butanedione 16h

From vinyl sulfone: To a hot stirred solution of thiazolium salt (236 mg, 0.88 mmol) and sodium acetate (144 mg, 1.76 mmol) in absolute ethanol (20 mL) was added the aldehyde **14c** (200 mg, 8.8 mmol) in one portion. The vinyl sulfone (530 mg, 4.4 mmol) was added dropwise to the solution. The mixture was refluxed overnight and then poured into water. The aqueous solution was extracted with chloroform and the combined organic extracts were suction filtered. The filtrate was washed with saturated NaCl solution and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo gave the crude product which was flash column chromatographed over silica gel using $CHCl_3$ as eluent to give 1.33 g (63%) of **16h**. Recrystallization of **16h** from chloroform gave yellow crystal: m.p. 208-210°C; ^{1}H NMR: δ 3.10 (s, 4H), 6.48 (dd, J=3.4, 1.8Hz, 2H), 6.64 (d, J=3.6 Hz, 2H), 6.69 (d, J=3.4 Hz, 2H), 6.74 (d, J=3.7 Hz, 2H), 6.90 (d, J=3.6 Hz, 2H), 7.32 (d, J=3.7 Hz, 2H), 7.45 (d, J=1.7 Hz, 2H); ^{1}H NMR: (DMSO-d_6) δ 3.26 (s, 4H), 6.66 (dd, J=3.3, 1.[illegible] Hz, 2H), 6.88 (d, J=3.2 Hz, 2H), 6.90 (d, J=3.7 Hz, 2H), 7.02 (d, J=3.7 Hz, 2H), 7.13 (d, J=3.6 Hz,

2H), 7.66 (d, J=3.6 Hz, 2H), 7.81 (dd, J=1.8, 0.6 Hz, 2H); ^{13}C NMR: δ 32.04, 106.52, 107.32, 107.44, 110.57, 111.64, 119.40, 142.54, 144.28, 145.80, 147.40, 149.54, 151.22, 186.92; MS: m/e (rel. intensity) 482 (M^+, 14), 255 (56), 40 (100); UV-vis: λ_{max} (ϵ_M) 377.5 (7.40×10^4); IR: cm^{-1} 1660; Exact mass calcd for $C_{28}H_{18}O_8$: 482.1002, found 482.1018.

Anal. Calcd for $C_{28}H_{18}O_8(\frac{1}{2}H_2O)$: C, 68.43; H, 3.90

Found: C, 68.49; H, 4.06

From diamide 19: n-BuLi (3.5 mmol) was added to a solution of α-terfuran **12** (0.7 g, 3.5 mmol) in dry ether (15 mL) at -60°C. The solution was raised slowly to room temperature and stirred at room temperature for 2h. The solution was cooled to 0°C and the diamide **19** (0.3 g, 1.74 mmol) was added in one portion. The solution was allowed to stir at room temperature for 24h. Work-up as described before and purified by flash column chromatography over silica gel gave 410 mg (49%) of **16h**.

1,4-Bis(5-2,2':5',2'':5'',2'''-quaterfuryl)-1,4-butanedione 16i

To a hot stirred solution of thiazolium salt (9.2 mg, 0.034 mmol) and sodium acetate (5.6 mg, 0.068 mmol) in absolute ethanol (5 mL) was added the aldehyde **14d** (100 mg, 0.34 mmol) in one portion. The vinyl sulfone (23.5 mg, 0.20 mmol) was also added in one portion via a syringe. The suspension was refluxed for 24h. The cooled solution was suction filtered. The residue was suspended in $CHCl_3$ (5 mL) and stirred overnight. The solution was suction filtered to

give 28.6 mg (28%) of 1,4-diketone **16i** as egg yellow solid: m.p. 242-245°C (dec); ^{1}H NMR: ($CDCl_3$ with CF_3CO_2H) δ 3.43 (s, 4H), 6.50 (m, 2H), 6.67 (m, 4H), 6.78 (m, 4H), 6.83 (d, J=3.8 Hz, 2H), 7.00 (d, J=3.6 Hz, 2H), 7.46 (s, 2H), 7.58 (d, J=3.8 Hz, 2H); MS: m/e (rel. intensity) 614 (M^+, 66), 321 (82), 237 (25), 215 (30), 95 (35), 44 (100); UV-vis: λ_{max} (ϵ_M) 401.0 (2.30×10^4); IR: cm^{-1} 1671; Exact mass calcd for $C_{36}H_{22}O_{10}$: 614.1213, found 614.1235.

2,2'-Bifuran 11

The α-bifuran **11** was synthesized according to the procedure of Kauffmann.[21c] The desired product **11** (4.1 g, 41%) was obtained as colorless liquid from the oxidative coupling of 2-furyllithium (150 mmol) by anhydrous copper (II) chloride (16.13 g, 120 mmol): b.p. 76-77°C/20 mmHg (lit.[21e] b.p. 63-64/11 mmHg); ^{1}H NMR: δ 6.42 (dd, J=3.3, 1.8 Hz, 2H), 6.52 (d, J=3.3 Hz, 2H), 7.40 (d, J=1.8 Hz, 2H).

2,2':5',2''-Terfuran 12

<u>From dehydration by acid catalyst:</u> To a cooled solution of 1,4-diketone **16a** (10 g, 45.9 mmol) in acetic anhydride (300 mL) was added concentrated hydrochloric acid (15 mL) portion-wise. The solution was stirred at room temperature for 4 days. The solution was poured into water (600 mL) and stirred for 1h. The aqueous solution was extracted with CCl_4 (4x150 mL). The combined organic layers were washed successively with water, saturated $NaHCO_3$ solution and saturated NaCl

solution. After drying over anhydrous $MgSO_4$, the solvent was removed in vacuo to give a brown oil which was purified by flash column chromatography over silica gel using Et_2O:hexanes (v/v=1/5) as eluent to give 5.8 g (63%) of α-terfuran **12** as white solid: m.p. 63-64°C (lit.[21c] m.p. 65°C); ^1H NMR: δ 6.45 (dd, J=3.3, 1.8 Hz, 2H), 6.58 (s, 2H), 6.60 (d, 2H), 7.45 (d, J=1.7 Hz, 2H); ^{13}C NMR: δ 105.40, 106.91, 111.43, 141.93, 145.72, 146.25; MS: m/e (rel. intensity) 200 (M^+, 100), 115 (22); UV-vis: λ_{max} (ϵ_M) 330 (1.66×10^4), 350 (1×10^4).

From dehydration under neutral condition: To the methyl ester of polyphosphoric acid P-Me[42] (2.0 g) was added a solution of 1,4-diketone **16a** (103.9 mg, 0.48 mmol) in chloroform (1 mL). The solution was heated at 100°C for 24h. After cooling, the solution was poured into ice-water mixture. The aqueous solution was extracted with CH_2Cl_2. The combined organic layers were washed with water, then brine solution and dried over anhydrous $MgSO_4$. Evaporation of the solvent in vauco gave the crude product which was flash column chromatographed over silica gel using Et_2O/hexanes (v/v=1/5) as eluting solvent to give 14.8 mg (15.4%) of **12** as white solid.

2,2':5',2'':5'',2'''-Quaterfuran 13

To a solution of 1,4-diketone **16b** (150 mg, 0.53 mmol) in acetic anhydride (4.0 mL) was added concentrated hydrochloric acid (0.2 mL) in one portion. The solution was stirred at room temperature for 36h. The solution was poured into water (120 mL) and neutralized with solid sodium carbonate. The

solution was extracted with chloroform (3x40 mL). The combined organic layers were washed with saturated NaCl solution and dried over anhydrous $MgSO_4$. Evaporation of the solvent in vacuo gave the crude product which was flash column chromtographed over silica gel using Et_2O:hexanes (v/v=1/5) to give 48.9 mg (42% based on recovered 1,4-diketone) of desired **13**. Recrystallization from pet. ether (60-90°C) gave pale yellow crystals: m.p. 160-162°C (lit.[21c] m.p. 158°C); ^1H NMR: δ 6.48 (dd, J=3.3, 1.8 Hz, 2H), 6.61-6.68 (m, 4H), 6.70 (d, J=3.6 Hz, 2H), 7.43 (d, J=1.8 Hz, 2H); ^{13}C NMR: δ 105.52, 107.05, 107.26, 111.49, 142.00, 145.37, 145.90, 146.22; MS: m/e (rel. intensity) 266 (M^+, 100), 237 (3), 181 (5); UV-vis: λ_{max} (ϵ_M) 275.5 ($1.04x10^4$), 366.0 ($2.49x10^4$), 390.0 ($1.80x10^4$).

2,2':5',2'':5'',2''':5''',2''''-Quinquefuran 23

From 1,4-diketone **16c:** To a solution of 1,4-diketone **16c** (434.9 mg, 1.24 mmol) in acetic anhydride (15 mL) was added concentrated hydrochloric acid (0.4 mL) in one portion. The solution was stirred at room temperature for 24h. The solution was poured into water (150 mL) and neutralized with solid sodium carbonate. The aqueous solution was extracted with $CHCl_3$ (3x50 mL). The combined organic layers were washed with saturated NaCl solution and dried over anhydrous $MgSO_4$. Evaporation of the solvent in vacuo gave the crude product which was chromatographed over silica gel by flash technique using CH_2Cl_2:hexanes (v/v=3/5) to give 154.9 mg (40% based on

recovered 1,4-diketone) of desired compound **23**. Recrystallization from methylene chloride gave yellow crystal : m.p. 207-209°C; ^{1}H NMR: δ 6.48 (dd, J=3.6, 1.8 Hz, 2H), 6.63 (t, 4H), 6.68-6.70 (m, 4H), 7.43 (d, J=1.7 Hz, 2H); ^{13}C NMR: δ 105.58, 107.08, 107.40, 111.52, 142.05, 145.34, 145.57, 145.99 146.22; MS: m/e (rel. intensity) 332 (M^+, 100), 166 (35), 95 (40), 40 (68); UV-vis: λ_{max} (ϵ_M) 313.5 (1.24×10^4), 389.5 (2.10×10^4), 415 (1.38×10^4).

Anal. Calcd for $C_{20}H_{12}O_5$: C, 72.29; H, 3.64

Found: C, 72.12; H, 3.72

From 1,4-diketone **16d:** Using the procedure described above except the solution was stirred at room temperature for 96h, the 1,4-diketone **16d** (600 mg, 1.71 mmol) gave 247.8 mg (47%) of **23** after purification.

2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2'''''-Sexifuran 24

From 1,4-diketone **16e:** To a solution of 1,4-diketone **16e** (187.6 mg, 0.45 mmol) in $CHCl_3$ (7 mL) was added acetic anhydride (3 mL) and concentrated hydrochloric acid (0.15 mL) in one portion. The resulting solution was stirred at room temperature for 96h. The solution was poured into water (60 mL) and neutralized with solid sodium carbonate. The aqueous solution was extracted with $CHCl_3$ (3x40 mL). The combined organic layers were washed with saturated NaCl solution and dried over anhydrous $MgSO_4$. Evaporation of the solvent in vacuo gave the crude product which was flash column chromatographed over silica gel using CH_2Cl_2 as eluent to give

25.8 mg (20% based on recovered 1,4-diketone) of α-sexifuran **24.** An analytical sample was obtained from the recrystallization in CH_2Cl_2 to give yellow crystal : m.p. 252-254°C; ^1H NMR: δ 6.49 (dd, J=3.4, 1.8 Hz, 2H), 6.65 (d, 4H), 6.69-6.72 (m, 6H), 7.45 (d, J=1.8 Hz, 2H); ^{13}C NMR: δ 105.61, 107.14, 107.46, 107.58, 111.55, 142.08, 143.40, 145.34, 145.54, 145.66, 146.25; MS: m/e (rel. intensity) 398 (M^+, 100), 199 (37), 95 (40); UV-vis: λ_{max} (ϵ_M) 285.0 (7.01×10^3), 337.5 (6.93×10^3), 405.0 (2.44×10^4); Exact mass calcd for $C_{24}H_{14}O_6$: 398.0790, found 398.0804.

Anal. Calcd for $C_{24}H_{14}O_6$: C, 72.36; H, 3.54

Found: C, 71.90; H, 3.66

From oxidative coupling: To a solution of α-terfuran **12** (1.0 g, 5 mmol) in dry ether/THF (3:1, 10 mL) at -60°C was added n-BuLi (5 mmol) in one portion. The solutin was then stirred at room temperature for 2h. The solution was cooled at -60°C and anhydrous copper (II) chloride (800 mg, 6 mmol) was added in one portion. The temperature was raised slowly to -10°C and the solution was stirred at this temperature for 1h. The solution was quenched with methanol (1 mL) and poured into a saturated glycine solution. The solution was filtered and the residue was washed with glycine solution and thoroughly with $CHCl_3$. The two layers of the filtrate were separated and the aqueous layer was extracted with $CHCl_3$. The combined organic layers were washed with water, saturated NaCl solution and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo gave dark brown oil which was flash column

chromatographed over silica gel using Et_2O:hexanes (v/v=1/5) as eluent to recover the α-terfuran **12** (147.8 mg). Further elution using CH_2Cl_2 gave 44.7 mg (5.3% based on recovered **12**) of desired α-sexifuran **24**. Crystallization from CH_2Cl_2 gave yellow crystal.

2,2':5',2'':5'',2''':5''',2'''':5'''',2''''':5''''',2'''''':5'''''',2''''''-Septifuran 25

A mixture of 1,4-diketone**16h** (200 mg, 0.42 mmol), acetic acid (12.5 mL) and acetic anhydride (0.5 mL) was refluxed for 48h. After cooling, the solution was poured into water and neutralized with solid Na_2CO_3. The solution was suction filtered. The residue was suspended in $CHCl_3$ (250 mL) and stirred overnight. The solution was filtered and dried over anhydrous $MgSO_4$. Removal of solvent in vacuo gave a dark brown solid which was flash column chromatographed over silica gel using CH_2Cl_2 as eluent to give 3.2 mg (1.7%) of **25**: ^{1}H NMR: δ 6.50 (m, 2H), 6.67 (m, 4H), 6.75 (m, 8H), 7.46 (m, 2H); MS: m/e (rel. intensity) 464 (M^+, 100), 232 (33); UV-vis: λ_{max} 416.5, 441.0.

2,5-Bis(2-furyl)-thiophene 26

A mixture of the 1,4-butanedione **16a** (100 mg, 0.46 mmol) and Lawesson's reagent (111.3 mg, 0.28 mmol) in dry toluene (100 mL) was refluxed for 6h. The solution was evaporated in vacuo to dryness and the solid obtained was flash column chromatographed over silica gel using ether:pet. ether (30-

60°C) (v/v=1/1) to give **26** as pale greyish solid (55.1 mg, 56%): m.p. 65-66°C (lit.[43] m.p. 67-69°C); ^{1}H NMR: δ 6.43 (dd, J=3.3, 1.8 Hz, 2H), 6.49 (d, J=3.3 Hz, 2H), 7.15 (s, 2H), 7.39 (d, J=1.8 Hz, 2H); ^{13}C NMR: δ 105.23, 111.78, 123.03, 132.25, 141.76, 149.15; MS: m/e (rel. intensity) 216 (M^+, 100), 187 (56), 159 (84), 134 (35), 115 (75), 108 (34); UV-vis: λ_{max} (ϵ_M) 348.5 (2.75×10^4), 369.0 (1.92×10^4).

2,5-Bis(5-2,2'-bifuryl)-thiophene 27

Using the procedure described for **26** except the solution was refluxed for 24h, compound **27** (284 mg, 57%) was obtained from the 1,4-butanedione **16c** (50 mg, 0.14 mmol) as a yellowish brown solid: m.p. 109-111°C; ^{1}H NMR: δ 6.47 (dd, J=3.3, 1.8 Hz, 2H), 6.56 (d, J=3.5 Hz, 2H), 6.60 (d, J=3.5 Hz, 2H), 6.63 (d, J=3.5 Hz, 2H), 7.22 (s, 2H), 7.42 (d, J=1.7 Hz, 2H); ^{13}C NMR: δ 105.49, 107.18, 107.35, 111.52, 123.26, 131.85 142.00, 145.73, 146.18, 148.30; MS: m/e (rel. intensity) 348 (M^+, 100), 233 (10), 216 (29), 149 (61), 129 (47), 83 (41), 69 (79), 57 (77); UV-vis: λ_{max} (ϵ_M) 320.5 (8.70×10^3), 408.5 (2.10×10^4), 432.0 (1.57×10^4); Exact mass calcd for $C_{20}H_{12}O_4S$: 348.0465, found 348.0461.

2,5-Bis(5-2,2':5',2''-terfuryl)-thiophene 28

Using the procedure described for **26** except the solution was refluxed for 24h, the 1,4-diketone **16h** (40 mg, 0.083 mmol) gave 15.9 mg (40%) of **28**. Crystallization from the eluent gave yellowish brown leaflet: m.p. 182-183°C; ^{1}H NMR:

δ 6.48 (dd, J=3.5, 1.8 Hz, 2H), 6.59 (d, J=3.5 Hz, 2H), 6.63 (d, J=3.3 Hz, 4H), 6.69 (t, 4H), 7.24 (s, 2H), 7.44 (d, J=1.3 Hz, 2H); MS: m/e (rel. intensity) 480 (M^+, 100), 152 (56); UV-vis: λ_{max} (ϵ_M) 311.0 (1.70×10^4), 361.5 (2.35×10^4), 436.0 (4.30×10^4), 464.0 (3.02×10^4). Exact mass calcd for $C_{28}H_{16}O_6S$: 480.0667, found 480.0654.

2,5-Bis(2-furyl)-pyrrole 29

A mixture of 1,4-diketone **16a** (100 mg, 0.46 mmol), ammonium acetate (353.6 mg, 4.6 mmol), acetic acid (5 mL) and acetic anhydride (0.4 mL) was refluxed overnight. The mixture was cooled and poured into water (50 mL) and neutralized with solid Na_2CO_3. The aqueous solution was extracted with $CHCl_3$ (3x30 mL). The combined organic layers were washed with saturated NaCl solution and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo gave a dark green oil which was purified by flash column chromatography over silica gel using Et_2O:pet. ether (30-60°C)(v/v=2/1) as eluent to give 20.4 mg (22%) of desired **29** as white solid: m.p. 70-72°C; ^1H NMR: δ 6.39 (d, J=3.3 Hz, 2H), 6.42-6.44 (m, 4H), 7.36 (d, J=1.8 Hz, 2H), 9.70-9.80 (bs, 1H); ^{13}C NMR: δ 102.74, 106.79, 111.58, 124.17, 140.53, 147.81; MS: m/e (rel. intensity) 199 (M^+, 100), 170 (26), 142 (43), 133 (20), 104 (19); UV-vis: λ_{max} 331.5, 345.5.

2,5-Bis(5-2,2'-bifuryl)-pyrrole 30

Using the procedure described for **29**, compound **30** (96.3

mg, 51%) was obtained from the 1,4-diketone **16c** (200 mg, 0.57 mmol) as a yellowish brown solid: m.p. 128-130°C; ^{1}H NMR: δ 6.47 (dd, J=3.0, 1.8 Hz, 4H), 6.56-6.65 (m, 6H), 7.37-7.50 (bs, 2H), 8.80-8.95 (bs, 1H); ^{1}H NMR: ($CDCl_3$ with D_2O) δ 6.48 (dd, 4H), 6.56-6.65 (m, 6H), 7.37-7.50 (bs, 2H); ^{1}H NMR: (DMSO-d_6) δ 6.53 (d, J=2.1 Hz, 2H), 6.63 (m, 2H), 6.74-6.81 (m, 6H), 7.74 (d, J=1.2 Hz, 2H), 11.70 (s, 1H); ^{1}H NMR: (DMSO-d_6 with D_2O) δ 6.62 (s, 2H), 6.68 (d, 2H), 6.80-6.92 (m, 6H), 7.81 (d, 2H); ^{13}C NMR: (DMSO-d_6) δ 105.33, 107.54, 111.84, 124.37, 142.37, 142.64, 143.80, 145.58, 147.25; MS: m/e (rel. intensity) 331 (M^+, 100), 166 (15); UV-vis: λ_{max} (ϵ_M) 306.0 (1.24×10^4), 389.5 (1.96×10^4), 411.0 (1.23×10^4); Exact mass calcd for $C_{20}H_{13}NO_4$: 331.0844, found 331.0865.

2,5-Bis(5-2,2':5',2''-terfuryl)-pyrrole 31

Using the procedure described for **29**, the 1,4-diketone **16h** (300 mg, 0.62 mmol) gave 43.1 mg (15%) of **31**. Crystallization from the eluent gave bright yellow crystal : m.p. 249-251°C; ^{1}H NMR: (DMSO-d_6) δ 6.60 (dd, J=3.4, 1.8 Hz, 2H), 6.65 (m, 2H), 6.79-6.87 (m, 10H), 7.78 (d, J=1.5 Hz, 2H), 11.76 (bs, 1H); ^{1}H NMR: (DMSO-d_6 with D_2O) δ 6.62 (s, 2H), 6.66 (m, 2H), 6.82-6.90 (m, 10H), 7.78 (s, 2H); ^{13}C NMR: (DMSO-d_6) δ 105.54, 106.11, 107.29, 107.61, 107.80, 108.26, 111.93, 124.36, 143.06, 143.23, 144.88, 145.10, 147.53; MS: m/e (rel. intensity) 463 (M^+, 1), 270 (100), 184 (87), 79 (93); UV-vis: λ_{max} (ϵ_M) 304.0 (1.03×10^4), 354.5 (1.87×10^4), 418.0 (2.24×10^4), 441.0 (1.62×10^4); Exact mass calcd for

$C_{28}H_{17}NO_6$: 463.1056, found 463.1034.

5-Formyl-2,2'-bifuran 14b

Freshly distilled phosphorous oxychloride (6.58 g, 42.9 mmol) was added dropwise over a period of 15 min to a solution of dry dimethylformamide (3.49 g, 47.8 mmol) in dry 1,2-dichloroethane (15 mL) at 0°C. The mixture was stirred at 0°C for 2h with white precipitate formation. A solution of α-bifuran **11** (4.82 g, 36.0 mmol) in dry 1,2-dichloroethane (50 mL) was added to the cooled reagent slurry over a period of 5 min. After the resulting solution had been stirred at room temperataure overnight, the reddish brown solution was cooled in an ice bath and a solution of sodium acetate (40 g, 0.49 mol) in water (200 mL) was added. The two-phase mixture was stirred at room temperature for 8h. The layers were separated and the aqueous phase was extracted with chloroform (3x50 mL). The combined organic phases were washed with water (50 mL), saturated $NaHCO_3$ solution (50 mL), sataurated NaCl solution (50 mL), dried over anhydrous $MgSO_4$ and filtered. Removal of the solvent in vacuo gave a brownish oil which was chromatographed over silica gel by flash technique using Et_2O:hexanes (v/v=1/5) as eluent to give 5.3 g (91%) of aldehyde **14b** as pale brown solid: m.p. 53-54°C (lit.[21e] m.p. 54°C); ^1H NMR: δ 6.52 (dd, J=3.4, 1.8Hz, 1H), 6.72 (d, J=3.8 Hz, 1H), 6.90 (d, J=3.5 Hz, 1H), 7.30 (d, J=3.9 Hz, 1H), 7.52 (d, J=1.7 Hz, 1H), 9.60 (s, 1H); ^{13}C NMR: δ 107.20, 109.38, 111.87, 123.36, 143.81, 144.63, 151.10, 151,34, 176.71; MS:

m/e (rel. intensity) 162 (M^+, 100), 105 (88), 51 (85); UV-vis: λ_{max} (ϵ_M) 347.0 (3.87×10^4).

5-Formyl-2,2':5',2''-terfuran 14c

Freshly distilled phosphorous oxychloride (1.8 g, 11.8 mmol) was added dropwise over a period of 3 min to a solution of dry DMF (1.04 g, 14.2 mmol) in dry 1,2-dichloroethane (5 mL) at 0°C. The mixture was stirred at 0°C for 2h with white precipitate formation. A solution of α-terfuran **12** (2.0 g 10 mmol) in dry 1,2-dichloroethane (20 mL) was added to the cooled reagent slurry. After 5 min, orange precipitate appeared and the resulting orange suspension was stirred at room temperature overnight. The suspension was cooled in ice bath and hydrolyzed by a solution of sodium acetate (10 g) in water (50 mL). The two-phase mixture was stirred at room temperature for 8h and the layers were separated. The combined organic layers were washed successively with water, saturated $NaHCO_3$ solution and saturated NaCl solution. The organic solution was dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo gave yellowish solid which was purified by flash column chromatography over silica gel using CH_2Cl_2 as eluent to give 2.2 g (97%) of aldehyde **14c** as yellow solid. Recrystallization of the aldehyde **14c** from dichloromethane and hexanes gave yellow leaflets: m.p. 110-111°C; ^{1}H NMR: δ 6.50 (dd, J=3.4, 1.8 Hz, 1H), 6.68 (d, J=3.6 Hz, 1H), 6.70 (d, J=3.4 Hz, 1H), 6.78 (d, J=3.8 Hz, 1H) 6.95 (d, J=3.7 Hz, 1H), 7.30 (d, J=3.9 Hz, 1H), 7.48 (d, J=1.8 Hz, 1H), 9.62

(s, 1H); ^{13}C NMR: δ 106.77, 107.38, 107.52, 111.52, 111.64, 123.48, 142.66, 143.78, 145.58, 147.78, 150.98, 151.63, 176.75; MS: m/e (rel. intensity) 228 (M^+, 100), 171 (33), 115 (41), UV-vis: λ_{max} (ϵ_M) 279.0 (1.95×10^4), 382.0 (4.34×10^4); IR: cm^{-1} 1667.

Anal. Calcd. for $C_{13}H_8O_4$: C, 68.42; H, 3.53

Found: C, 68.06; H, 3.73

5-Formyl-2,2':5',2'':5'',2'''-quaterfuran 14d

Freshly distilled phosphorous oxychloride (439.5 mg, 3.2 mmol) was added dropwise to a solution of dry dimethylformamide (280 mg, 3.8 mmol) in dry 1,2-dichloroethane (1 mL) at 0°C. The mixture was stirred at 0°C for 2h. A solution of α-quaterfuran **13** (600 mg, 2.26 mmol) in dry 1,2-dichloroethane (2 mL) was added to the cooled Vilsmeier reagent. After the solution had been stirred at room temperature overnight, the reddish brown solution was cooled in an ice bath and hydrolyzed by NaOAc solution. The two-phase mixture was stirred at room temperature for 8h and the layers were separated. The aqueous phase was extracted with chloroform (3x20 mL). The combined organic layers were washed with water, saturated $NaHCO_3$ solution, saturated NaCl solution and then dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo gave the crude product which was chromatographed over silica gel by flash technique using $CHCl_3$ as eluent to give 435.3 mg (66%) of aldehyde **14d** as yellowish orange solid: m.p. 188-189°C; ^1H NMR: δ 6.50 (dd, J=3.3, 1.8 Hz, 1H), 6.65 (t, J=3.7 Hz,

2H), 6.72 (d, J=3.7 Hz, 1H), 6.75 (d, J=3.6 Hz, 1H), 6.79 (d, J=3.8 Hz, 1H), 6.99 (d, J=3.6 Hz, 1H), 7.32 (d, J=3.8 Hz, 1H), 7.45 (d, J=1.7 Hz, 1H), 9.60 (s, 1H); ^{13}C NMR: δ 106.05, 107.14, 107.64, 107.70, 108.68, 111.58, 111.72, 123.54, 142.31, 143.22, 145.96, 146.60, 147.49, 150.98, 151.69, 176.78; MS: m/e (rel. intensity) 294 (M^+, 100); UV-vis: λ_{max} (ϵ_M) 407.0 (8.82×10^4); IR: cm^{-1} 1679; Exact mass calcd for $C_{17}H_{10}O_5$: 294.0528, found 294.0522.

5-Formyl-2,2':5',2'':5'',2''':5''',2''''-quinquefuran 14e

Using the procedure described for **14d** except using ethyl acetate:chloroform (v/v=1/20) as eluent for the flash column chromatography, the aldehyde **14e** (52.1 mg, 46%) was obtained from α-quinquefuran (105.5 mg, 0.32 mmol) as yellowish orange solid: m.p. 236-238°C; ^{1}H NMR: δ 6.50 (dd, J=3.3, 1.8 Hz, 1H), 6.65 (d, 2H), 6.71-6.81 (m, 5H), 6.99 (d, J=3.6 Hz, 1H), 7.32 (d, J=3.7 Hz, 1H), 7.45 (d, J=1.8 Hz, 1H), 9.63 (s, 1H); ^{13}C NMR: δ 105.80, 107.15, 107.50, 107.69, 107.85, 107.93 108.87, 111.58, 111.79, 123.53, 142.19, 144.08, 144.86, 145.05, 146.13, 146.28, 147.49, 151.01, 151.74, 176.83; MS: m/e (rel. intensity) 360 (M^+, 100); UV-vis: λ_{max} (ϵ_M)418.5 (3.52×10^4); IR: cm^{-1} 1675; Exact mass calcd for $C_{21}H_{12}O_6$: 360.0634, found 360.0620.

5-Bromo-5'-formyl-2,2'-bifuran 32a

A solution of N-bromosuccinimide (NBS) (368.5 mg, 2.1 mmol) in dry DMF (5 mL) was added dropwise to an ice cold

solution of aldehyde **14b** (304.9 mg, 1.88 mmol) in dry DMF (5 mL). The solution was then stirred at room temperature for 36h. The solution was poured into water (50 mL) and the aqueous solution was extracted with chloroform (3x50 mL). The combined organic layers were washed thoroughly with water (10x30 mL) and then saturated NaCl solution (30 mL). After drying over anhydrous $MgSO_4$ and filtered, the solvent was removed in vacuo to give the crude product which was purified by flash column chromatography over silica gel using Et_2O:hexanes (v/v=2/1) as eluent to give 397 mg (80%) of the bromoaldehyde **32a** as white solid: m.p. 113-115°C; ^{1}H NMR: δ 6.45 (d, J=3.6 Hz, 1H), 6.74 (d, J=3.8 Hz, 1H), 6.84 (d, J=3.6 Hz, 1H), 7.29 (d, J=3.8 Hz, 1H), 9.63 (s, 1H); ^{13}C NMR: δ 107.76, 111.61, 113.93, 123.23, 124.26, 146.63, 150.01, 151.60, 176.93; MS: m/e (rel. intensity) 242 (M^++2, 67), 240 (M^+, 79), 211 (100), 213 (79), 133 (63), 76 (50), 50 (53); UV-vis: λ_{max} (ϵ_M) 348.5 (1.64×10^4); IR: cm^{-1} 1668.

5-Bromo-5''-formyl-2,2':5',2''-terfuran 32b

Using the procedure described for **32a** except using CH_2Cl_2 as eluent for flash column chromatography, the bromoaldehyde **32b**(182 mg, 68%) was obtaind from the aldehyde **14c** (200 mg, 0.88 mmol) and NBS (156.1 mg, 0.88 mmol). Crystallization from the eluent gave yellow solid: m.p. 172-174°C; ^{1}H NMR: δ 6.42 (d, J=3.3 Hz, 1H), 6.64 (d, J=3.5 Hz, 1H), 6.68 (d, J=3.6 Hz, 1H), 6.78 (d, J=3.7 Hz, 1H), 6.95 (d, J=3.6 Hz, 1H), 7.31 (d, J=3.7 Hz, 1H), 9.63 (s, 1H); ^{13}C NMR: δ 107.78,

107.94, 108.92, 111.51, 113.49, 122.56, 123.44, 146.57, 147.37, 150.78, 151.75, 176.84; MS: m/e (rel. intensity) 308 (M^++2, 6), 306 (M^+, 5), 199 (30), 133 (24), 105 (100), 77 (40); UV-vis: λ_{max} (ϵ_M) 384.5 (3.79×10^4); IR: cm^{-1} 1668; Exact mass calcd for $C_{13}H_7BrO_4$: 305.9528, found 305.9519.

5-Bromo-5'''-formyl-2,2':5',2'':5'',2'''-quaterfuran 32c

A solution of NBS (13.3 mg, 0.07 mmol) in dry DMF (1 mL) was added dropwise to an ice cold solution of aldehyde **14d** (20 mg, 0.068) in dry DMF (2 mL). The solution was then stirred at room temperature for 36h. The solution was poured into water (50 mL) and the aqueous solution was extracted with $CHCl_3$ (3x50 mL). The combined organic layers were washed thoroughly with water (10x30 mL) and then saturated NaCl solution (30 mL). After drying over anhydrous $MgSO_4$ and filtered, the solvent was removed in vacuo to give brown solid which was flash column chromatographed over silica gel using CH_2Cl_2:EtOAc (v/v=40/1) as eluent to give the bromoaldehyde **32c** (18.8 mg, 74%) as yellowish brown solid: m.p. 203-205°C (dec); ^{1}H NMR: δ 6.41 (d, J=3.4 Hz, 1H), 6.61 (d, J=3.4 Hz, 1H, 1H), 6.66 (d, J=3.6 Hz, 1H), 6.75 (t, 2H), 6.80 (d, J=3.8 Hz, 1H), 6.98 (d, J=3.7 Hz, 1H), 7.32 (d, J=3.8 Hz, 1H), 9.63 (s, 1H); MS: m/e (rel. intensity) 374 (M^++2, 24), 372 (M^+, 31), 293 (28), 265 (100), 264 (20), 152 (46), 76 (36); UV-vis: λ_{max} (ϵ_M) 406.0 (3.74×10^4); IR: cm^{-1} 1667; Exact mass calcd for $C_{17}H_9BrO_5$: 371.9634, found 371.9623.

5-Bromo-5''''-formyl-2,2':5',2'':5'',2''':5''',2''''-quinquefuran 32d

Using the procedure described for **32c**, the bromoaldehyde **32d** (17.4 mg, 72%) was obtained from the aldehyde **14e** (20 mg, 0.055 mmol) and NBS (10.9 mg, 0.06 mmol) as yellowish brown solid: m.p. 214-216^{o}C (dec); ^{1}H NMR: δ 6.41 (d, J=3.5 Hz, 1H), 6.59 (d, J=3.5 Hz, 1H), 6.66 (d, J=3.6 Hz, 1H), 6.72 (m, 2H), 6.75 (d, J=3.7 Hz, 1H), 6.79 (d, J=3.7 Hz, 1H), 6.80 (d, J= 3.9 Hz, 1H), 7.00 (d, J=3.7 Hz, 1H), 7.32 (d, J=3.8 Hz, 1H), 9.64 (s, 1H); MS: m/e (rel. intensity) 440 (M^{+}+2, 25), 438 (M^{+}, 28), 359 (47), 331 (99), 219 (29), 189 (65), 165 (33), 137 (51), 123 (100), 105 (65), 75 (35), 57 (33); UV-vis: λ_{max} (ϵ_{M}) 420.5 (2.83x10^{4}); IR: cm^{-1} 1667; Exact mass calcd for $C_{21}H_{11}BrO_{6}$: 437.9739, found 437.9723.

5,5'-Diformy-2,2'-bifuran 33a

n-BuLi (25 mmol) was added to a solution of α-bifuran **11** (1.5 g, 11.2 mmol) in dry ether (30 mL) at -60^{o}C. The solution was then stirred at room temperature for 2h. The solution was cooled at -60^{o}C and dry dimethylformamide (2.8 g, 38.7 mmol) in dry ether (5 mL) was added dropwise. The resulting suspension was stirred at room temperature overnight. The suspension was cooled in an ice bath and 10% HCl (30 mL) was added. The mixture was stirred for 4h. The two layers were separated and the aqueous layer was extracted with $CHCl_{3}$ (5x50 mL). The combined organic layers were washed with water, saturated NaCl solution and dried over anhydrous $MgSO_{4}$.

Removal of the solvent in vacuo gave brownish solid. Recrystallization of the crude product from DMF with charcoal decolorization gave the desired dialdehyde **33a** (189.1 mg, 9%) as pale brownish needle: m.p. 262-264°C (dec) (lit. [28d] m.p. 263-265°C (dec)); ^{1}H NMR: δ 7.05 (d, J=3.7 Hz, 2H), 7.34 (d, J=3.7 Hz, 2H), 9.71 (s, 2H); ^{13}C NMR: ($CDCl_3$ with CF_3CO_2H) δ 112.70, 127.42, 150.56, 152.14, 180.00; MS: m/e (rel. intensity) 190 (M^+, 100), 189 (18), 133 (57), 105 (14); UV-vis: λ_{max} (ϵ_M) 348.5 (2.23×10^4), 367.5 (1.98×10^4); IR: cm^{-1} 1660.

5,5''-Diformy-2,2':5',2''-terfuran 33b

Using the procedure described for **33a**, the α-terfuran **12** (2.0 g, 10 mmol) gave the dialdehyde **33b** (1.0 g, 39%) as tiny yellowish plates after recrystallization from DMF: m.p. 232-234°C; ^{1}H NMR: δ 6.88 (d, J=3.5 Hz, 2H), 7.04 (s, 2H), 7.35 (d, J=3.5 Hz, 2H), 9.65 (s, 2H); ^{13}C NMR: δ 108.73, 111.69, 123.10, 145.87, 150.18, 152.12, 177.04; MS: m/e (rel. intensity) 256 (M^+, 100), 199 (39), 171 (10), 115 (25); UV-vis: λ_{max} (ϵ_M) 285.5 (5.27×10^3), 390.0 (3.45×10^4), 409.5 (3.02×10^4); IR: cm^{-1} 1665; Exact mass calcd for $C_{14}H_8O_5$: 256.0372; found 256.0378.

5,5'''-Diformyl-2,2':5',2'':5'',2'''-quaterfuran 33c

Freshly distilled phosphorous oxychloride (494.5 mg, 3.2 mmol) was added dropwise to a solution of dry dimethylformamide (283.2 mg, 3.8 mmol) in dry 1,2-dichloroethane (1 mL)

at 0°C. The mixture was stirred at 0°C for 2h. A solution of α-quaterfuran **13** (400 mg, 1.5 mmol) in dry 1,2-dichloroethane (2 mL) was added to the cooled Vilsmeier reagent. After the solution had been stirred at room temperature overnight, the reddish brown solution was cooled in an ice bath and hydrolyzed by NaOAc solution with yellow precipitate formation. The two-phases mixture was stirred at room temperature for 8h and the yellow precipitate was collected by suction filtration. The residue was suspended in $CHCl_3$ (20 mL) and stirred overnight. Suction filtration gave the dialdehyde **33c** (287.4 mg, 65%) as yellow solid: m.p. 260 (dec); ^{1}H NMR: ($CDCl_3$ with CF_3CO_2H) δ 6.92 (d, J=3.8 Hz, 2H), 6.95 (d, J=4.0 Hz, 2H), 7.12 (d, J=3.8 Hz, 2H), 7.64 (d, J=4.0 Hz, 2H), 9.64 (s, 2H); ^{13}C NMR: δ ($CDCl_3$ with CF_3CO_2H) 109.39, 110.07, 113.96, 130.22, 144.26, 147.57, 150.56, 153.48, 178.65; MS: m/e (rel. intensity) 322 (M^+, 39), 294 (7), 265 (6), 149 (16), 57 (38), 44 (100); UV-vis: λ_{max} (ϵ_M) 417.0 (1.22×10^4), 439.0 (8.94×10^3), IR: cm^{-1} 1670.

5,5''''-Diformyl-2,2':5',2'':5'',2''':5''',2''''-quinquefuran 33d

Using the procedure described for **33c**, the dialdehyde **33d** (66.5 mg, 57%) was obtained from the α-quinquefuran **23** (100 mg, 0.3 mmol) as orange solid: m.p.>300°C; ^{1}H NMR: ($CDCl_3$ with CF_3CO_2H) δ 6.48 (d, J=3.8 Hz, 2H), 6.87 (s, 2H), 6.90 (d, J=3.8 Hz, 2H), 7.09 (d, J=3.7 Hz, 2H), 7.57 (d, J=3.9 Hz, 2H), 9.43 (s, 2H); ^{13}C NMR: ($CDCl_3$ with CF_3CO_2H) δ 109.74

109.25, 109.94, 114.48, 131.28, 143.46, 145.69, 148.49, 150.16, 154.31, 179.95; MS (FAB)[47]: m/e 389 (M^++1); UV-vis: λ_{max} (ϵ_M) 300.0 (4.31×10^3), 430.5 (1.41×10^4), 456 (1.08×10^4); IR: cm^{-1} 1668.

5,5'-Dibromo-2,2'-bifuran 34a

A solution of NBS (2.7 g, 15.1 mmol) in dry DMF (20 mL) was added dropwise to an ice cold solution of α-bifuran **11** (1.0 g, 7.5 mmol) in dry DMF (30 mL). The solution was then stirred at room temperature for 24h. The solution was poured into water (100 mL) and the aqueous solution was extracted with methylene chloride (3x50 mL). The combined organic layers were washed with water (10x30 mL) and saturated NaCl solution (30 mL). After drying over anhydrous $MgSO_4$, the solvent was removed in vacuo to give the crude product which was flash column chromatographed over silica gel using Et_2O:hexanes (v/v=1/5) as eluent to give 1.23 g (56%) of dibromide **34a** as off-white solid: m.p. 73-75°C (lit.[44] m.p. 76°C); ^1H NMR: δ 6.35 (d, J=3.3 Hz, 2H), 6.50 (d, J=3.3 Hz, 2H); ^{13}C NMR: δ 107.91, 113.20, 121.75, 147.23; MS: m/e (rel. intensity) 294 (M^++4, 38), 292 (M^++2, 73), 290 (M+, 36), 213 (100), 211 (99), 185 (51), 183 (49), 157 (28), 155 (28), 76 (56); UV-vis: λ_{max} (ϵ_M) 300.5 (1.10×10^4), 314.0 (6.67×10^3).

5,5''-Dibromo-2,2':5'2''-terfuran 34b

Using the procedure as described for **34a** except the

solution was stirred at room temperature for 48h, the dibromide **34b** (1.29 g, 72%) was obtained from the α-terfuran **12** (1.0 g, 5 mmol) and NBS (2.0 g, 11.2 mmol) as pale yellow solid: m.p. 148-150°C; ^{1}H NMR: δ 6.40 (d, J=3.3 Hz, 2H), 6.58 (d, J=3.3 Hz, 2H), 6.61 (s, 2H); ^{13}C NMR: δ 107.49, 107.81, 113.26, 121.73, 144.72, 147.81; MS: m/e (rel. intensity) 360 (M^++4, 44), 358 (M^++2, 100), 356 (M+, 46), 279 (24), 277 (24), 170 (54), 142 (75), 125 (53), 114 (65), 76 (43); UV-vis: λ_{max} (ϵ_M) 348.5 (1.69x10^4), 368.0 (1.15x10^4).

5,5'''-Dibromo-2,2':5',2'':5'',2'''-quaterfuran 34c

Using the procedure as described for **34a** except the solution was stirred at room temperature for 48h and using Et_2O:hexanes (v/v=1/1) as eluent for flash column chromatography, the dibromide **34c** (243.9, 77%) was obtained from the α-quaterfuran **13** (200 mg, 0.75 mmol) and NBS (270 mg, 15.2 mmol). Crystallization from the eluent gave yellow solid: m.p. 204-206°C; ^{1}H NMR: δ 6.41 (d, 2H), 6,59 (d, 2H), 6.66 (d, 2H), 6.69 (d, 2H); MS: m/e (rel. intensity) 426 (M^++4, 8), 424 (M^++2, 19), 422 (M^+, 8), 345 (10), 343 (10), 317 (12), 315 (13), 208 (17), 152 (27), 104 (68), 76 (100), 50 (50); UV-vis: λ_{max} (ϵ_M) 295.0 (9.68x10^3), 375.4 (2.04 x10^4), 396 (1.41x10^4).

5-Acetyl-2,2'-bifuran 17b and 5,5'-diacetyl-2,2'-bifuran 37a

To a solution of α-bifuran **11** (1.0 g, 7.5 mmol) in dry ether (40 mL) at -60°C was added n-BuLi (7.5 mmol) in one

portion. The solution was stirred at room temperature for further 2h. The solution was cooled at -60°C and a solution of N,N-dimethylacetamide (DMAC) (755.2 mg, 10.3 mmol) in dry ether (5 mL) was added dropwise. The solution was stirred at room temperature overnight. The solution was cooled in an ice bath and 10% HCl (40 mL) was added. The mixture was stirred for 4h and the two layers were separated. The aqueous layer was extracted with $CHCl_3$ (3x50 mL). The combined organic layers were washed with water, saturated NaCl solution and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo gave the crude product which was chromatographed over silica gel by flash technique using Et_2O:hexanes (v/v=1/1) as eluent to give 793.8 mg (60%) of ketone **17b** as yellow solid: m.p. 53-55°C; ^1H NMR: δ 2.50 (s, 3H), 6.51 (dd, J=3.4, 1.8 Hz, 1H), 6.66 (d, J=3.7 Hz, 1H), 6.84 (d, J=3.5 Hz, 1H), 7.25 (d, J=3.7 Hz, 1H), 7.49 (d, J=1.8 Hz, 1H); ^{13}C NMR: δ 25.84, 107.14, 108.49, 111.82, 119.19, 143.43, 145.22, 149.78, 151.46, 185.98; MS: m/e (rel. intensity) 176 (M^+, 100), 161 (55), 105 (69), 43 (36); UV-vis: λ_{max} (ϵ_M) 335.0 ($2.29x10^4$); IR: cm^{-1} 1660.

The column was flushed by air to dryness. The silica gel from the top of the column was suspended in $CHCl_3$ (150 mL) and the suspension was stirred for 2h. Filtration and evaporation of the solvent gave the crude diketone which was purified by recrystallization from methylene chloride and hexanes to give 16.4 mg (1%) of the diketone **37a** as pale yellow leaflet: m.p. 201-203°C; ^1H NMR: δ 2.50 (s, 6H), 6.95

(d, J=3.7 Hz, 2H), 7.26 (d, J=3.7 Hz, 2H); ^{13}C NMR: δ 26.07, 110.10, 118.97, 148.08, 152.52, 186.19; MS: m/e (rel. intensity) 218 (M^+, 76), 203 (54), 147 (72), 43 (100); UV-vis: λ_{max} (ϵ_M) 276.5 (4.85×10^4), 344.5 (3.51×10^4), 362 (2.88×10^4); IR: cm^{-1} 1668.

5-Acetyl-2,2':5',2''-terfuran 17c and **5,5''-diacetyl-2,2':5'2''-terfuran 37b**

Using the procedure described for **17b** except using $CHCl_3$:EtOAc (v/v=9/1) as eluent for flash column chromatography, the monoketone **17c** (282.1 mg, 47%) and the diketone **37b** (42.6 mg, 6%) were obtained from the α-terfuran **12** (500 mg, 2.5 mmol) and DMAC (236 mg, 3.33 mmol).

Recrystallization of compound **17c** from ethanol gave tiny yellow plates: m.p. 142-144°C; ^1H NMR: δ 2.51 (s, 3H), 6.50 (d, J=3.3, 1.8 Hz, 1H), 6.65 (d, J=3.6 Hz, 1H), 6.68 (d, J= 3.4 Hz, 1H), 6.72 (d, J=3.6 Hz, 1H), 6.90 (d, J=3.5 Hz, 1H), 7.25 (d, J=3.7 Hz, 1H), 7.46 (d, J=1.8 Hz, 1H); ^{13}C NMR: δ 25.81, 106.44, 107.17, 107.29, 110.41, 111.55, 119.38, 142.46, 144.13, 145.66, 147.28, 149.43, 151.46, 185.86; MS: m/e (rel. intensity) 242 (M^+, 100), 227 (10), 171 (78), 143 (16), 115 (46), 43 (80); UV-vis: λ_{max} (ϵ_M) 372.5 (1.83×10^4); IR: cm^{-1} 1664; Exact mass calcd for $C_{14}H_{10}O_4$: 242.0579, found 242.0565.

Recrystallization of the diketone **37b** from methylene chloride and hexanes gave golden yellow crystal : m.p. 253-255°C; ^1H NMR: δ 2.52 (s, 6H), 6.79 (d, J=3.7 Hz, 2H), 6.94

(s, 2H), 7.26 (d, J=3.4 Hz, 2H); ^{13}C NMR: ($CDCl_3$ with CF_3CO_2H) δ 25.26, 109.29, 112.05, 123.44, 145.89, 150.77, 150.90, 189.64; MS: m/e (rel. intensity) 284 (M^+, 63), 269 (4), 213 (45), 43 (100); UV-vis: λ_{max} (ϵ_M) 283.5 (6.75×10^3), 383.5 (4.39×10^4), 402.5 (3.63×10^4); IR: cm^{-1} 1662.

5-Benzoyl-2,2'-bifuran 36a and **5,5'-dibenzoyl-2,2'-bifuran 37c**

n-BuLi (3.7 mmol) was added to a solution of α-bifuran **11** (500 mg, 3.7 mmol) in dry ether (15 mL) at -60°C. The solution was stirred at room temperature for additional 2h. The solution was cooled at -60°C and a solution of N,N-dimethylbenzamide (600 mg, 4 mmol) in dry ether (3 mL) was added dropwise. The solution was then stirred at room temperature overnight. The solution was cooled in an ice bath and 10% HCl (20 mL) was added. The mixture was stirred for 4h and the layers were separated. The aqueous layer was extracted with $CHCl_3$ (3x50 mL). The combined organic layers were washed with water, saturated NaCl solution and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo gave a dark brown oil which was purified by flash column chromatography over silica gel using Et_2O:hexanes (v/v=1/1) as eluent to give 525.6 mg (59%) of ketone **36a** as yellowish viscous oil. Recrystallization of **36a** from methylene chloride and hexanes gave tiny yellowish brown plates: m.p. 62-64°C; ^{1}H NMR: δ 6.52 (dd, J=3.6, 1.8 Hz, 1H), 6.71 (d, J=3.7 Hz, 1H), 6.88 (d, J=3.5 Hz, 1H), 7.26 (d, J=3.8 Hz, 1H),

7.47-7.59 (m, 4H), 7.97 (dd, J=8.3, 1.4 Hz, 1H); ^{13}C NMR: δ 107.15, 108.97, 111.96, 122.76, 128.39, 129.17, 132.39, 137.52, 143.60, 145.23, 150.56, 150.94, 181.93; MS: m/e (rel. intensity) 238 (M^+, 91), 105 (100), 77 (82), 51 (65); UV-vis: λ_{max} (ϵ_M) 357.5 (2.27×10^4); IR: cm^{-1} 1640.

The column was flushed by air to dryness. The silica gel on the top of the column was suspended in $CHCl_3$ (150 mL) and the suspension was stirred for 2h. Filtration and evaporation of the solvent in vacuo gave the crude diketone which was recrystallized from methylene chloride and hexanes to give **37c** (81.9 mg, 6%) as small yellow plates: m.p. 185-187°C; ^1H NMR: δ 7.04 (d, J=3.7 Hz, 2H), 7.32 (d, J=3.7 Hz, 2H), 7.49-7.66 (m, 6H), 7.99 (d, J=8.0 Hz, 4H); ^{13}C NMR: δ 110.36, 122.31, 128.52, 129.23, 132.75, 137.14, 148.73, 152.11, 182.01; MS: m/e (rel. intensity) 342 (M^+, 53), 209 (11), 105 (100), 77 (77); UV-vis: λ_{max} (ϵ_M) 367.5 (3.47×10^4), 385.5 (3.26×10^4); IR: cm^{-1} 1638.

5-Benzoyl-2,2':5',2''-terfuran 36b and **5,5''-dibenzoyl-2,2':5',2''-terfuran 37d**

Using the procedure described for **36a**, the desired ketone **36b** (1.27 g, 42%) was obtained from α-terfuran **12** (2.0 g, 10 mmol) and N,N-dimethylbenzamide (2.3 g, 15.4 mmol). Recrystallization of the ketone **36b** from methylene chloride and hexanes gave golden yellow needles: m.p. 85-87°C; ^1H NMR: δ 6.50 (dd, J=3.0, 1.8 Hz, 1H), 6.68 (t, J=4.0 Hz, 2H), 6.68 (d, J=3.7 Hz, 1H), 6.95 (d, J=3.6 Hz, 1H), 7.28 (d,

J=3.6 Hz, 1H), 7.46 (d, J=1.8 Hz, 1H), 7.47-7.60 (m, 3H), 7.97 (d, J=7.0 Hz, 2H); ^{13}C NMR: δ 106.52, 107.32, 110.90, 111.61, 122.90, 128.37, 129.10, 132.34, 137.51, 142.52, 144.13, 145.69, 147.42, 150.98, 181.77; MS: m/e (rel. intensity) 304 (M^+, 2), 171 (8), 149 (38), 105 (31), 57 (65), 43 (100); UV-vis: λ_{max} (ϵ_M) 304.0 ($4.64x10^3$), 395.0 ($1.26x10^4$); IR: cm^{-1} 1638; Exact mass calcd for $C_{19}H_{12}O_4$: 304.0735, found 304.0733.

The diketone **37d** was obtained similarly from the silica gel on the top of the column. Recrystallization of the crude diketone **37d** from methylene chloride and hexanes gave bright yellow fluffy solid (250 mg, 6%) : m.p. 171-172°C; ^1H NMR: δ 6.88 (d, J=3.7 Hz, 2H), 7.02 (s, 2H), 7.33 (d, J=3.7 Hz, 2H), 7.49-7.68 (m, 6H), 8.00 (d, J=7.0 Hz, 4H); ^{13}C NMR: δ 108.31, 111.05, 122.64, 128.42, 129.14, 132.52, 137.80, 145.81, 149.42, 151,37, 181.83; MS: m/e (rel. intensity) 408 (M^+, 100), 275 (15), 105 (68); UV-vis: λ_{max} (ϵ_M) 404.5 ($3.75x10^4$), 423.5 ($3.43x10^4$); IR: cm^{-1} 1636; Exact mass calcd for $C_{26}H_{16}O_5$: 408.0998, found 408.1008.

5-(4-Methoxybenzoyl)-2,2'-bifuran 36c and
5,5'-Di-(4-methoxybenzoyl)-2,2'-bifuran 37e

To a solution of α-bifuran **11** (500 mg, 3.7 mmol) in dry ether (15 mL) at -60°C was added n-BuLi (3.7 mmol) in one portion. The solution was stirred at room temperature for further 2h. The solution was cooled at -60°C and a solution of N,N-dimethyl-(4-methoxy)-benzamide (700 mg, 3.9 mmol) in

dry ether (3 mL) was added dropwise. The solution was stirred at room temperature overnight. The solution was cooled in an ice bath and 10% HCl (20 mL) was added. The mixture was stirred for 2h and the two layers were separated. The aqueous layer was extracted with $CHCl_3$ (3x50 mL). The combined organic layers were washed with water, saturated NaCl solution and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo gave the crude product which was chromatographed over silica gel by flash technique using Et_2O:hexanes (v/v=1/1) as eluent to give 557.1 mg (56%) of ketone **36c**. Recrystallization from methylene chloride and hexanes gave the ketone **36c** as pale yellow cubes: m.p. 102-104°C; ^1H NMR: δ 3.89 (s, 3H), 6.52 (dd, J=3.6, 1.8 Hz, 1H), 6.71 (d, J=3.7 Hz, 1H), 6.86 (d, J=3.5 Hz, 1H), 6.98 (d, J=8.8 Hz, 2H), 7.27 (d, J=3.7 Hz, 1H), 7.50 (d, J=1.7 Hz, 1H), 8.03 (d, J=8.8 Hz, 2H); ^{13}C NMR: δ 55.43, 107.06, 108.58, 111.89, 113.69, 121.74, 130.05, 131.58, 143,42, 145.35, 149.98, 151.34, 163.18, 180.52; MS: m/e (rel. intensity) 268 (M^+, 53), 135 (100), 77 (37); UV-vis: λ_{max} (ϵ_M) 356.5 ($3.16x10^4$); IR: cm^{-1} 1630.

The column was flushed by air to dryness. The silica gel on the top of the column was suspended in $CHCl_3$ (150 mL) and the suspension was stirred for 2h. Filtration and evaporation of the solvent gave the crude diketone which was recrystallized from methylene chloride and hexanes to give **37e** (89.6 mg, 6%) as pale yellow leaflet: m.p. 182-183°C; ^1H NMR: δ 3.90 (s, 6H), 6.99-7.02 (m, 6H), 7.31 (d, J=3.7 Hz, 2H), 8.06 (d, J=8.8 Hz, 4H); ^{13}C NMR: δ 55.47, 109.99, 113.80,

121.34, 129.70, 131.69, 148.31, 152.45, 163.43, 180.47; MS: m/e (rel. intensity) 402 (M^+, 16), 152 (28), 135 (54), 84 (55), 49 (100); UV-vis: λ_{max} (ϵ_M) 372.0 (4.24×10^4), 389.0 (3.98×10^4); IR: cm^{-1} 1632.

5-(4-Methoxybenzoyl)-2,2':5',2''-terfuran 36d and **5,5''-Di-(4-methoxybenzoyl)-2,2':5',2''-terfuran 37f**

Using the procedure described for **36c** except using Et_2O:hexanes (v/v=3/1) as eluent for flash column chromatography, the monoketone **36d** (1.53 g, 46%) was obtained from α -terfuran **12** (2.0 g, 10 mmol) and N,N,-dimethyl-(4-methoxy)-benzamide (2.0 g, 11.1 mmol). Recrystallization from methylene chloride and hexanes gave **36d** as yellowish brown leaflet: m.p. 102-104°C; ^1H NMR: δ 3.90 (s, 3H), 6.49 (dd, J=3.6, 1.8 Hz, 1H), 6.68 (t, 2H), 6.78 (d, J=3.7 Hz, 1H), 6.92 (d, J=3.6 Hz, 1H), 7.00 (d, J=9.0 Hz, 2H), 7.28 (d, J=3.8 Hz, 1H), 7.46 (d, J=1.8 Hz, 1H), 8.04 (d, J=9.0 Hz, 2H); ^{13}C NMR: δ 55.38, 106.40, 106.61, 107.23, 110.47, 111.58, 113.67, 121.81, 130.05, 131.52, 142.45, 144.29, 145.75, 147.25, 149.61, 151.40, 163.16, 180.35; MS: m/e (rel. intensity) 334 (M^+, 100), 135 (34); UV-vis: λ_{max} (ϵ_M) 304.0 (2.81×10^4), 393.0 (4.61×10^4); IR: cm^{-1} 1636; Exact mass calcd for $C_{20}H_{14}O_5$: 334.0841, found 334.0851.

The diketone **37f** was obtained similarly from the silica gel on the top of the column. Recrystallization of the crude diketone from methylene chloride and hexanes gave **37f** (218 mg, 5%) as bright yellow fluffy solid: m.p. 183-185°C;

^{1}H NMR: δ 3.91 (s, 6H), 6.48 (d, J=3.7 Hz, 2H), 6.98 (s, 2H), 7.01 (d, J=8.9 Hz, 4H), 7.30 (d, J=3.9 Hz, 2H), 8.05 (d, J= 8.7 Hz, 4H); ^{13}C NMR: δ 55.44, 108.16, 110.67, 113.75, 121.67, 129.90, 131.61, 145.84, 148.98, 151.78, 163.31, 180.42; MS: m/e (rel. intensity) 468 (M^+, 100), 135 (58); UV-vis: λ_{max} (ϵ_M) 302.0 (2.41×10^4), 404.0 (2.47×10^4), 424.0 (1.35×10^4); IR: cm^{-1} 1628.

Bis(5-2,2'-bifuryl) ketone 39a

n-BuLi (3.7 mmol) was added in one portion to a solution of α-bifuran **11** (500 mg, 3.7 mmol) in dry ether (20 mL) at -60°C. The solution was stirred at room temperature for additional 2h. The solution was cooled at -60°C and a solution of carbamate **38** (200 mg, 1.9 mmol) in dry ether (2 mL) was added dropwise. The solution was stirred at room temperature overnight. The solution was cooled in an ice bath and 10% HCl (20 mL) was added. The mixture was stirred for 2h and the two layers were separated. The aqueous layer was extracted with $CHCl_3$ (3x50 mL). The combined organic layers were washed with water, saturated NaCl solution and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo gave a dark brown oil which was chromatographed over silica gel by flash technique using Et_2O:hexanes (v/v=4/1) as eluent to give 270.9 (49%) of ketone **39a** as yellow viscous oil. Recrystallization of the oil from methylene chloride and hexanes gave dark brown needles: m.p. 121-122°C; ^{1}H NMR: δ 6.53 (dd, J=3.5, 1.8 Hz, 2H), 6.74 (d, J=3.7 Hz, 2H), 6.88

(d, J=3.5 Hz, 2H), 7.51 (d, J=1.6 Hz, 2H), 7.62 (d, J=3.7 Hz, 2H); ^{13}C NMR: δ 107.40, 108.76, 111.93, 121.34, 143.54, 145.28, 149.98, 150.37, 167.27; MS: m/e (rel. intensity) 294 (M^+, 100), 161 (23), 105 (69); UV-vis: λ_{max} (ϵ_M) 274.0 (1.48×10^4), 394.0 (2.53×10^4); IR: cm^{-1} 1625; Exact mass calcd for $C_{17}H_{10}O_5$: 294.0528, found 294.0535.

Bis(5-2,2':5',2''-terfuryl) ketone 39b

Using the procedure described for **39a**, the symmetrical ketone **39b** (852 mg, 40%) was obtained from α-terfuran **12** (2.0 g, 10 mmol) and carbamate **38** (515 mg, 5 mmol). Crystallization from the eluent gave yellowish orange fluffy solid: m.p. 199-201°C; ^1H NMR: δ 6.51 (dd, J=3.4, 1.8 Hz, 2H), 6.69 (t, J=3.6 Hz, 4H), 6.82 (d, J=3.8 Hz, 2H), 6.96 (d, J=3.6 Hz, 2H), 7.46 (d, J=1.4 Hz, 2H), 7.64 (d, J=3.8 Hz, 2H); ^{13}C NMR: δ 106.61, 107.41, 107.70, 110.82, 111.67, 121.50, 142.60, 144.34, 145.84, 147.48, 149.75, 150.66, 167.13; MS: m/e (rel. intensity) 426 (M^+, 100), 171 (20); UV-vis: λ_{max} (ϵ_M) 319.5 (2.15×10^4), 431.5 (3.15×10^4); IR: cm^{-1} 1630; Exact mass calcd for $C_{25}H_{14}O_7$: 426.0739, found 426.0716.

5,5'-d-2,2'-Bifuran 40a

To a solution of α-bifuran **11** (1.0 g, 7.5 mmol) in dry ether (15 mL) at -60°C was added n-BuLi (15 mmol) in one portion. The solution was stirred at room temperature for 2h. The solution was cooled at -70°C and quenched with D_2O (1 mL) via a syringe. After the solution was stirred at room

temperature for 3h, water (10 mL) was added. The two layers were separated and the aqueous solution was extracted with ether (2x10 mL). The combined organic layers were washed with saturated NaCl solution and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo gave a brown liquid which was vacuum distilled to give the deuteriated **40a** (666.6 mg, 65%) as pale yellow liquid: b.p. 60-61°C/10 mmHg; ^{1}H NMR: δ 6.40 (d, J=3.4 Hz, 2H), 6.51 (d, J=3.4 Hz, 2H); ^{13}C NMR; δ 105.02, 111.07, 140.94, 141.43, 141.93, 146.54; MS: m/e (rel. intensity) 137 (M^++1, 53), 136 (M^+, 100), 106 (30), 80 (66).

5,5''-d-2,2':5',2''-Terfuran 40b

Using the procedure described for **40a** except the crude product was purified by flash column chromatography over silica gel using Et_2O:hexanes (v/v=1/5) as eluent. The deuteriated **40b** (378.6 mg, 75%) was obtained as a white solid from α-terfuran **12** (500 mg, 2.5 mmol): m.p. 60-61°C; ^{1}H NMR: δ 6.44 (d, J=3.5 Hz, 2H), 6.59 (s, 2H), 6.60 (d, J=3.5 Hz, 2H); ^{13}C NMR: δ 105.38, 106.87, 111.22, 141.19, 141.69, 142.19, 145.69, 146.16; MS: m/e (rel. intensity) 202 (M^+, 100), 172 (15), 117 (53); UV-vis: λ_{max} (ϵ_M) 333.0 (2.52x10^4), 351.0 (1.52x10^4).

5,5'''-d-2,2':5',2'':5'',2'''-Quaterfuran 40c

Using the procedure described for **40a** except the aqueous solution was extracted with $CHCl_3$ (3x30 mL) and the crude product was purified by flash column chromatography over

silica gel using Et_2O:hexanes (v/v=1/5) as eluent. The α-quaterfuran **13** (200 mg, 0.75 mmol) gave the deuteriated derivative **40c** (34.8 mg, 17%) as pale yellow solid: m.p. 161-162°C; ^1H NMR: δ 6.47 (d, J=3.4 Hz, 2H), 6.63 (dd, J=3.4, 1.8 Hz, 4H), 6.67 (d, J=3.5 Hz, 2H); ^{13}C NMR: δ 105.53, 107.03, 107.24, 111.28, 141.28, 141.77, 142.28, 145.36, 145.91, 146.14; MS: m/e (rel. intensity) 269 (M^++1, 74), 268 (M^+, 100); UV-vis: λ_{max} (ϵ_M) 274.5 ($7.14x10^3$), 366.0 ($2.93x10^4$), 385.5 ($1.88x10^4$).

5,5'-Dimethyl-2,2'-bifuran 41a

To a solution of α-bifuran **11** (700 mg, 5.2 mmol) in dry ether (15 mL) at -60°C was added n-BuLi (11 mmol) in one portion. The solution was stirred at room temperature for 2h. The solution was cooled at -70°C and quenched with MeI (1 mL) via a syringe. After the solution was stirred at room temperature overnight, water (10 mL) was added. The two layers were separated and the aqueous solution was extracted with ether (2x10 mL). The combined organic layers were washed with saturated NaCl solution and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo gave a brown liquid which was vacuum distilled to give 93 mg of α-bifuran **11**. The residue was flash column chromatographed over silica gel using Et_2O:hexanes (v/v=1/5) as eluent to give the dimethyl derivative **41a** (352.5 mg, 48% based on recovered **11**) as pale yellow liquid which crystallized upon vacuum drying: m.p. 37-38°C (lit.[45] b.p. 41-43°C/2.8 mmHg); ^1H NMR: δ 2.32 (d,

J=0.7 Hz, 6H), 5.99 (dd, J=3.1, 0.8 Hz, 2H), 6.34 (d, J=3.1 Hz, 2H); ^{13}C NMR: δ 13.53, 105.05, 107.18, 145.23, 151.22, MS: m/e (rel. intensity) 162 (M^+, 100), 119 (75), 43 (84); UV-vis: λ_{max} (ϵ_M) 296.5 (1.33×10^4), 309.0 (8.64×10^3).

5,5''-Dimethyl-2,2':5',2''-terfuran 41b

Using the procedure described for **41a**, the dimethyl compound **41b** (459.8 mg, 81%) was obtained as a white solid from α-terfuran **12** (500 mg, 2.5 mmol): m.p. 92-93°C (lit.[21f] m.p. 91°C); ^{1}H NMR: δ 2.35 (s, 6H), 6.03 (d, J=3.2 Hz, 2H), 6.47 (d, J=3.2 Hz, 2H), 6.50 (s, 2H); ^{13}C NMR: δ 13.61, 105.90, 106.18, 107.46, 144.78, 145.63, 151.88; MS: m/e (rel. intensity) 228 (M^+, 100), 185 (42); UV-vis: λ_{max} (ϵ_M) 342.0 (2.48×10^4), 360.0 (1.55×10^4).

5,5'''-Dimethyl-2,2':5',2'':5'',2'''-quaterfuran 41c

Using the procedure described for **41a** except the aqueous solution was extracted with $CHCl_3$ (3x30 mL), the α-quaterfuran **13** (200 mg, 0.75 mmol) gave the desired dimethyl derivative **41c** (19.2 mg. 9%) as yellow solid: m.p. 178-180°C; ^{1}H NMR: δ 2.36 (s, 6H), 6.04-6.05 (m, 2H), 6.50 (d, J=3.2 Hz, 2H), 6.53 (d, J=3.5 Hz, 2H), 6.63 (d, J=3.5 Hz, 2H); ^{13}C NMR: δ 13.63, 106.06, 106.48, 107.02, 107.55, 144.66, 145.10, 146.12, 152.07; MS: m/e (rel. intensity) 294 (M^+, 100), 147 (30), 109 (21); UV-vis: λ_{max} (ϵ_M) 281.5 (6.38×10^3), 373.0 (2.36×10^4), 393.0 (1.64×10^4).

5,5''-Dibenzoyl-2,2':5',2''-terfuran 37d

n-BuLi (20 mmol) was added in one portion to a solution of α-terfuran **12** (2.0 g, 10 mmol) in dry ether (40 mL) at -60°C. The solution was stirred at room temperature for 2h with precipitate formation. The suspension was cooled at -60°C and a solution of N,N-dimethylbenzamide (3.5 g, 23.5 mmol) in dry ether (10 mL) was added dropwise. After the solution was stirred at room temperature overnight, 10% HCl (40 mL) was added and the mixture was stirred for 4h. The two layers were separated and the aqueous layer was extracted with $CHCl_3$ (4x50 mL). The combined organic layers were washed with water, saturated NaCl solution and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo gave dark brown solid. The crude product was recrystallized from methylene chloride and hexanes with charcoal decolorization to give **37d** (1.24 g, 30%) as yellow fluffy solid: spectra data for **37d**, see page 96.

2,2-Bis(5-formyl-2-furyl)propane 44

Freshly distilled phosphorous oxychloride (15.3 g, 0.1 mol) was added dropwise to a solution of dry dimethylformamide (8.0 g, 0.11 mol) in dry 1,2-dichloroethane (25 mL) at 0°C. The mixture was stirred at 0°C for additional 2h with white precipitate formation. A solution of 2,2-difuryl-propane **46**[30] (8.0 g, 45.5 mmol) in dry 1,2-dichloroethane (75 mL) was added to the cooled reagent slurry over a period of 10 min. After the resulting solution had been stirred at

room temperature overnight, the yellowish brown solution was cooled in an ice bath and a solution of sodium acetate (80 g, 0.98 mol) in water (400 mL) was added. The two-phase mixture was stirred at room temperature for 8h. The layers were separated and the aqueous phase was extracted with $CHCl_3$ (5x50 mL). The combined organic layers were washed with water (100 mL), saturated $NaHCO_3$ solution (100 mL), saturated NaCl solution (100 mL), dried over anhydrous $MgSO_4$ and filtered. Removal of the solvent in vacuo gave the crude product which was recrystallizaed from ethanol to give the dialdehyde **44** (9.4 g, 89%) as pale yellow crystal : m.p. 81-83°C; ^1H NMR: δ 1.75 (s, 6H), 6.35 (d, J=3.6 Hz, 2H), 7.20 (d, J=3.6 Hz, 2H), 9.35 (s, 2H); ^{13}C NMR: δ 25.62, 38.33, 108.30, 122.41, 152.01, 164.61, 177.27; MS: m/e (rel. intensity) 232 (M^+, 23), 217 (100); UV-vis: λ_{max} (ϵ_M) 286.0 ($4.00x10^4$); IR: cm^{-1} 1665.

2,2-Bis(5-acetyl-2-furyl)propane 47

To a solution of 2,2-difurylpropane **46** (2.0 g, 11.4 mmol) in acetic anhydride (5 mL) at 0°C was added freshly distilled BF_3.OEt (0.3 mL) in one portion via a syringe. The solution was stirred at 0°C for 30 min and then at room temperature for another 30 min. The solution was poured into water (50 mL) and neutralized with solid Na_2CO_3. The aqueous solution was extracted with CH_2Cl_2 (3x50 mL). The combined organic layers were washed with water (30 mL), saturated NaCl solution and dried over anhydrous $MgSO_4$. Filtration and

evaporation of the solvent in vacuo gave an orange oil which was flash column chromatographed over silica gel using Et_2O:hexanes (v/v=3/1) as eluent to give 1.5 g (49%) of diketone **47** as pale brown viscous oil: ^1H NMR: δ 1.78 (s, 6H), 2.45 (s, 6H), 6.26 (d, J=3.7 Hz, 2H), 7.11 (d, J=3.6 Hz, 2H); ^{13}C NMR: δ 25.72, 25.78, 38.16, 107.70, 118.17, 151.81, 163.07, 186.21; MS: m/e (rel. intensity) 260 (M^+, 19), 245 (100); UV-vis: λ_{max} (ϵ_M) 287.5 (2.79×10^4); IR: cm^{-1} 1675.

Bis-Mannich base 45

A mixture of diketone **47** (2.0 g, 7.7 mmol), paraformaldehyde (550 mg, 18.3 mmol), dimethylamine hydrochloride (1.50 g, 18.3 mmol) and concentrated HCl (0.08 mL) in 95% ethanol (5 mL) was heated under reflux for 16h. After cooling in the freezer for several days, the precipitate was collected and washed with ice-cold ethanol to give the bis-Mannich base hydrochloride (1.39 g, 40%) as white solid: m.p. 179-181°C; ^1H NMR: (D_2O, DSS) δ 1.78 (s, 6H), 2.92 (s, 12H), 3.53 (s, 8H), 6.61 (d, J=3.7 Hz, 2H), 7.54 (d, J=3.8 Hz, 2H); MS: m/e (rel. intensity) 450, 448, 446 (M^++4, M^++2, M^+ (not observed)), 374 (0.4), 329 (23), 269 (53), 58 (100); IR: cm^{-1} 1660.

The bis-Mannich base hydrochloride was treated with an aqueous ammonium solution and extracted with ether (3x50 mL). The combined organic extracts were washed with water (10 mL), then saturated NaCl solution (10 mL) and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo gave the free bis-Mannich base **45** which was used immediately: ^1H NMR: δ

1.75 (s, 6H), 2.25 (s, 12H), 2.74 (t, 4H), 2.97 (t, 4H), 6.28 (d, 2H), 7.18 (d, 2H).

2-Furyl-(5-formyl-2-furyl)-2,2-propane 50

Freshly distilled phosphorous oxychloride (5.2 g, 33.9 mmol) was added dropwise to a solution of dry dimethylformamide (2.7 g, 36.9 mmol) in dry 1,2-dichloroethane (15 mL) at 0°C. The mixture was stirred at 0°C for additional 2h with white precipitate formation. A solution of 2,2-difuryl-propane **46** (5.0 g, 28.4 mmol) in dry 1,2-dichloroethane (35 mL) was added to the cooled reagent slurry over a period of 5 min. After the resulting solution had been stirred at room temperature overnight, the yellowish brown solution was cooled in an ice bath and a solution of sodium acetate (30 g, 0.37 mol) in water (150 mL) was added. The two-phase mixture was stirred at room temperature for 8h. The layers were separated and the aqueous phase was extracted with $CHCl_3$ (3x50 mL). The combined organic layers were washed with water, saturated $NaHCO_3$ solution, saturated NaCl solution and dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent in vacuo gave a brown oil which was chromatographed over silica gel by flash technique using Et_2O:hexanes (v/v=1/1) as eluent to give the aldehyde **50** (5.2 g, 90%) as yellow solid: m.p. 50-52°C; ^1H NMR: δ 1.75 (s, 6H), 6.14 (d, J=3.2 Hz, 1H), 6.21 (d, J=3.6 Hz, 1H), 6.35 (dd, J=3.2, 1.8 Hz, 1H), 7.15 (d, J=3.6 Hz, 1H), 7.36 (d, J= 1.7 Hz, 1H), 9.56 (s, 1H); ^{13}C NMR: δ 25.87, 37.86, 104.79,

107.76, 110.05, 122.40, 141.58, 151.81, 158.16, 166.81, 177.30, MS: m/e (rel. intensity) 204 (M^+, 15), 189 (100); UV-vis: λ_{max} (ϵ_M) 289.5 (1.59×10^4); IR: cm^{-1} 1665.

1,4-Bis(2,2-difurylpropane)-1,4-butanedione 51

To a hot stirred solution of thiazolium salt (400 mg, 1.49 mmol) and sodium acetate (240 mg, 2.93 mmol) in absolute ethanol (20 mL) was added the aldehyde **50** (3.0 g, 14.7 mmol) in one portion. The vinyl sulfone (882.8 mg, 7.5 mmol) was added dropwise to the hot solution. The mixture was refluxed overnight and then poured into water. The aqueous solution was extracted with chloroform and the combined organic extracts were suction filtered. The filtrate was washed with saturated NaCl solution and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo gave the crude product which was flash column chromatographed over silica gel using Et_2O:hexanes (v/v=3/5) as eluent to give 2.53 g (79%) of 1,4-diketone **51** as pale yellow viscous oil: ^1H NMR: δ 1.70 (s, 12H), 3.20 (s, 4H), 6.11 (d, J=3.2 Hz, 2H), 6.16 (d, J= 3.6 Hz, 2H), 6.30 (dd, J=3.3, 1.8 Hz, 2H), 7.15 (d, J=3.6 Hz, 2H), 7.35 (d, J=1.8 Hz, 2H); ^{13}C NMR: δ 25.98, 31.75, 37.74, 104.62, 107.26, 109.99, 118.11, 141.46, 151.19, 158.51, 164.69, 187.21; MS: m/e (rel. intensity) 434 (M^+, 5), 419 (3), 205 (100), 189 (70), 137 (20), 109 (19); UV-vis: λ_{max} (ϵ_M) 289.5 (3.62×10^4); IR: cm^{-1} 1675.

5,5''-Bis(dimethylfurfuryl)-2,2':5',2''-terfuran 52

To an ice-cold solution of 1,4-diketone **51** (2.22 g, 5.12 mmol) in acetic anhydride (35 mL) was added concentrated HCl (1.5 mL) in one portion. The solution was stirred at room temperature for 4 days. The solution was poured into water (150 mL) and stirred for 2h. The aqueous solution was extracted with $CHCl_3$ (3x50 mL). The combined organic layers were washed with water, saturated $NaHCO_3$ solution and saturated NaCl solution. After drying over anhydrous $MgSO_4$, the solvent was removed in vacuo to give an oil which was purified by flash column chromatography over silica gel using Et_2O:hexanes (v/v=1/3) as eluent to give the furan compound **52** (1.24 g, 58%) as white solid: m.p. 69-71°C; ^{1}H NMR: δ 1.67 (s, 12H), 6.04 (d, J=3.5 Hz, 2H), 6.06 (d, J=3.3 Hz, 2H), 6.28 (dd, J= 3.3, 1.8 Hz, 2H), 6.47 (d, J=3.3 Hz, 2H), 6.50 (s, 2H), 7.31 (d, J=1.8 Hz, 2H); ^{13}C NMR: δ 26.34, 37.48, 104.20, 105.82, 106.11, 106.29, 109.93, 141.19, 145.04, 145.66, 159.66, 159.72; MS: m/e (rel. intensity) 416 (M^+, 100), 410 (85); UV-vis: λ_{max} (ϵ_M) 344.5 (3.81×10^4), 363.5 (2.42×10^4); Exact mass calcd for $C_{26}H_{24}O_5$: 416.1624, found 416.1619.

5,5''-Bis(5-formyl-dimethylfurfuryl)-2,2':5',2''-terfuran 48

Using the procedure described for **44**, the furan compound **52** (3.4 g, 8.17 mmol) gave 2.5 g (65%) of dialdehyde **48**. Recrystallization of **48** from ethanol gave yellow solid: m.p. 172-174°C; ^{1}H NMR: δ 1.75 (s, 12H), 6.19 (d, J=3.3 Hz, 2H), 6.24 (d, J=3.6 Hz, 2H), 6.52 (s, 4H), 7.16 (d, J=3.6 Hz, 2H),

9.57 (s, 2H); ^{13}C NMR: δ 26.01, 38.10, 105.99, 106.64, 106.93, 107.99, 122.40, 145.40, 145.51, 151.94, 157.86, 166.51, 177.39; MS: m/e (rel. intensity) 472 (M^+, 100), 457 (63), 137 (32); UV-vis: λ_{max} (ϵ_M) 286.5 (4.13×10^4), 344.5 (3.78×10^4), 361.5 (2.47×10^4); IR: cm^{-1} 1680; Exact mass calcd for $C_{28}H_{24}O_7$: 472.1522; found 472.1529.

5,5''-Bis(5-acetyl-dimethylfurfuryl)-2,2':5',2''-terfuran 53

To a solution of furan compound **52** (1.21 g, 2.9 mmol) in acetic anhydride (2 mL) at 0°C was added freshly distilled BF_3.OEt (0.07 mL) in one portion via a syringe. The solution was stirred at 0°C for 30 min and then at room temperature for another 30 min. The solution was poured into water and neutralized with solid Na_2CO_3. The aqueous solution was extracted with $CHCl_3$. The combined organic layers were washed with water, saturated NaCl solution and dried over anhydrous $MgSO_4$. Filtration and evaporation of the solvent in vacuo gave the crude product which was flash column chromatographed over silica gel using Et_2O:hexanes (v/v=5/1) as eluent to give the diketone **53** (316 mg, 22%) as white solid: m.p. 109-110°C; ^1H NMR: δ 1.74 (s, 12H), 2.43 (s, 6H), 6.17 (t, J= 3.8 Hz, 4H), 6.51 (d, J=3.7 Hz, 4H), 7.09 (d, J=3.5 Hz, 2H); ^{13}C NMR: δ 25.81, 26.10, 37.95, 105.94, 106.55, 106.70, 107.52, 118.25, 145.34, 145.54, 151.75, 158.19, 164.45, 186.45; MS: m/e (rel. intensity) 500 (M^+, 100), 485 (69), 280 (29), 235 (17), 151 (21), 43 (15); IR: cm^{-1} 1682.

Cyclization of 14c to 42b

To a solution of aldehyde **14c** (100 mg, 0.44 mmol) in dry CH_2Cl_2 (20 mL) at 0^oC was added Et_2AlCl (1.0M, 0.5 mL) in one portion. The resulting reddish brown solution was stirred at 0^oC for 3h and then at room temperature for additional 48h. The solution was passed through a column of silica gel by flash technique using CH_2Cl_2 as eluent to give 57.4 mg of **42b** as yellowish brown viscous oil: ^1H NMR: δ 1.01 (t, 3H), 2.10 (q, 2H), 4.05 (broad m, 1H), 6.18 (d, 2H), 6.50 (m, 4H); ^{13}C NMR: δ 12.02, 25.56, 26.06, 26.33, 26.47, 40.73, 106.05, 106.42, 107.85, 145.19, 145.61, 154.85; MS: m/e (rel. intensity) 720 (M^+ for n=3, 9), 691 (M^+-Et, 11), 40 (100); UV-vis: λ_{max} 346.0, 366.5.

Cyclization of α-terfuran 12 with benzaldehyde to 42c

Phosphorous oxychloride (329 mg, 2.1 mmol) was added to a solution of α-terfuran **12** (200 mg, 1 mmol) and benzaldehyde (2.0 g, 20 mmol) in methylene chloride (100 mL). The solution was stirred at room temperature for 24h. Evaporation of the solvent to one-fifth volume and flash column chromatography of the reaction mixture over silica gel using CH_2Cl_2 as eluent gave 144.7 mg of **42c** as pale greenish solid: ^1H NMR: δ 5.55 (broad s, 1H), 6.08 (broad s, 2H), 6.52 (m, 4H), 7.32 (m, 5H); ^{13}C NMR: δ 45.11, 106.18, 106.83, 109.82, 127.35, 128.43, 128.61, 139.02, 145.54, 145.78, 153.83; MS: m/e (rel. intensity) 864 (M^+ for n=3, 7), 369 (29), 355 (36), 295 (54), 281 (51), 221 (100), 207 (78), 147 (48);

MS (FD)[46]: m/e (rel. intensity) 1440 (M^+ for n=5, 14), 1276 (41), 1152 (M^+ for n=4, 100), 864 (M^+ for n=3, 20), 721 (25), 576 (M^+ for n=2, 34); UV-vis: λ_{max} 338.5, 346.0, 369.0.

Phenylbis(5-2,2':5',2''-terfuryl)methane 55a and **5,5''-bis(phenyl(5-2,2':5',2''-terfuryl)methyl)-terfuran 56a**

To a solution of ketone **36b** (100 mg, 0.33 mmol) in absolute methanol (15 mL) at 0°C was added sodium borohydride (100 mg, 2.6 mmol) portionwise. The temperature was raised slowly to room temperature and the solution was stirred at room temperature for additional 15 min. The solution was poured into water (30 mL) and then extracted with CH_2Cl_2 (3x30 mL). The combined organic extracts were washed with saturated NaCl solution (20 mL) and dried over anhydrous $MgSO_4$. Removal of the solvent in vacuo gave the alcohol **57a** quantitatively as pale yellow oil: ^{1}H NMR: δ 2.42 (bs, 1H), 5.87 (s, 1H), 6.14 (d, J=3.3 Hz, 1H), 6.46 (dd, J=3.3, 1.8 Hz, 1H), 6.50-6.64 (m, 5H), 7.27-7.50 (m, 5H); MS: m/e (rel. intensity) 306 (M^+, 26), 289 (27), 115 (40), 105 (100), 95 (54), 77 (82), 51 (56); IR: cm^{-1} 3200-3600 (broad).

The alcohol **57a** was redissolved in dry CH_2Cl_2 (20 mL). α -Terfuran **12** (200 mg, 1 mmol) and a catalytic amount of p-TsOH was added and the solution was then stirred at room temperature for 4h. The solution was washed with saturated $NaHCO_3$ solution (10 mL), saturated NaCl solution (10 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed in vacuo to give a mixture of products which was

purified by flash column chromatography over silica gel using Et_2O:hexanes (v/v=1/5) as eluent to give **55a** (83.5 mg, 52% based on ketone **36b**) as colorless viscous oil: ^1H NMR: δ 5.54 (s, 1H), 6.11 (d, J=3.3 Hz, 2H), 6.44 (dd, J=3.3, 1.8 Hz, 2H), 6.52-6.58 (m, 8H), 7.27-7.37 (m, 5H), 7.39 (d, J=1.7 Hz, 2H); ^{13}C NMR: δ 45.09, 105.37, 106.20, 106.82, 106.91, 109.85, 111.43, 127.34, 128.40, 128.61, 138.02, 141.90, 145.63, 145.75, 146.28, 153.87; MS: m/e (rel. intensity) 488 (M^+, 100), 411 (50), 327 (20), 289 (33), 244 (39), 161 (88), 95 (67).

Further elution of the column gave **56a** (29.3 mg, 11% based on ketone **36b**) as pale greenish viscous oil: ^1H NMR: δ 5.53 (s, 2H), 6.09 (m, 4H), 6.43 (dd, J=3.3, 1.8 Hz, 2H), 6.50-6.58 (m, 12H), 7.27-7.38 (m, 10H), 7.39 (d, J=1.6 Hz, 2H); ^{13}C NMR: δ 45.09, 105.36, 106.14, 106.20, 106.82, 106.91, 109.82, 111.43, 127.33, 128.40, 128.60, 139.02, 141.90, 145,54, 145.63, 145.77, 146.28, 153.81, 153.89; MS: m/e (rel. intensity) 776 (M^+, 100), 699 (4).

4-Methoxyphenylbis(5-2,2':5',2''-terfuryl)methane 55b and 5,5''-bis(4-methoxyphenyl-(5-2,2':5',2''-terfuryl)methyl)-terfuran 56b

Using the procedure described for 55a and 56a except using Et_2O:hexanes (v/v=3/5) as eluting solvent for the flash column chromatography, the ketone 36d (200 mg, 0.60 mmol) gave the alcohol 57b quantitatively which in turn gave the open-chain compound 55b (152 mg, 49% based on ketone 36d) as colorless viscous oil: ^1H NMR: δ 3.75 (s, 3H), 5.48 (s,

1H), 6.08 (d, J=3.3 Hz, 2H), 6.41 (dd, J=3.3, 1.8 Hz, 2H), 6.51-6.58 (m, 8H), 6.85 (d, J=8.7 Hz, 2H), 7.20 (d, J=8.7 Hz, 2H), 7.37 (d, J=1.4 Hz, 2H); ^{13}C NMR: δ 44.30, 55.15, 105.32, 106.17, 106.76, 106.87, 109.64, 111.40, 113.96, 129.37, 131.08, 141.86, 145.64, 146.25, 154.24, 158.84; MS: m/e (rel. intensity) 518 (M^+, 12), 411 (3), 161 (60), 105 (55), 95 (100).

Further elution of the column gave **56b** (55.8 mg, 11% based on ketone **36d**) as pale greenish viscous oil: ^1H NMR: δ 3.78 (s, 6H), 5.47 (s, 2H), 6.09 (m, 4H), 6.45 (dd, 2H), 6.46-6.58 (m, 12H), 6.86 (d, 4H), 7.21 (d, 4H), 7.39 (d, 2H); ^{13}C NMR: δ 44.33, 55.21, 105.35, 106.14, 106.20, 106.76, 106.90, 109.62, 111.43, 114.02, 129.40, 131.13, 141.87, 145.57, 145.70, 146.31, 154.19, 154.28, 158.87; MS: m/e (rel. intensity) 836 (M^+, 100), 295 (26), 221 (29), 105 (45).

Spectra data for the alcohol **57b**: MS: m/e (rel. intensity) 336 (M^+, 55), 319 (77), 135 (100), 95 (48), 77 (46); IR: cm^{-1} 3200-3600 (broad).

Cyclization of 55a with benzaldeyde to 42c

Phosphorous oxychloride (32.9 mg, 0.2 mmol) was added to a solution of linear compound **55a** (83.5 mg, 0.17 mmol) and benzaldehyde (177.5 mg, 1.7 mmol) in methylene chloride (50 mL). The solution was stirred at room temperature for 9 days until **55a** completely disappeared. Evaporation of the sovent to one-fifth volume and flash column chromatography of the reaction mixture over silica gel using CH_2Cl_2 as eluent gave 53.7 mg of **42c** as pale green solid: m.p. 128-131°C;

^{1}H NMR: δ 5.52 (broad s, 1H), 6.04-6.08 (m, 2H), 6.48-6.52 (m, 4H), 7.31-7.35 (m, 5H); ^{13}C NMR: δ 45.08, 106.16, 106.81, 109.80, 127.34, 128.41, 128.60, 138.97, 145.52, 145.75, 153.82; MS: m/e (rel. intensity) 576 (M^+ for n=2, 17), 221 (28), 207 (68), 44 (100); MS (FAB)[47]: m/e (rel. intensity) 1152 (M^+ for n=4, 2), 576 (M^+ for n=2, 3); UV-vis: λ_{max} 337.0, 344.5, 368.0.

Cyclization of 55b with 4-methoxybenzaldehyde to 42d

Phosphorous oxychloride (49.4 mg, 0.32 mmol) was added to a solution of linear compound **55b** (135.6 mg, 0.26 mmol) and 4-methoxybenzaldehyde (335.7 mg, 2.5 mmol) in methylene chloride (60 mL). The solution was stirred at room temperature for 18 days until **55b** completely disappeared. Evaporation of the solvent to one-fifth volume and flash column chromatography of the reaction mixture over silica gel using CH_2Cl_2 as eluent gave 56.4 mg of **42d** as pale green solid: m.p. 149-153^{o}C; ^{1}H NMR: δ 3.84 (s, 3H), 5.50 (broad s, 1H), 6.02-6.10 (m, 2H), 6.44-6.54 (m, 4H), 6.85-6.94 (m, 2H), 7.25-7.35 (m, 2H); ^{13}C NMR: δ 44.30, 55.26, 106.16, 106.77, 109.62, 114.00, 129.47, 131.08, 145.54, 145.70, 154.22, 158.85; MS: m/e (rel. intensity) 636 (M^+ for n=2, 11), 207 (4), 142 (11), 44 (100); MS (FAB)[47]: m/e (rel. intensity) 1272 (M^+ for n=4, 3), 636 (M^+ for n=2, 5); UV-vis: λ_{max} 337.0, 345.0, 368.0.

APPENDIX

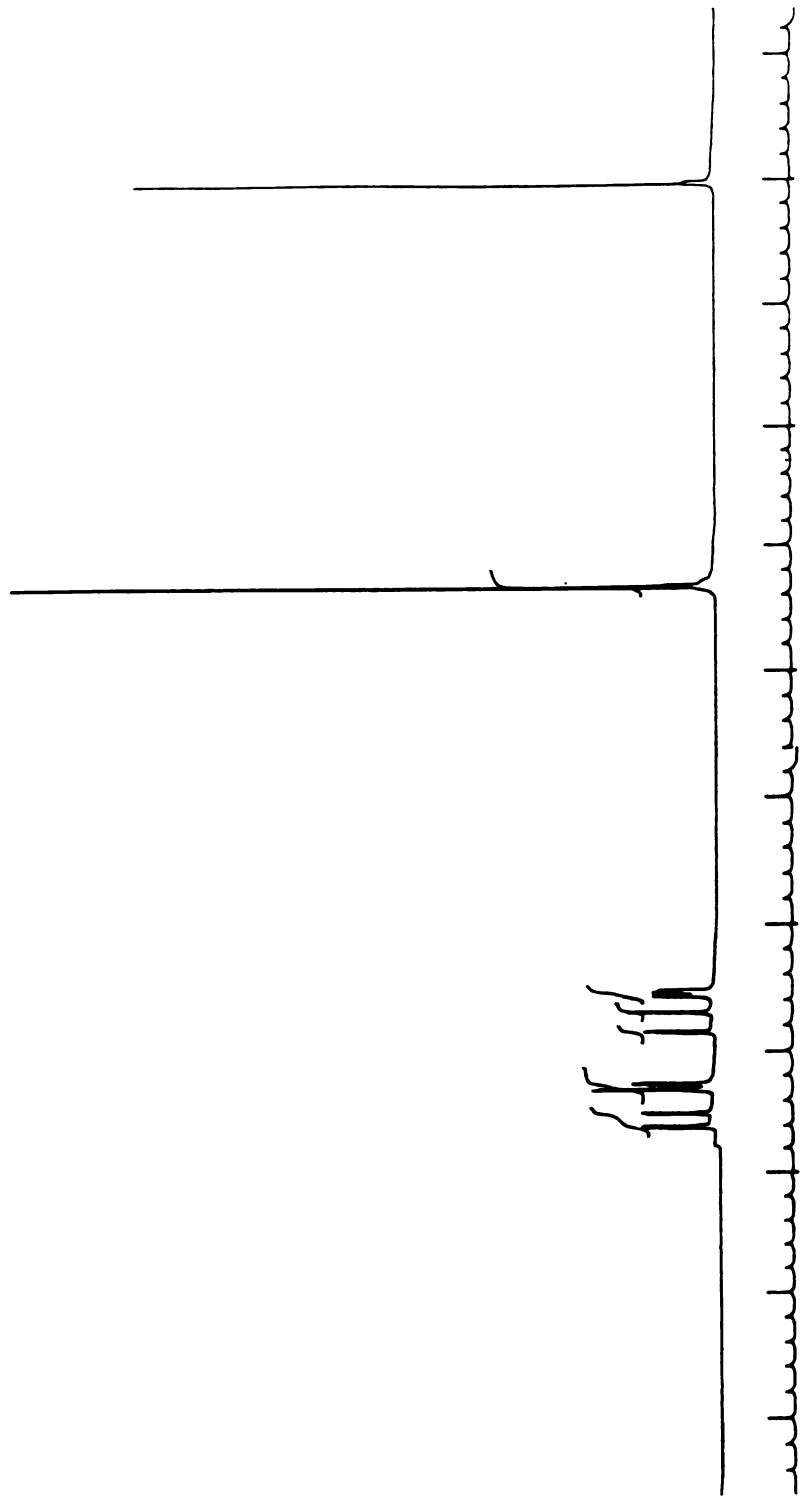


Figure A1. 250 MHz ^{1}H NMR spectrum of 1-(2-furyl)-4-(5-2,2'-bifuryl)-1,4-butanedione **16b.**

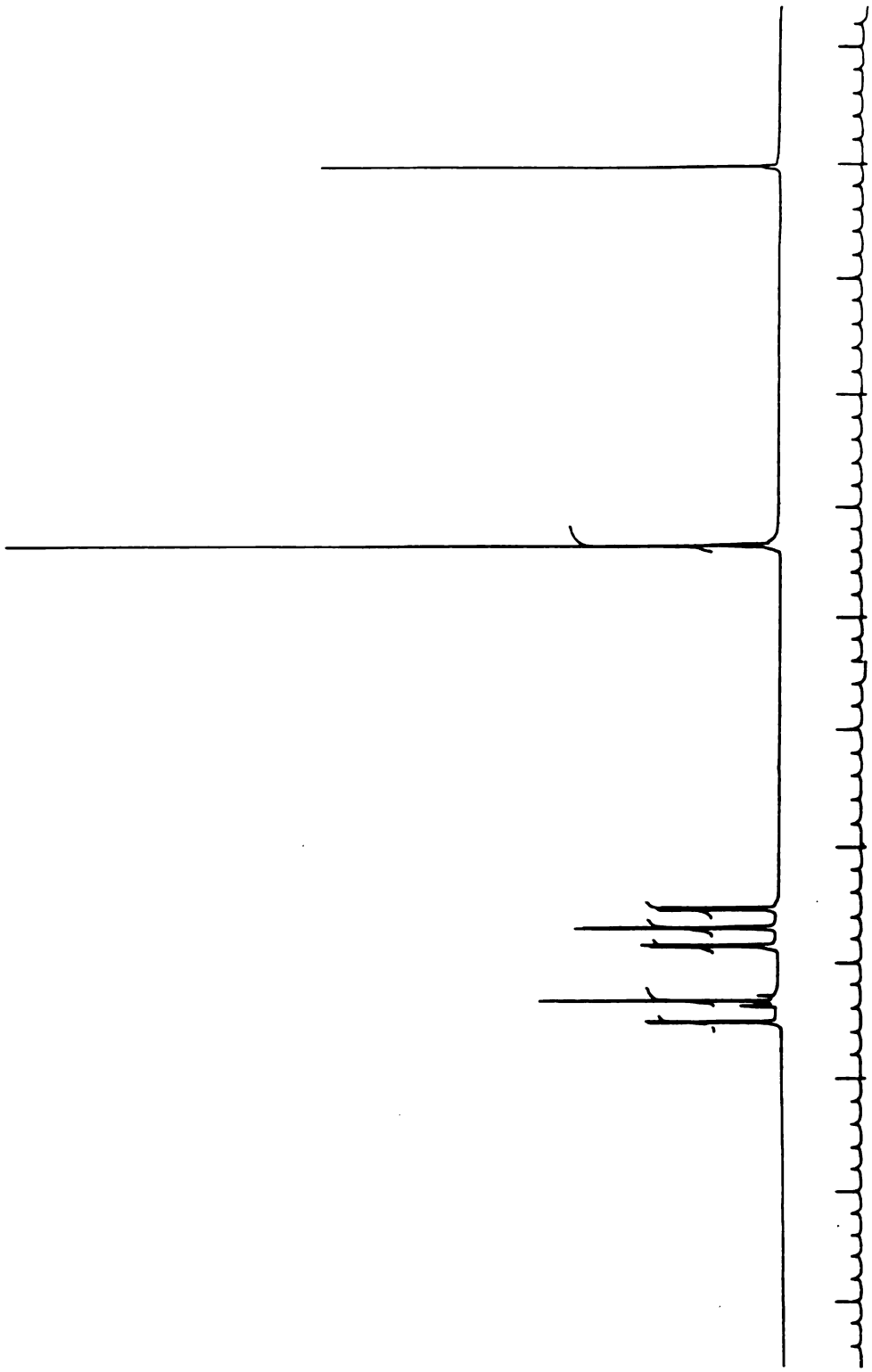


Figure A2. 250 MHz ^{1}H NMR spectrum of 1,4-bis(5-2,2'-bifuryl)-1,4-butanedione **16c.**

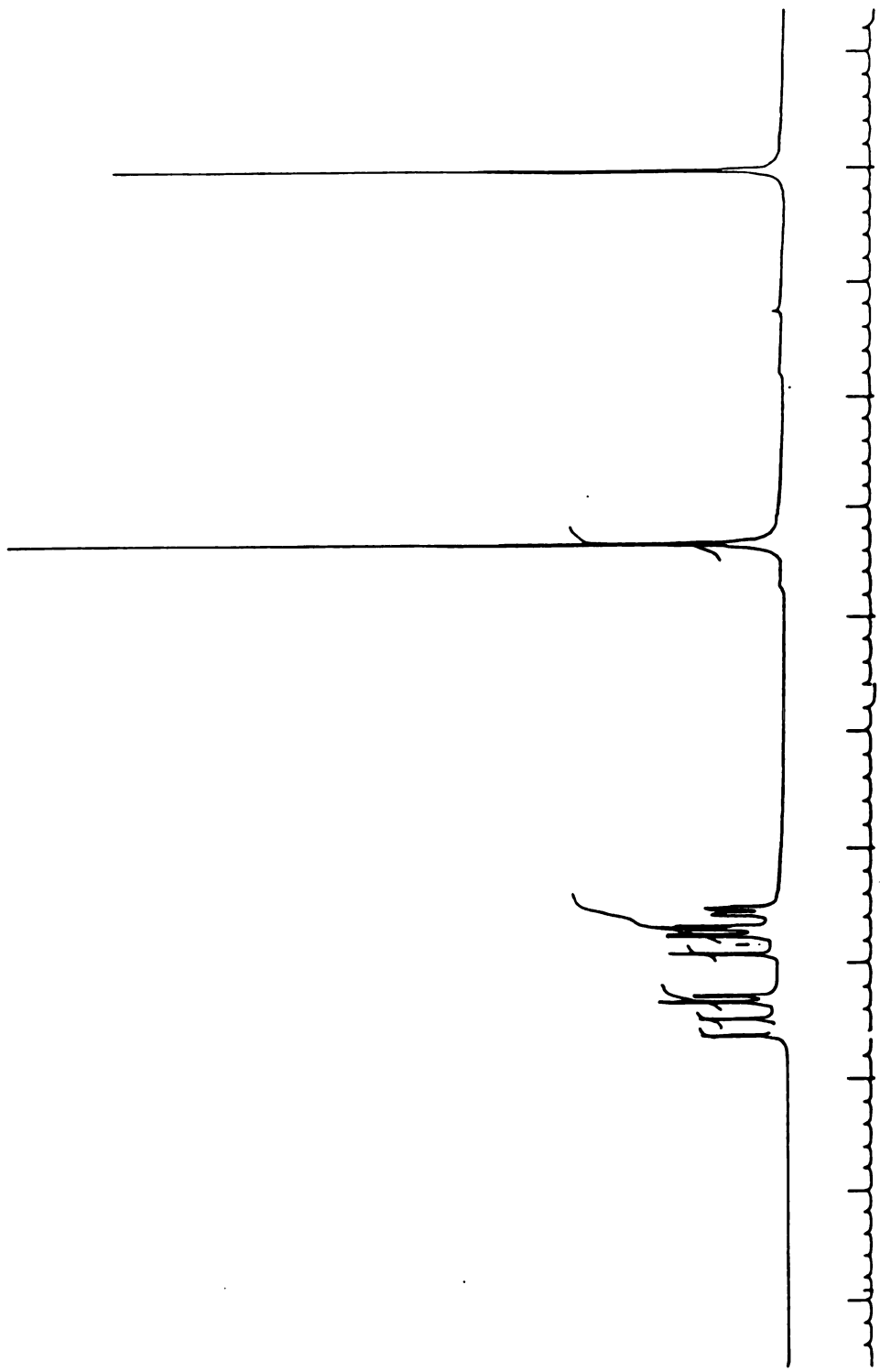


Figure A3. 250 MHz ^{1}H NMR spectrum of 1-(2-furyl)-4-(5-2,2':5',2''-terfuryl)-1,4-butanedione **16d**.

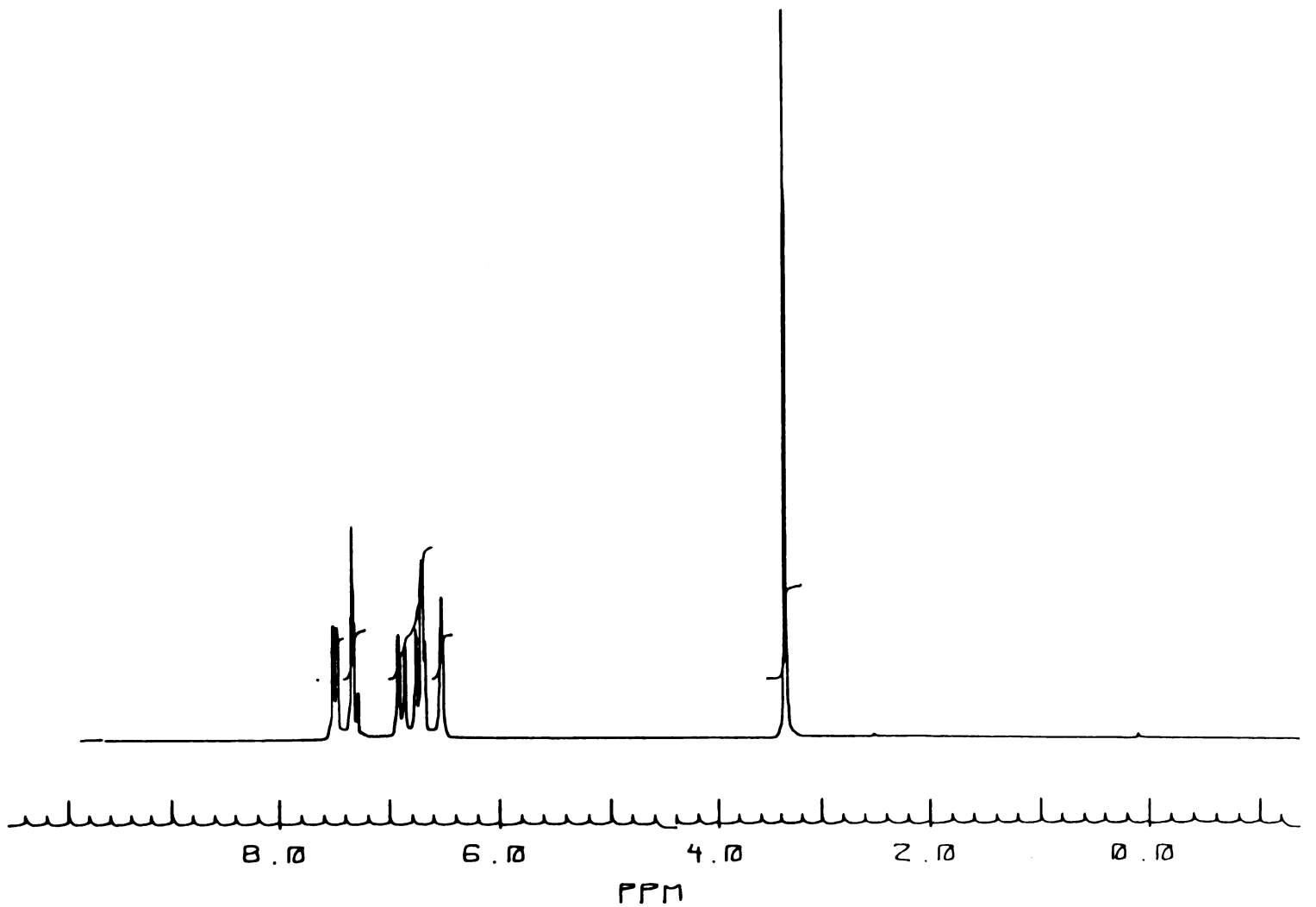


Figure A4. 250 MHz ^{1}H NMR spectrum of 1-(5-2,2'-bifuryl)-4-(5-2,2':5',2''-terfuryl)-1,4-butanedione **16e**.

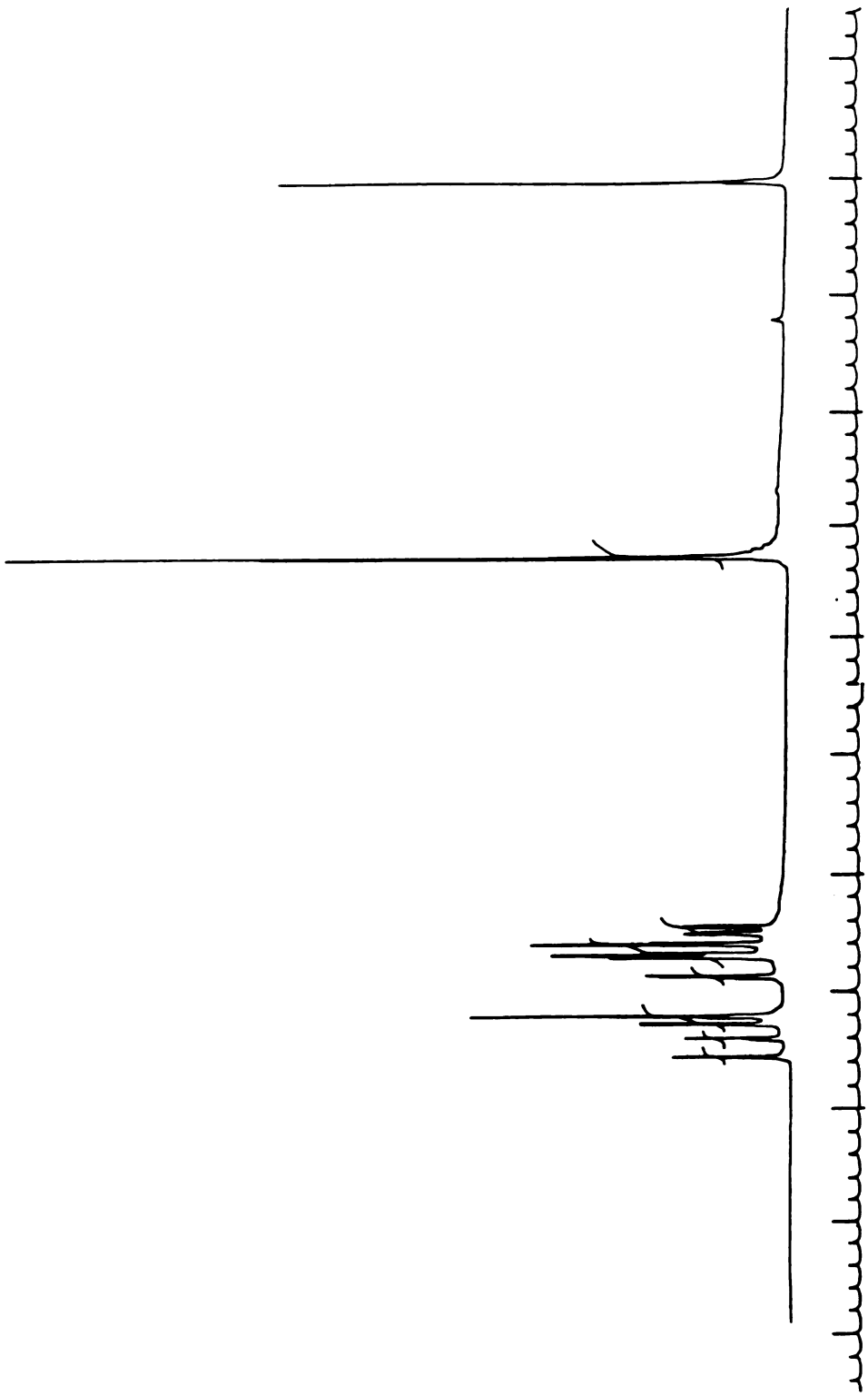


Figure A5. 250 MHz ^{1}H NMR spectrum of 1-(2-furyl)-4-(5-2,2':5'2'':5'',2'''-quaterfuryl)-1,4-butanedione **16f.**

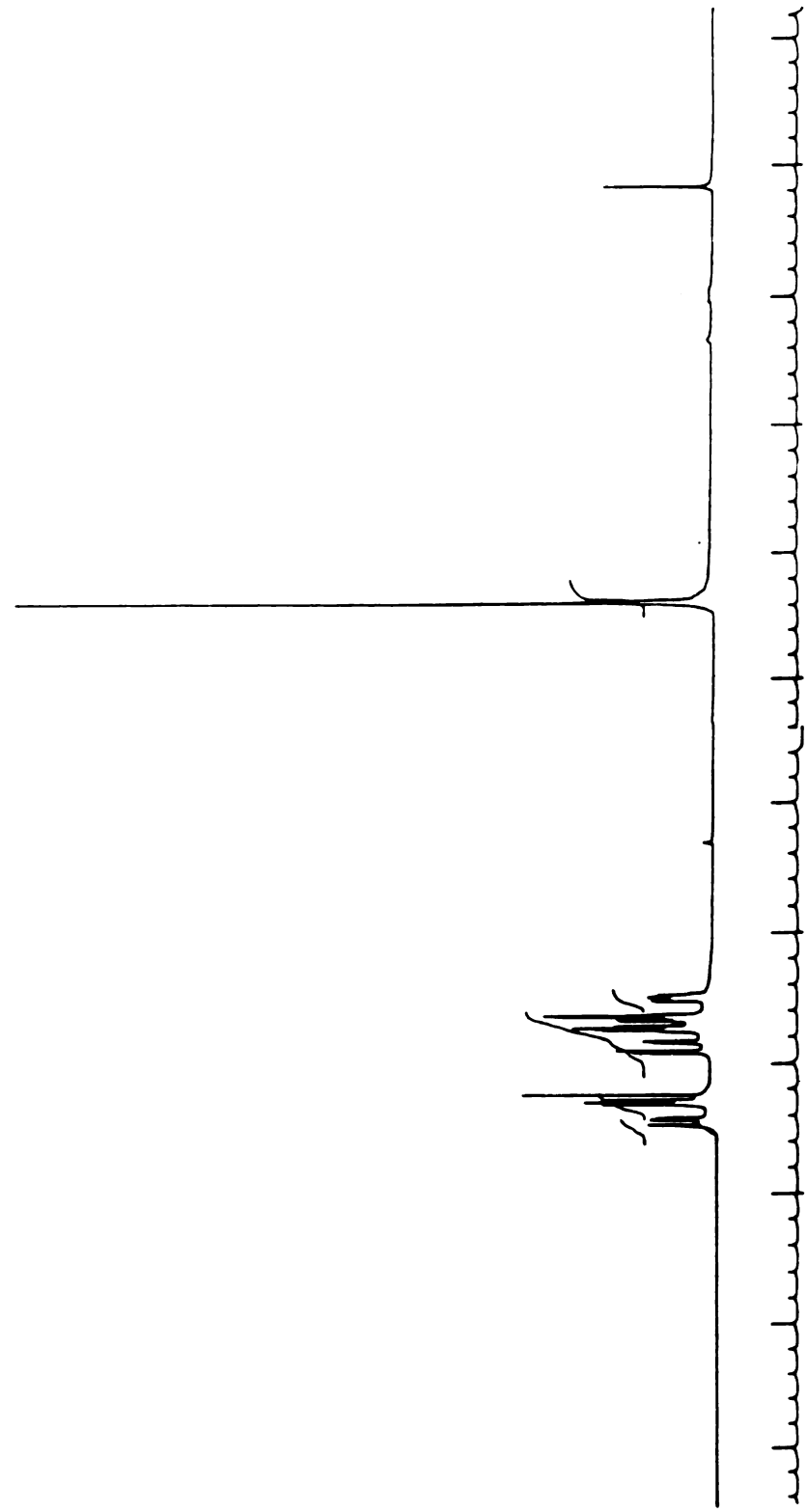


Figure A6. 250 MHz ^{1}H NMR spectrum of 1-(5-2,2'-bifuryl)-4-(5-2,2':5',2'':5'',2'''-quaterfuryl)-1,4-butanedione **16g**.

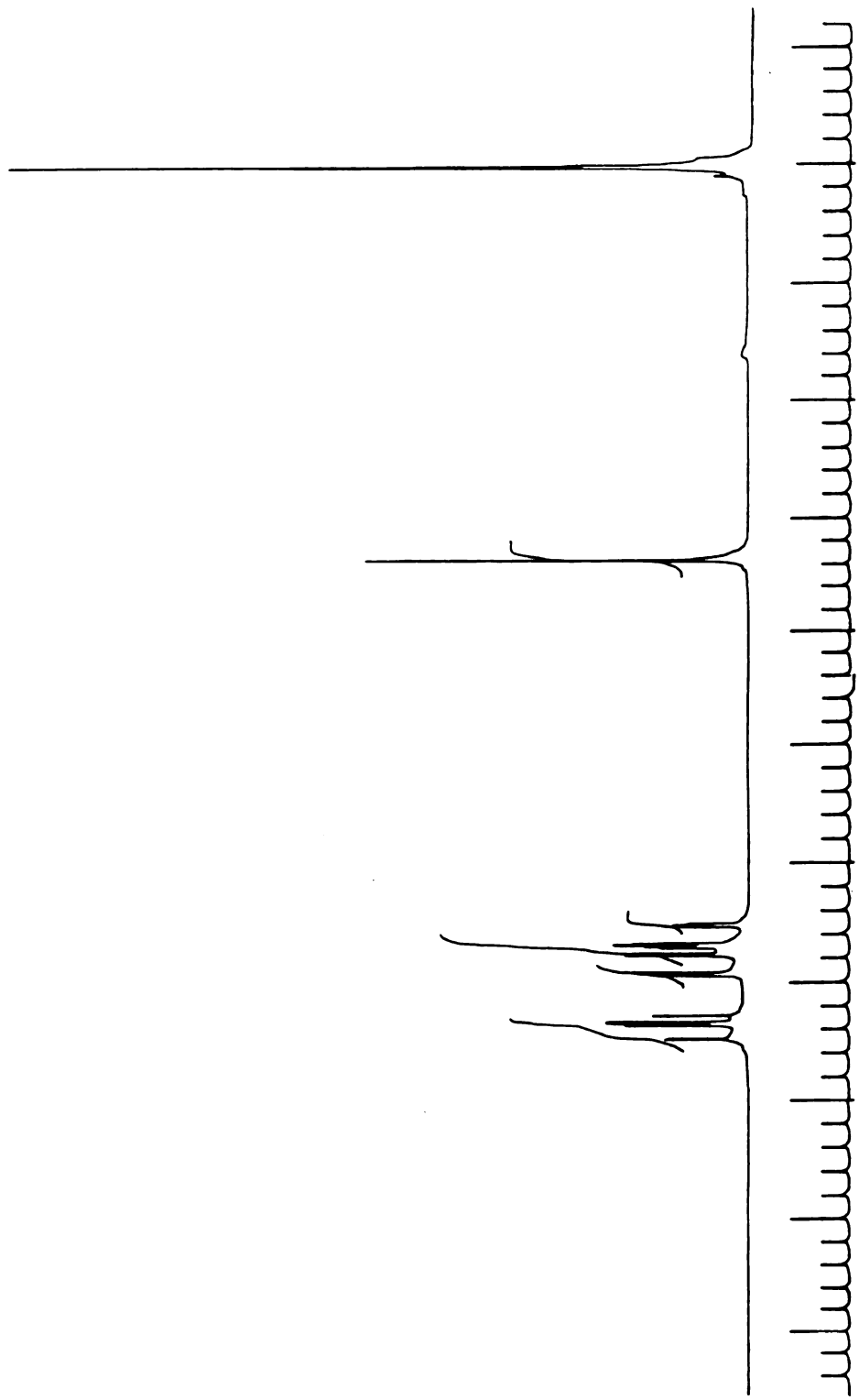


Figure A7. 250 MHz ^{1}H NMR spectrum of 1,4-bis(5-2,2':5',2''-terfuryl)-1,4-butanedione **16h.**

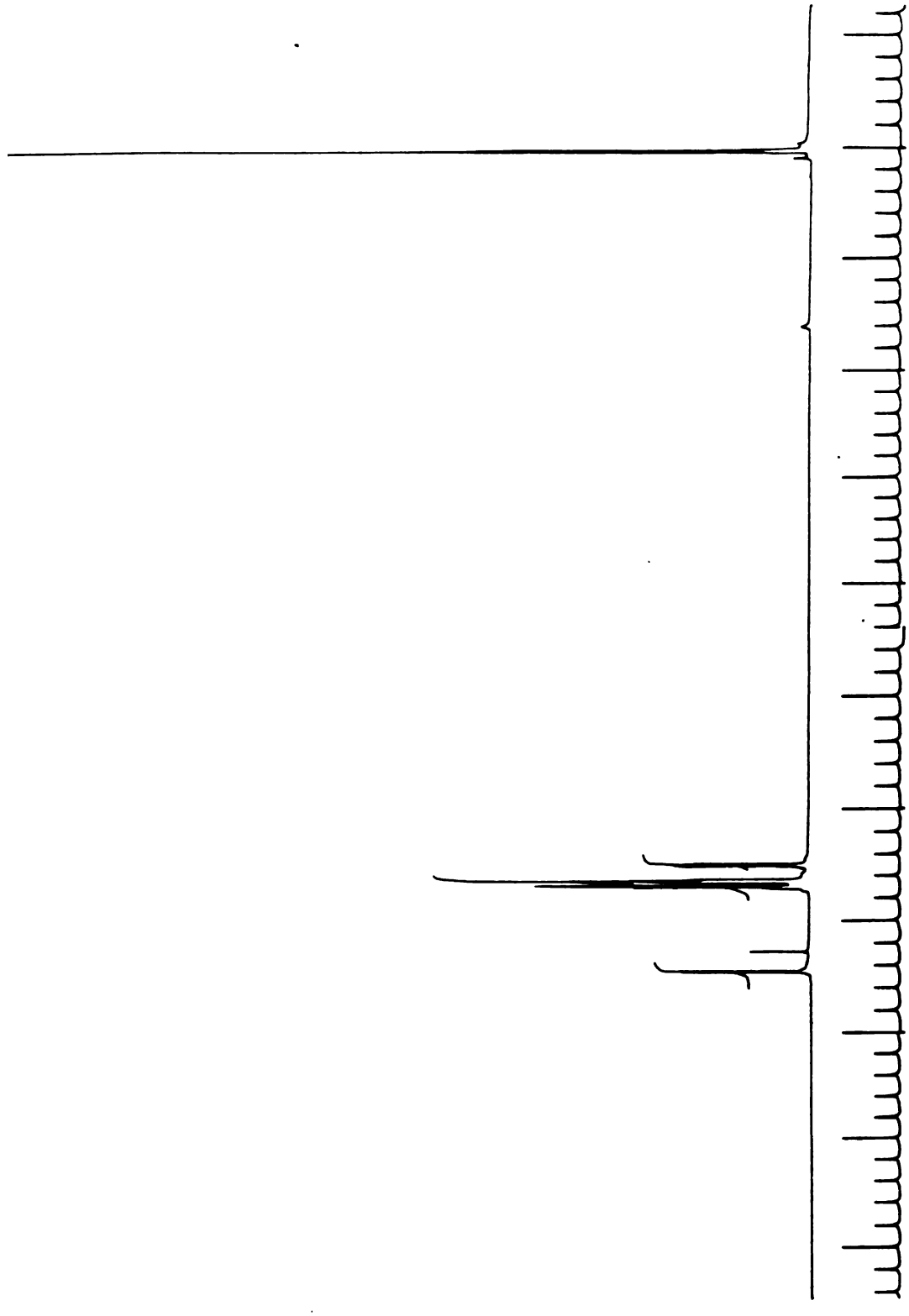


Figure A8. 250 MHz ^{1}H NMR spectrum of 2,2':5',2'':5'',2'''-quaterfuran 13.

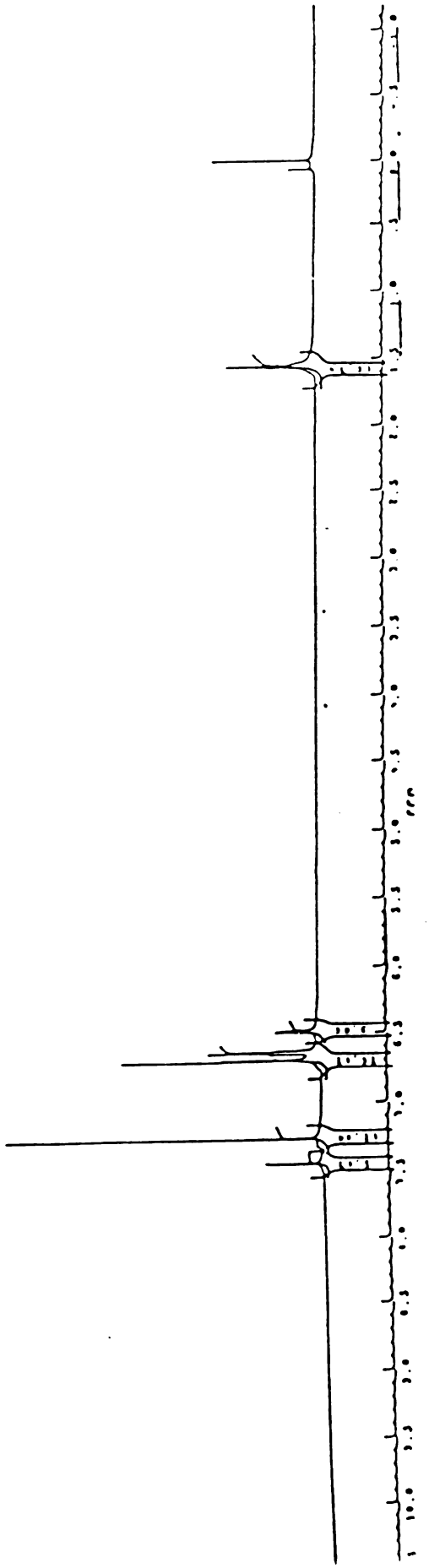


Figure A9. 250 MHz ^{1}H NMR spectrum of 2,2':5',2'':5'',2''':5''',2''''-quinquefuran **23**.

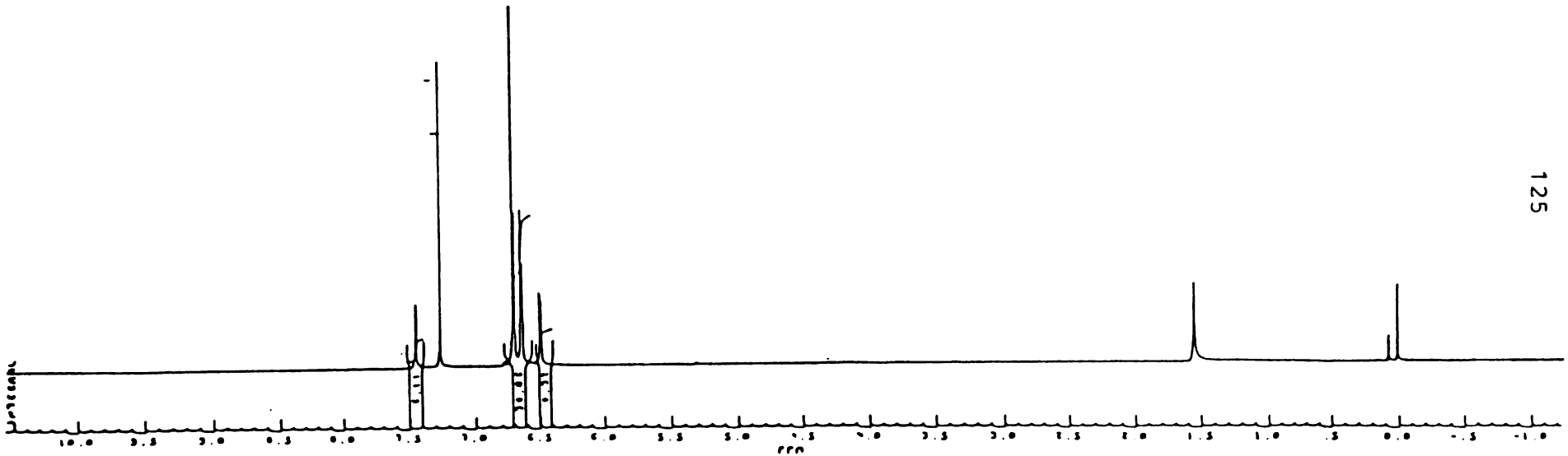


Figure A10. 250 MHz ^{1}H NMR spectrum of 2,2':5',2'':5'',2''':5''',2'''':5'''',2'''''-sexifuran **24**.

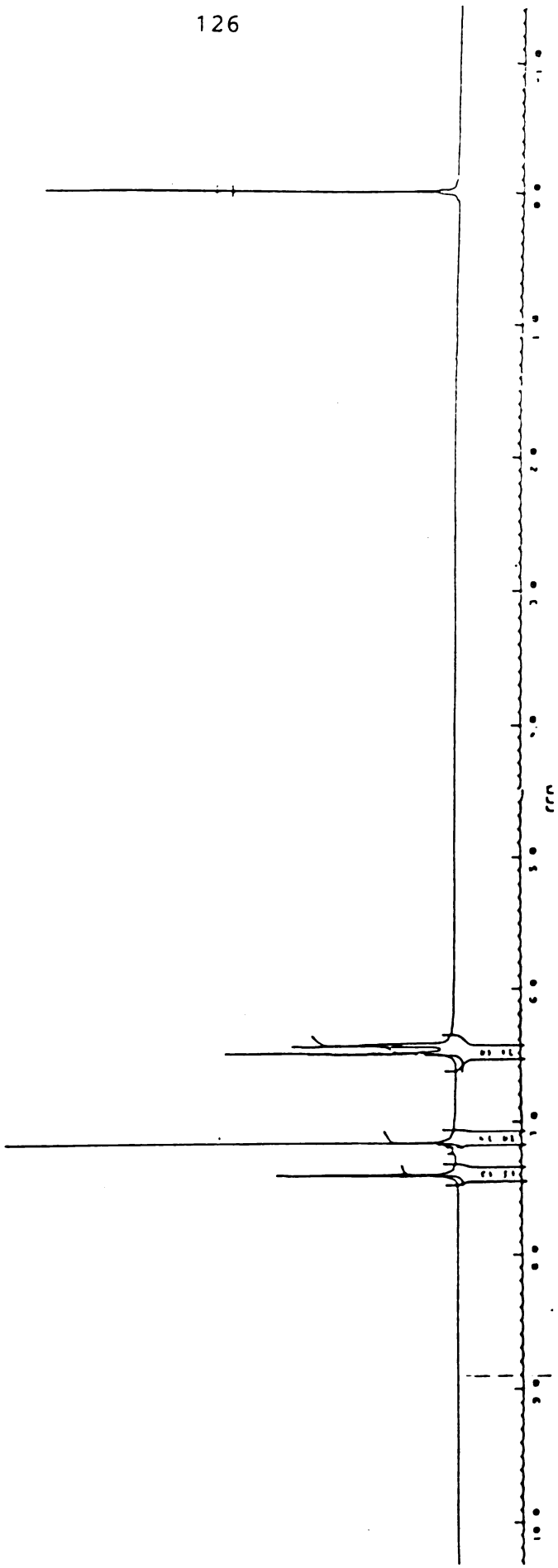


Figure A11. 250 MHz ^{1}H NMR spectrum of 2,5-bis(2-furyl)-thiophene **26**.

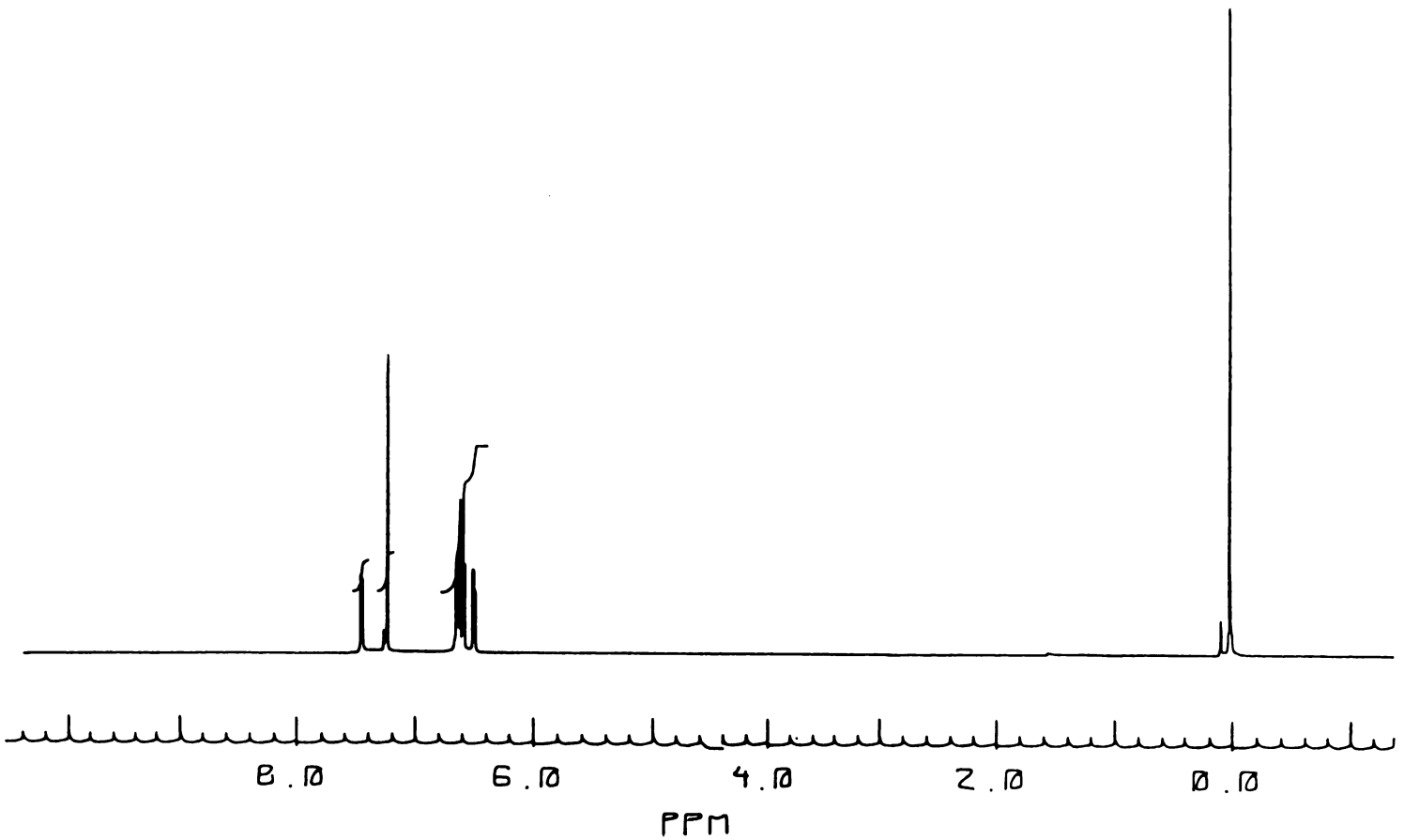


Figure A12. 250 MHz ^{1}H NMR spectrum of 2,5-bis(5-2,2'-bifuryl)-thiophene **27.**

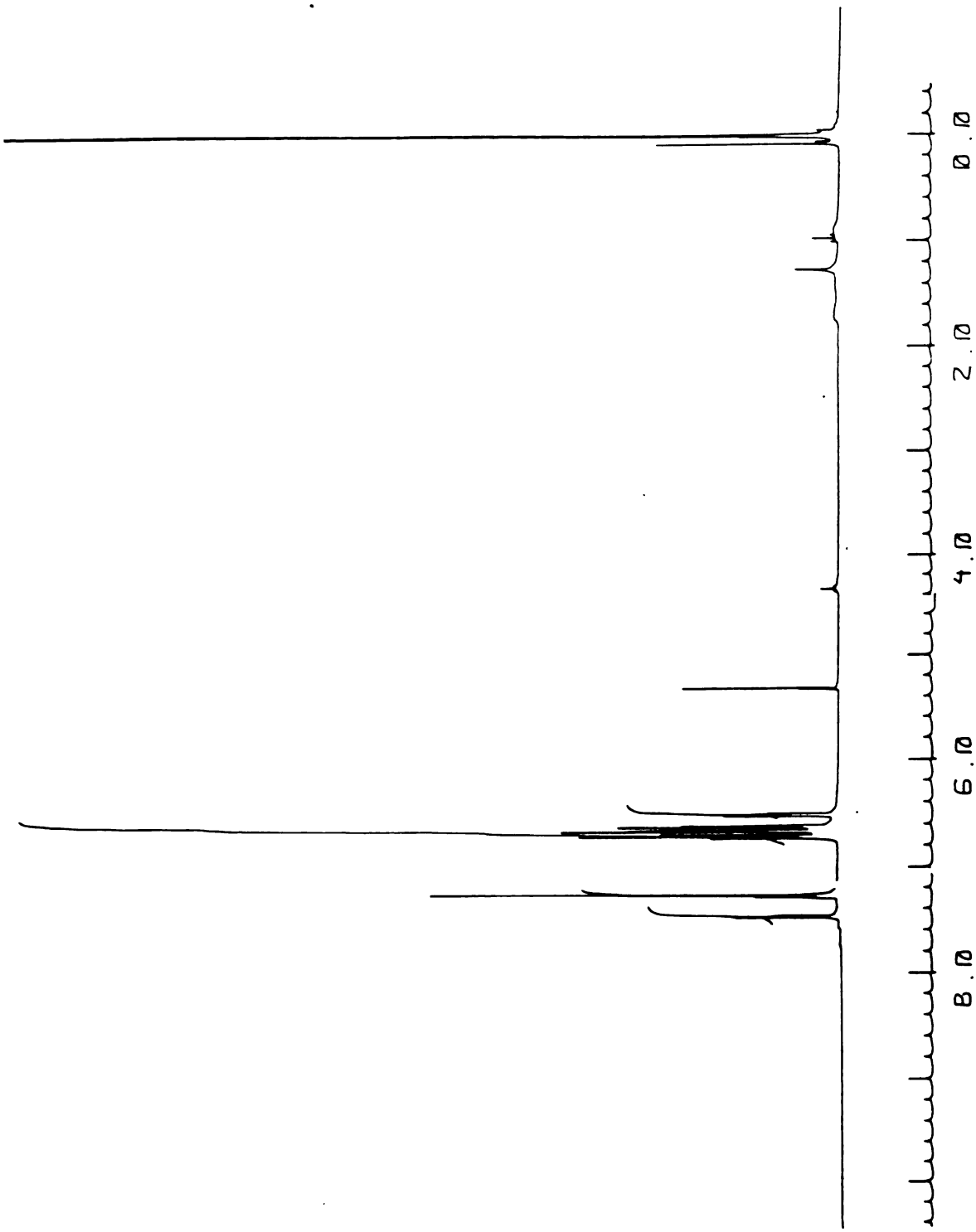


Figure A13. 250 MHz ^{1}H NMR spectrum of 2,5-bis(5-2,2':5',2''-terfuryl)-thiophene **28**.

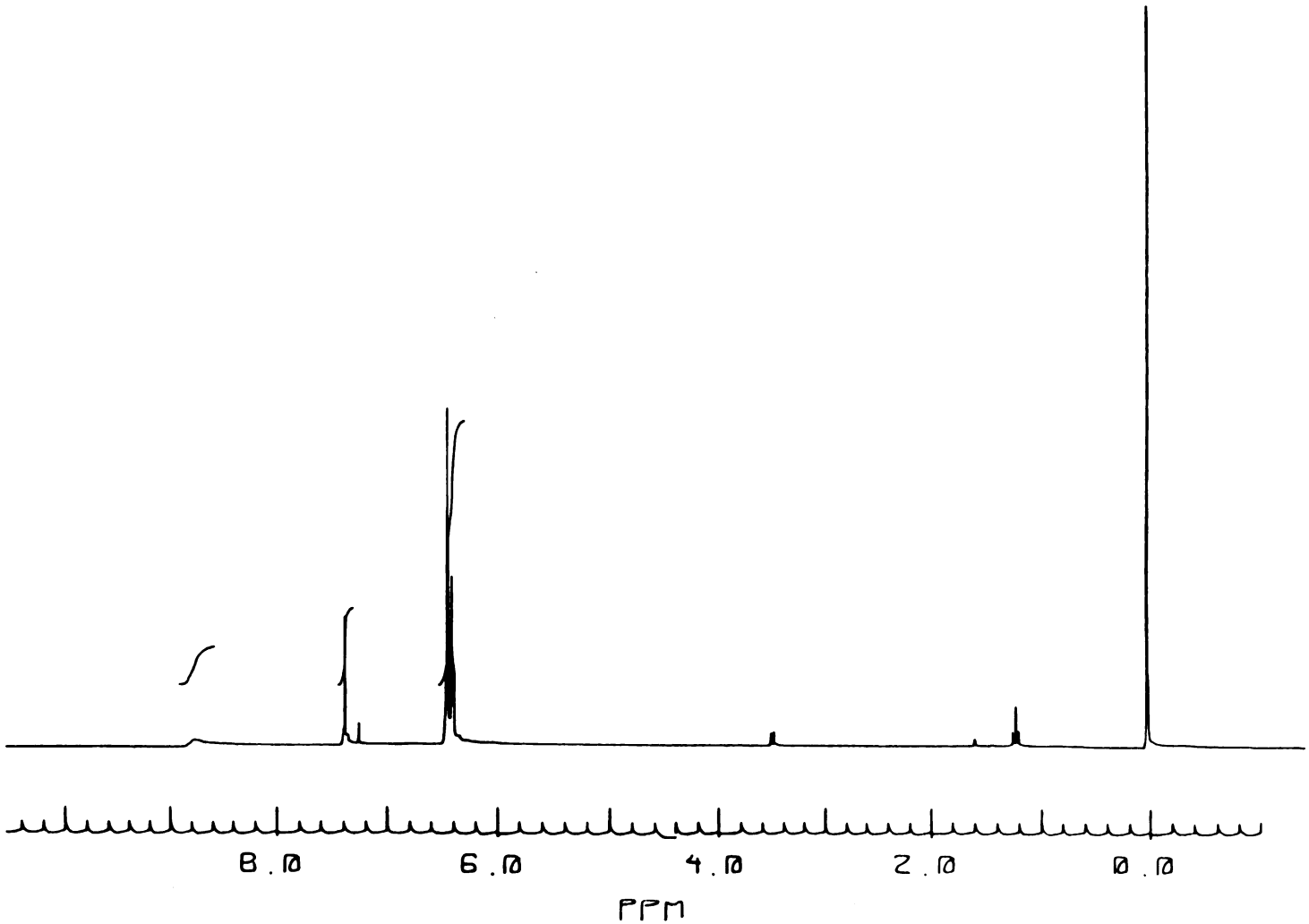


Figure A14. 250 MHz ^{1}H NMR spectrum of 2,5-bis(2-furyl)-pyrrole **29.**

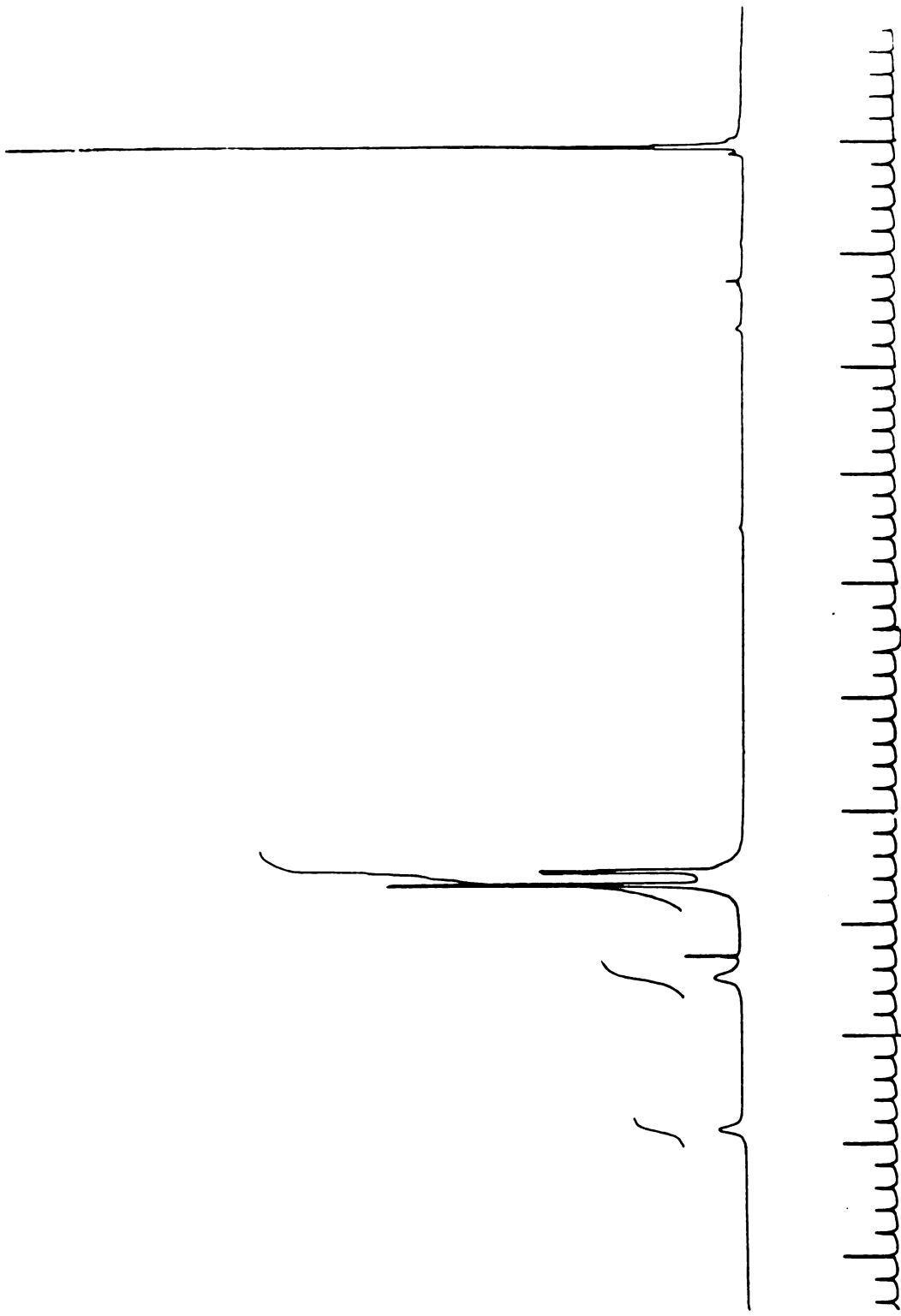


Figure A15. 250 MHz ^{1}H NMR spectrum of 2,5-bis(5-2,2'-bifuryl)-pyrrole 30.

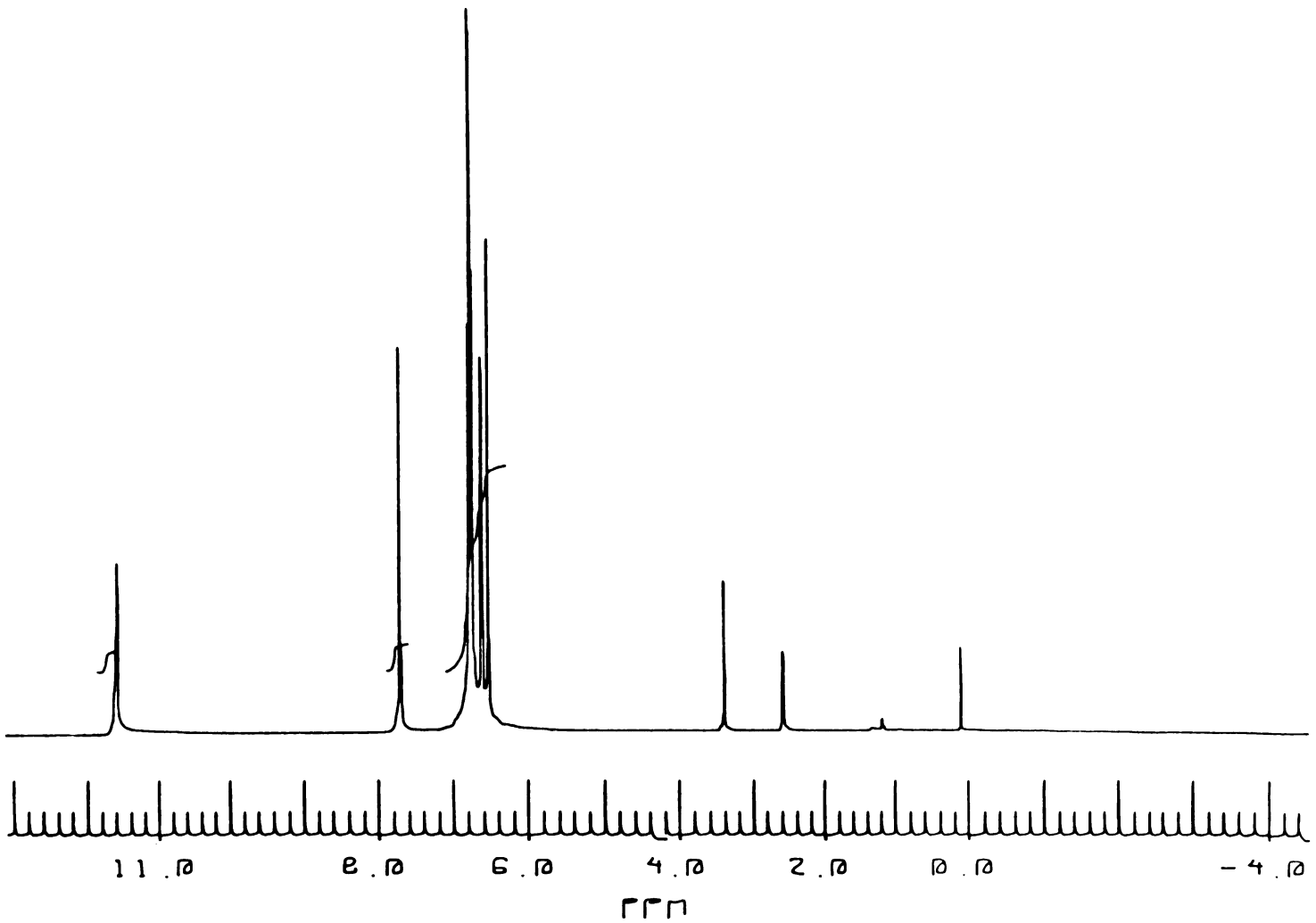


Figure A16. 250 MHz ^{1}H NMR spectrum of 2,5-bis(5-2,2'-bifuryl)-pyrrole **30** in DMSO-d_6.

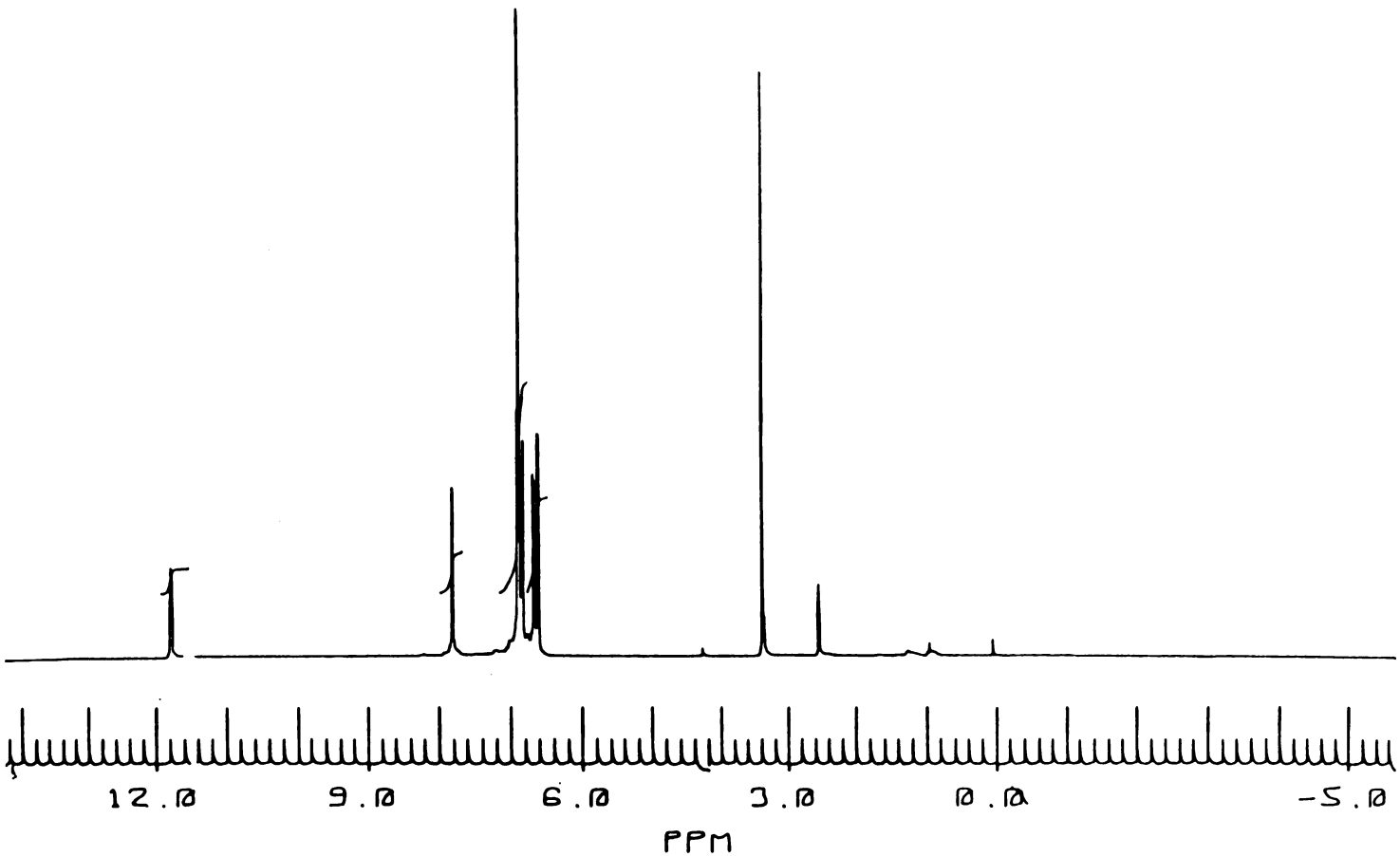


Figure A17. 250 MHz ^{1}H NMR spectrum of 2,5-bis-(5-2,2':5',2''-terfuryl)-pyrrole 31 in DMSO-d_6.

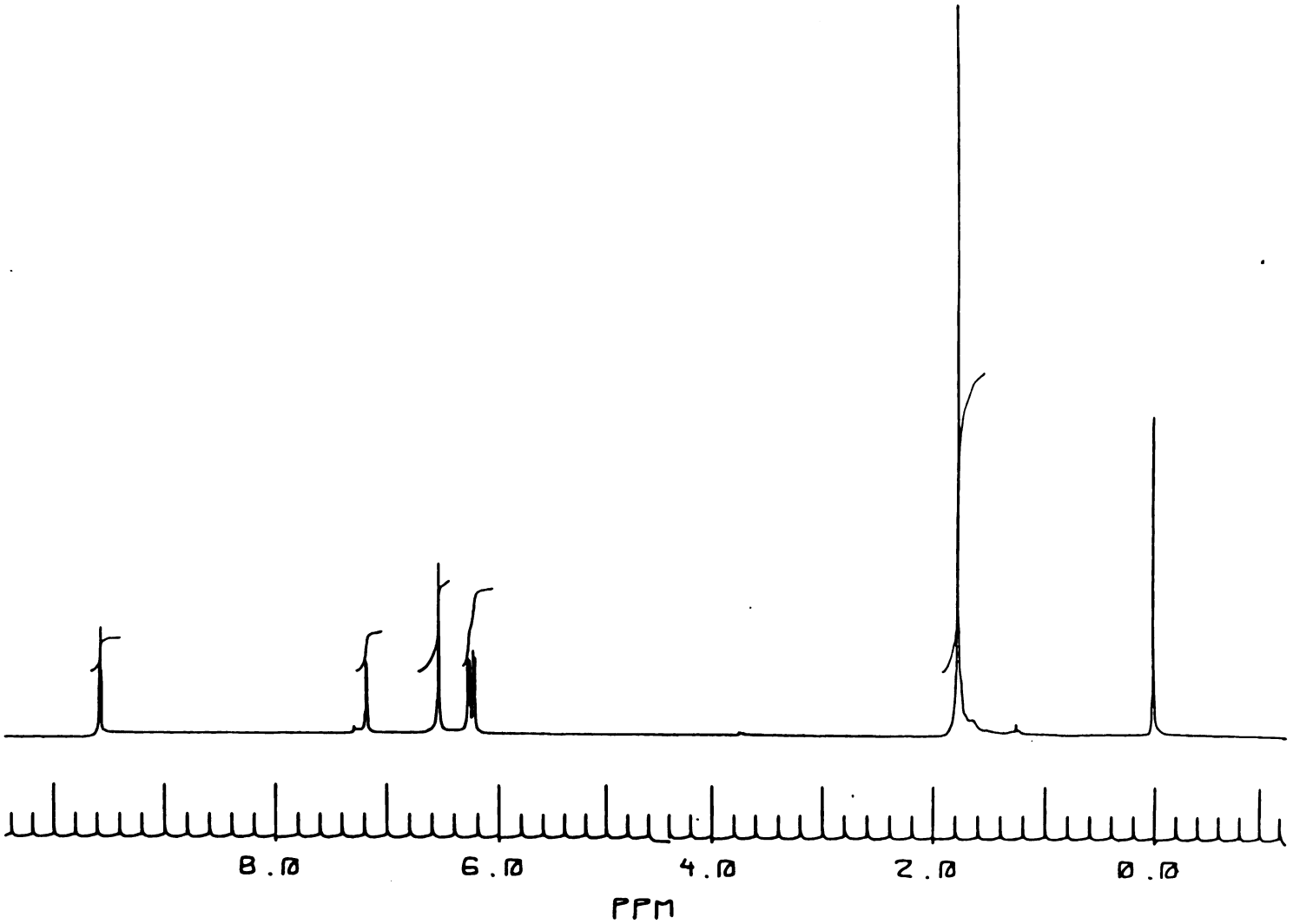


Figure A18. 250 MHz ^{1}H NMR spectrum of 5,5''-bis(5-formyl-dimethylfurfuryl)-2,2':5',2''-terfuran **48**.

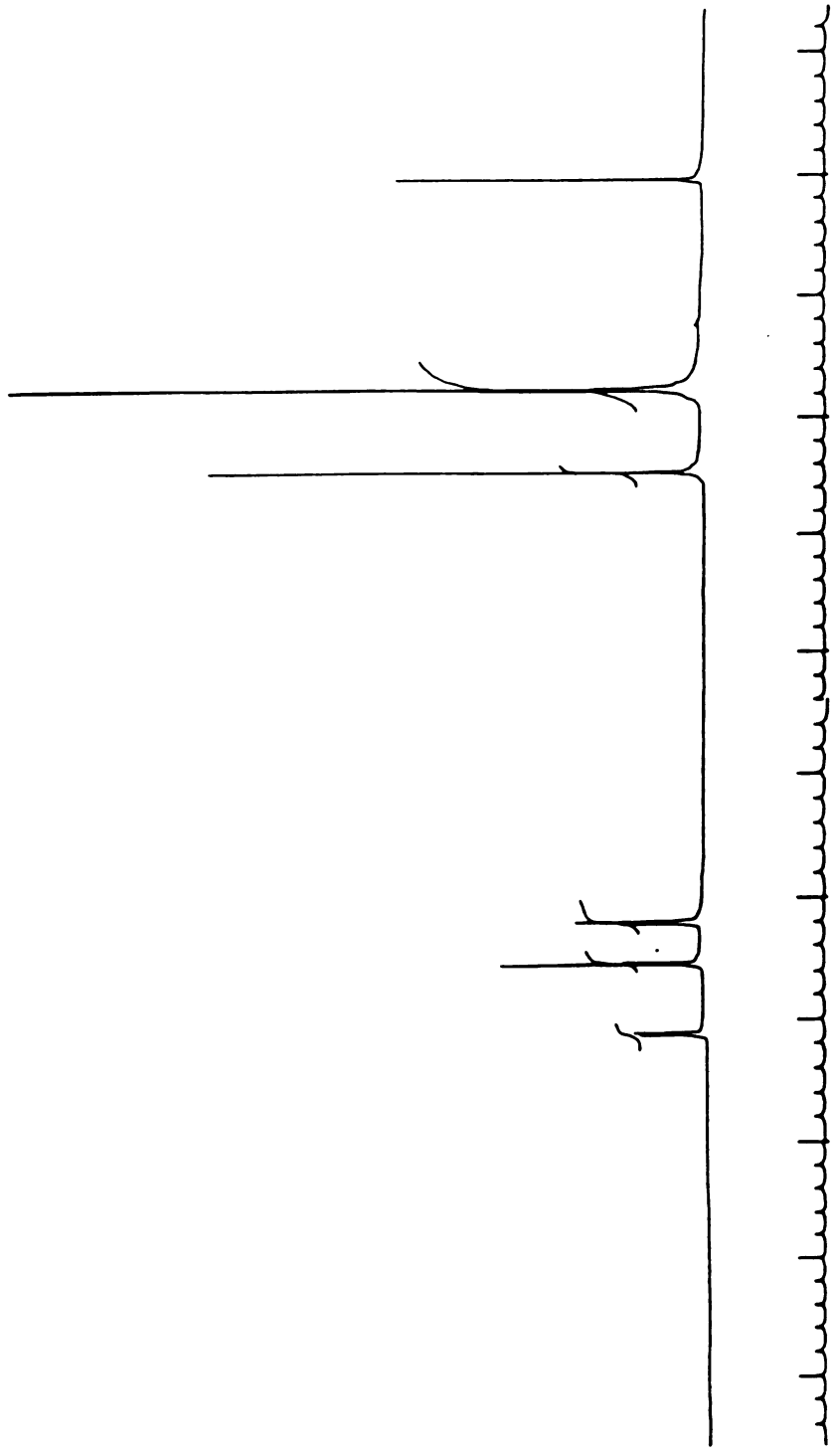


Figure A19. 250 MHz ^{1}H NMR spectrum of 5,5''-bis(5-acetyl-dimethylfurfuryl)-2,2':5,2''-terfuran 53.

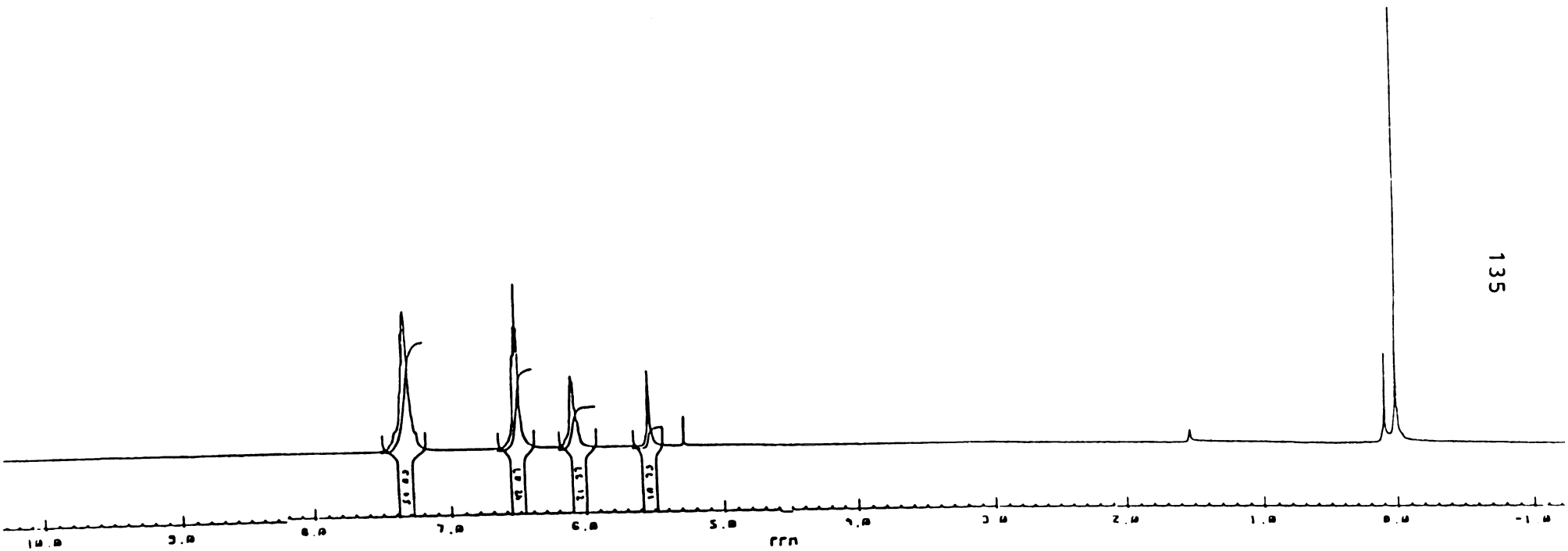


Figure A20. 250 MHz ^{1}H NMR spectrum of **42c** from the reaction bewteen α-terfuran **12** and benzaldehyde at $1x10^{-2}M$.

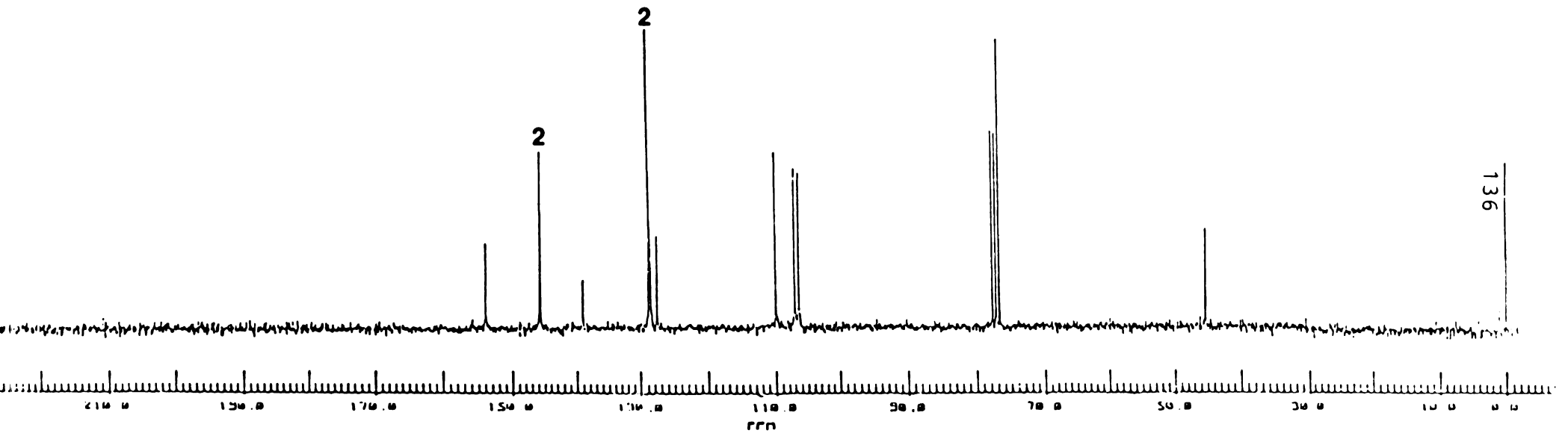


Figure A21. 62.9 MHz ^{13}C NMR spectrum of **42c** from the reaction bewteen α-terfuran 12 and benzaldehyde at $1x10^{-2}M$.

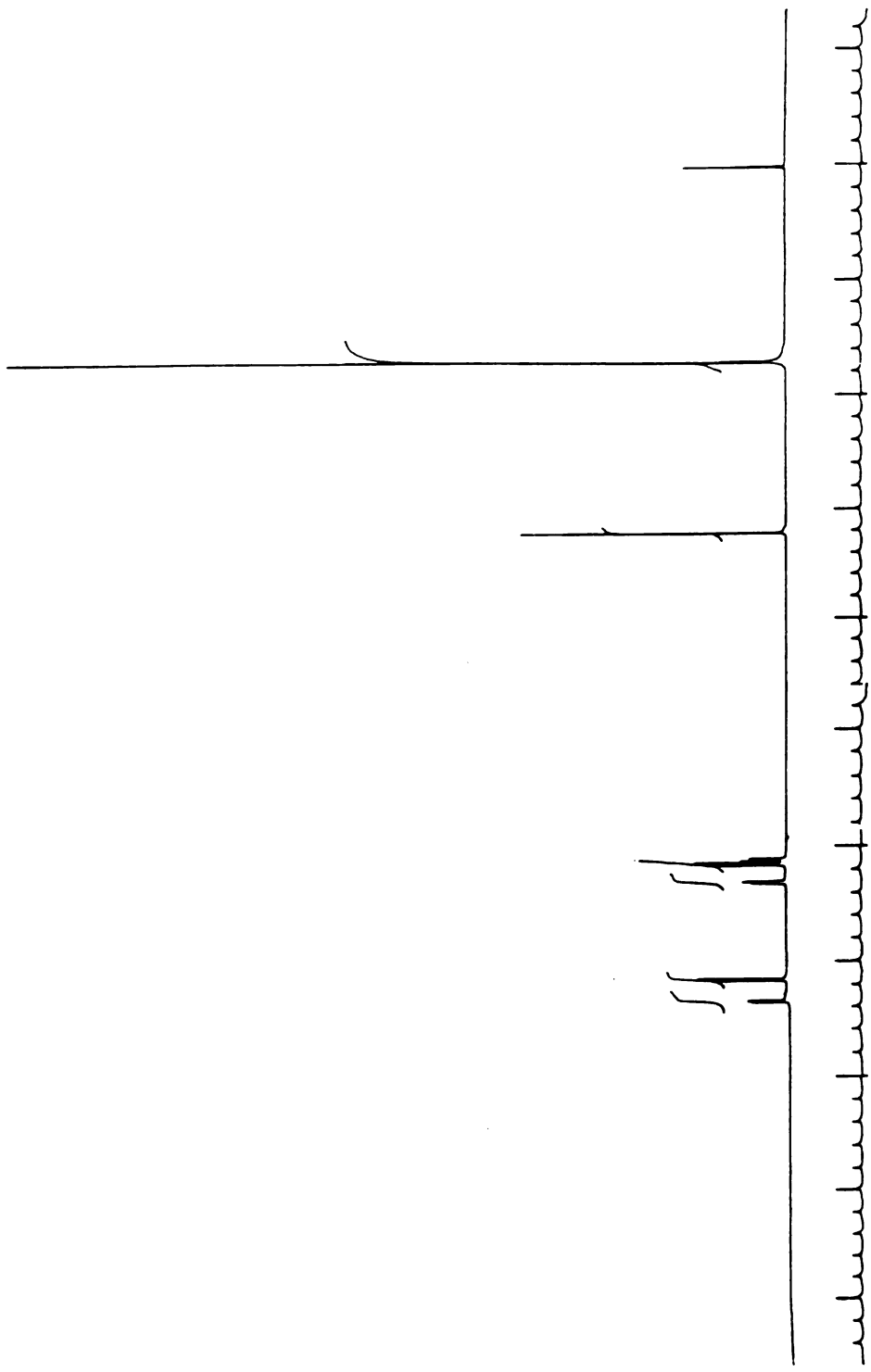


Figure A22. 250 MHz ^{1}H NMR spectrum of 1,4-bis(2,2-difurylpropane)-1,4-butanedione **51**.

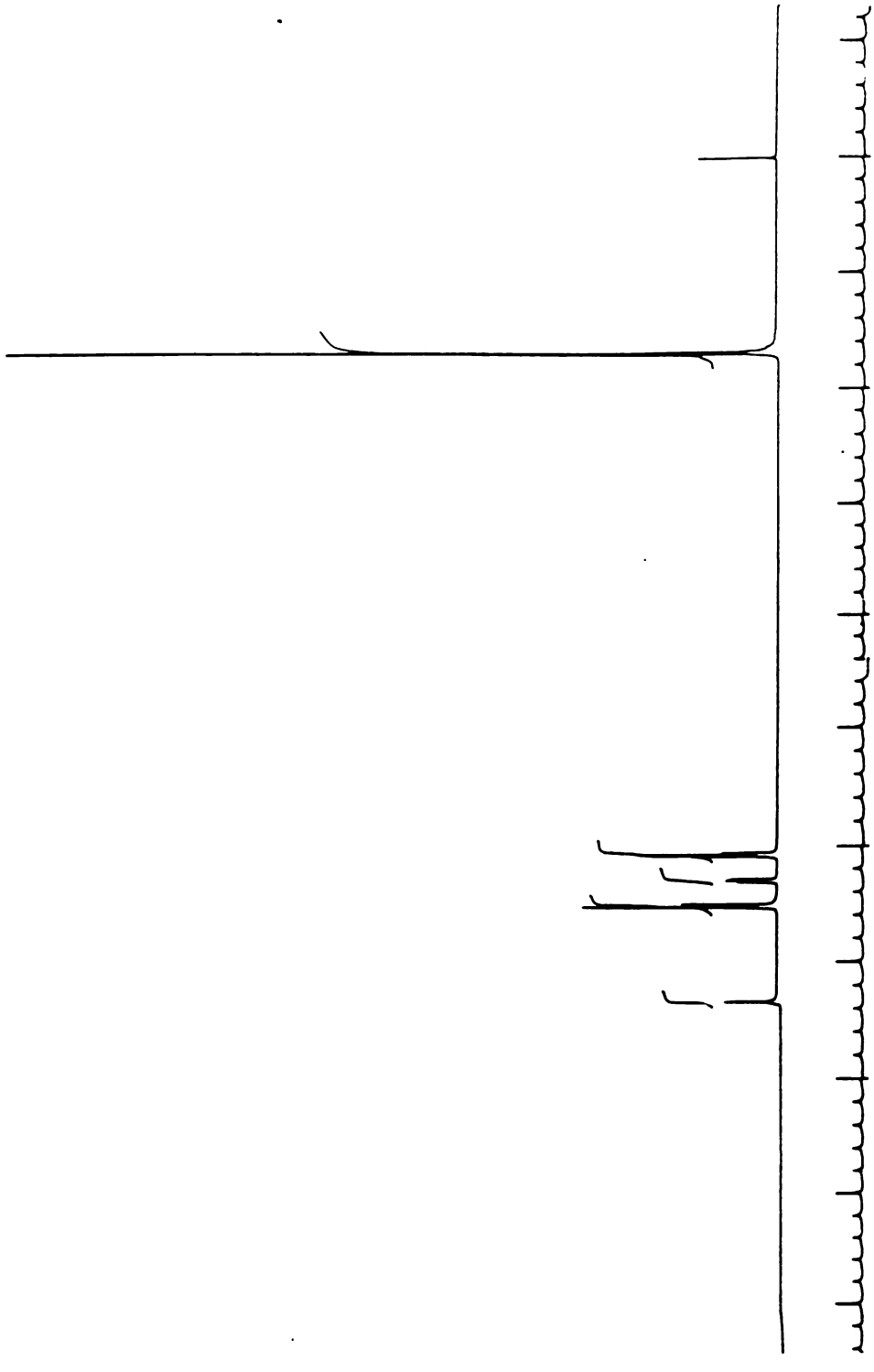


Figure A23. 250 MHz ^{1}H NMR spectrum of 5,5''-bis(dimethylfurfuryl)-2,2':5',2''-terfuran 52.

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