PART I

SYNTHESIS OF A NEW DIARYNE EQUIVALENT AND ITS APPLICATION TO ORGANIC SYNTHESIS

PART II

ACID-CATALYZED AND PHOTOCHEMICAL REARRANGEMENTS OF NOVEL KETONES

By

Dong Ok

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ABSTRACT

PART I

SYNTHESIS OF A NEW DIARYNE EQUIVALENT AND ITS APPLICATION TO ORGANIC SYNTHESIS

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In the first part of this thesis the synthesis of a new diaryne equivalent and its application to bis-annulation was investigated.

Treatment of benzo[1,2-d:4,5-d']bistriazole **1** in aqueous potassium hydroxide solution at 66-68°C with hydroxylamine-O-sulfonic acid provided a mixture of 1,5- 1,6- and 1,7-diaminobenzo[1,2-d:4,5-d']bistriazole (**2**, **3**, and **4**) and two mono-aminated products in 45 and 48% yield respectively. The three isomers were separated in excellent purity by fractional recrystallization from ethanol. The mono-aminated products could then be recycled to give additional **2-4**.

Reaction of either **2** or **4** with lead tetraacetate (LTA) and two equivalents of a diene gave bis-annulation products. For example, reaction of **2** with diethyl 2,5-dimethylfuran-3,

4-dicarboxylate and LTA gave tetraethyl 1,4,5,8-tetramethyl-1,4,5,8-tetrahydroanthracene-1,4:5,8-diendoxide-2,3,6,7-tetracarboxylate as a single isomer in 67% yield. Similar reactions with the following symmetric dienes are also described: furan, 2,5-dimethylfuran, 1,3,4-trimethyl-2,5-diphenylpyrrole, 2,3-bis-(methylene)-bicyclo[2.2.1]heptane, diethyl 3,4-furandicarboxylate.

The question of regioselectivity arises when the diene is unsymmetric. Two regioisomers, as well as syn and anti stereoisomers, are possible. However, in practice only the 'trans'-type isomers were formed with several dienes. For example, treatment of **2** with methyl 2-furoate and LTA gave dimethyl 1,4,5,8-tetrahydroanthracene-1,4:5,8-diendoxide-1,5-dicarboxylate in 47% yield. The following unsymmetrical dienes were studied: 3-bromofuran, dimethyl 4,5-diphenylfuran-2,3-dicarboxylate, 2,3,4,5,6,6-hexamethylcyclohexa-2,4-dien-1-one **5**.

Cycloaddition to 1,3-dipoles is also possible. Here too the reaction was highly regioselective. For example, the reaction of **2** with N-methyl-α-phenylnitrone and LTA gave the only the 'trans' regioisomer. The remarkable degree of regio- and stereospecificity in these cycloadditions strongly suggests that they occur in a stepwise manner, the regiochemistry being controlled by the mono-aryne adduct.

Bis-annulation has been extended to the synthesis of various polyphenyl arenes. For example, treatment of **2** with two equivalents of tetraphenylcyclopentadienone and

LTA gave 1,2,3,4,5,6,7,8-octaphenylanthracene. Similarly, reaction of **2** with 1,3-diphenylisobenzofuran furnished the diadduct, 5,7,12,14-tetraphenyl-5,7,12,14-tetrahydropentacene-5,14,7,12-diendoxide **6** in 88% yield. Removal of the oxygen bridges from **6** by treatment with Zn-$TiCl_4$ in boiling THF gave 5,7,12,14-tetraphenylpentacene **7** in 81% yield. Diels-Alder reaction of the pentacene **7** with dimethyl acetylenedicarboxylate or maleic anhydride gave the expected adduct at the central aromatic ring.

Part II of this thesis deals with aromatic acid-catalyzed and photochemical rearrangements of novel ketones, obtained directly or indirectly from the chemistry developed in Part I.

The acid-catalyzed rearrangment of a β,γ-unsaturated ketone, 1,3,3,4,7,8,10,12,12,13,16,17-dodecamethyl-benzo-[1,2-e:4,5-e']bisbicyclo[2.2.2]oct-7.16-dien-2,11-dione **8** (obtained from the reaction of diene **5** with **2** and LTA), in trifluroacetic acid gave an equilibrium mixture of four isomeric ketones (**9-12**), 1,5,6,7,8,8,10,11,12,14,17,17-dodecamethyl-benzo[1,2-c:4,5-f']bisbicyclo[3.2.1]oct-6,11-dien-2,13-dione **9** (48%), 1,5,6,7,8,8,10,11,11,13,16,17-dodecamethyl-benzo[1,2-c:4,5-e']bicyclo[3.2.1]octabicyclo[2.2.2]oct-6,-16-dien-2,12-dione **10** (20%) 1,5,6,7,8,8,10,11,12,13,17,17-dodecamethyl-benzo[1,2-c:4,5-c']bisbicyclo[3.2.1]oct-6,11-dien-2,14-dione **11** (15%) and 1,3,4,5,8,8,10,11,12,14,17,17-dodecamethyl-benzo[1,2-f:4,5-f']bisbicyclo[3.2.1]oct-3,11-dien-2,13-dione **12** (9%). The structure determination of ketones

(**9-12**) follows from their spectra and the results of deuterium labeling experiments.

A solution of **11** in acetone was irradiated for 12 h, using a 450 watt Hanovia lamp and a Pyrex filter, to give virtually pure photoisomer, 1,2,4,7,8,8,10,11,12,12,13,15-dodecamethyl-benzo[1,2-e:4,5-e']bistricyclo[2.1.1.$0^{2,7}$]oct-3,14-dione **13**. Irradiation of a benzene solution of syn-7,8-syn-16,17-diepoxy-1,3,3,4,7,8,10,12,12,16,17,17-dodecamethyl-benzo[1,2-e:,4,5-e']bisbicyclo[2.2.2]oct-2,11-dione **14**, prepared in 85% yield from the reaction of **8** and m-chloroperbenzoic acid, in a similar fashion gave a decarbonylated diepoxide in quantitative yield.

TO MY PARENTS

ACKNOWLEDGEMENTS

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

Appreciation is extended to Michigan State University, National Science Foundation, and National Institute of Health for financial support in the form of teaching and research assistantships.

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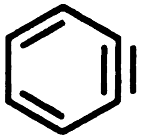
PART I. SYNTHESIS OF A NEW DI-ARYNE EQUIVALENT AND ITS APPLICATION TO ORGANIC SYNTHESIS

Introduction

This thesis deals with the preparation and chemistry of arynes. In particular, it concerns the chemistry of compounds capable of producing two aryne units on the same aromatic ring. Hence it is pertinent, in this introduction, to briefly review some of the history of aryne chemistry, the main literature methods for preparing arynes, and some of their chemistry, particularly their cycloaddition reactions.

The term benzyne[1] denotes ortho-benzyne, also known as 1,2-dehydrobenzene or in Chemical Abstracts 1,3-cyclohexadien-5-yne. The last name is somewhat misleading, since benzyne differs from benzene in having two less hydrogens but not in the stabilization associated with delocalization of double bonds.[2] It is commonly represented by any of the structures **1-3**.



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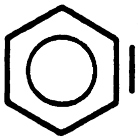

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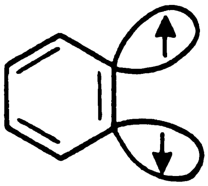
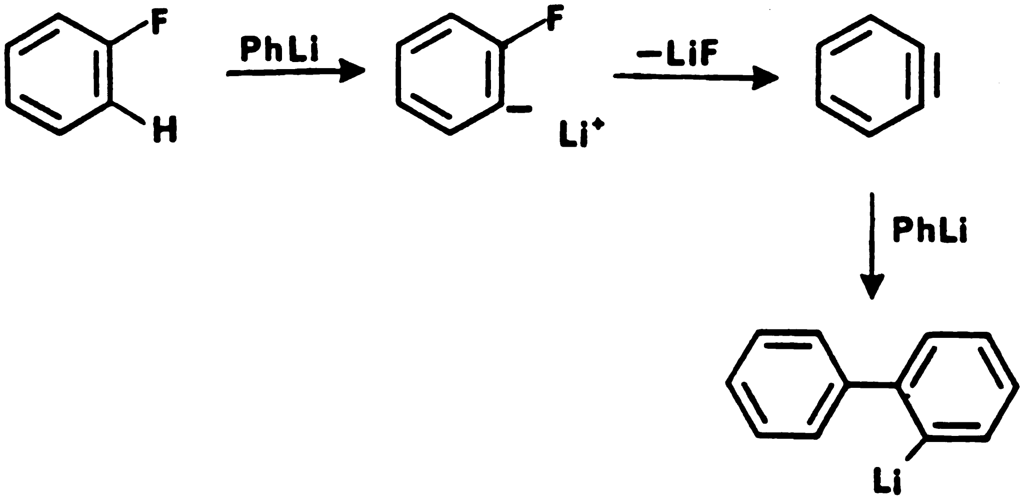


3

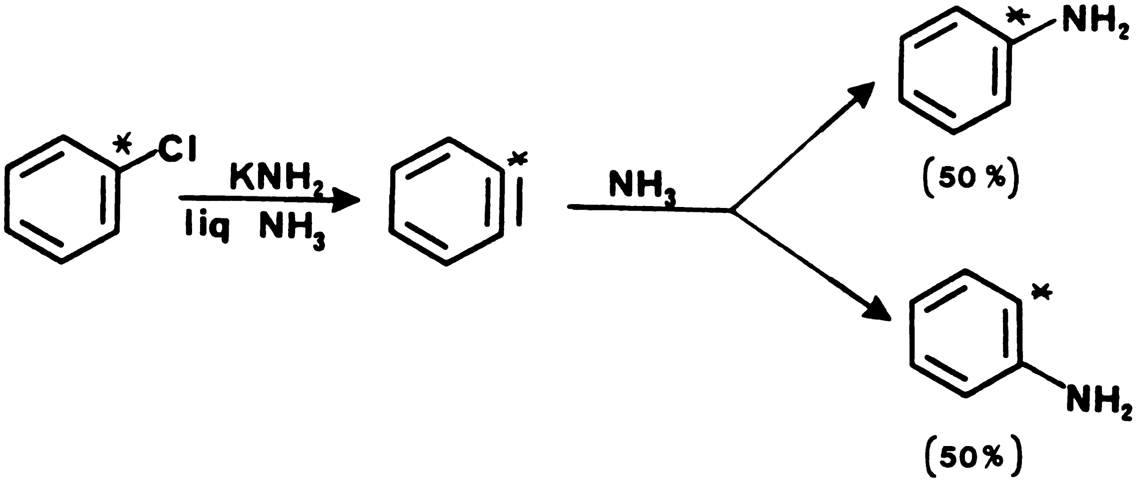
Note that the electrons in the so-called triple bond are in orbitals which to a first approximation are orthogonal to the aromatic electrons, and also that the orbitals are canted and not parallel, thus decreasing the overlap from what is present in an ordinary triple bond; hence the increased reactivity of benzyne relative to ordinary alkynes.

Since 1902 there have been suggestions that benzynes might be intermediates in various aromatic substitution reactions.[3] Wittig was the first to put the suggestion clearly and convincingly during the 1940's.[4] He studied the reaction of halobenzenes with phenyllithium and found that biphenyl was formed, but that its rate of formation from fluorobenzene was greater than from the other halobenzenes. A direct displacement of fluoride by the phenyl anion was therefore unlikely. Wittig suggested that the inductive effect of the fluorine facilitated removal of the o-hydrogen and its replacement by lithium. Thus an o-fluorophenyl anion was generated, which then lost fluoride to give benzyne. Phenyllithium could then react rapidly with the benzyne to give o-lithiobiphenyl, which Wittig showed to be the primary product of the reaction.



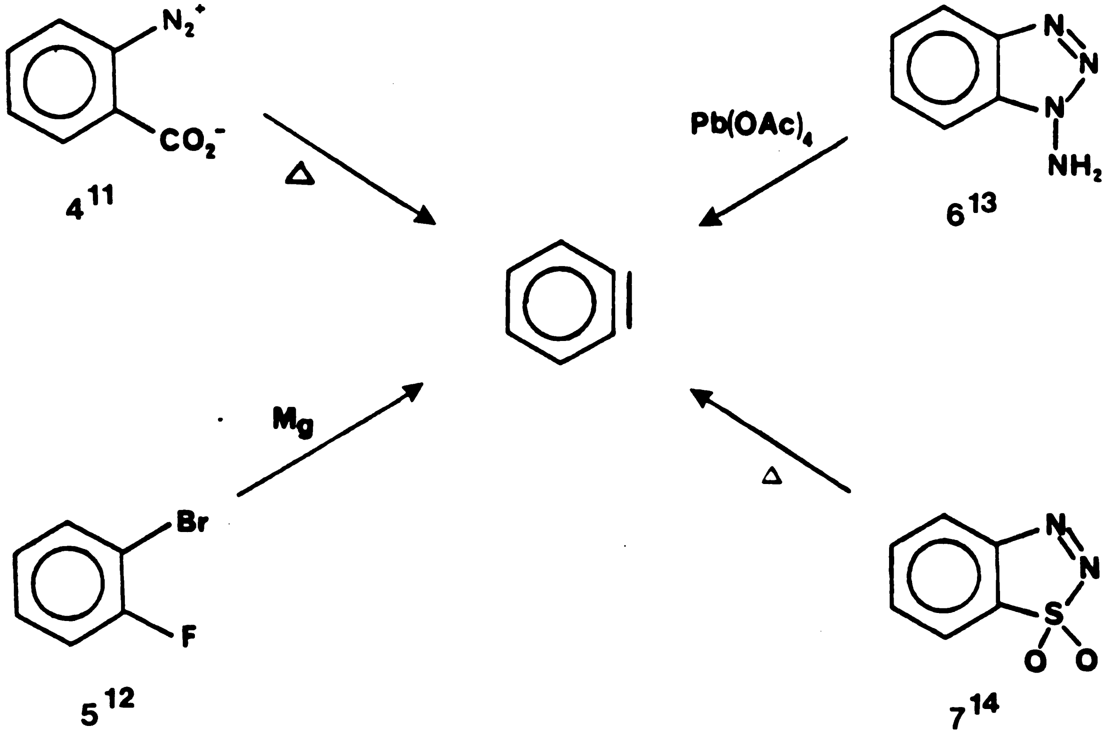
In this reaction phenyllithium has a dual role: it acts as a strong base to remove the o-hydrogen, generating the o-fluorophenyl anion, and it acts as a nucleophile in its addition to benzyne.

In 1953, J. D. Roberts established the presence of arynes in reactions of 1-C^{14} chlorobenzene with potassium amide in liquid ammonia.[5] The product consisted of aniline, half of which was labeled in the 1-position and half in the 2-position. A mechanism which can explain all the observations involves elimination followed by addition:

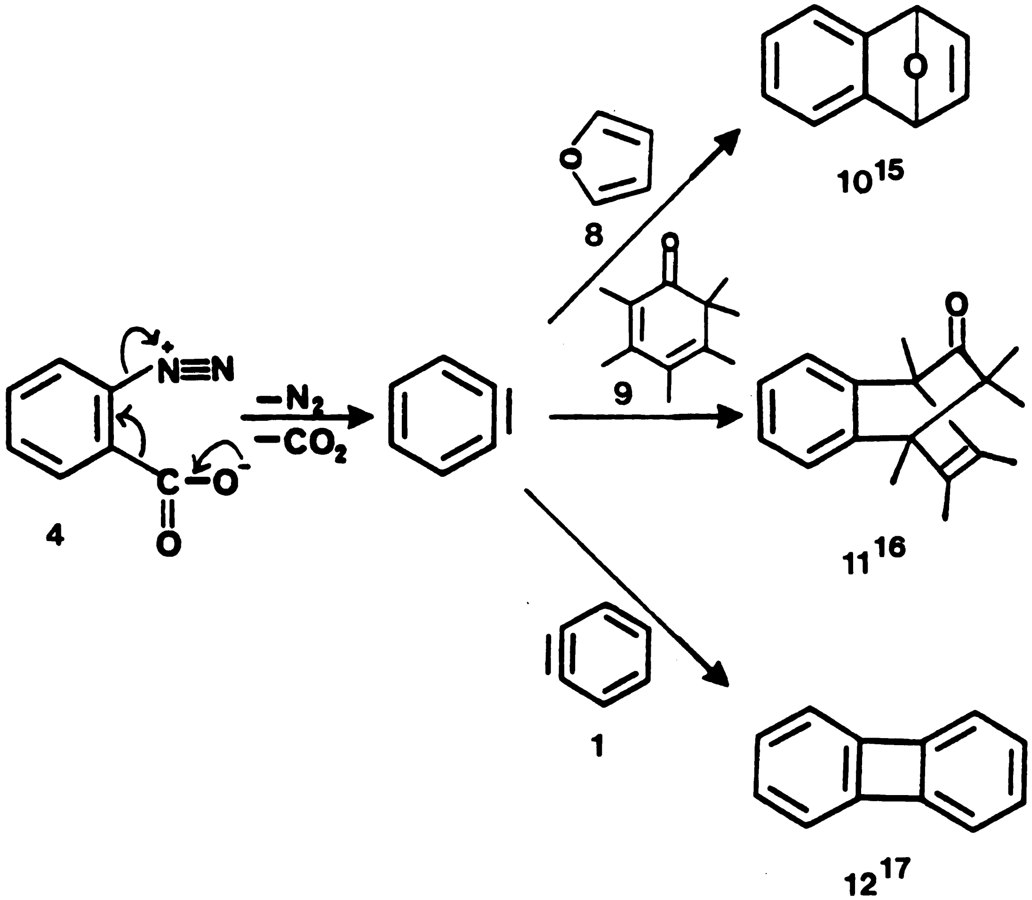


Observations of the UV absorption attributable to benzyne in the vapor phase,[6] evidence from time-resolved mass spectrometry,[7] and more recently of the IR spectrum of benzyne in an argon matrix at very low temperatures[8] leave no doubt as to the existence of benzyne as a discrete molecular species. There is now a very extensive chemistry of ortho-benzyne and of some of its substituted derivatives (arynes), but much less is known of meta-[9] and para-benzyne[10] isomers.

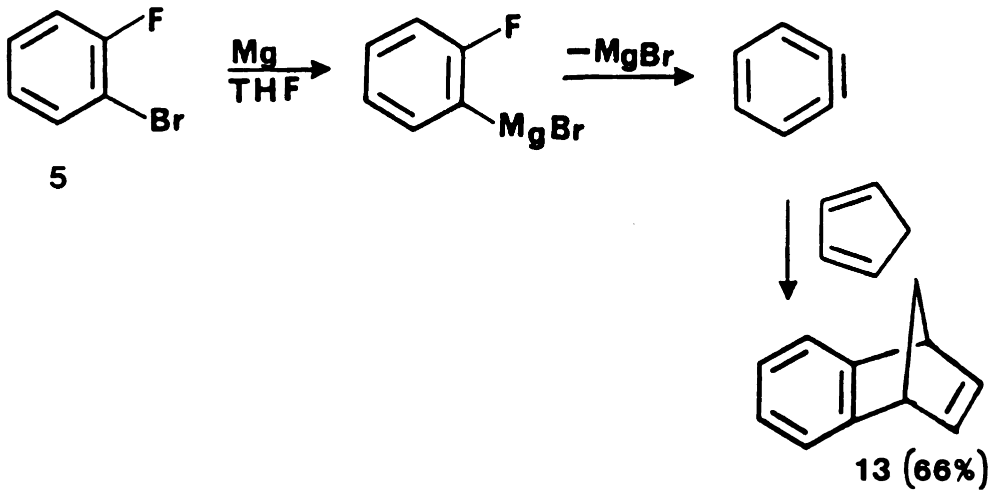
A variety of methods are described in the literature for the preparation of benzyne. However they all fall into two categories. One common way to generate benzyne is to remove two adjacent substituents from an aromatic nucleus. Another useful general route to benzyne is the fragmentation of heterocyclic rings fused to the ortho positions of the aromatic system. Some of the different conditions that can be used to generate benzyne are shown below:



Probably the most convenient method involves thermal decomposition of the product **4** of diazotization of anthranilic acid.[11] Both substituents are excellent leaving groups, one leaving with an electron pair, the other leaving without. When **4** decomposes in the presence of an added nucleophile, the benzyne intermediate is trapped by the nuclophile as it is formed. If a conjugated diene **8** or a dienone **9** is present, benzyne will react with it to give [4 + 2] cycloadduct, **10** or **11**, respectively. In the absence of other compounds with which it can react, benzyne will undergo [2 + 2] cycloaddition to itself to give biphenylene **12**.

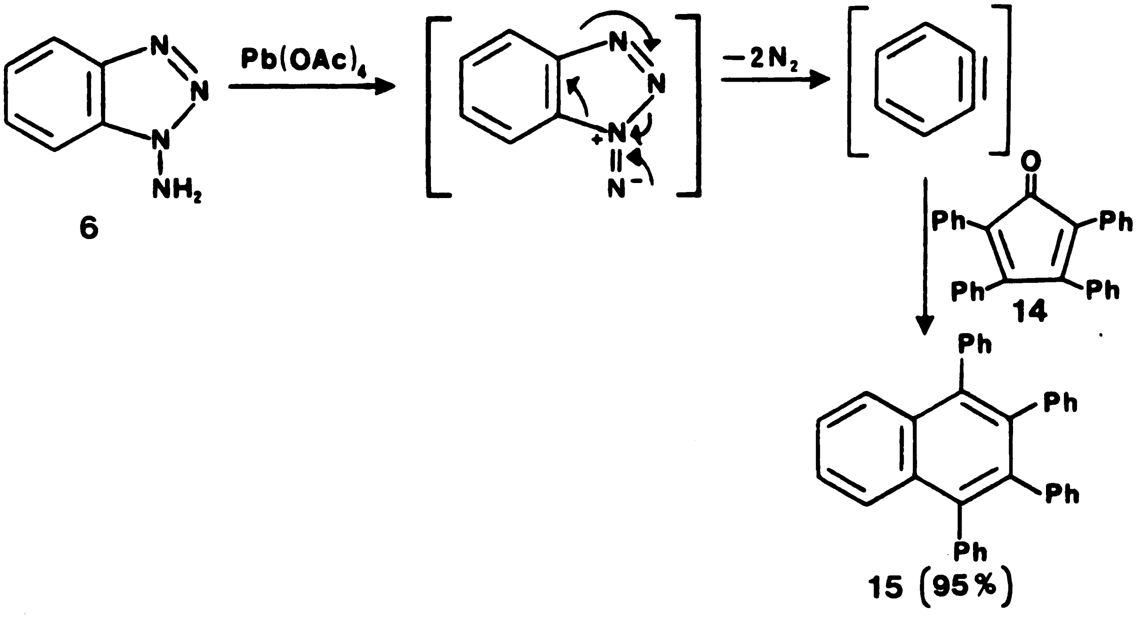


Another route to benzynes involves organometallic compounds derived from aryl halides.[12] An example is the generation of benzyne from 1-bromo-2-fluorobenzene **5** with magnesium in tetrahydrofuran. If the temperature is kept near 0°C, 2-fluorophenylmagnesium bromide is formed. At higher temperatures, magnesium halide is eliminated and benzyne results. With cyclopentadiene, the [4 + 2] cycloadduct **13** was obtained in 66% yield.[12] However, in this



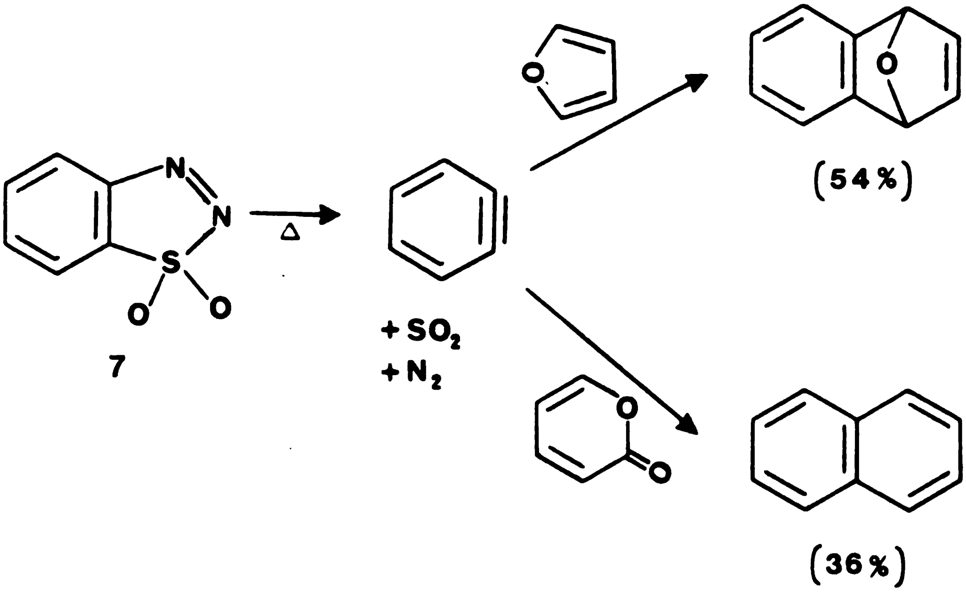
reaction, the diene may not contain carbonyl or similar groups that are reactive toward the Grignard reagent. In fact, the synthetic utility of benzyne reaction depends in large part on the success with which the benzyne can be generated by one reagent, but trapped by another.

Oxidation of 1-aminobenzotriazole with lead tetraacetate also serves as a source of benzyne under mild conditions.[18] An oxidized intermediate (nitrene) decomposes with loss of two molecules of nitrogen:



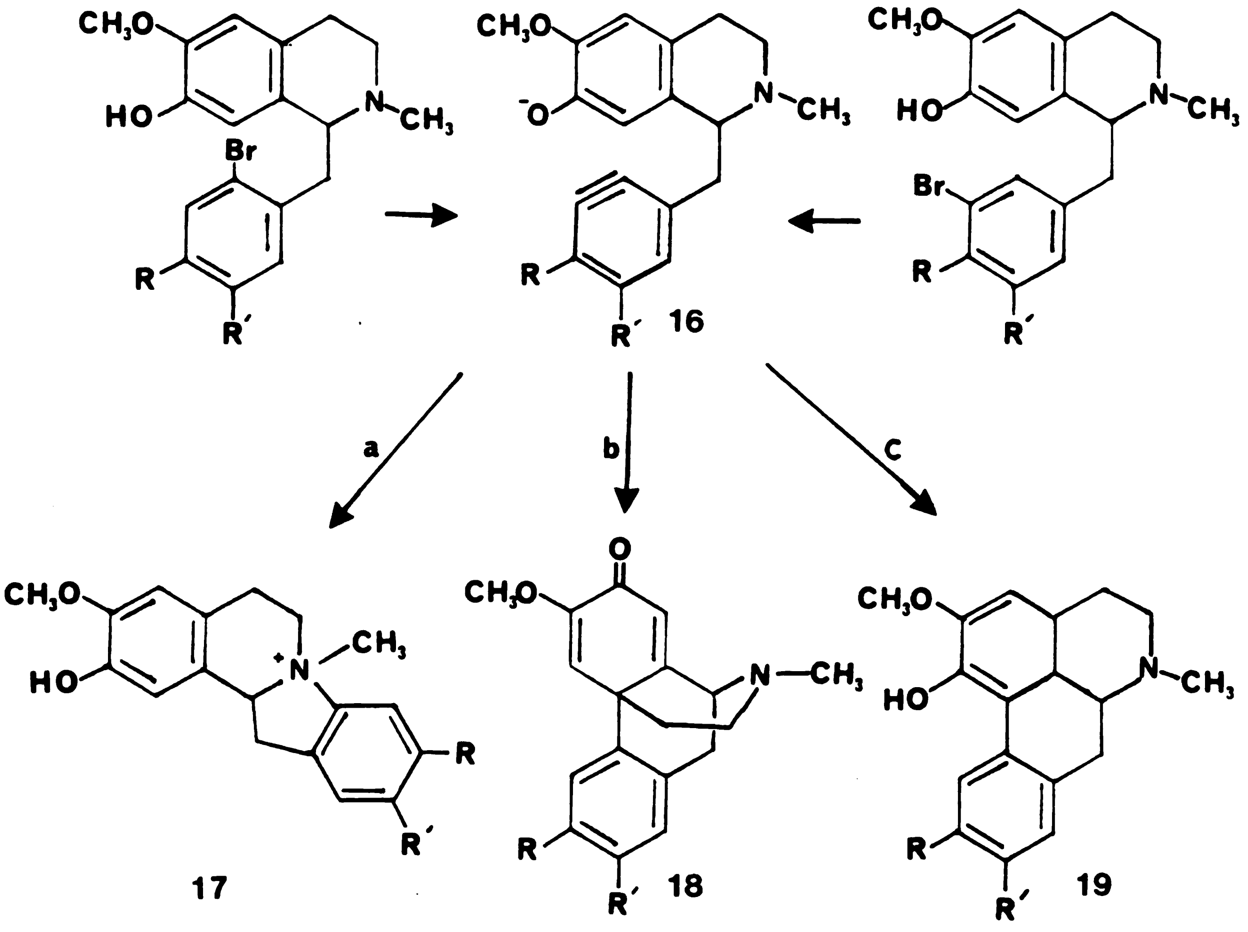
When the oxidation was carried out in the presence of tetraphenylcyclopentadienone **14**, 1,2,3,4-tetraphenylnaphthalene **15** was obtained in high yield.[18]

Another heterocycle that can serve as a benzyne precursor is benzothiadiazole-1,1-dioxide.[14] With selected dienes, moderate yields of cycloadducts were obtained. The preparation of this benzyne precursor is lengthy and the compound explodes at about 60°C, but it decomposes slowly at about 10°C to give benzyne, nitrogen, and sulfur dioxide.



Reactions of benzyne have been used to synthesize compounds that were otherwise difficultly accessible. For example, intramolecular additions to aryne intermediates **16** from 1-(2-bromobenzyl)- or 1-(3-bromobenzyl)-1,2,3,4-tetrahydroisoquinoline derivatives are the basis of some elegant syntheses of natural products.[19] In Scheme 1, paths a, b, and c define cyclizations through 2-, 4a and 8-positions

Scheme 1



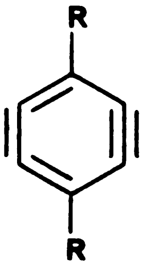
17 — R,R′ = OCH_2O
R = R′ = OCH_3
R = OCH_3, R′ = H

18 R,R′ = OCH_2O

19 — R,R′ = OCH_2O
R = R′ = OCH_3
R = OCH_3, R′ = H

of the isoquinoline moiety, leading to dibenzoindolizines **17**, morphinandienones **18**, and aporphines **19**, respectively.

Bis-arynes such as **20** and **21** could be useful synthetic precursors to polysubstituted arenes or other novel structures.[20] However, very few bis-aryne equivalents, or precursors of bis-arynes,[20-21] are known. Bis-arynes have been postulated in certain mass spectral fragmentations



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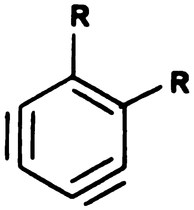
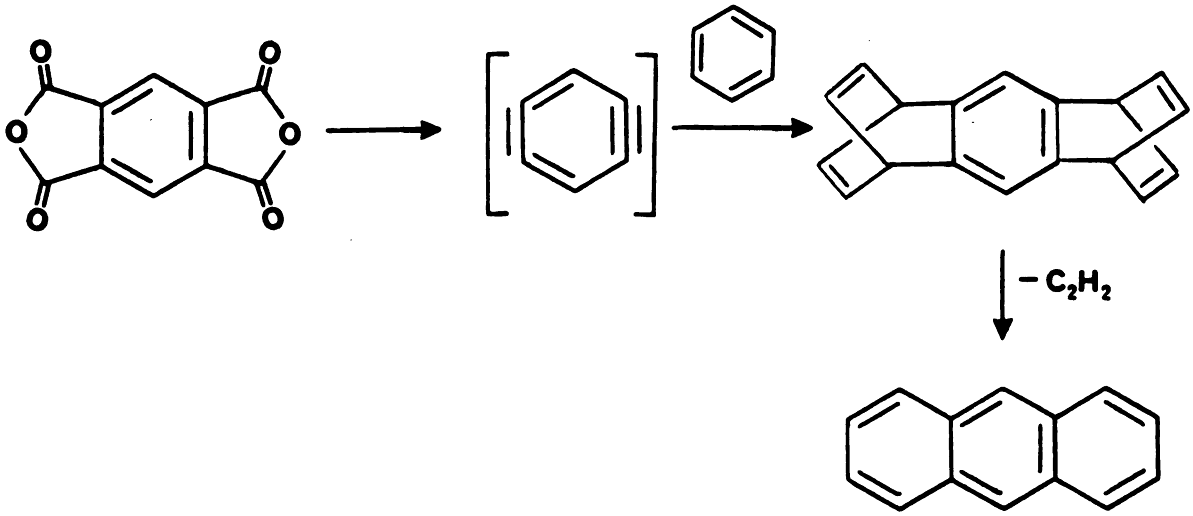


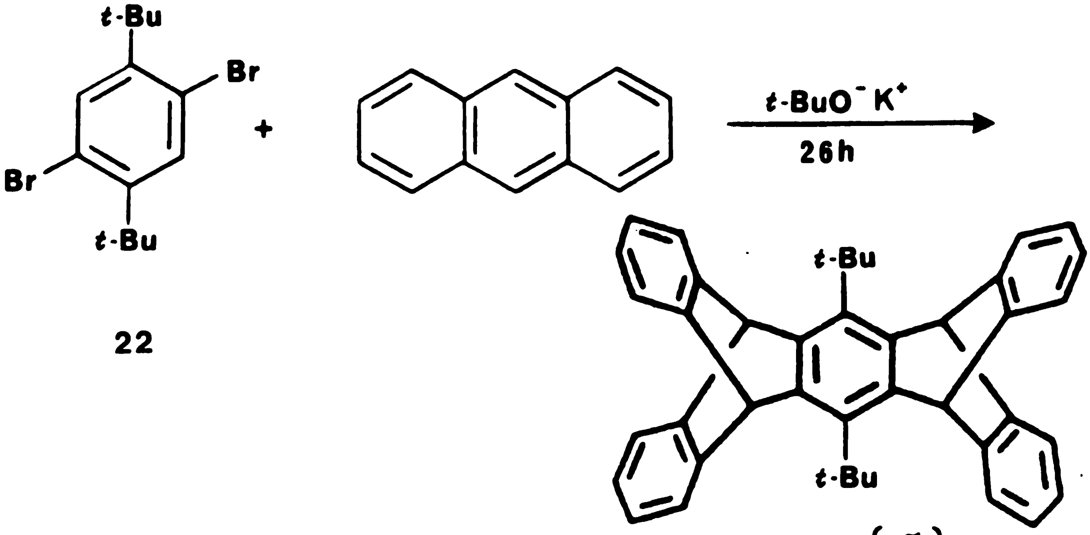
21

and to rationalize products from the copyrolyses of benzene with pyromellitic or mellophanic anhydrides.[22]



These reactions may not really involve a bis-aryne, however, since they could occur in a stepwise fashion.

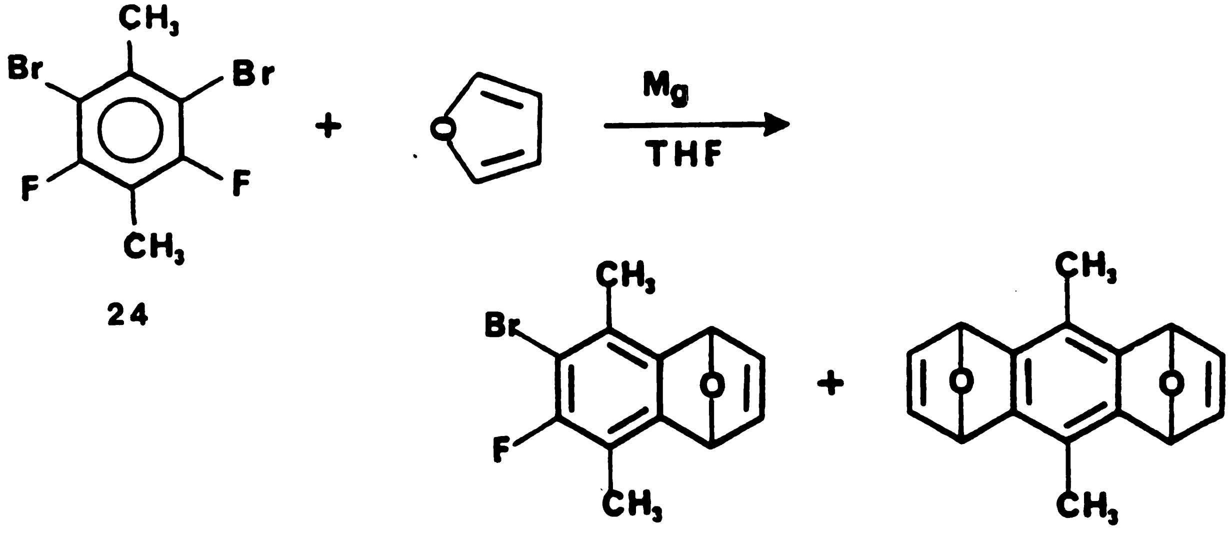
Compound **23** was synthesized, albeit in very low yield, via bis-aryne equivalent **22** by treatment with strong base.[21a]



22

23 (2%)

The reaction of furan with benzyne, discovered by Wittig and Harle,[23] was the earliest example of benzyne behaving as a dienophile. In a possible extension of this reaction to bis-arynes, Wittig found that with magnesium in tetrahydrofuran **24** gave mainly mono-adduct **25** (34%) and only 5% of the bis-adduct **26**. With butyllithium in place of magnesium, a 15% yield of bis-adduct and no mono-adduct was obtained.

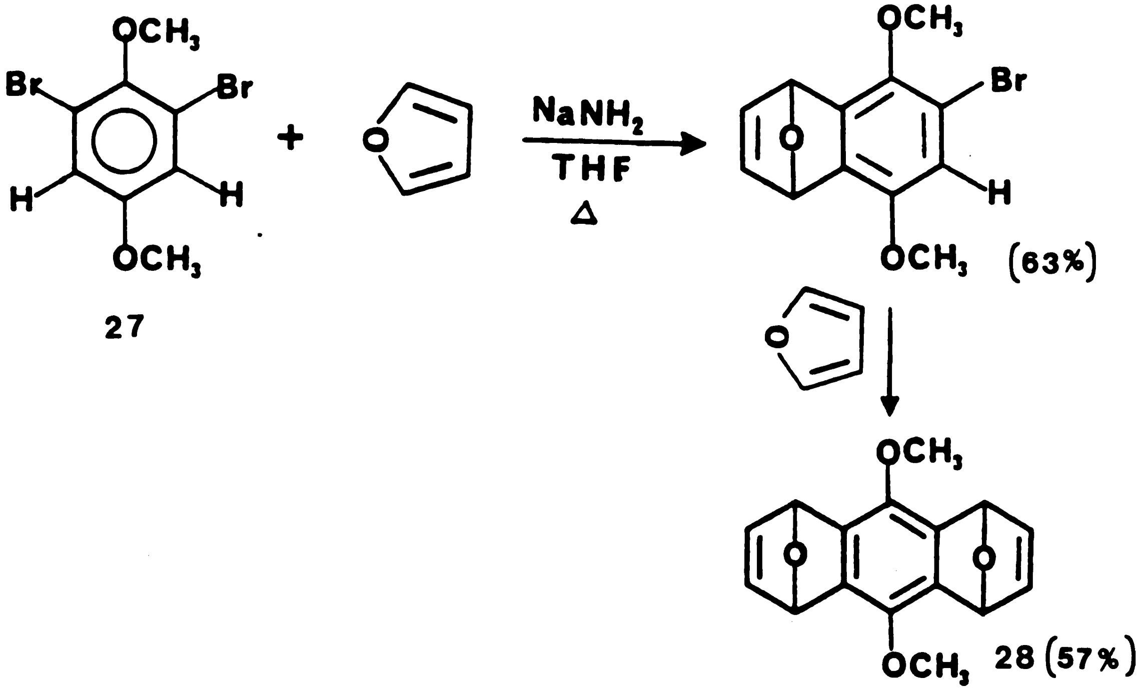


24

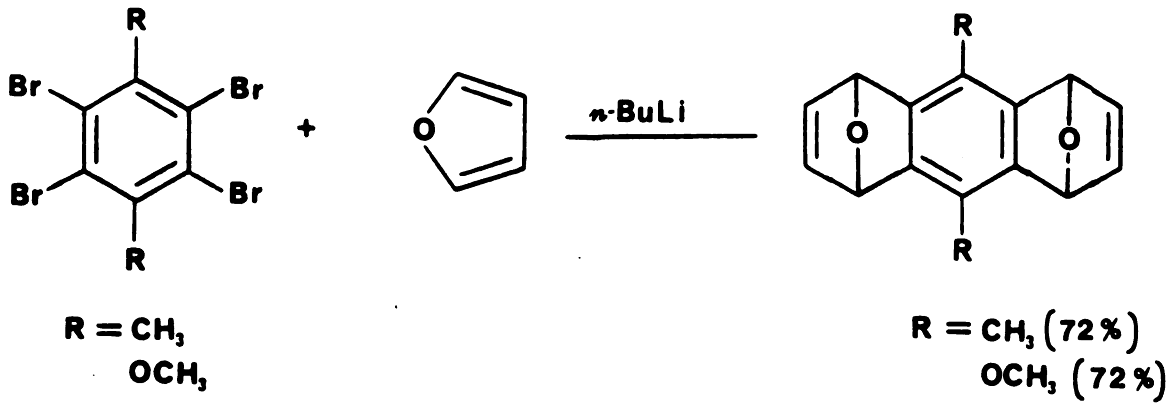
25 (34%)

26 (5%)

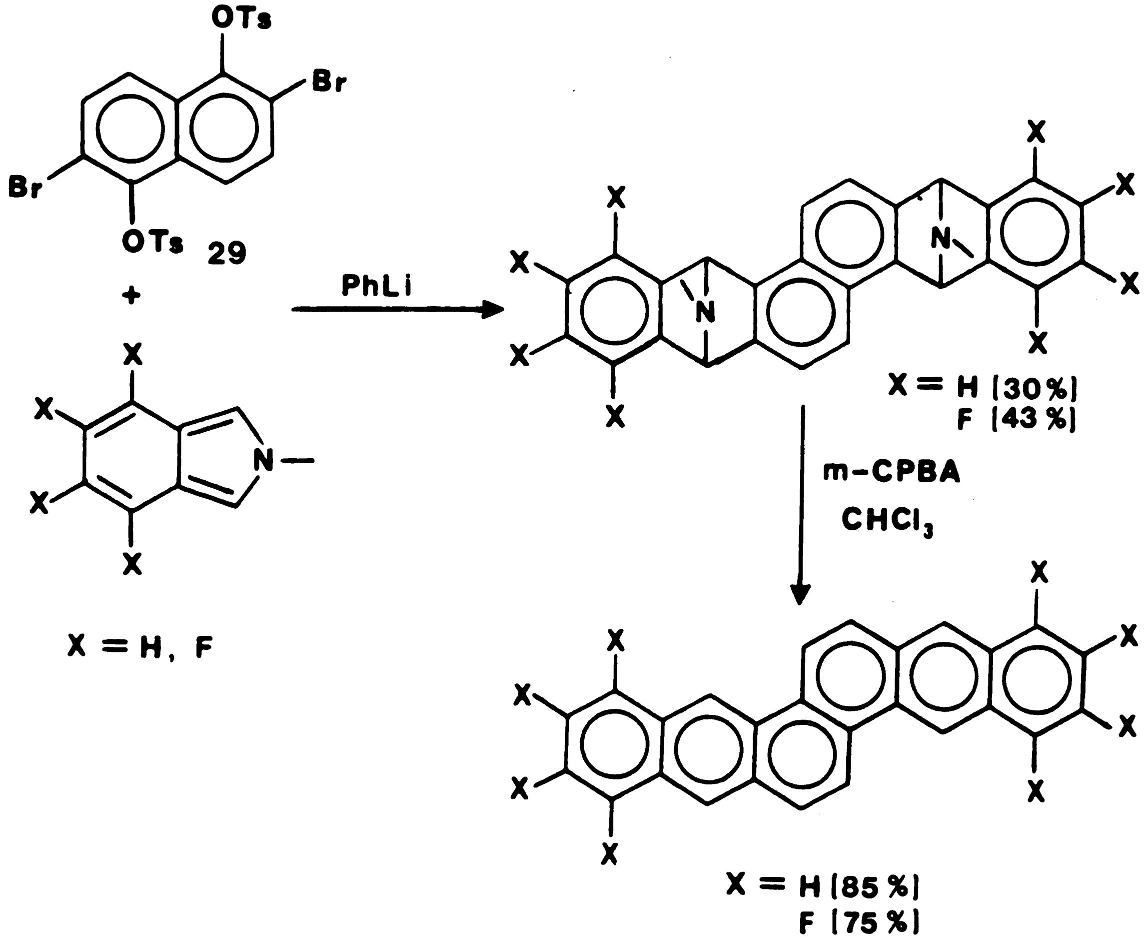
The bis-epoxide **28** was synthesized in 36% yield via a di-aryne equivalent **27** by Guiles and coworkers.[24] The reaction was carried out in two steps, however, since addition of the second furan molecule required a higher temperature than that of the first.



Hart and coworkers have developed a much improved method of generating arynes from diaryne equivalents,[20b] and have improved the synthetic utility of these reactions. For example:

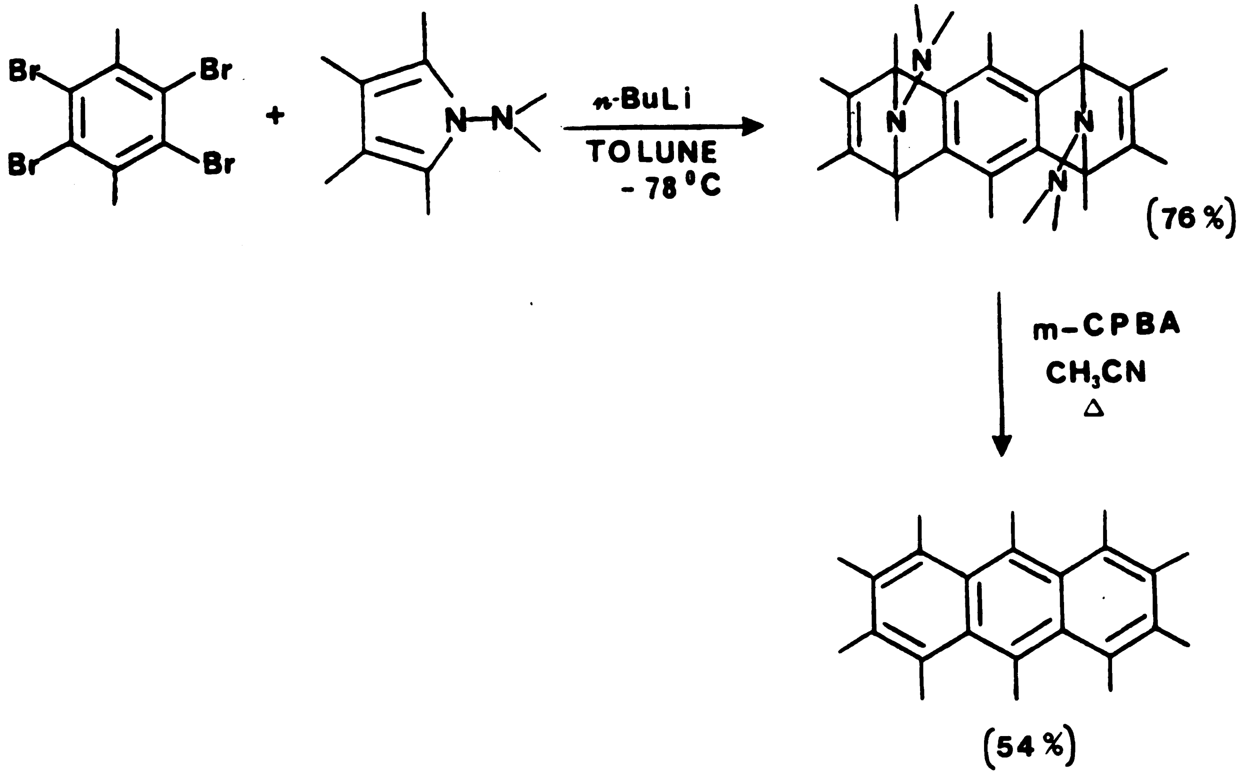


Recently, bis-annulation of naphthalene via a 1,5-naphthodiyne synthon **29** was reported by Gribble and LeHoullier.[21c]

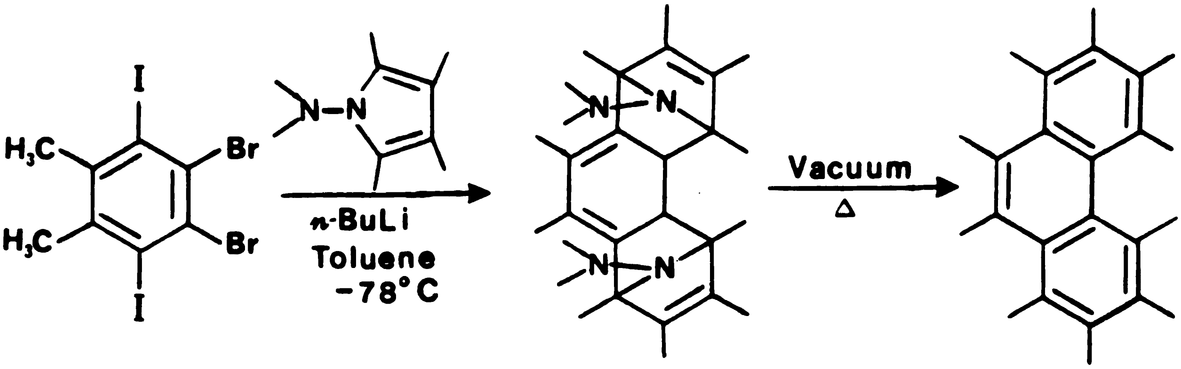


Wege and Stringer reported the preparation of some novel furan derivatives related to triphenylene (**31** and **33**) by a strategy involving sequential Diels-Alder additions of arynes to furan. However, the yields (**30** and **32**) in the key steps are low.[21b]

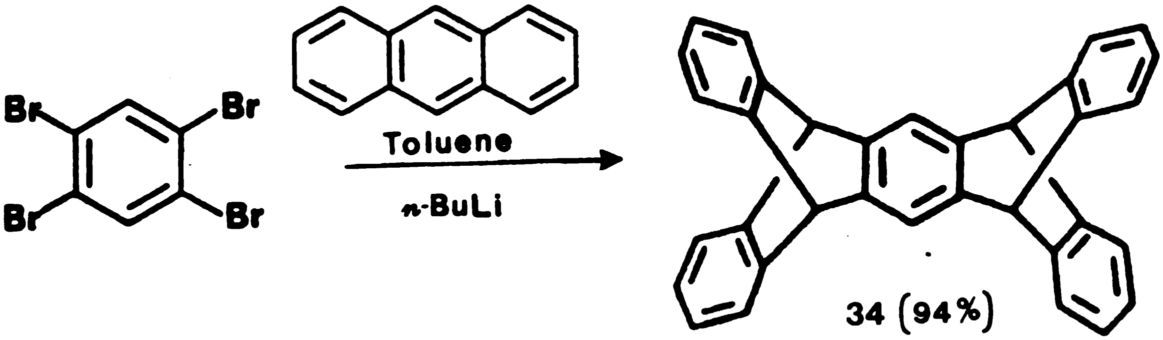
Much of the work in this area has been done in recent years in this laboratory. Hart and coworkers described the use of tetrahalobenzenes as di-aryne equivalents. When treated with two equivalents of an organolithium reagent in the presence of certain dienes, they readily form bis-cycloadducts. With these reagents benzenes could be converted to anthracenes or phenanthrenes in just two steps.[20] For example, decamethylanthracene was prepared in overall 54% yield.[20b] The para di-benzyne equivalent tetrabromo-p-xylene reacts with n-butyllithium in the presence of N-substituted pyrroles to give bis-adducts. Removal of nitrogen bridges then gives the anthracene:



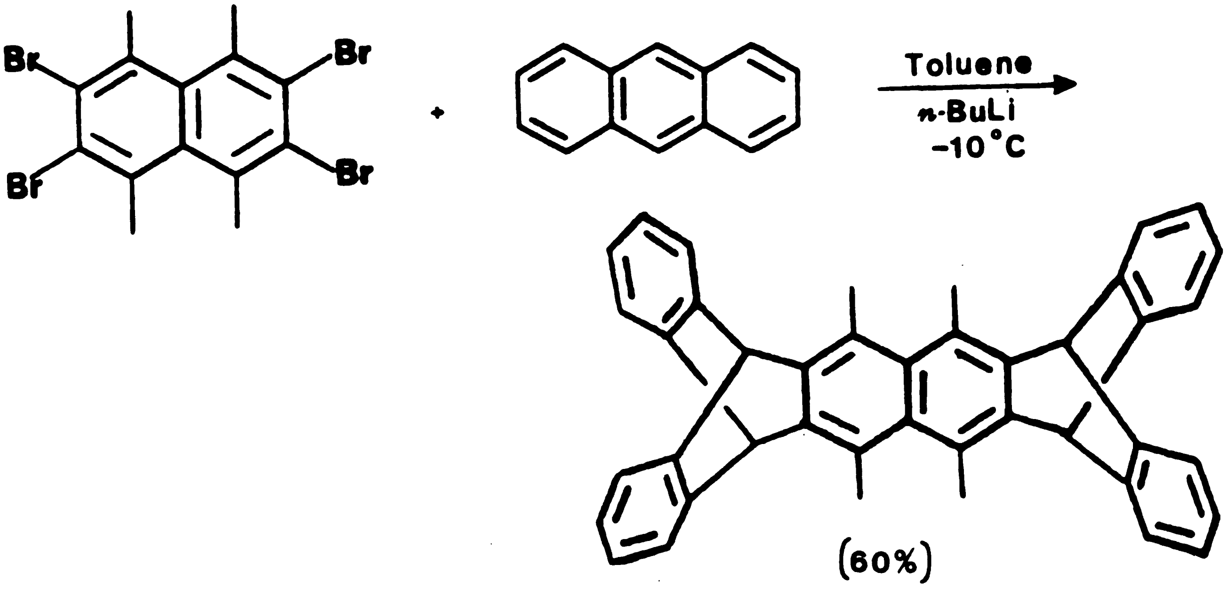
This methodology was applied to a phenanthrene synthesis:



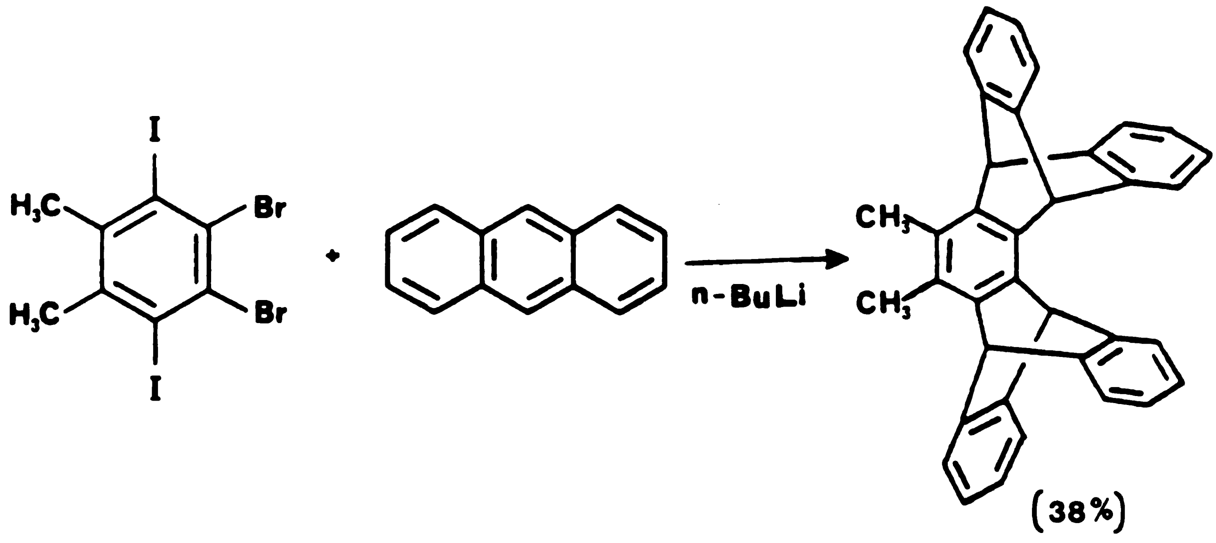
Hart and coworkers have developed a simple one-step synthesis of pentiptycene[20d] using diaryne equivalents.[20d] A toluene solution of anthracene and tetrabromoarene, when treated with n-butyllithium in hexane around -10°C gave pentiptycene **32** in high yield.



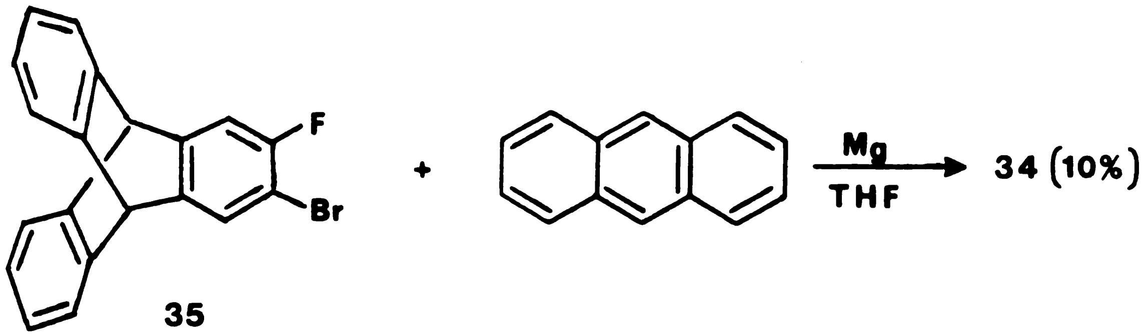
34 (94%)



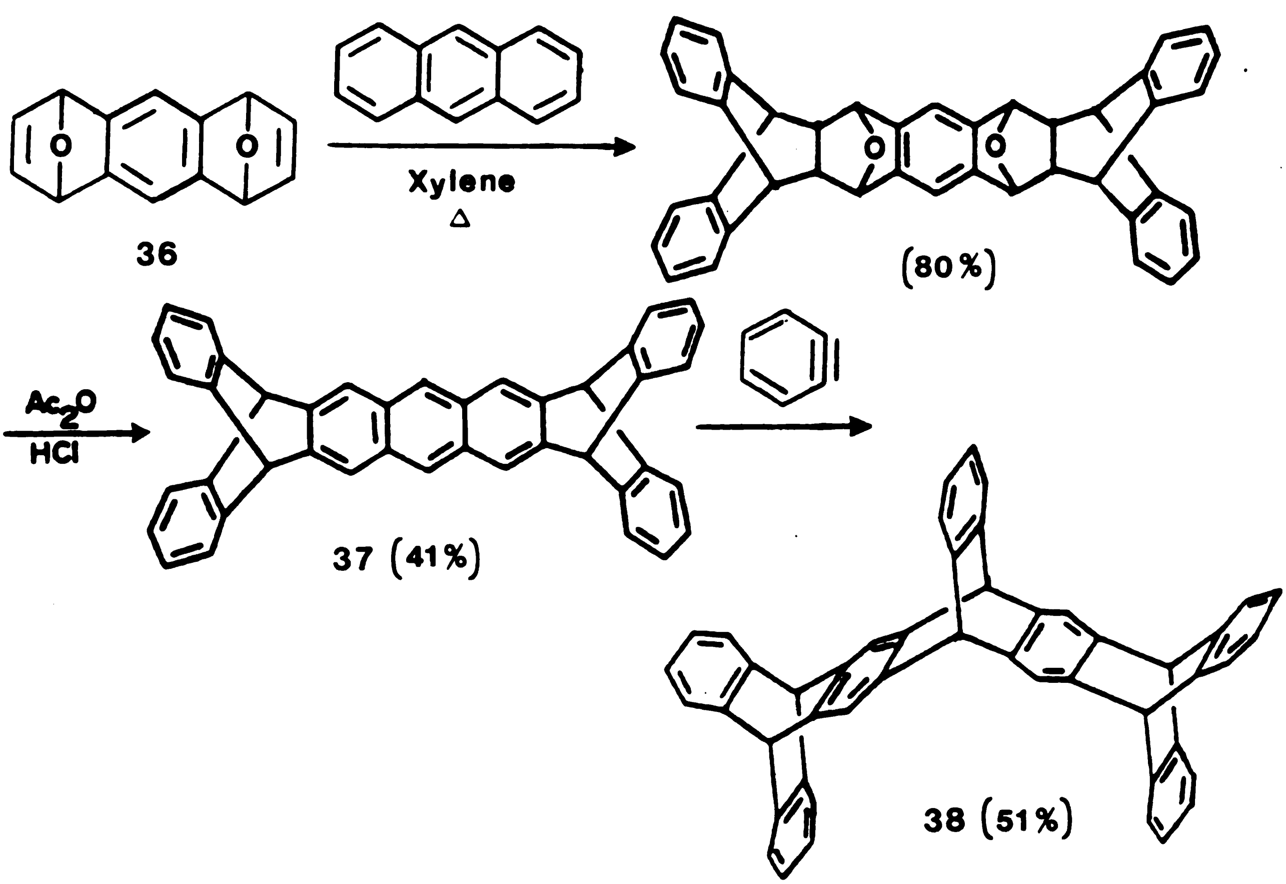
(60%)



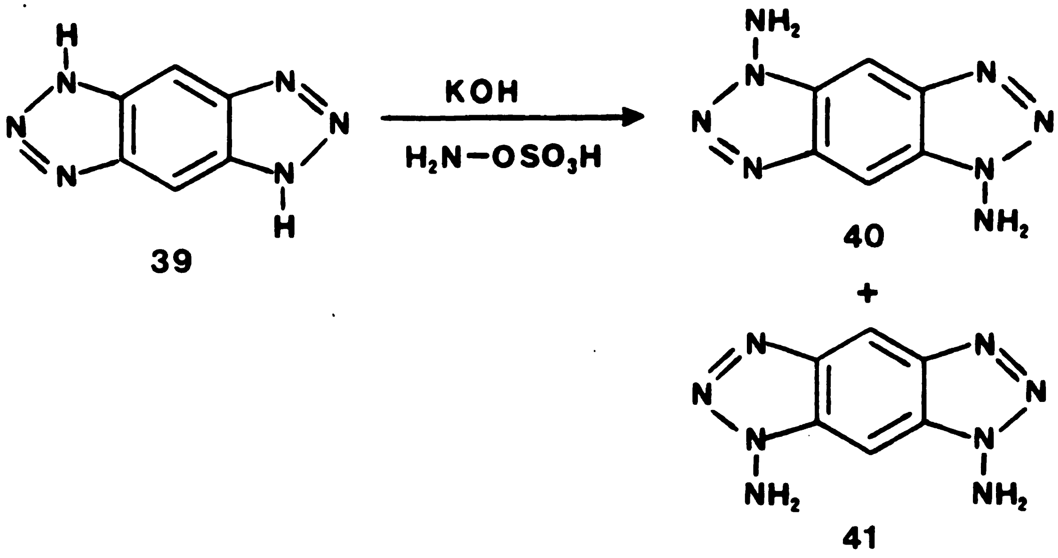
Pentiptycene **34** had been prepared previously, but in low yield (10%) by Russian workers.[25] The required fluorobromotriptycene **35** had to be synthesized from anthracene in four steps, so that the overall yield from readily available starting material was quite low.



Heptiptycene **38** was synthesized using a 2,3:6,7-anthradiyne equivalent **36** in three steps via a pentiptycene intermediate **37**[21d].



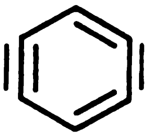
1,2,4,5- and 1,2,3,4-Tetrahaloarenes are versatile synthetic equivalents of 1,4- and 1,3-diarynes (**20** and **21** respectively). One synthetic limitation of this method, however, is that the receptor diene may not contain functionality which will compete with the tetrahaloarene for the organolithium reagent. In practice this means that the diene usually must not contain carbonyl, halogen, or similar groups. Therefore it seemed worthwhile to pursue alternative ways of generating bis-benzynes to circumvent this problem. One obvious type of diaryne precursor would be the bis-diazonium carboxylates derived from appropriate diamino tere- or isophthalic acids (analogous to the anthranilic acid route to arynes). We synthesized 2,5-diamino-1,4-benzenedicarboxylic acid by a modified literature procedure. So far, however, attempts to tetrazotize this bis-anthranilic acid have failed. We also synthesized 1,5- and 1,7-diamino-benzo[1,2-d:4,5-d']bistriazole (DABT) **40** and **41** from the known precursor **39**.[26] In our attempt to explore the scope of this bis-annulation technique, a variety of dienes and a 1,3-dipole (nitrone) were used. Bromofuran, esters, dienones and nitrones, all of which are presumably incompatible with the butyllithium used to generate arynes from tetrahaloarenes gave bis-adducts in good yields. It is the purpose of this part of the thesis to describe the synthesis and synthetic applications of these new diaryne precursors.



Results and Discussion

A. Synthesis of Diamino-benzo[1,2-d:4,5-d']bistriazole (DABT), A New Useful 1,4-dibenzyne Equivalent.

This investigation was directed toward the synthesis of the synthetic equivalent of a reactive intermediate, dibenzyne **20**. The problem could be approached by the preparation of an appropriate group of dibenzyne precursors,



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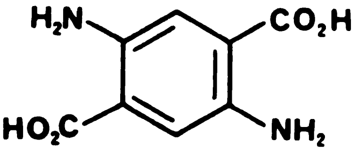
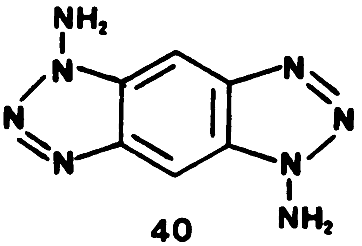
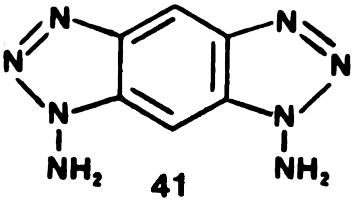
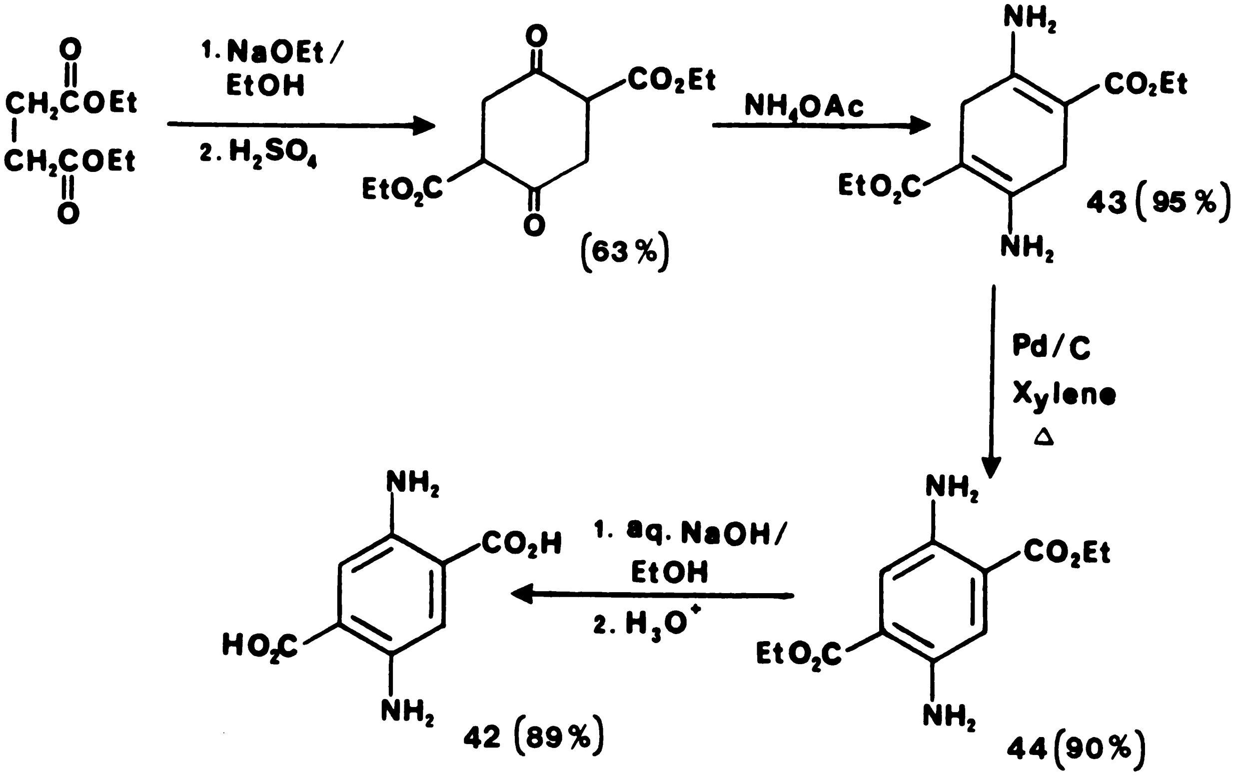
and an examination of the reactivity of these compounds with members of representative classes of dienes. The following dibenzyne precursors were chosen as worthy of study; they appeared to offer the most promising routes to arynes (Table 1).

The first study began with the synthesis of 1,4-diaminoterephthalic acid, **42**, that contains the anthranilic acid grouping twice. Several syntheses of **42** are reported in literature.[27,28] One method involved the preparation of **42** from its corresponding diester **44**, via diethyl 2,5-diamino-1,4-dihydroterephthalate **43**. Aromatization of **43** by action of iodine[28] according to Eremeeva and coworkers always gave product which was contaminated with iodine. Purification of the product was quite troublesome and therefore it was desirable to improve the preparation of **44**. When compound **43** was refluxed in xylene in the presence of a catalytic amount of palladium on charcoal, the aromatic

Table 1. Potential Diaryne precursors

Precursor	Method of Generation
 **42**	Thermal decomposition after diazotization
 **40**	Oxidative nitrogen extrusion
 **41**	

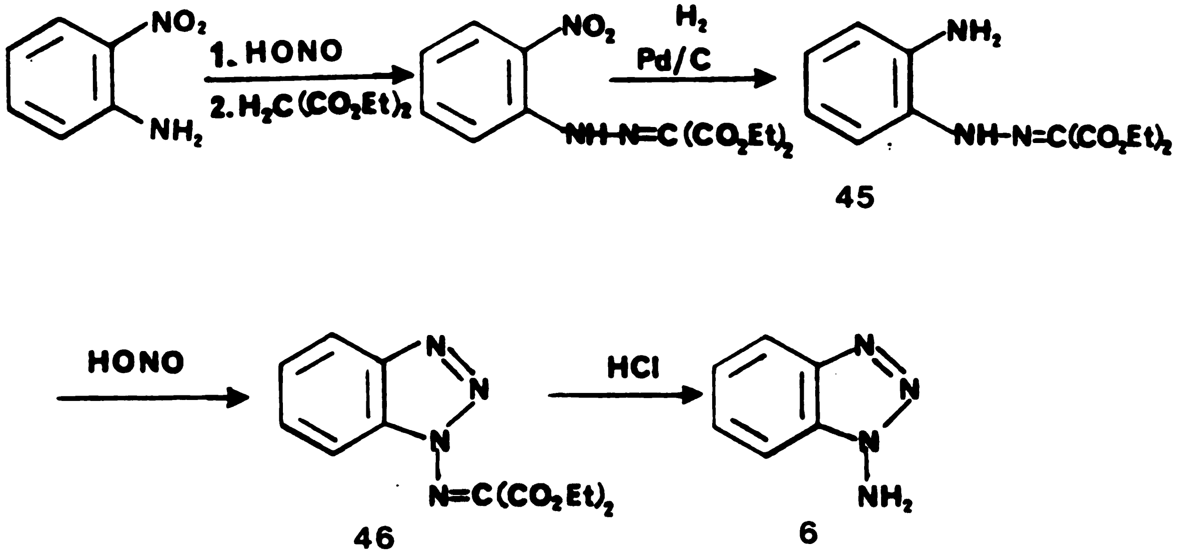
compound **44** was obtained in 90% yield. Purification from ethanol afforded orange needles which had the same melting point as in the literature.[28]



The diaminoterephthalic acid **42** was readily prepared by hydrolysis of **44**. However, an immediate problem arose with its solubility. The compound is practically insoluble in most organic solvents, as reported in the literature.[27] In fact, compound **42** is even insoluble in hot dimethylsulfoxide. All attempts to tetrazotize **42** were unsuccessful. Some efforts were also made to prepare the corresponding mono-acid with the hope that it might serve as a diaryne equivalent in a stepwise manner. Saponification of **44** with one equivalent of sodium hydroxide, followed by acidification gave only the starting ester. At this point this approach to a diaryne equivalent was abandoned in favor of another approach.

The next goal was the synthesis of 1,5-diamino-benzo[1,2-d:4,5-d']bistriazole **40** which is analogous to 1-aminobenzotriazole, **6**. Compound **6** had previously been prepared by two routes, either diazotization of a suitably protected o-aminoarylhydrazine **45** followed by removal of the protecting group of **46** (Scheme 2) or by direct amination of the parent triazole **47** (Scheme 3).[18] As can be seen, the former method requires more steps but it provides only the desired product

Scheme 2

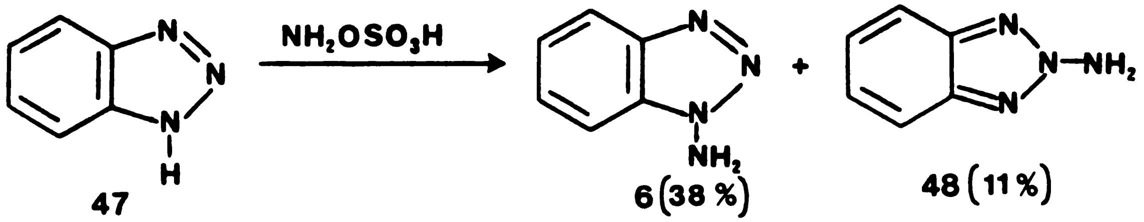


45

46

6

Scheme 3

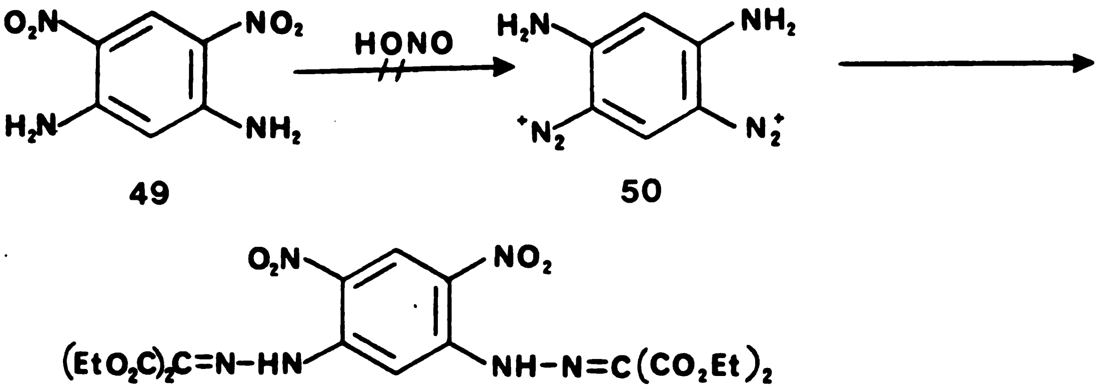


47

6 (38 %)

48 (11 %)

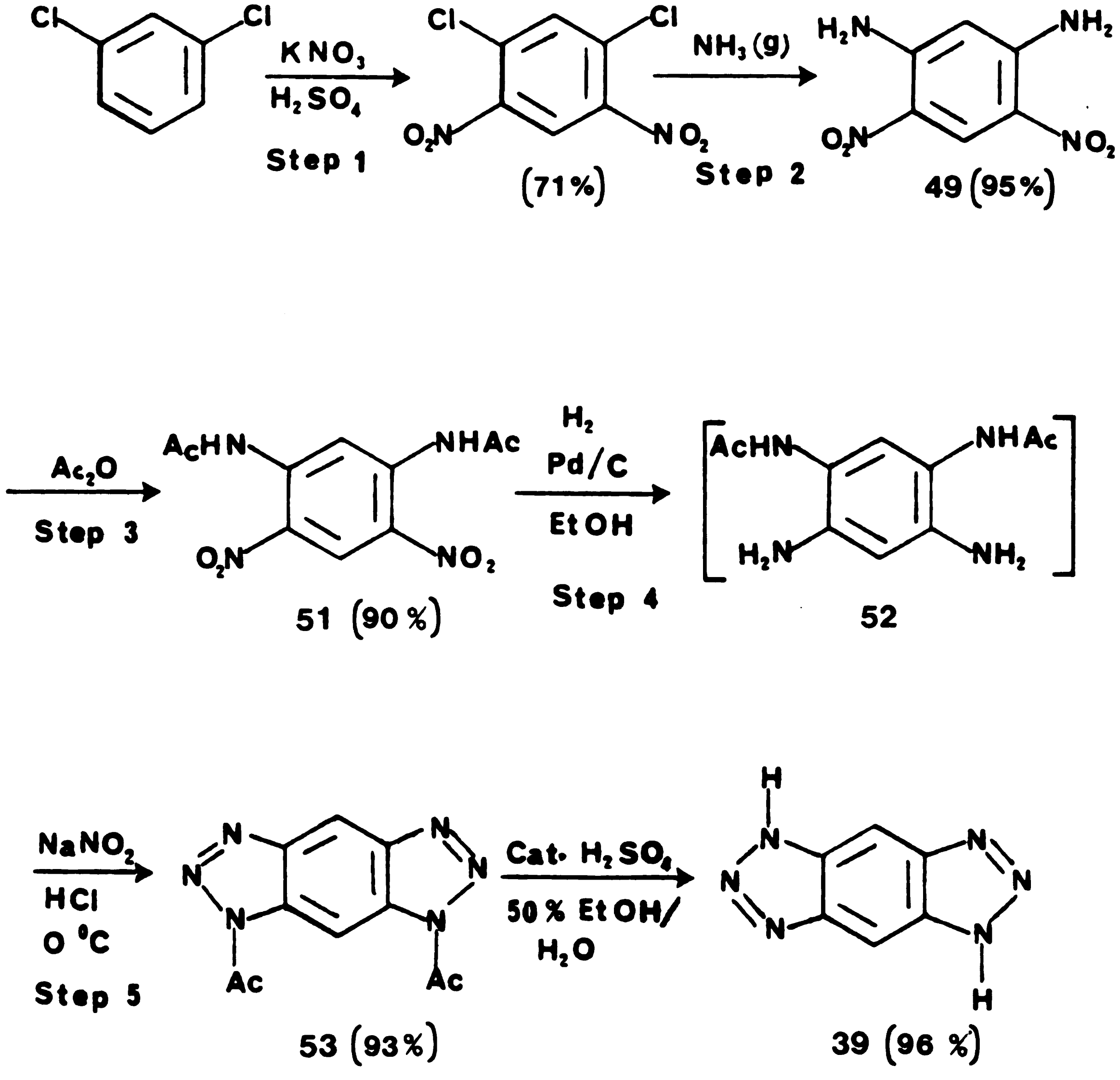
in high yield (over 54%) whereas the latter method gives a mixture of 1- and 2-isomers in good yield (49%). But in the case of diamino-benzo[1,2-d:4,5-d']bistriazole **40** (DABT) the direct amination method appeared more promising



because difficulties were encountered in the preparation of the required tetrazotized intermediate **50** from the corresponding diamino compound **49**. Also the desired DABT could be prepared in a single-stage synthesis by amination of the known benzo[1,2-d:4,5-d']bistriazole **39** (Scheme 4)[29,30] with an appropriate aminating agent.

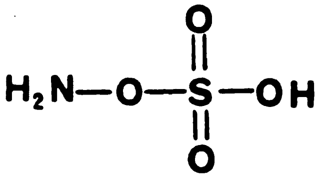
Several attempts to repeat the literature procedure for the preparation of **39** always gave low yields in some steps (steps 4 and 5, yields <3%). The literature procedure has been improved as described here and each step now works well. Compound **39** can be prepared in good yield (overall 54%) by a six-step process starting from m-dichlorobenzene. The most important improvement involves the conversion of 1,5-bis[acetylamino]-2,4-dinitrobenzene **51** to 1,7-diacetyl-

Scheme 4

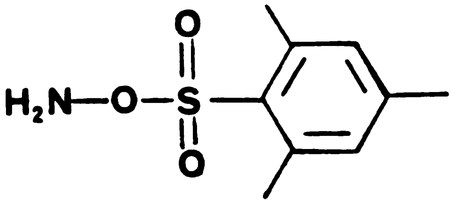

KNO$_3$
H$_2$SO$_4$
Step 1
(71%)
NH$_3$(g)
Step 2
49 (95%)
Ac$_2$O
Step 3
51 (90%)
H$_2$
Pd/C
EtOH
Step 4
52
NaNO$_2$
HCl
0 °C
Step 5
53 (93%)
Cat. H$_2$SO$_4$
50% EtOH/
H$_2$O
39 (96%)

benzo[1,2-d:4,5-d']bistriazole **53** where the yield has been improved from a reported 60% to 93%. The major differences from the literature procedure are as follows: 1. hydrogenation of **51** in ethanol instead of acetic acid using a weight ratio of 4:1 1,5-bis[acetylamino]2,4-dinitrobenzene **51**: 10% palladium on charcoal. For example, when the compound **51** (12 g, 0.0425 mol) was hydrogenated in ethanol (150 mL) over 10% palladium on charcoal (1 g) under 60 psi for 72 h, only partial reduction was observed. However, when 3 g of 10% palladium on charcoal was used under otherwise similar conditions, the reduction was complete in 3 h. The catalyst used in the reduction was recovered and recycled. 2. The diazotization of compound **52** was accomplished in H_2O at 0°C instead of in acetic acid at 25°C.

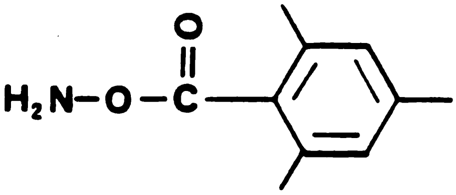
Many nitrogen heterocycles can be aminated on nitrogen using various aminating agents such as hydroxylamine-O-sulfonic acid **54**,[31] O-sulfonyl **55**,[32] O-actyl- **56**[33] and O-nitrophenylhydroxyl amines **57**.[34] These amines can be represented



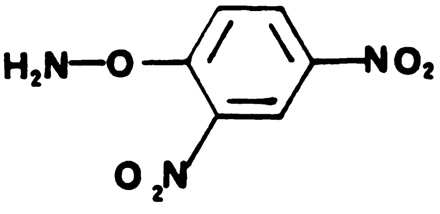
54



55

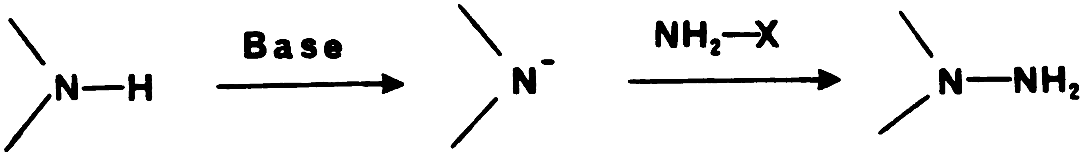


56

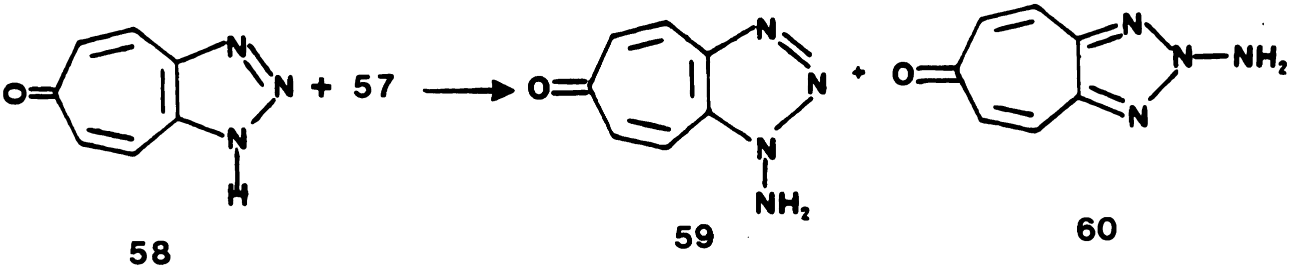


57

by the general structure, NH_2-X, where X is a good leaving group. The procedure involves removal of the acidic proton of the heteroaromatic compounds using an appropriate base, followed by nucleophilic displacement on the amino group. Among the reagents listed above, hydroxylamine-O-sulfonic acid is the most easily accessible and is known to aminate benzotriazole **47**[18] and other analogous systems.[31] For example, N-amination of benzotriazole was reported by Campbell and Rees, who treated **47** in aqueous potassium hydroxide solution at 70-75°C with hydroxylamine-O-sulfonic acid **54** to give 1-aminobenzotriazole **6** and 2-aminobenzotriazole **48**. The yields of pure material obtained after chromatography were 38 and 11%, respectively. Also, the starting benzotriazole was recovered (32%) after acidification of the basic solution followed by ether extraction.

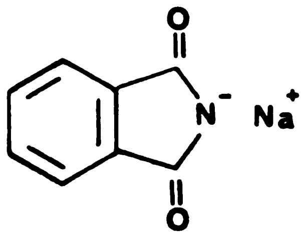
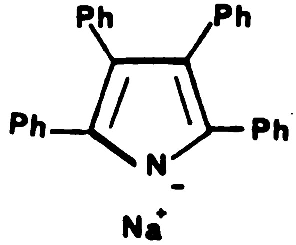


O-(2,4-Dinitrophenyl)-hydroxylamine **57** and O-mesitylenesulfonylhydroxylamine **55** are also reported to aminate triazole systems. For example, reaction of 1H-cycloheptatriazole-6-one **58** with **57** afforded 1-aminocycloheptatrizole-6-one **59** and



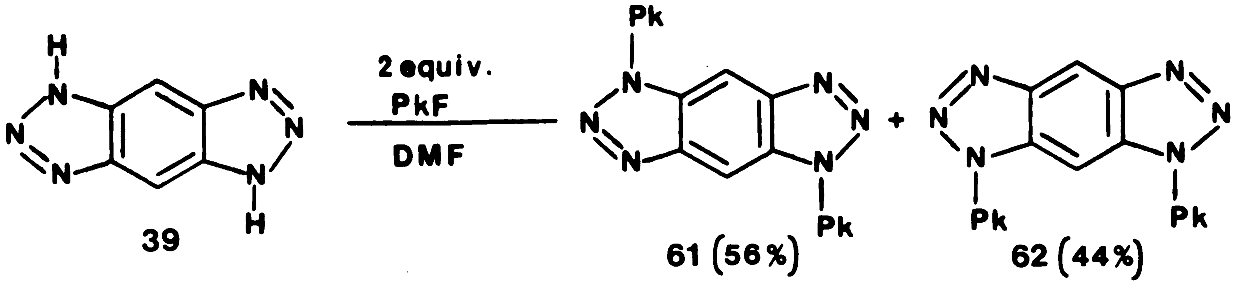
the 2-amino-2H isomer **60** in a ratio of 1.7:1 in 75% yield.[35] It is important to notice that amination of the triazole system, regardless of the reagent employed, always provided a mixture of 1- and 2-amino isomers. Some selected examples of N-amination with O-substituted hydroxylamines are summarized in Table 2.

Table 2. Selected Examples of N-amination

Aromatic Nitrogen Compound	**Hydroxylamine**	**Yield (%)**	**Reference**
	57	88	34
	56	37	36

Although not an amination reaction, treatment of **39** with picryl fluoride belongs to this type of reaction. Thus the reaction of **39** with two equivalents of picryl fluoride gave a mixture of two dipicryl derivatives, which was resolved by extraction with hot acetone to give 1,5- and

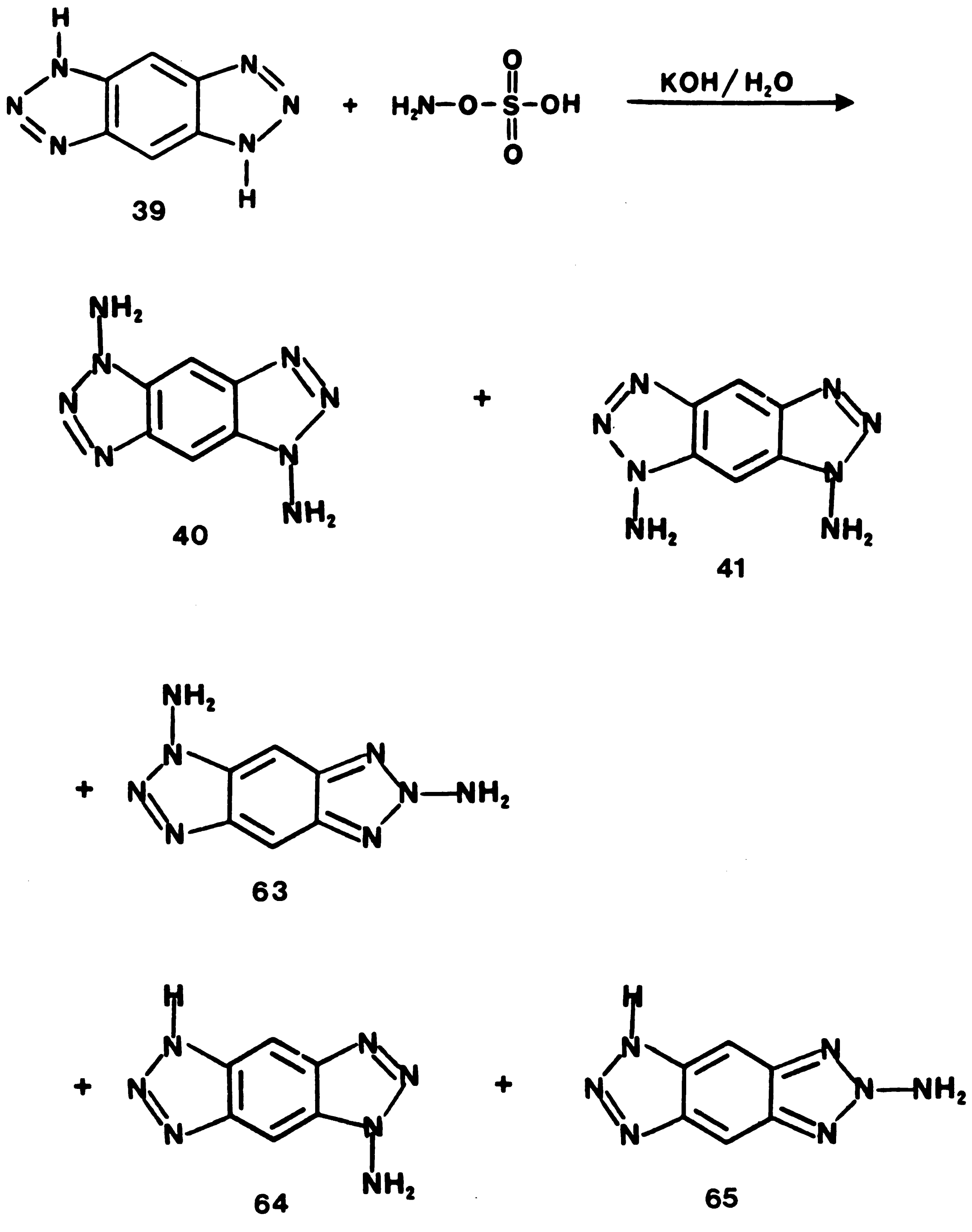
1,7-dipicrylbenzo[1,2-d:4,5-d']bistriazole (**61** and **62**) in 56 and 44% yield, respectively.[37] This reaction encouraged me to try the amination reaction.



Pk = 2,4,6,–tri–nitrophenyl

Reaction of benzo[1,2-d:4,5-d']bistriazole **39** in aqueous potassium hydroxide solution at 66-68°C with hydroxylamine-O-sulfonic acid **54** gave the di-aminated products as a mixture of 1,5-, 1,7- and 1,6-isomers (**40**, **41** and **63**) and two mono-aminated products (**64** and **65**) in 45 and 48% yields, respectively. No other products were detected from the reaction mixture. The ratio of isomers **40**, **41** and **63** was determined to be 53:12:35 by integrating the peaks at δ 8.24 (1,5-isomer), 8.69, 7.71 (1,7-isomer) and 8.59, 7.96 (1,6-isomer) in the 250 MHz ^{1}H NMR spectrum. The recovered mono-aminated compounds were recycled for further amination using the same reaction conditions.

The three isomers were separated in excellent purity by fractional recrystallization from ethanol taking advantage of their different solubilities. The 1,6-isomer is very soluble in hot ethanol and the 1,5-isomer is less soluble than the 1,7-isomer. The structures of **40**, **41** and **63** were assigned mainly from their spectral data. Compound **40**, mp 292°C (dec) gave excellent analytical values in agreement


39
KOH / H_2O
40
41
63
64
65

with formula, $C_6H_6N_8$ and its mass spectrum showed a parent peak at m/e 190 (intensity 16), a fragmentation peak at m/e 162 (M^+-nitrogen) and a base peak at m/e 105. The 250 MHz ^1H NMR spectrum consisted of two signals at δ 8.24 and 7.18 for the aromatic and amine protons, respectively. A single peak for the aromatic protons is only consistent with the symmetry of the 1,5-isomer. The ^{13}C NMR spectrum of **40** showed only three signals as required by symmetry, at δ 144.16, 131.40 and 97.43. The infrared spectrum showed strong primary amine absorptions at 3386 and 3610 cm^{-1}.

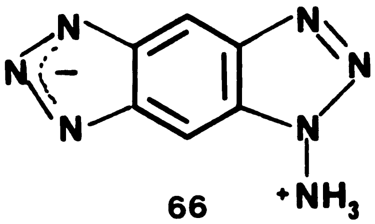
The ^1H NMR (250 MHz) spectrum of **41**, mp 263°C, showed two equal doublets at δ 8.69 and 7.71 for the aromatic C_4- and C_8-protons which were mutually coupled (J = 1 Hz), whereas at δ 7.09 there was a sharp singlet for the amine protons. The ^{13}C NMR spectrum showed four peaks at δ 142.93, 133.32, 108.42 and 87.43, consistent with the C_{2v} symmetry of **41**.

The unsymmetrical diamine structure **63** was clear from its spectra. Thus **63**, mp 271-273°C, showed six peaks in its ^{13}C NMR spectrum at δ 143.36, 139.98, 138.87, 132.72, 104.63 and 91.08. The 250 MHz ^1H NMR consisted of two equal aromatic doublets at δ 8.59 (C_4-H, J = 1 Hz) and 7.96 (C_8-H, J = 1 Hz) and a singlet at δ 7.09 for the amine protons.

It was noticed that two signals ($\sim \delta$ 100) with higher intensity than the others in each ^{13}C spectrum of the three isomers are notably shifted to higher field than normal aromatic region. On the basis of intensity, the shifted bands were suspected to be due to those carbons with hydrogen substituents. It was thought that a ^{13}C off-resonance coupling NMR experiment might confirm this assignment because each shifted carbon band would be split into two by the adjacent hydrogen.

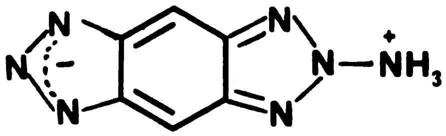
The coupled ^{13}C spectrum of **40** had four bands at δ 144.38 ($\underline{J}$ = 1 Hz), 131.65 ($\underline{J}$ = 1 Hz), 99.13 and 96.37 confirming that the band at δ 97.43 (decoupled) was responsible for the carbon with a hydrogen substituent. The coupled ^{13}C spectrum of **41**, with six signals at δ 142.92 ($\underline{J}$ = 1 Hz), 133.26 ($\underline{J}$ = 1 Hz), 109.78, 107.07, 88.83 and 86.04 also proved that the relatively high field bands are due to the carbons with hydrogen substituents.

The ratio of the recovered mono-amines **64** and **65** was determined to be 79:21 by integrating the peaks at δ 8.10 (d, $\underline{J}$ = 1 Hz), 7.65 (d, $\underline{J}$ = 1 Hz) and 7.99 (s) in the 250 MHz ^{1}H NMR spectrum. The mono-amine **64** was isolated in pure form by recrystallization from ethanol. The melting point of **64** is much higher (> 400°C) than those of the diamino compounds, probably due to a dipolar ion structure **66** since the amine contains both an acidic proton and a basic amine in the same molecule. The ^{1}H NMR (250 MHz) spectrum of **64** had two equal doublets for the aromatic protons at δ 8.10 ($\underline{J}$ = 1 Hz) and 7.65 ($\underline{J}$ = 1 Hz) and a singlet at δ 6.83 for the amine protons. The ^{13}C NMR spectrum showed the expected six peaks at δ 146.19, 144.96, 142.18, 130.54, 101.60 and 90.66.



66

Compound **65** was not isolated pure, but was always contaminated with **64**. The mono-amines (**64** and **65**), unlike the diamino compounds (**40**, **41** and **63**), did not readily separate on being warmed in ethanol (i.e., during recrystallization). The structure of **65** was deduced by comparing the ^{1}H NMR spectrum of **64** with that of the mixture of recovered mono-aminated compounds. The singlet at δ 7.99 was thought to be due to the structure **67** (dipolar ion form of **65**).



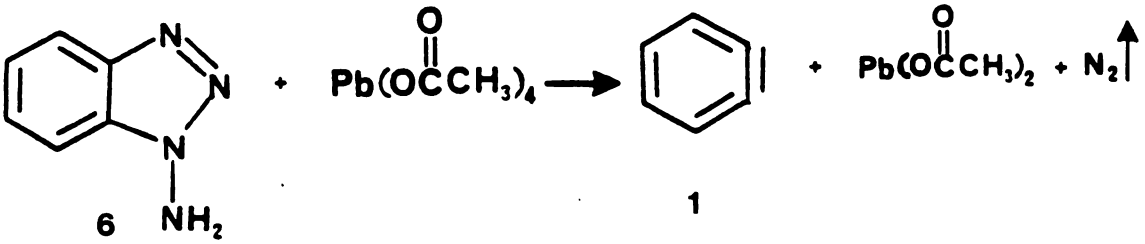
67

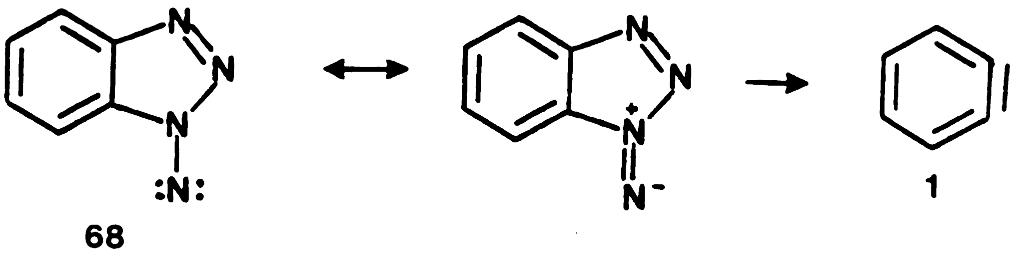
Amination of **39** with O-(2,4-dinitrophenyl)hydroxylamine **57** was capricious and gave no better yield and more difficult workup than with hydroxylamine-O-sulfonic acid.

B. Use of a New Diaryne Equivalent, (DABT), in Bis-annulation.

The bis-annulation of tetrahalobenzenes with various classes of dienes including furans, pyrroles and cyclopentadienes with no other functionalities is now well established.[20] However, similar annulation with dienes which contain carbonyl or similar groups, or with 1,3-dipoles, has not been possible with these or other diaryne precursors. This work represents the first study of those dienes or of a 1,3-dipole with the new di-aryne equivalent 1,5-diaminobenzo[1,2-d:4,5-d']-bis-triazole (DABT) **40**, using lead tetraacetate (LTA) as the oxidizing agent to generate an aryne.

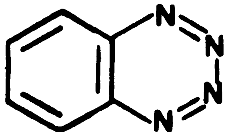
The initial study began with the development of an oxidation method for DABT **40**. Generation of benzyne from 1-aminobenzotriazole was reported by Campbell and Rees and their general procedure was as follows:[18] 1-aminobenzotriazole **6** was dissolved in a dry solvent such as benzene, methylene chloride, toluene, acetic anhydride or carbon tetrachloride and this solution was added dropwise to a stirred suspension of lead tetraacetate in the same dry solvent at room temperature. The reaction was always instantaneous (evolution of N$_2$). Work-up involved filtration, evaporation of the solvent, and chromatography of the residue. The reaction pathway involves oxidative removal of the amino hydrogens from 1-aminobenzotriazole **6**, producing a nitrene **68**, which might be expected to fragment to benzyne **1** and two molecules of nitrogen. This framentation process could occur by a concerted process, or by a radical mechanism, or by nitrene insertion to give benzotetrazine **69**, followed by decomposition; or by ring opening of **69** to produce a dipolar species **70**, which could lose two nitrogen molecules.



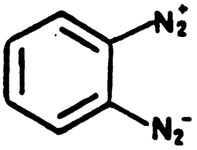


68

1



69



70

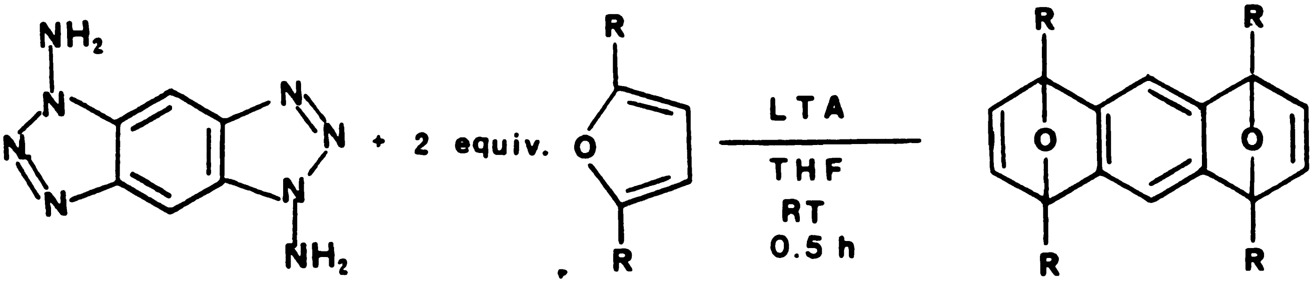
In terms of solubility, DABT is markedly different from 1-aminobenzotriazole. DABT is almost insoluble in common organic solvents such as benzene, chloroform or toluene in which 1-aminobenzotriazole is soluble, However, DABT is very slightly soluble in tetrahydrofuran (THF) at room temperature (ca. 3 mg in 100 mL). Several attempts to adapt the above method to the oxidation of DABT met with no success. For example, when DABT suspended in THF was added to a stirred suspension of lead tetraacetate in the same solvent at room temperature (or at reflux) over 1 h, no reaction took place (no evolution of N_2) and the unreacted DABT was recovered quantitatively. With several other solvents, e.g., benzene, toluene, ether or dimethyl sulfoxide, similar results were obtained.

However, it was suspected that the reaction might occur by using inverse addition, since the oxidation of 1-aminobenzotriazole with LTA is very fast. Therefore, even a small amount of DABT dissolved in THF may initiate the reaction.

Indeed, when LTA suspended in THF was added to a stirred suspension of DABT in the same solvent at room temperature, nitrogen evolution was almost instantaneous and ceased on completion of addition of LTA. Apparently, reaction between LTA and the DABT dissolved in THF increased the further solubility of DABT driving the equilibrium to the right. However ether, methylene chloride and toluene proved to be unsuitable solvents for the reaction due to an even lower solubility of DABT in those solvents. Throughout the course of this bis-annulation study, only THF was used as the reaction medium. The failure of the reaction when DABT was added to the LTA suspended in THF is probably due to insolubility of DABT.

To test the utility of DABT-LTA, simple furans were chosen as the dienes. The following is a general oxidation procedure for the use of DABT as a diaryne equivalent. To a mixture of 2 mmol of diene and 1 mmol of DABT in 100 mL of dry THF at room temperature was added in portions 2.2 mmol of LTA over a period of 30 min. After 10 min. additional stirring, the lead diacetate was filtered, and the filtrate was usually worked up by extraction of the adduct into methylene chloride and purification by chromatography and/or recrystallization.

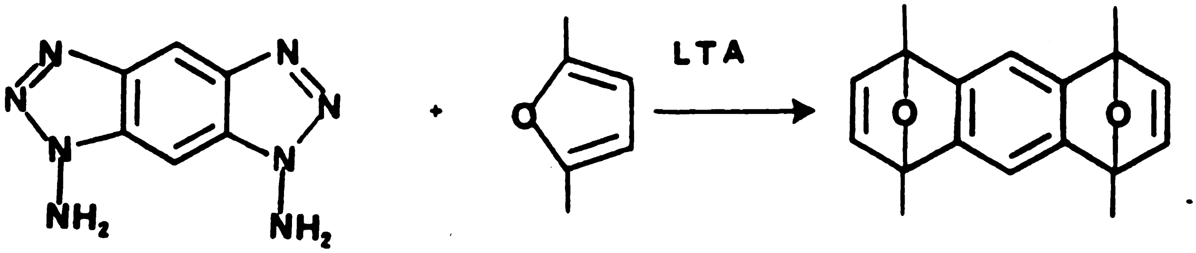
Reaction of 1,5-diamino[1,2-d:4,5-d']bistriazole (DABT) **40** with furan **8** and lead tetraacetate (LTA) gave the first bis-annulation example **71** derived from DABT, in 79% yield as a mixture of two stereoisomers. The ratio was determined to be 77:23 by integrating the peaks at δ 7.20 and 7.19 for the aromatic hydrogens in the 250 MHz ^{1}H NMR spectrum. The ^{13}C NMR spectrum showed six bands indicating a mixture of two isomers. When the sequence was repeated with excess furan (ten fold), a similar yield (80%) was obtained. With 2,5-dimethylfuran **72**, the bis-adduct **73** was obtained in 81% yield. The 250 MHz ^{1}H NMR spectrum had five singlets at 6.96, 6.78 (minor), 6.76 (major), 1.87 (major) and 1.86 (minor) indicating a mixture of two isomers in a ratio of 19:81 integrating the peaks at δ 6.78 and 6.76. The ^{13}C NMR spectrum showed seven peaks confirming the presence of two isomers.



8 R = H
72 R = CH_3

71 R = H (79%) (77:23)
73 R = CH_3 (81%) (81:19)

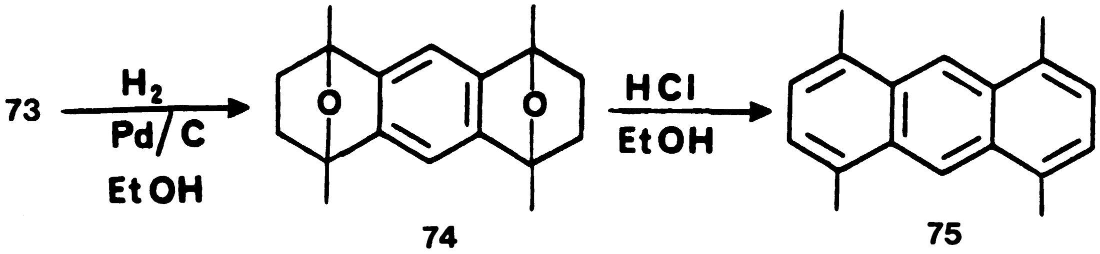
Treatment of 1,7-diamino-benzo[1,2-d:4,5-d']bistriazole **41** with 2,5-dimethylfuran and LTA also afforded **73** as a mixture of two stereoisomers, in 80% yield in the same ratio as observed before, 19:81.



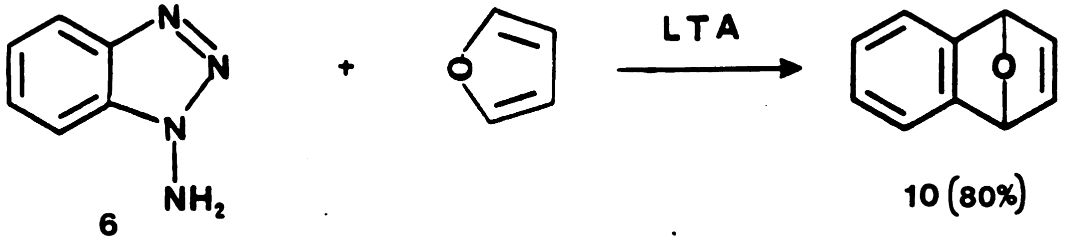
41

73

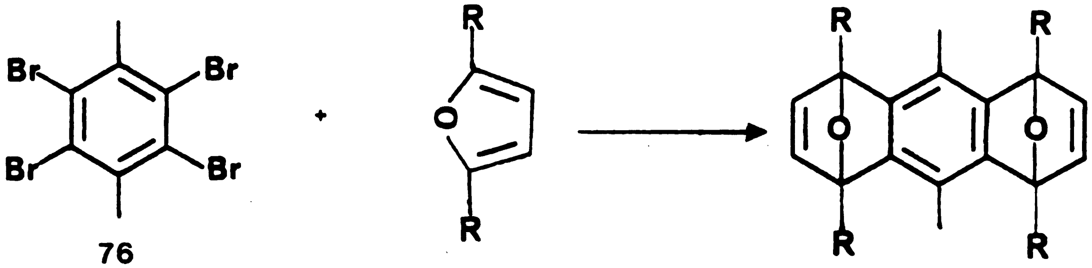
The oxygen bridges of **73** were easily removed in overall 83% yield to give 1,4,5,8-tetramethylanthracene **75**[38] by catalytic hydrogenation of **73**, followed by dehydration of the resulting **74**.



The yields in these bis-annulations were quite satisfactory compared to other analogous examples. For example, oxidation of 1-aminobenzotriazole and LTA in furan gave, on distillation, 1,4-epoxy-1,4-dihydronaphthalene **10** in 80% yield.[18]



Hart and coworkers prepared similar bis-adducts (**77** and **78**) using tetrabromo-p-xylene **76** as a diaryne precursor.[20b] Treatment of **76** and furan **8** with n-butyllithium gave the diadduct **77** in 77% yield as a mixture of two isomers in a ratio of 53:47. When the sequence was repeated with 2,5-dimethylfuran **72**, the diadduct **78** was obtained in 78% yield as a mixture of two isomers, but in a slightly higher ratio (57:43). It is noteworthy that DABT with both dienes provided a higher stereoselectivity than did tetrabromo-p-xylene **76**, and between the two dienes 2,5-dimethylfuran gave a better stereoselectivity.

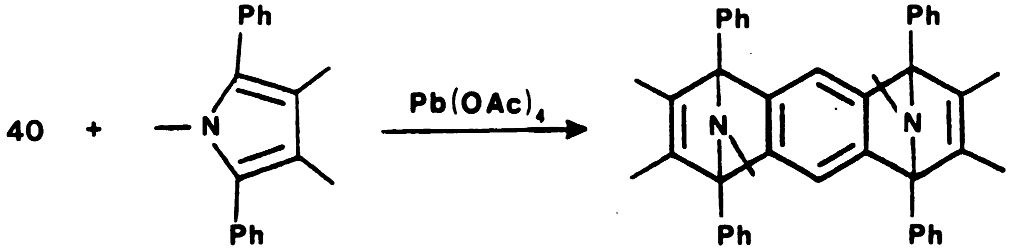


76

8 R = H
72 R = CH_3

77 R = H (77%)(53:47)
78 R = CH_3(78%)(57:43)

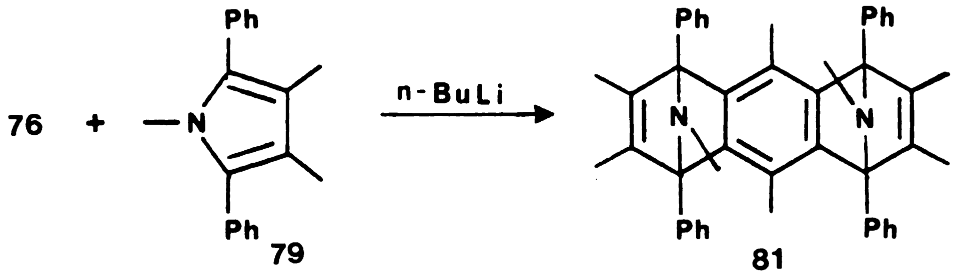
In order to explore the generality of the bis-annulation technique with **40**, different classes of dienes were employed. Treatment of **40** with 1,3,4-trimethyl-2,5-diphenylpyrrole **79** and LTA gave the diadduct **80**, mp, 273-275°C identified from its analytical and spectral properties. The 250 MHz ^1H NMR spectrum of **80** consisted of aromatic multiplets



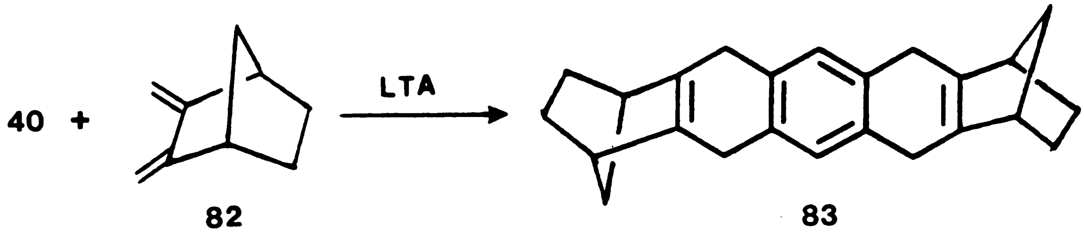
79

80 (77%)

(δ 7.6-7.2, 22 H) and two broad singlets (δ 1.8, 12 H and 1.6, 6H). The ^{13}C NMR spectrum had ten major peaks as required by a single isomer with appropriate chemical shifts. Similarly, diadduct **81** was prepared in 57% yield from the reaction of tetrabromo-p-xylene **76** and **79** with n-butyllithium as a mixture of two isomers (ratio not known).[39]



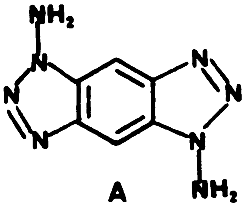
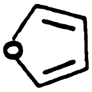
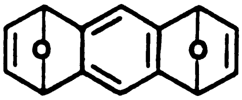
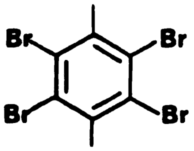
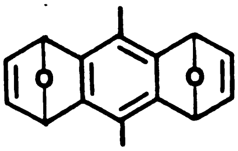
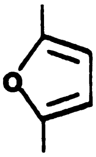
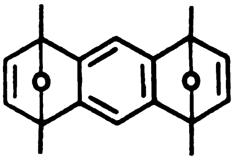
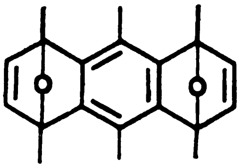
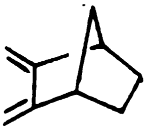
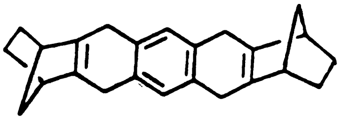
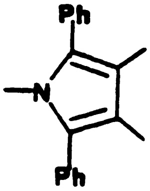
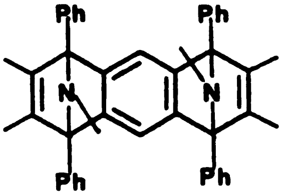
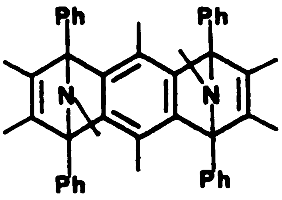
Similar treatment of **40** with 2,3-bis-(methylene)-bicyclo[2.2.1]heptane **82**[40] afforded the bis-adduct **83** in 93% yield. The 250 MHz ^{1}H NMR indicated a mixture of two isomers in a ratio of 91/9 integrating the two small equal singlets (syn) at δ 7.56 and 7.43 and one large singlet (anti) at δ 6.96.



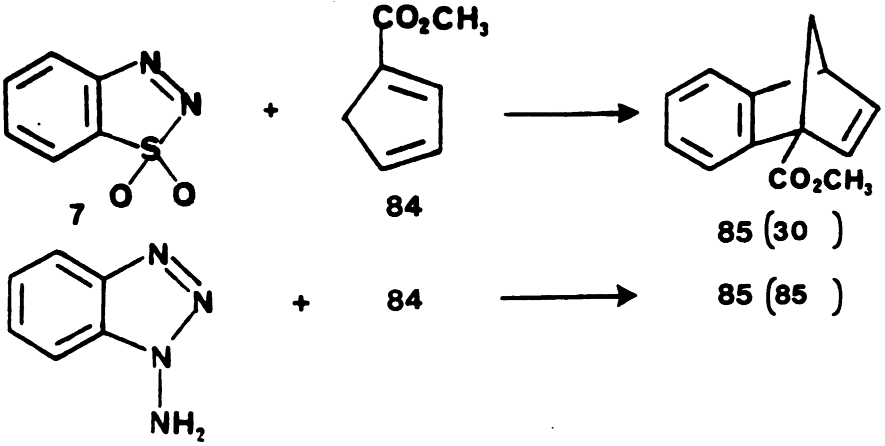
Apparently, more substituted dienes gave the higher stereoselectivity regardless of precursors and the results are summarized in Table **3**.

Examples of benzyne cycloadditions to dienes containing carbonyl functionality are rarely found in the literature. Benzyne, generated by thermal decomposition of 1,2,3-benzothiadiazole-1,1-dioxide **7** added to methyl cyclopentadienyl-1-carboxylate **84** providing methyl benzonorbornadienyl-1-carboxylate **85** in 30% yield (based on o-nitrobenzenesulfonic acid from which the benzyne precursor was prepared).[41]

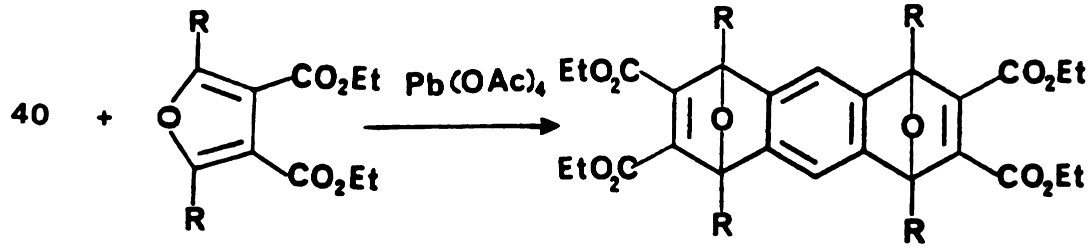
Table 3. Adducts derived from two diaryne equivalents with various dienes.

Precursor	Diene	Bis-adduct	Yield (%)	Isomer Ratio
 A	 C		79	77:23
 B	C		77	53:47
A	 D		81	81:19
B	D		78	57:43
A			93	91:9
A	 E		77	Mainly single isomer
B	E		57	ratio not known

The dimerization of cyclopentadienyl-1-carboxylate **84** is very facile at 10-25°C which is necessary for the thermal decomposition. Irie and Tanida considered that a benzyne generated at a lower temperature might give a better result and used for this purpose 1-aminobenzotriazole and LTA. Thus the benzyne generated at -60°C in methylene chloride was successfully added to **84** giving **85** in 85% yield.[42]



As the first example using DABT with a carbonyl-containing diene, reaction of **40** with diethyl 3,4-furandicarboxylate **86**[43] and LTA gave the desired bis-adduct **87** in 40% yield. This substance melted fairly sharply at 188-190°C, suggesting that it was mainly one isomer. The structure of **87** is based on its spectral properties. The 250 MHz ^1H NMR spectrum had a two-proton aromatic singlet at δ 7.45 and a four-proton bridgehead singlet at δ 5.90 in addition to a typical triplet and quartet for the ethoxyl group (δ 4.30, 8H, q, $\underline{J}$ = 7 Hz and 1.35, 12 H, t, $\underline{J}$ = 7 Hz). The ^{13}C NMR spectrum of **87** showed the seven major peaks which are required for a single isomer. The compound showed a parent peak at m/e 498 and 425 (M^+-ester) in its mass spectrum and had an infrared spectrum showing strong carbonyl absorption at 1695 cm^{-1}.



86 R=H

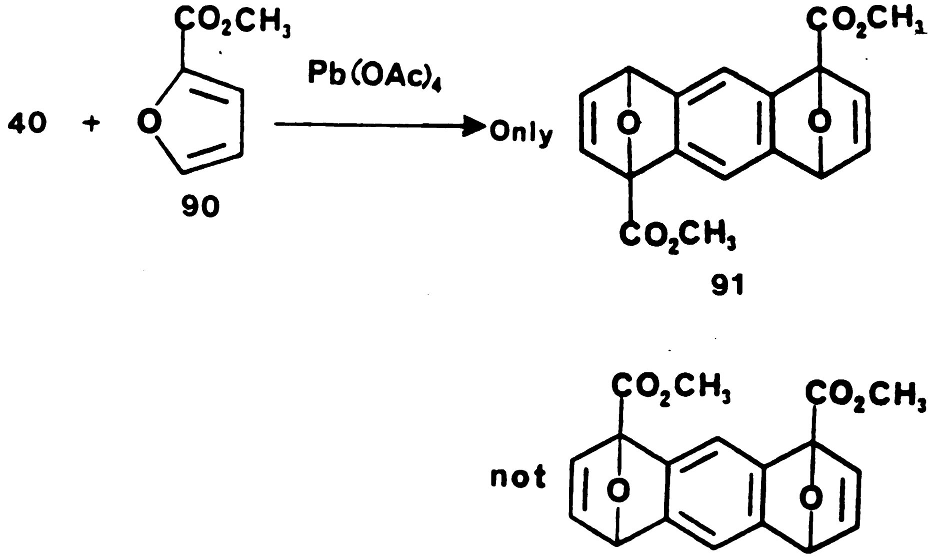
88 R=CH_3

87 R=H (40%)

89 R=CH_3(67%)

Reaction of **40** with diethyl 2,5-dimethylfuran-3,4-dicarboxylate **88**[44] gave the bis-adduct **89**, mp 233-236°C in 67% yield. Compound **89** gave the correct analysis for a bis-adduct and its mass spectrum contained a parent peak at m/e 554. The ^{13}C NMR spectrum had eight major peaks indicating that **93** was mainly a single isomer.

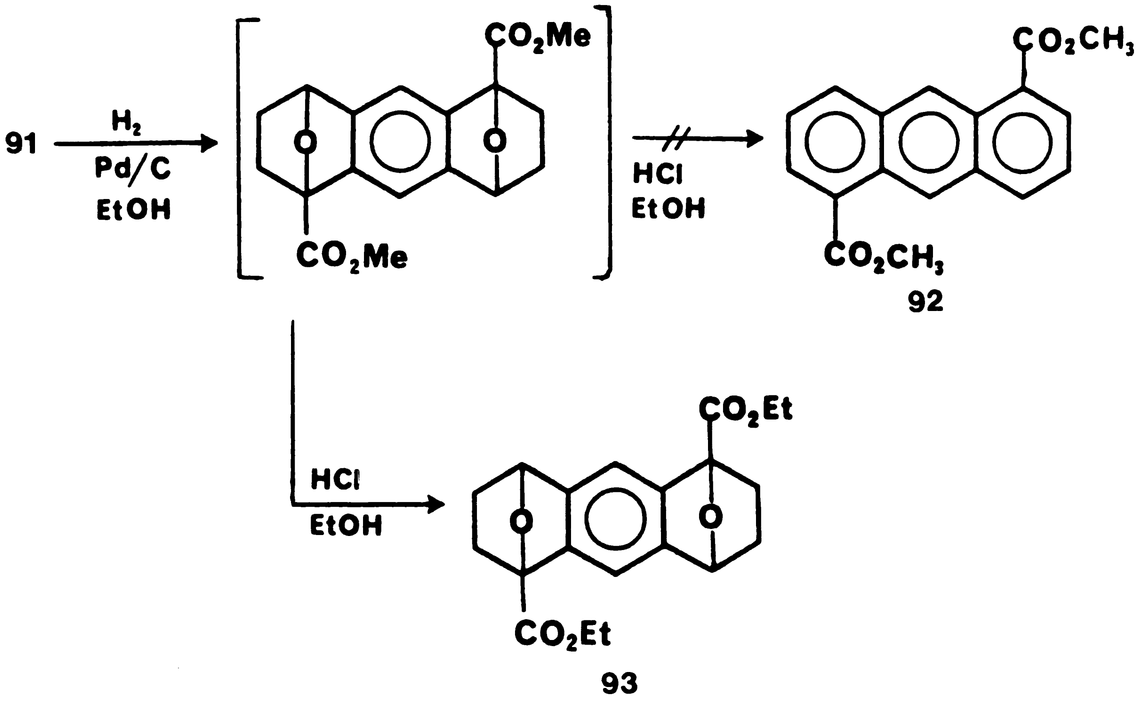
In contrast to symmetrical dienes, a question of regioselectivity arises when the dienes are unsymmetrically substituted. The Diels-Alder reaction of **40** with unsymmetrical dienes could give rise to two regiochemically distinct products each of which again provides two stereoisomers, syn and anti, thus resulting in four isomers altogether. It was found in practice, however, that only the "trans"-type isomer formed with several dienes. For example, treatment of **40** and methyl 2-furoate **90**[43] at room temperature with LTA gave the diadduct **91** in 47% yield. The structure of **91** was unequivocally determined by its spectral properties and chemical transformations. The adduct melted fairly sharply at 240-242°C suggesting that it was mainly one isomer. The 250 MHz ^1H NMR spectrum contained a singlet at δ 7.35 for the aromatic protons clearly indicating one regioisomer and four other singlets at δ 7.10, 7.08, 5.74, and 4.07 for vinyl, bridghead, and methyl protons. The adduct analyzed correctly for $C_{18}H_{14}O_6$ and the infrared spectrum showed the expected carbonyl band at 1760 cm^{-1}. The ^{13}C NMR had mainly nine peaks confirming the presence of a single isomer.

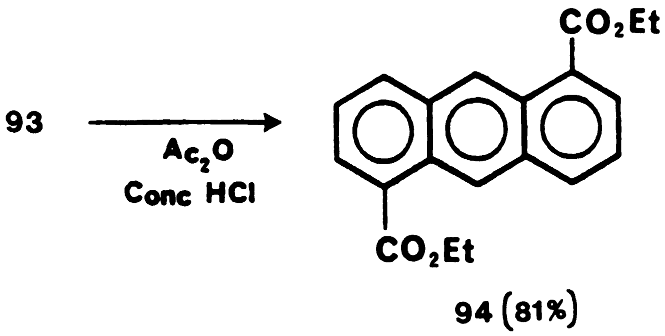


90

91

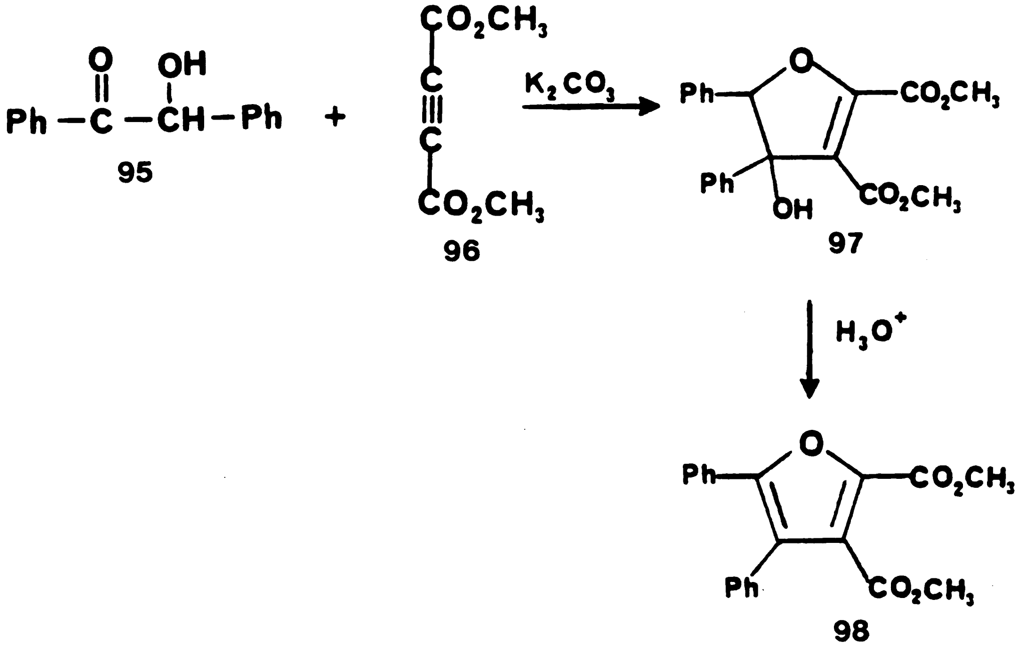
In order to prove structure 91 with certainty, it was desired to aromatize compound 91. Among many other possibilities, aromatizations by dehydration[45] was adapted. The bis-adduct 91 was reduced catalytically, followed by acid treatment in refluxing ethanol with the hope that it would provide the anthracene derivative 92. However, the corresponding trans-esterified material 93 was obtained along with only a trace of aromatized product 92. Therefore it was thought that more severe conditions might be required for the dehydration. When the aromatization of **93** was carried out in acetic anhydride in the presence of conc. hydrochloric acid, the desired product **94**, mp 185°C [lit.[46] 185°C] was obtained in 81% yield. Compound **94** has a singlet for the two central aromatic protons at δ 9.67, two aromatic multiplets centered at δ 8.31 and 7.50, and typical ethyl signals at δ 4.53 and 1.51 (J = 7 Hz) confirming the 'trans' arrangement of the ester functions.



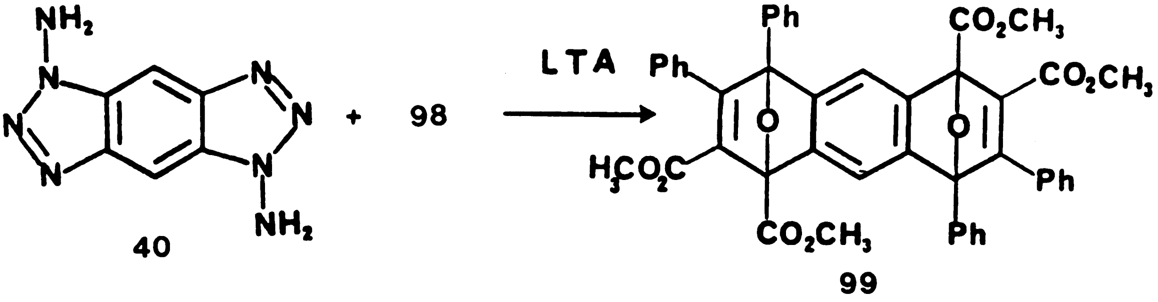


The Diels-Alder reaction of **40** with dimethyl 4,5-diphenylfuran-2,3-dicarboxylate **98** was particularly interesting because the diene is not only unsymmetrically substituted but also contains two electron-withdrawing (ester) groups. It should be mentioned that the vast majority of Diels-Alder reactions involve an electron-rich diene and an electron-deficient dienophile.

The diene **98** used in this reaction was prepared in overall 34% yield by condensation of benzoin **95** with dimethyl acetylenedicarboxylate **96** and potassium carbonate, followed by dehydration of **97**[47]. Treatment of **40** with **98** and LTA in refluxing tetrahydrofuran gave the bis-adduct **99**, mp 283-287°C in 78% yield. However, when the reaction was carried out at room temperature, no bis-adduct was observed and only the starting diene was recovered quantitatively.

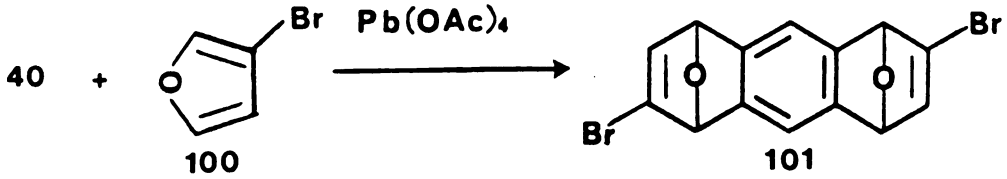


So far, this is the only diene which required vigorous

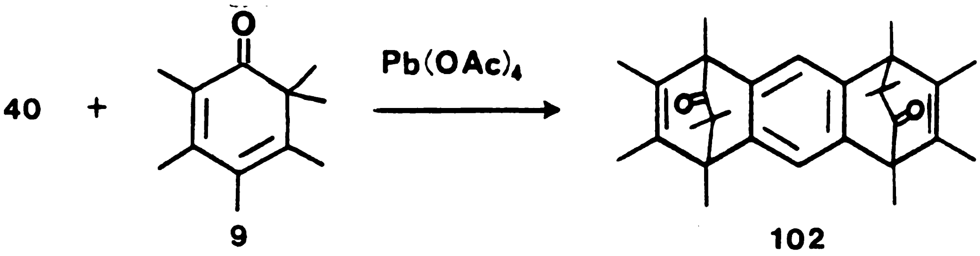


conditions for bis-annulation. The structure of **99** rests on its spectral properties and elemental analysis. The 250 MHz ^{1}H NMR spectrum of **99** had a singlet at δ 8.11 for the two central aromatic protons, a broad twenty-proton aromatic multiplet (δ 7.45-7.1) and two singlets at δ 3.97 and 3.61 for the two ester methyl groups. The infrared spectrum had two strong ester carbonyl absorptions at 1755 and 1725 cm^{-1}.

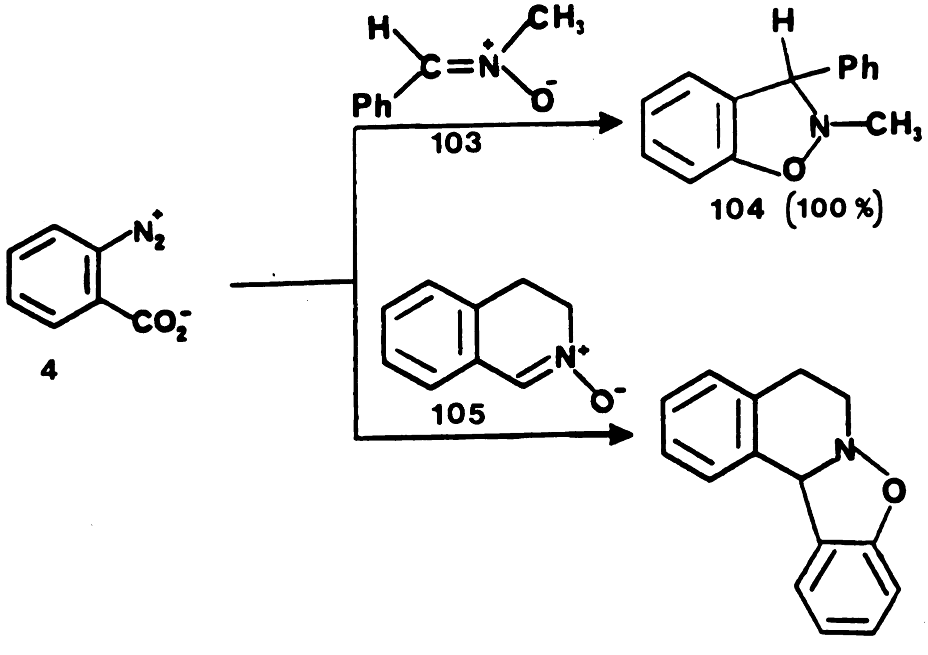
A valuable result which further demonstrates the usefulness of the precursor **40** was obtained from the reaction with a halogen-substituted furan. Treatment of **40** with 3-bromofuran **100** furnished the bis-adduct **101**, mp 115°C (decomp) in 69% yield. The 250 MHz ^{1}H NMR spectrum of **101** revealed a singlet at δ 7.32 for the aromatic protons suggesting that the product was the 'trans' isomer, as well as a doublet ($\underline{J}$ = 2 Hz) at δ 6.96 for the vinyl protons and a broad singlet for the bridgehead protons (α to bromine), and doublet ($\underline{J}$ = 2 Hz) for the other bridgehead protons (β to bromine) at δ 5.69 and 5.38 respectively. Compound **101** gave the correct analysis for the bis-adduct, and its mass spectrum had a parent peak at m/e 368 with the typical isotope pattern for two bromines, and a peak at m/e 289 (M^+-bromine).



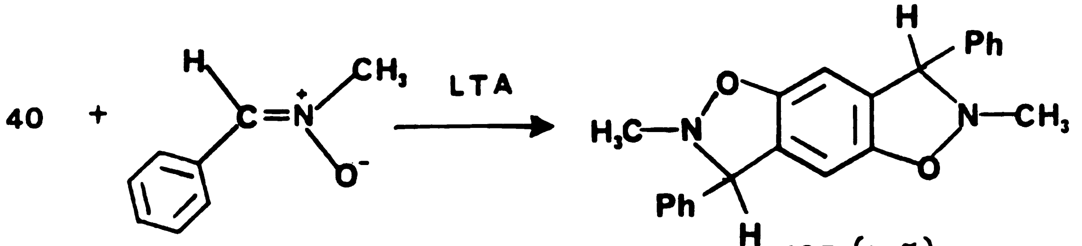
Another important group of dienes studied was the fully methyl-substituted dienone **9**. 2,3,4,5,6,6-Hexamethylcyclohexadiene-1-one **9** formed the bis-adduct **102** with DABT--LTA in 79% yield. Its structure determination is somewhat complicated and will be discussed in detail in a separate chapter (see page 103).



1,3-Dipolar cycloaddition is one of the most useful methods for preparing five-membered heterocycles. Numerous possibilities for variations are available by changing the structures of both the dipole and dipolarophile. The cycloaddition reaction between benzyne and nitrones (azomethine oxides) was first reported by Huisgen in 1961.[48] For example, benzyne generated from benzenediazonium carboxylate adds to N-methyl-α-phenyl nitrone **103** to give a stable adduct **104** in quantitative yield. Similarly, cyclic nitrone **105** gave the adduct **106** with benzyne in excellent yield.



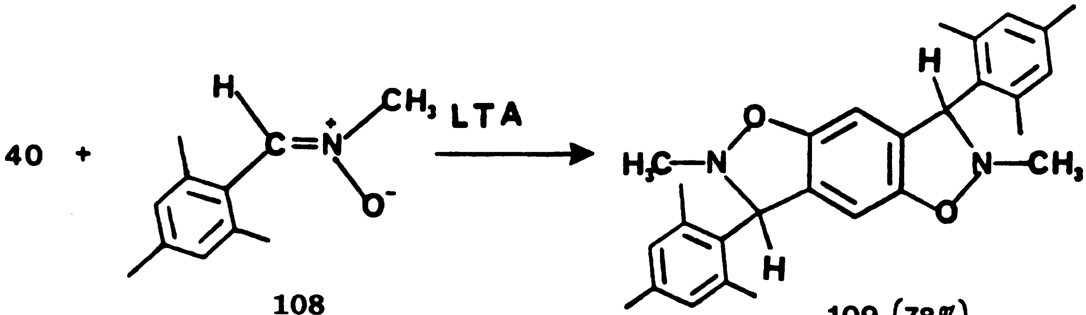
In principle, any reaction between **40** and a nitrone could give four products, i.e., two regioisomers with two stereoisomers as in the case of unsymmetrical dienes. However, regioselectivity was also observed in the dipolar cycloaddition of **40** with nitrones. The reaction of 1,5-diamino-benzo[1,2-d:4,5-d']bistriazole **40** with N-methyl-α-phenyl nitrone **103**[49] and LTA gave the only 'trans' regioisomer **107**, mp 142-143°C, in 91% yield. The structure of **107** follows from its analytical and spectral properties. The 250 MHz ^{1}H NMR spectrum had three singlets at δ 6.42, 5.04 and 2.94 for the central aromatic, benzylic and N-methyl hydrogens in a ratio of 1:1:3, and multiplets at δ 7.38-7.33 for the ten aromatic hydrogens. The mass spectrum showed a parent and base peak at m/e 344 and major fragmentation peaks at *m*/*e* 329 (M^+-methyl) and 267 (M^+-phenyl). The ^{13}C NMR spectrum showed mainly nine peaks indicating the presence of a single isomer.



103

107 (91%)

Similarly, the reaction of **40** with the bulky nitrone **108** at room temperature afforded the bis-adduct **109**, mp 239-241°C in 78% yield. The 250 MHz ^{1}H NMR spectrum consisted of six singlets showing mesityl, central aromatic and benzylic hydrogens at δ 6.85, 6.14 and 5.66 in a ratio of 4:2:2 and three methyl signals at δ 2.96, 2.30 and 2.27 in a ratio of 6:12:6. The ^{13}C NMR spectrum showed mainly eleven peaks for a single isomer. The mass spectrum had a parent and base peak at *m*/*e* 428 and major fragmentation peaks at *m*/*e* 384 (84) and 309 (M^+-mesityl).

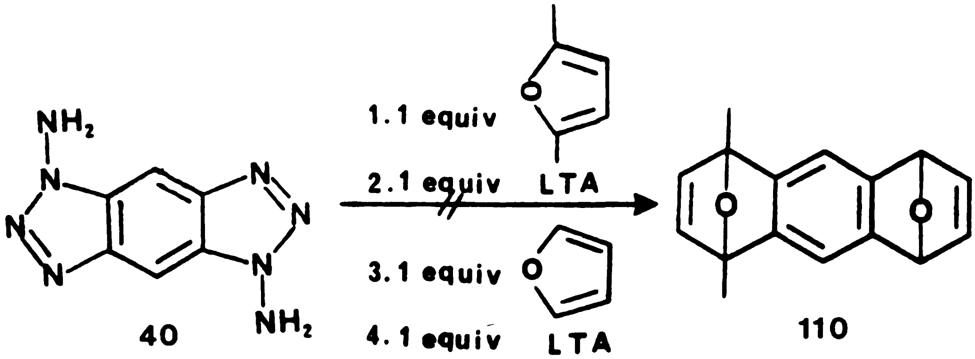


108

109 (78%)

The remarkable degree of regio and stereospecificity in these cycloadditions strongly suggests that they occur stepwise. The results are summarized in Table 4.

It was hoped that an unsymmetrical bis-adduct could be prepared by using two different dienes in succession as trapping agents. A mixture of DABT and 1 equiv. of 2,5-dimethylfuran in THF was treated with 1 equiv. of LTA.



Upon completion of the addition of LTA, furan was added to the reaction mixture followed by more LTA. The products, isolated after the usual workup, turned out to be 1,4,-5,8-tetramethyl-1,4,5,8-tetrahydroanthracene-1,4:5,8-diendoxide **73** and 1,4,5,8-tetrahydroanthracene-1,4,5,8-diendoxide **71** and no unsymmetrical adduct **110**. Probably the intermediate **111** resulting from the addition of one equivalent of aryne to the diene **72** is more soluble than DABT in the solvent and reacts further to give the symmetrical adduct **73**. In fact treatment of DABT and 1 equiv. of 2,5-dimethylfuran with LTA gave the bis-adduct **73** and the unsymmetrical adduct **111** was not observed.

Table 4. Adducts of DABT-LTA with various dienes with functionality.

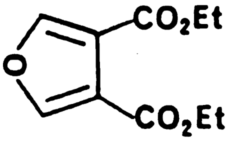
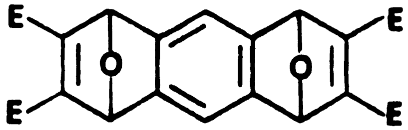
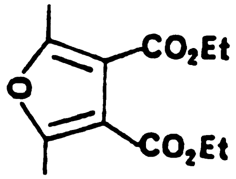
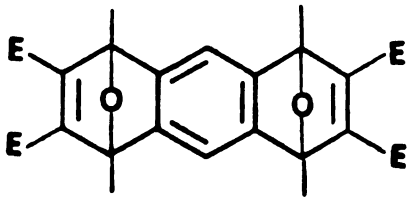
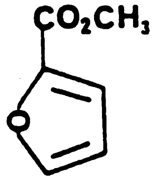
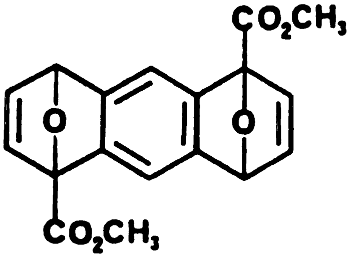
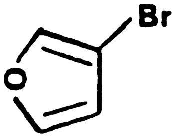
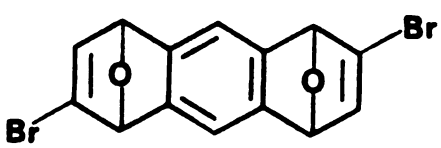
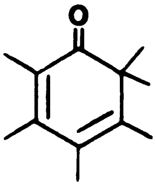
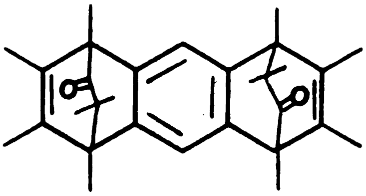
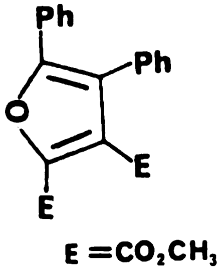
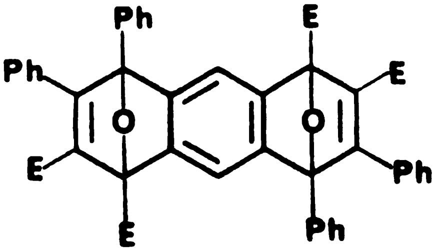
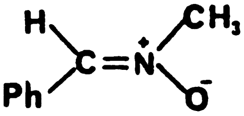
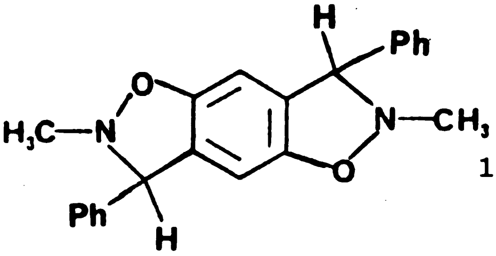
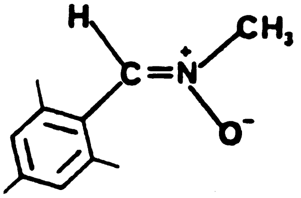
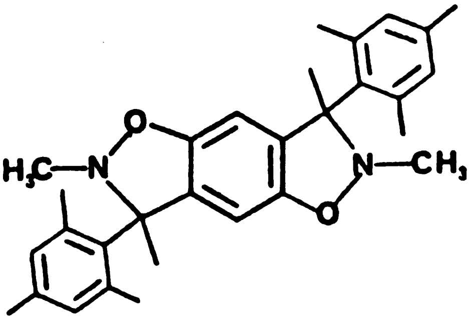
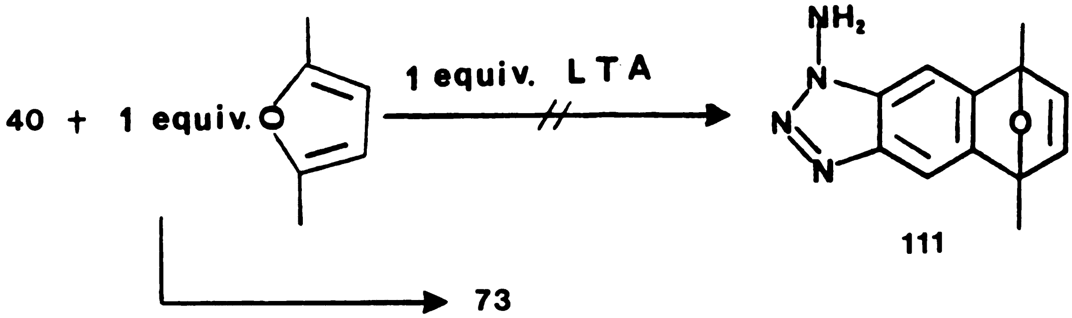
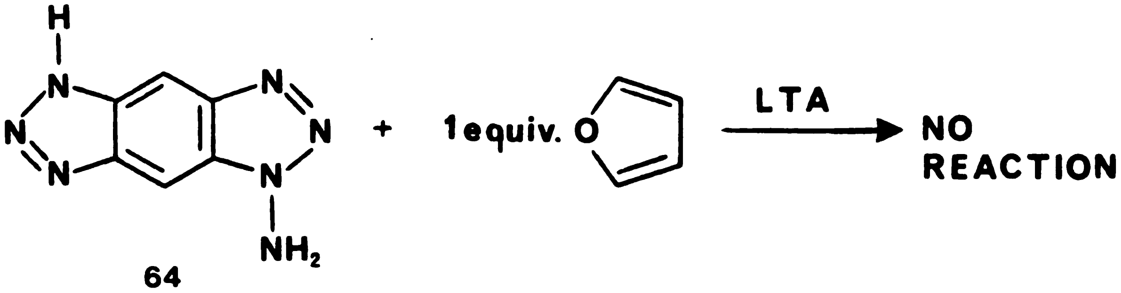
Diene	Adduct	mp, °C	Yield (%)
	 $E = CO_2CH_2CH_3$	188-190	40
	 $E = CO_2CH_2CH_3$	233-236	67
		240-242	47
		115 (dec)	69

Table 4 (continued)

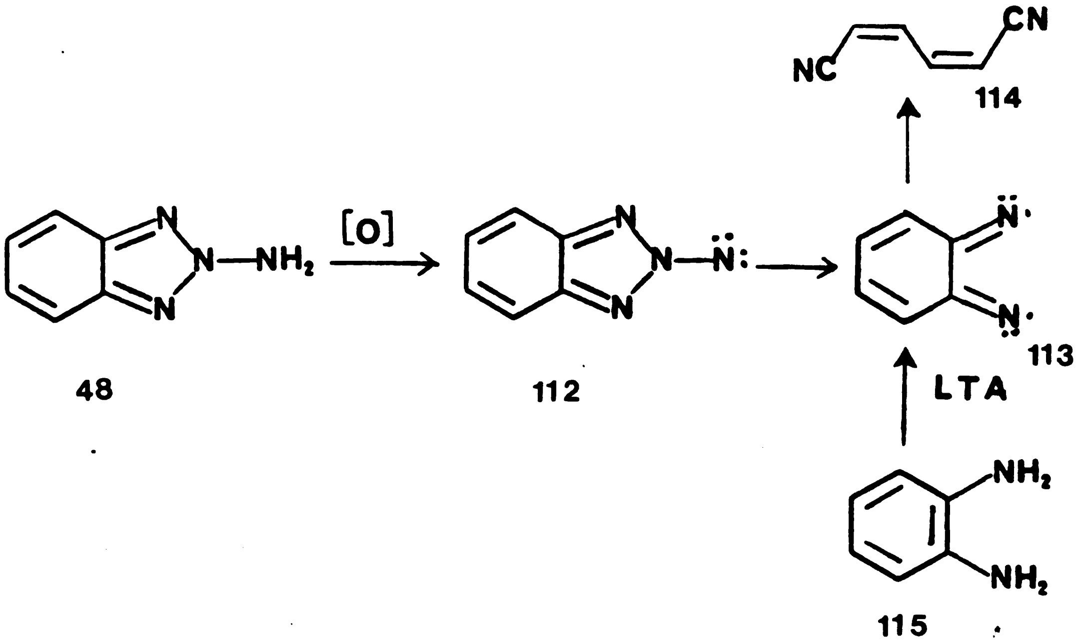
		338 (dec)	79
		283-287	78
		142-143	91
		239-241	78

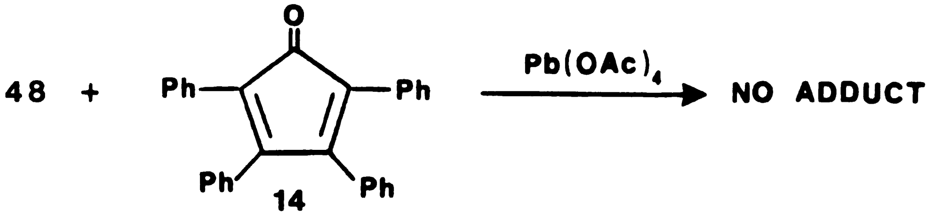


It was thought that mono-amino compound **64** might behave as a diaryne equivalent in a stepwise process, and that it might be a useful precursor of unsymmetrical adducts. However, 1-aminobenzo[1,2-d:4,5-d']bistriazole **64** didn't seem to react with LTA in THF probably due to its insolubility; the unreacted amino compound **64** was recovered unchanged.



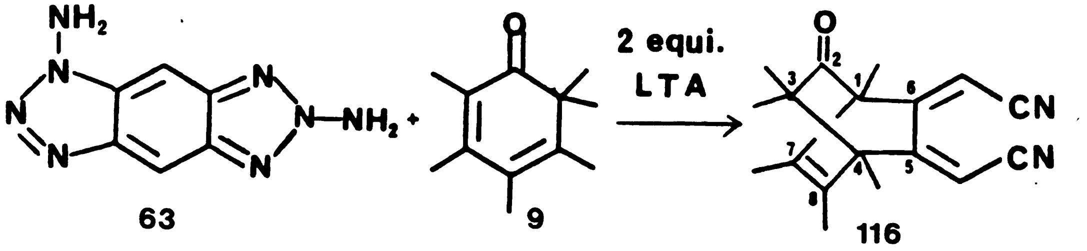
It was quite interesting to study the oxidation of 1,6-diamino-benzo[1,2-d:4,5-d']bistriazole **63** which contains 1-amino- and 2-amino-moieties in the same molecule. Unlike 1-aminobenzotriazole, 2-aminobenzotriazole **48** does not behave as a benzyne precursor.[18] Iodobenzene diacetate is known to oxidize 2-aminobenzotriazole **48** to cis,cis muconitrile **114** in 98% yield, presumably through the nitrenes **112** and **113**.[18] Compound **114** has also been obtained in 64% yield by the oxidation of o-phenylenediamine **115** with LTA, in which the nitrene **113** is a possible intermediate.[50] Thus, oxidation of **48** with LTA in the presence of 1,2,3,4-tetraphenylcyclopentadienone **14** gave no adduct and the diene **14** was recovered.[18]





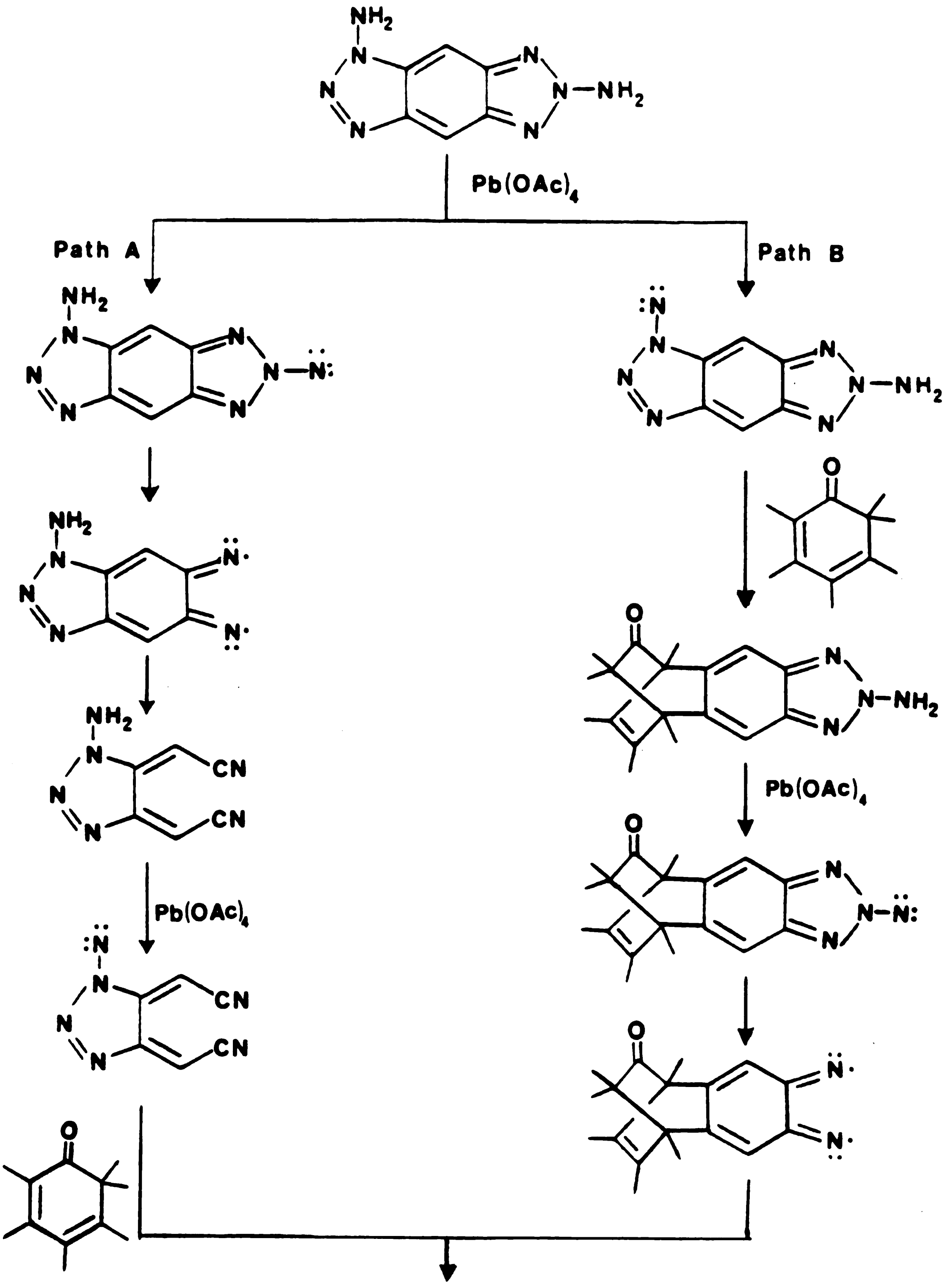
Oxidation of compound **63** with lead tetraacetate brought about a rapid evolution of nitrogen, and when 2,3,4,5,-

6,6-hexamethyl-2,4-cyclohexadienone **9** was present as the trapping agent, 1,3,3,4,7,8-hexamethyl-5,6-bis(Z,Z-cyanomethylene)-bicyclo[2.2.2]oct-7-ene-2-one **116** was obtained in 81% yield. The infrared spectrum showed both nitrile



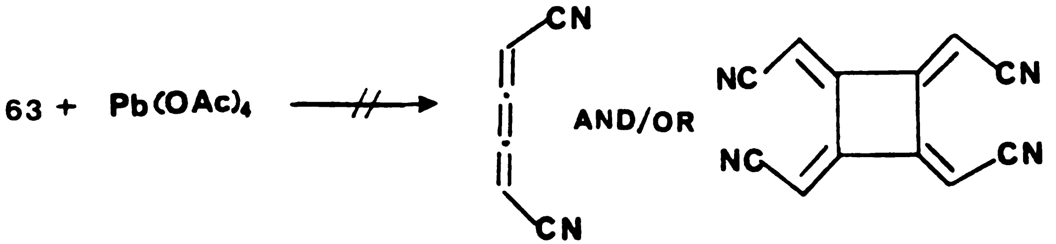
and carbonyl bands at 2215 and 1740 cm^{-1} respectively. The 250 MHz ^{1}H NMR (CDCl$_3$) spectrum of **116** had bands at δ 1.77 and 1.70 for two homoallylically coupled methyl groups (*J* = 1.0 Hz), four separate aliphatic methyl singlets at δ 1.46, 1.41, 1.09 and 0.89 and two vinyl singlets at δ 5.66 and 5.62. The ^{13}C NMR spectrum showed a carbonyl carbon at 199.50, eight vinyl and nitrile carbons at δ 161.28, 155.75, 139.52, 129.98, 116.54, 115.87, 98.06 and 96.13, three quaternary carbon signals at δ 60.06, 52.24 and 45.71 and six methyl carbon peaks at δ 23.58 (overlap), 14.25, 13.90, 11.99 and 11.62. High resolution mass spectral analysis established the elemental composition. The mass spectrum showed a parent peak at *m/e* 280, and a base peak at *m/e* 210 indicating a loss of dimethylketene (M^{+}-70). In view of previous oxidation studies of 1- and 2-aminobenzotriazoles, two pathways can be suggested to account for the formation of compound **116** (Scheme 5).

Scheme 5



116

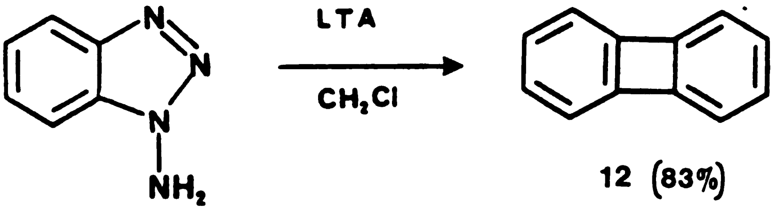
It was thought that the oxidation of **63** in the absence of any trapping agent might lead to the compounds **117** and/or **118**. However, the only product obtained was a polymeric oil.



117

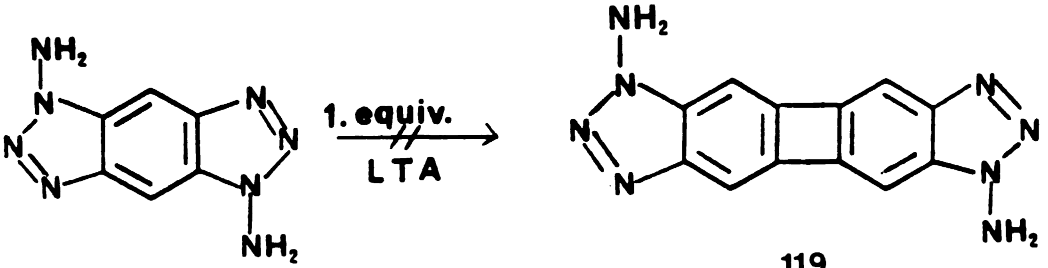
118

It was thought that 1,5-diamino-benzo[1,2-d;4,5-d']bistriazole **40**, might dimerize on oxidation with only one equivalent of lead tetraacetate. In the oxidation of 1-aminobenzotriazole with LTA in methylene chloride, the benzyne generated



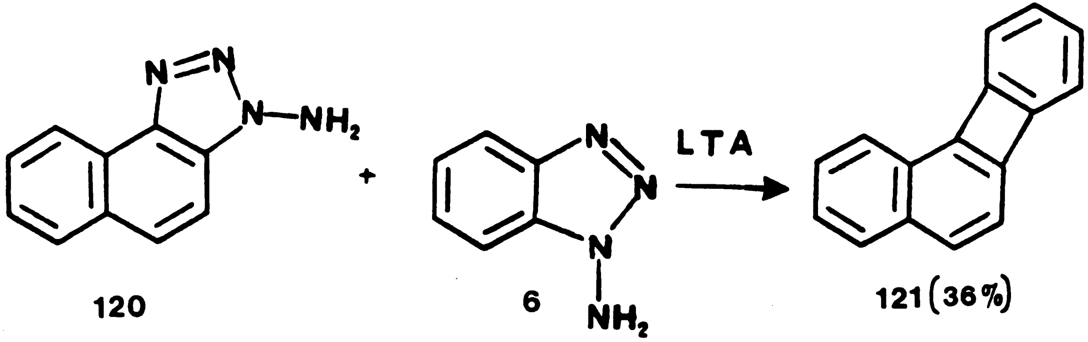
12 (83%)

dimerized to give biphenylene 12[18] in high yield. When DABT was oxidized with one equivalent of LTA, no desired biphenylene **119** or oligomer thereof was detected. It is tempting to assume that the failure of dimerization is due to further oxidation (as can be understood from the example given below) of the product **119** leading to more complicated products.



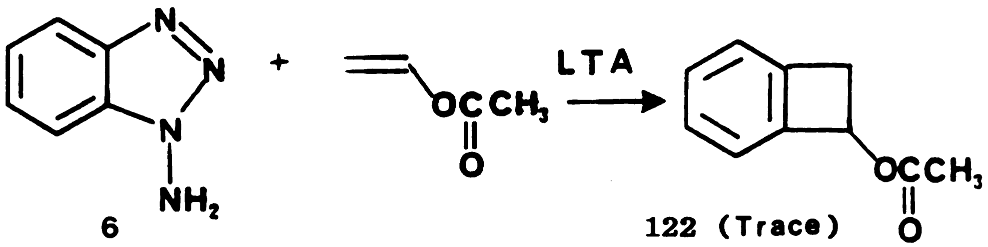
40 119

1-Aminobenzotriazole is known to undergo a cross-coupling reaction with other analogous aryne precursors by cooxidation with LTA.[51] Barton and Jones reported an unsymmetrical biphenylene **121** obtained from cooxidation of 1-amino-1H-naphtho[1,2-d]triazole **120** and 1-aminobenzotriazole **6**.[51a]



120 **6** **121**(36%)

Among the cycloaddition reactions that have some generality and synthetic utility are the [2+2] cycloadditions of benzyne with alkenes. Benzyne generated from benzenediazonium 2-carboxylate adds to vinyl acetate in good yield.[52] However, oxidative generation of benzyne in vinyl acetate gave biphenylene in high yield and only a trace of 1,2-adduct, benzocyclobutenyl acetate **122**[18]. Reaction of DABT with vinyl acetate and LTA gave no cycloadduct. An electron-rich dienophile, 1,1-dimethoxyethylene,[53] also showed no reactivity toward the DABT-LTA.



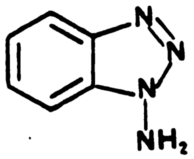
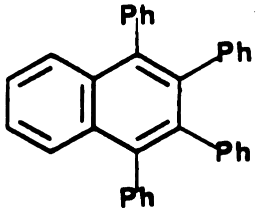
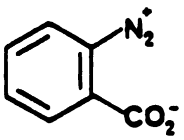
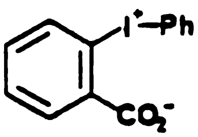
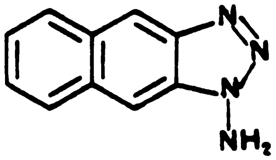
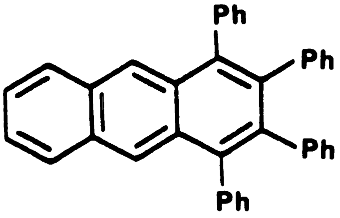
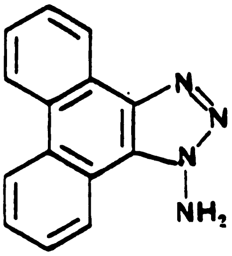
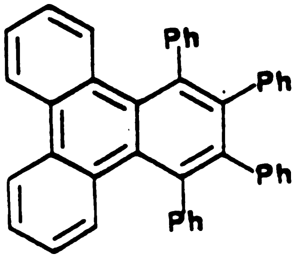
In conclusion, we have synthesized 1,5- and 1,7-diamino-benzo[1,2-d;4,5-d']bistriazole (DABT) and demonstrated their utility as diaryne precursors. The most interesting aspect of the Diels-Alder reaction with unsymmetrical dienes and 1,3-dipoles is that each reaction is regiospecific in that, of the two possible orientations, only the 'trans' product is produced. The remarkable degree of regio- and stereospecificity encourage one to further study the reasons for this specificity as well as to seek out further synthetic applications of DABT.

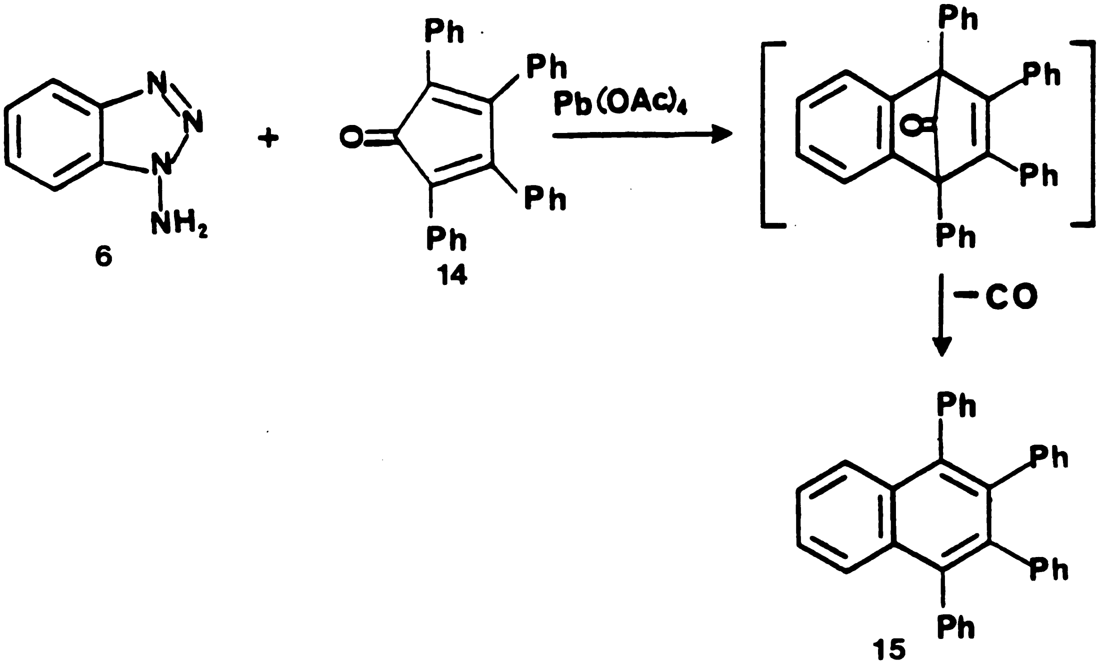
C. **Preparation of Polyphenylarenes Using DABT**

The bis-annulation technique has been usefully extended to the synthesis of various polyphenyl arenes, which are easily prepared in high yield by reaction of DABT and LTA with an appropriate diene.

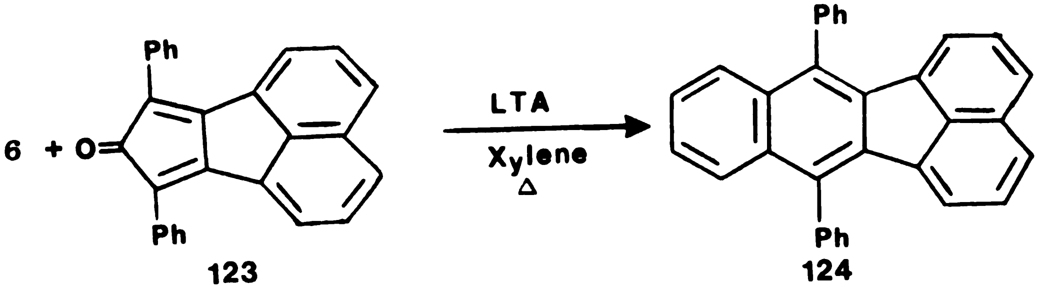
Among many dienes, tetraphenylcyclopentadienone **14** has always been a good candidate for testing aryne cyclization as shown in Table 5. For example, 1,2,3,4-tetraphenylnaphthalene **15** was readily synthesized by using this method.

Table 5. Adducts of 1,2,3,4-tetraphenylcyclopentadienone with various benzyne precursors.

Precursor	Product	Yield (%)	Reference
		95	18
	same	95	55
	same	82-90	56
		73	18
		50	51b

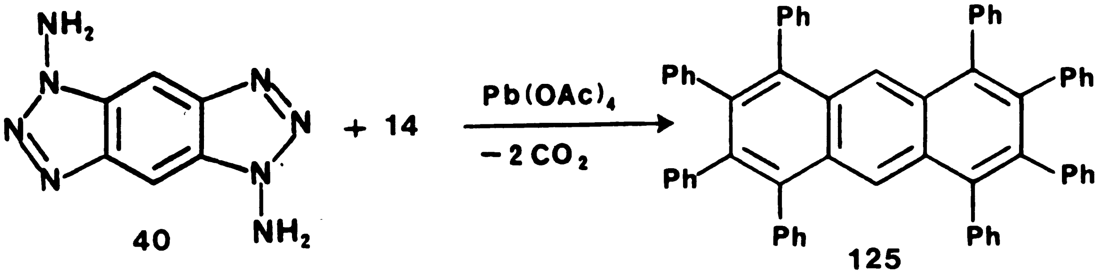


However, the addition of benzyne to the related dienone, 7,9-diphenyl-8-H-cyclopenta[a]acenaphthylene-8-one(acyclone, **123**) in boiling xylene gave the fluorescent adduct, 7,12-diphenylbenzo[k]fluoranthene **124** in only 8% yield, with a 50% yield of biphenylene. The low yield was due to insolubility of the dienone.[18]

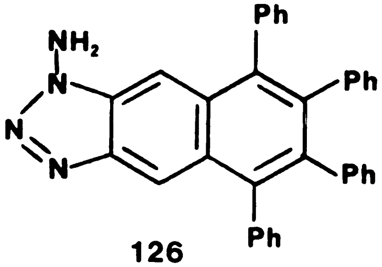


Treatment of DABT with two equivalents of **14** and LTA in boiling THF gave 1,2,3,4,5,6,7,8-octaphenylanthracene,

125, mp 415-417°C in 56% yield. However, when the reaction



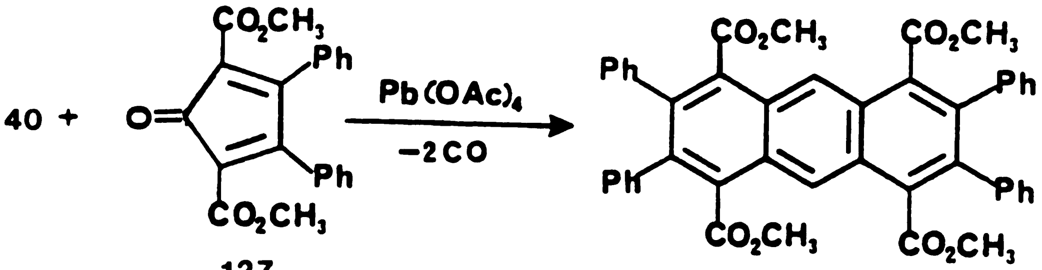
was carried out at room temperature, compound **125** was obtained in only low yield (7%) in addition to much unreacted dienone. Perhaps, the low yield was due to the poor solubility of the presumed intermediate **126** at room temperature.



126

The 250 MHz ^1H NMR spectrum (d_6-DMSO, 110°C) of **125** had a sharp singlet for the central aromatic hydrogens at δ 7.33 and aromatic multiplets at δ 7.1-6.7. The mass spectrum of **125** showed a strong M^+ peak (m/e, 786, intensity 71).

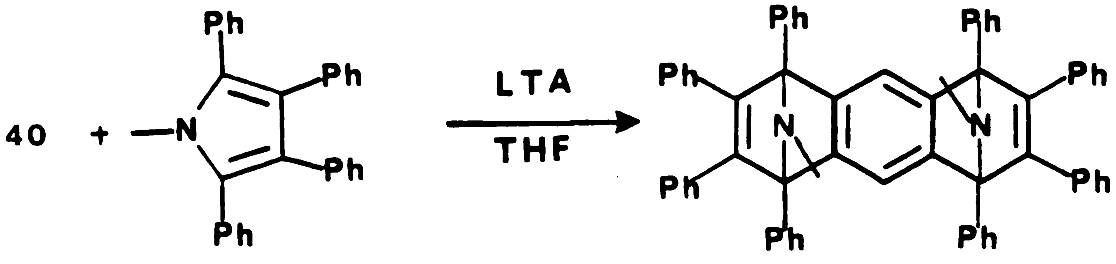
Treatment of **40** with LTA and 2,5-methoxycarbonyl-3,4-diphenylcyclopentadienone **127**[54] gave a yellowish green bis-adduct **128**, mp 375-376°C in excellent yield (93%). The structure of **128** was based upon its chemical and spectral properties. The 250 MHz ^1H NMR spectrum, with a singlet at δ 8.55 for the two central aromatic protons, twenty-proton aromatic multiplets at δ 7.25-7.07 and a singlet at δ 3.65 for four ester methyl groups, was consistent with the structure. The ^{13}C NMR spectrum of **128** had only ten peaks as required by symmetry with appropriate chemical shifts. The IR spectrum of **128** had a strong ester carbonyl band at 1721 cm^{-1}. The mass spectrum had a parent and base peak at m/e 714 and a weak fragmentation peak at m/e 683 (M^{+}-methoxyl).



127

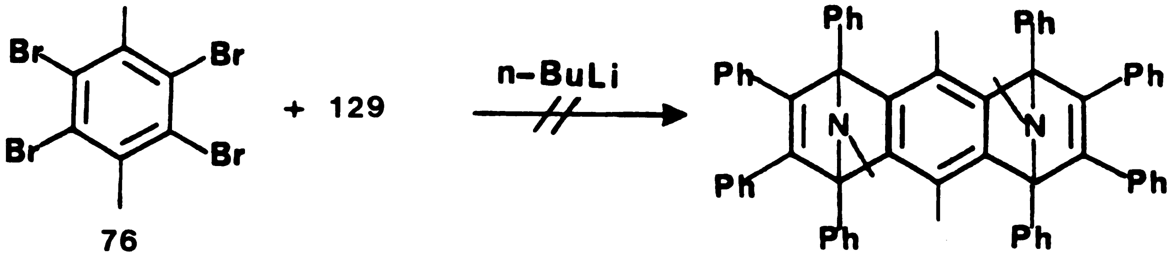
128

Reaction of DABT with LTA and N-methyl-2,3,4,5-tetraphenylpyrrole **129**[39] afforded the bis-adduct **130**, mp 205-207°C in 88% yield. Compound **130** gave the correct analysis for a bis-adduct and its 250 MHz ^{1}H NMR spectrum consisted of a multiplet at δ 7.8-6.6 for aromatic protons and a broad singlet at δ 2.12 for the methyl groups. Hart and Lai attempted to prepare a similar bis-adduct **131** from the reaction of tetrabromo-p-xylene **76** with the same diene **129** and n-BuLi. However, the bis-adduct was not formed.[39]



129

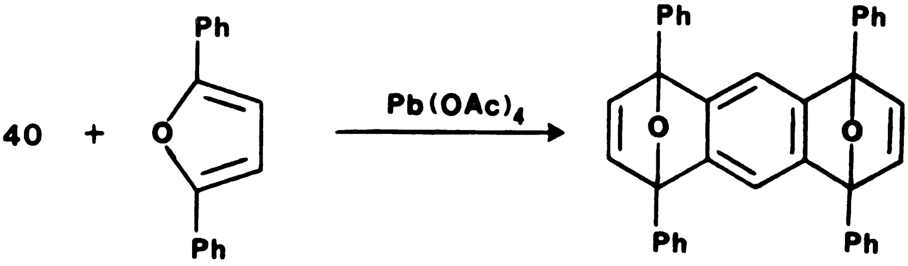
130



76

131

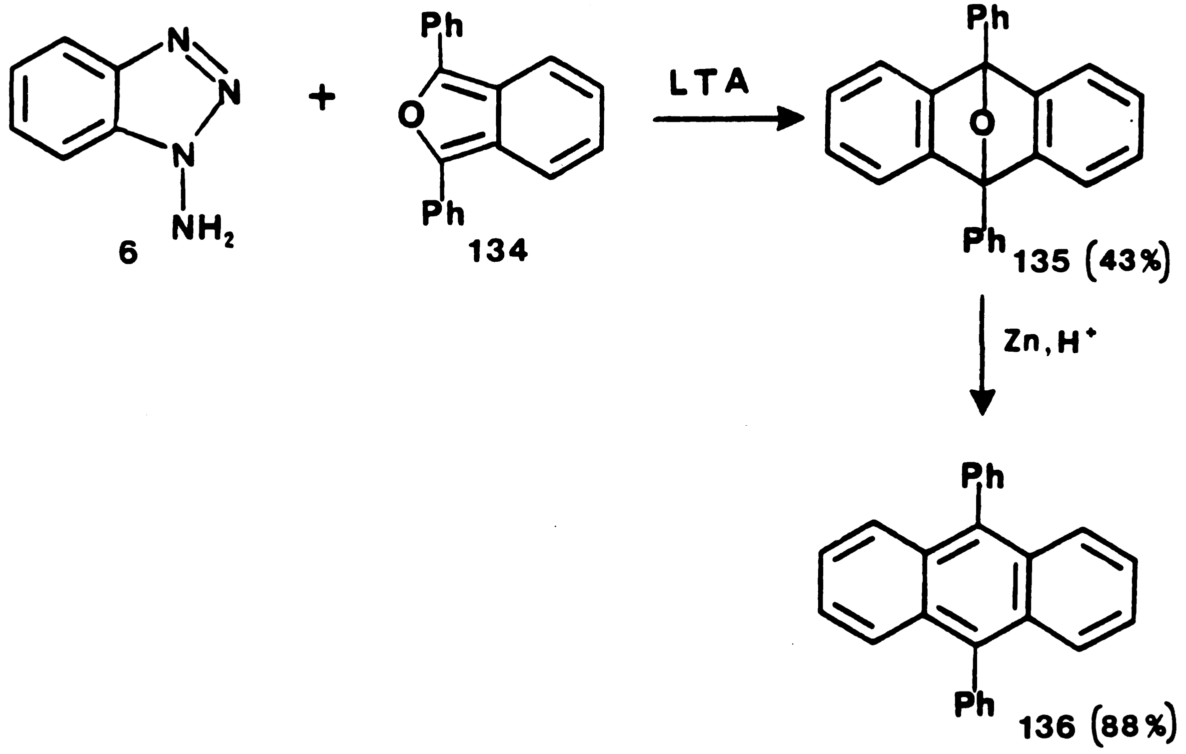
Treatment of DABT with 2,5-diphenylfuran **132** and LTA gave a bis-adduct, **133**, mp 264-265°C in 75% yield. Compound **133** gave a correct analysis. The 250 MHz ^{1}H NMR spectrum showed an aromatic multiplet at δ 7.67-7.25 and a vinyl singlet at δ 6.74. The mass spectrum of **133** had a parent and base peak at m/e 514 and a major fragmentation peak at m/e 498 (M^+-oxygen, intensity 18).



132

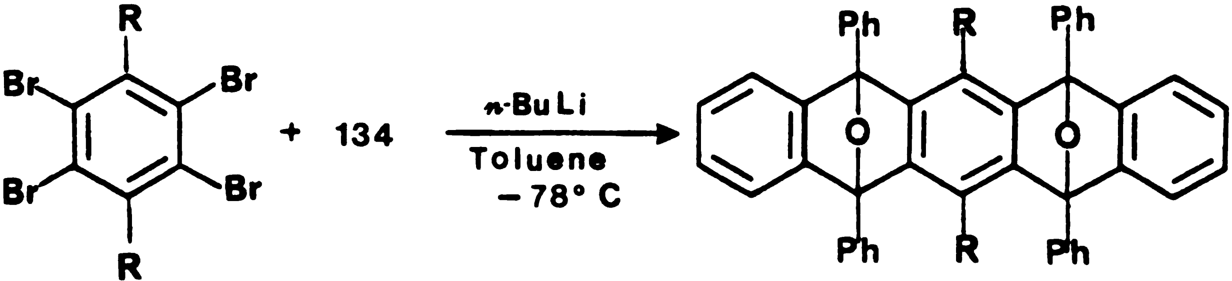
133

Campbell and Rees reported that the formation of benzyne adduct **135** was complicated by competing oxidation of the diene to o-dibenzoylbenzene, but with a large excess of the diene adduct **135** was obtained in reasonable yield (43%).[18] The oxygen bridge of **135** was easily removed to give 9,10-diphenylanthracene **136** in 88% yield.[57]



6 134 135 (43%) 136 (88%)

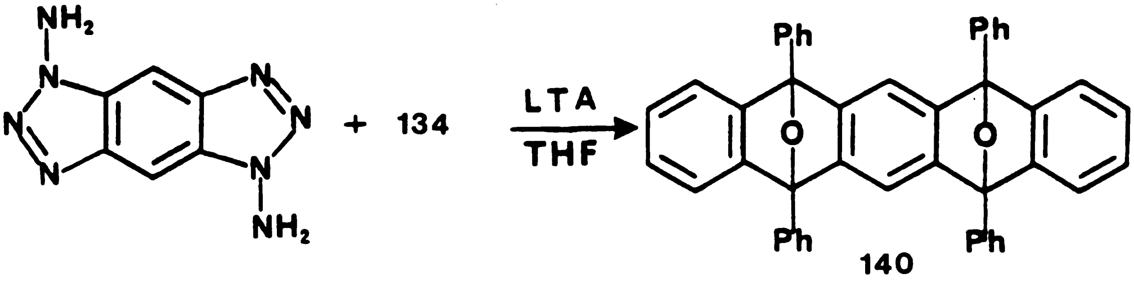
Similar bis-adducts were prepared in good yields in this laboratory using tetrabromobenzene derivatives (**76** and **138**) as diaryne equivalents.[58]



76 R = CH_3
138 R = OCH_3

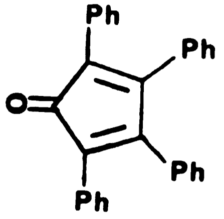
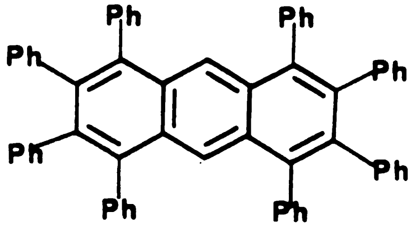
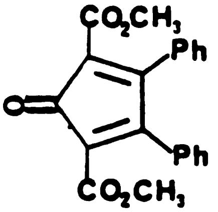
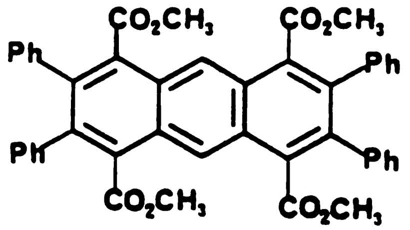
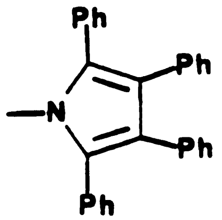
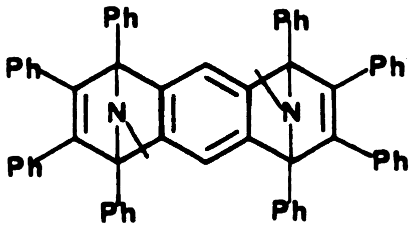
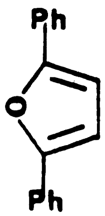
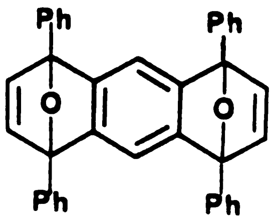
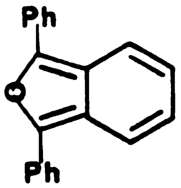
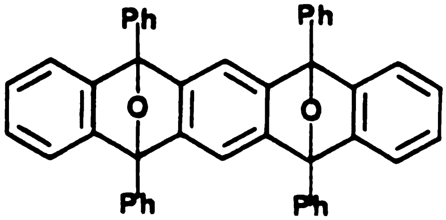
137 R = CH_3 (67%)
139 R = OCH_3 (42%)

The reaction of DABT with diene **134** gave a diadduct **140** in much higher yield (88%) than obtained in the analogous reaction with **6**. The difference in yields may be explained by the difference in reaction procedure. For the synthesis of **135** a solution of 1-aminobenzotriazole in dry benzene was added to a stirred suspension of LTA and the diene **134** at 25°C in the same solvent. In this case, LTA also oxidize the receptor diene to o-dibenzoylbenzene. On the other hand, for the bis-annulation of DABT, an inverse addition was always applied as described in previous chapter (i.e., addition of LTA to a mixture of DABT and diene). Since oxidation of DABT by LTA is very fast, the competing reaction between DABT and the diene **134** may not be possible. Compound **140** analyzed correctly. Although the 250 MHz ^1H NMR spectrum showed complicated multiplets in the aromatic region (8.2-6.85), the ^{13}C spectrum had mainly ten signals confirming that only one isomer was formed. All of these results are summarized in Table 6.

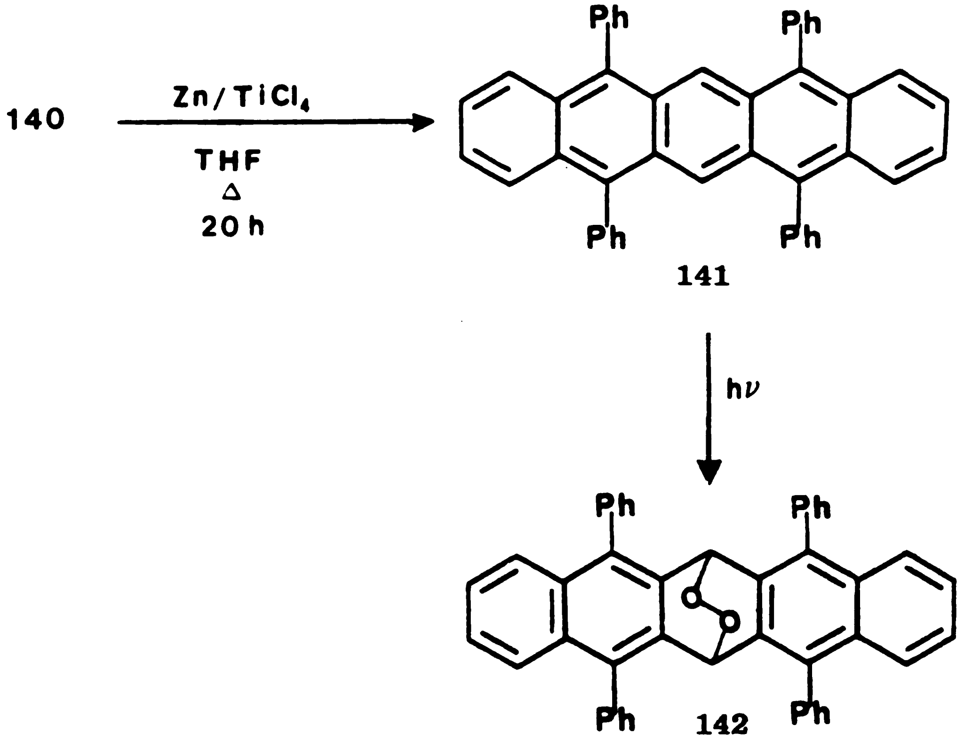


The removal of the oxygen bridges of **140** was performed by treatment with Zn-$TiCl_4$ in boiling THF for 20 h to yield 81% of 5,7,12,14-tetraphenylpentacene **141**.[59] Pentacene **141** is very reactive, and in solution absorbs atmospheric

Table 6. Di-adducts of DABT-LTA with various dienes.

Diene	**Di-adduct**	**Yield (%)**	**mp(°C)**
		56	415-417
		93	375-376
		88	205-207
		75	264-265
		88	306-308

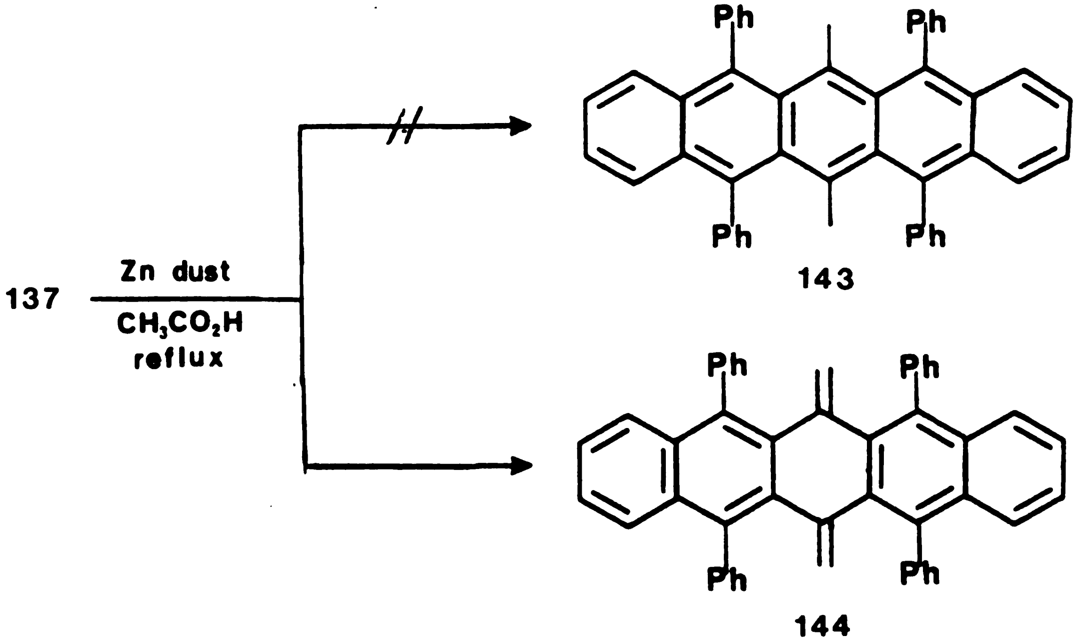
oxygen (very rapidly in sunlight) to give the peroxide



141

142

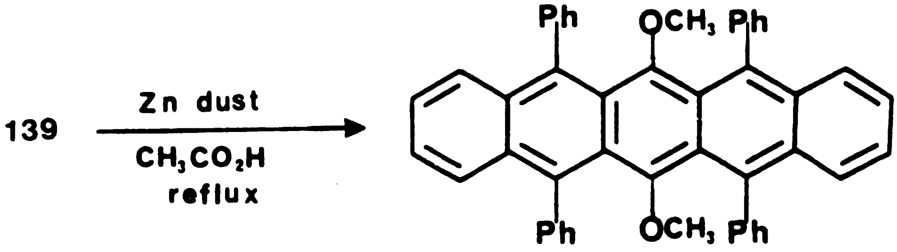
142 as reported in the literature.[59-60] The deoxygenation of 137 and 139 was studied by Hart and Shamouilian.[58] When compound 137 was refluxed in acetic acid with Zn dust



143

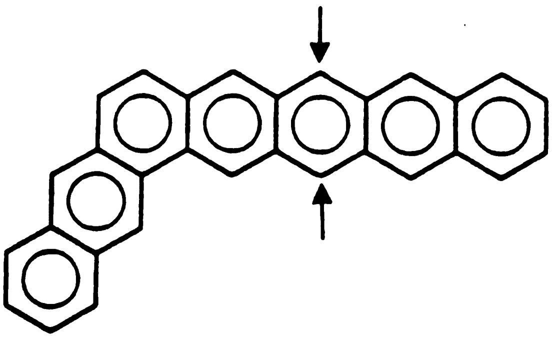
144

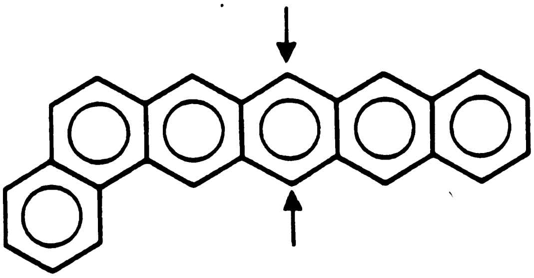
for 2 h, reaction did not proceed to give pentacene **143**; rather it gave the quinonedimethide **144** in quantitative yield. However, similar treatment of **139** with Zn in acetic acid provided the expected pentacene **145**.

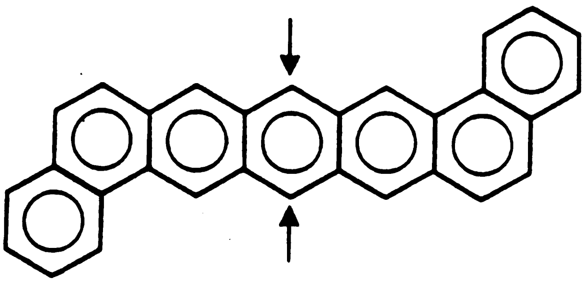


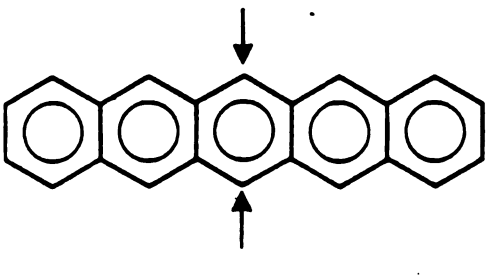
145

It was interesting to study the Diels-Alder reactivity of the 5,7,12,14-tetraphenylpentacene **141**. Biermann and Schmidt studied Diels-Alder reactivity of many polycyclic aromatic hydrocarbons with maleic anhydride.[61] The structures of the primary Diels-Alder adduct were deduced from the UV spectra of the reaction mixtures taken at regular intervals. Pentacenes were predicted to give adducts at the central aromatic ring as shown below:

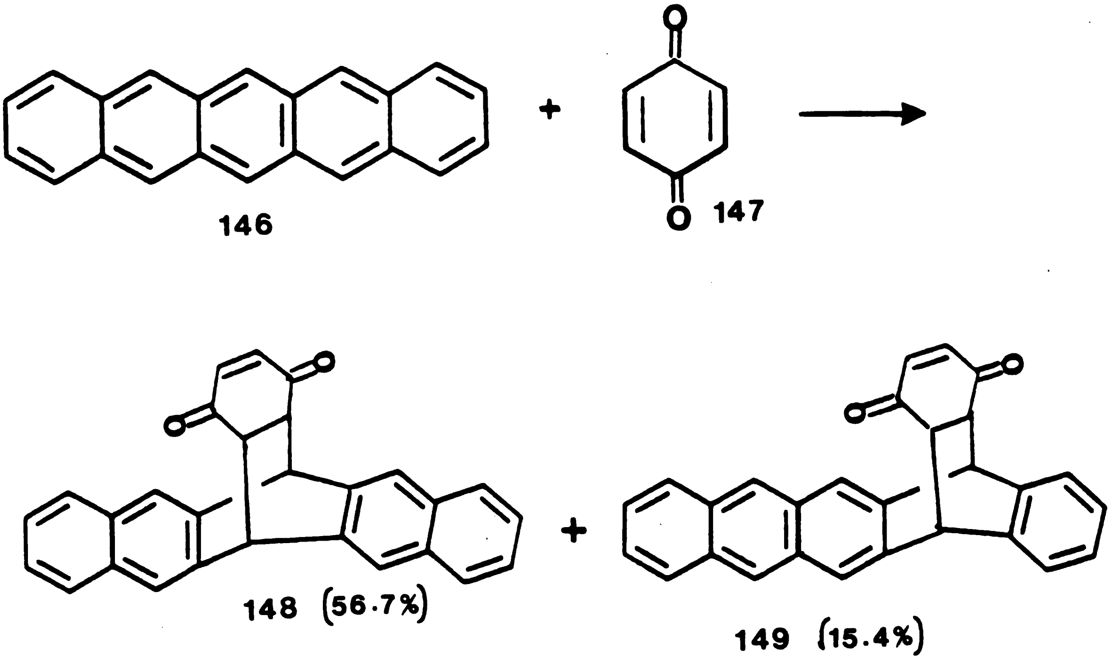








Interestingly, Russian workers reported that pentacene reacted with benzoquinone to yield two adducts, of symmetrical (**148**) and unsymmetrical (**149**) structure.^{62}



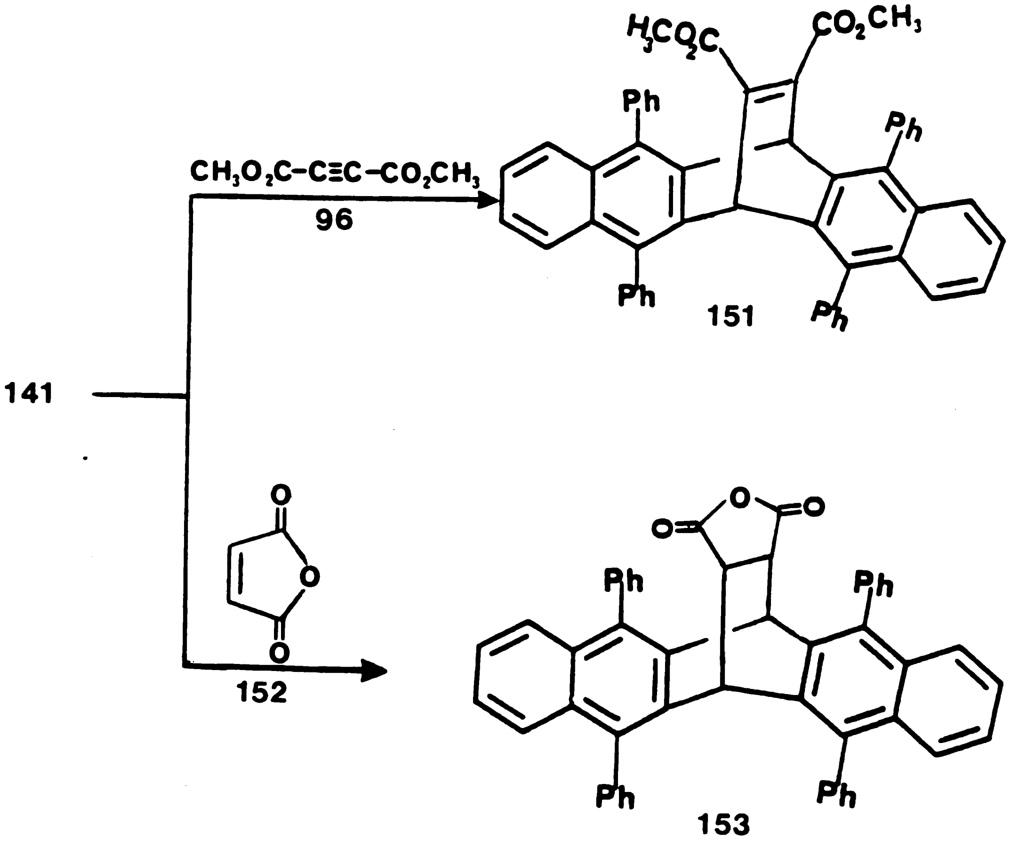
146

147

148 (56.7%)

149 (15.4%)

Compound **151**, mp 375-376°C, previously unknown, was prepared in high yield (85%) by treatment of pentacene **141** with one equivalent of dimethyl acetylenedicarboxylate. The structure follows from its analysis and spectral properties. The infrared spectrum of **151** had a strong carbonyl band at 1715 cm^{-1}. The 250 MHz ^{1}H NMR spectrum had a multiplet at δ 7.40-7.20 for the twenty phenyl protons and an AA'BB'; system centered at δ 7.50 and 7.13 ($\underline{J}$ = 4 Hz) for eight aromatic protons. In addition, there were two sharp singlets at δ 5.58 and 3.74 for two bridgehead protons and six ester protons, respectively. The ^{13}C NMR spectrum showed only thirteen signals as required by symmetry. The



mass spectrum had a parent and base peak at *m*/*e* 724. Compound **153** was obtained in fair yield (46%) from the reaction of **141** and maleic anhydride **152**. The 250 MHz NMR spectrum was clear-cut, with a peak for two bridgehead protons at δ 5.06 (*J* = 1 Hz) coupled to the two hydrogens α to the carbonyl groups at δ 3.52 (*J* = 1 Hz), in addition to multiplets at δ 7.45-6.95 for the aromatic hydrogens. The compound was found to be very unstable and even on mild heating underwent a retro Diels-Alder reaction. Therefore, compound **153** was isolated by washing the crude product with ethyl ether to remove impurities. Measurement of the melting point was attempted in a sealed capillary tube. Above 75°C, it showed a blue color and became a blue solution on further heating, presumably due to reformation of **141**. Its mass spectrum had a strong peak at m/e 582 (M^+-maleic anhydride, intensity 50) indicating a retro Diels-Alder reaction.

In summary, it was demonstrated the diaryne equivalent **40** can be converted to polyphenyl anthracenes or pentacene in one (or two) steps. This methodology can be applied as a powerful tool to synthesize various other polyphenylated arenes.

Experimental

1. **General Procedures.** ^1H NMR spectra were measured at 60 MHz (Varian T-60) or at 250 MHz on a Bruker WM-250 spectrometer using $(CH_3)_4Si$ as an internal standard. All chemical shifts are recorded in δ units. ^{13}C NMR spectra were measured at 62.89 MHz on a Bruker WM-250 spectrometer, IR spectra were determined on a Perkin Elmer Model 167 spectrometer. UV spectra were obtained on a Cary 219 spectrometer. Mass spectra were measured at 70 eV using a Finnigan 4000 spectrometer with the INCOS system, operated by Mr. Ernest Oliver or Mr. Richard Olson. Melting points were determined with an electro-thermal melting point apparatus (Fisher Scientific) or a Thomas Hoover Unimelt apparatus. Microanalyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, Michigan or by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada.

2. **Diethyl 2,5-diamino-1,4-benzenedicarboxylate (44).** A mixture of 20 g (78.7 mmol) of diethyl 2,5-diamino-1,4-dihydroterephthalate **43**[28] and 1 g of 10% palladium on carbon in 200 mL of cumene was refluxed for 12 h. The catalyst was removed by filtration and the filtrate was concentrated under reduced pressure to provide 17.6 g (89%) of crude product which was recrystallized from ethanol, mp 168°C, orange needles [lit.[28] 168°C]; ^1H NMR ($CDCl_3$) δ 7.2 (s, 2H), 4.3 (q, *J* = 7.1Hz, 4H), 5.4 (broad s, 4H), 1.35 (t, *J* = 7.1Hz, 6H); mass spectrum, *m*/*e* (relative intensity)

252 (100), 224 (20), 207 (26), 196 (15), 178 (63), 150 (23), 132 (53), 105 (13).

3. **1,5-Bis[acetylamino]-2,4-dinitrobenzene (51).** A mixture of 1,5-diamino-2,4-dinitrobenzene[30] (99 g, 0.5 mol), acetic anhydride (100 mL) and conc. sulfuric acid (20 mL) was heated under reflux for 6 h. The clear brown solution was then allowed to cool to room temperature and poured into water (3000 mL) with stirring. After the excess acetic anhydride had hydrolyzed, the brown solid was collected by filtration, washed with water and dried to yield 128 g (90%) of crude product (51). Recrystallization from acetic acid gave pure product: mp 226°C (lit.[29] mp 228°C); ^{1}H NMR ($CDCl_3$) δ 10.64 (broad s, NH—), 10.32 (s, 1H), 9.22 (s, 1H), 2.1 (s, 6H); mass spectrum, m/e (relative intensity), 282 (3), 236 (95), 194 (100), 168 (22), 148 (11).

4. **1,7-Diacetylbenzo[1,2-d:4,5-d']bistriazole (53).** 1,5-Bis[acetylamino]-2,4-dinitrobenzene (12 g, 0.0425 mol) suspended in absolute ethanol (150 mL) was hydrogenated over 3 g of 10% Pd on C on a Parr apparatus (60 psi). After removal of the solvent by filtration, the filtrate was dissolved in 400 mL of water and the catalyst* was removed by filtration. The filtrate was treated with conc. hydrochloric acid (20 mL) and a solution of sodium nitrite (8.89 g, 0.1275 mol) in water (40 mL) at 0°C over 30 min.

*The catalyst was recycled after washing with 20% aqueous potassium hydroxide solution and water.

The product was collected by filtration, washed with water and dried to yield 9.6 g (93%) of pure **53**: mp 205°C (recrystallized from ethyl acetate/hexane as yellow needles) (lit.[29] mp 239°C); ^{1}H NMR (250 MHz, $CDCl_3$) δ 9.14 (d, $\underline{J}$ = 1 Hz, 1 H), 8.87 (d, $\underline{J}$ = 1 Hz, 1H), 3.06 (s, 6H); mass spectrum, $\underline{m}/\underline{e}$ (relative intensity), 244 (16), 202 (38), 174 (8), 160 (56), 43 (100).

5. Amination of benzo[1,2-d:4,5-d']bistriazole 39 with hydroxylamine-O-sulfonic acid (54). Benzo[1,2-d:4,5-d']bistriazole[29] (6 g, 0.0375 mol) was dissolved in a solution of potassium hydroxide (19.8 g, 85% purity, 0.352 mol) in water (200 mL) at 60°C. Solid hydroxylamine-O-sulfonic acid (16.95 g, 0.15 mol) was added in portions during 1 h, the temperature being maintained at 66-68°C. The mixture was then stirred for 1 h at ca. 65°C, cooled and filtered. The alkaline solution was continuously extracted with ether for 72 h. Removal of the ether gave 3.2 g (45% yield) of a separable mixture of three isomers, 1,5-, 1,7-, and 1,6-diaminobenzo[1,2-d:4,5-d']bistriazoles in a ratio of 53:12:35. Recrystallization from ethanol afforded 1.4 g of pure 1,5-isomer (**40**) as an off-white solid. A few more crystals (0.58 g) (a mixture of 1,5- and 1,7-isomers) were obtained from the mother liquor. Concentration of the mother liquor gave mainly the 1,6-isomer (**63**) (1.2 g, purity >95%, determined by integrating the peak at δ 8.24 and δ 8.59, 7.96 of ^{1}H NMR spectrum). After extraction the resulting basic solution was neutralized with 10% aqueous hydrochloric acid to provide a mixture of mono-aminated products (3.2 g, 48% yield). For 1,5-Diamino-benzo[1,2-d:4,-5-d']bistriazole (DABT) (**40**): mp 292°C (decomp); ^{1}H NMR (250 MHz, d_6-DMSO) δ 8.24 (s, aromatic H), 7.18 (s, $-NH_2$); ^{13}C NMR (d_6-DMSO) δ 144.16, 131.40, 97.43 coupled ^{13}C NMR (d_6-DMSO) δ 144.38 (_J_ = 1 Hz), 131.65 (_J_ = 1 Hz), 99.13, 96.37; mass spectrum, _m_/_e_ (relative intensity) 190 (16), 162 (14), 133 (27), 118 (19), 105 (100), 78 (52), 63 (45), 51 (66); IR (KBr) 3386, 3610, 3020, 1600, 1520, 1440, 1310, 1040, 923 cm^{-1}. _Anal_ Calcd. for $C_6H_8N_8$: C, 37.90; H, 3.18; N, 58.92. Found: C, 37.96; H, 3.18; N, 58.81. For 1,7-diamino-benzo[1,2-d:4,5-d']bistriazole (**41**): mp 263°C; ^{1}H NMR (250 MHz, d_6-DMSO) δ 8.69 (d, 1H, _J_ = 1Hz), 7.71 (d, 1H, _J_ = 1Hz), 7.09 (s, 4H, $-NH_2$); ^{13}C NMR (d_6-DMSO) δ 142.93, 133.32, 108.42, 87.43; coupled ^{13}C NMR (d_6-DMSO) δ142.92 (_J_ = 1 Hz), 133.26 (_J_ = 1 Hz), 109.78, 107.07, 88.83, 86.04; mass spectrum, _m_/_e_ (relative intensity) 190 (13), 162 (12), 147 (7), 133 (39), 105 (100), 78 (61), 63 (29), 51 (57); IR (KBr) 3320, 3275, 3160, 1635, 1375, 1310, 1278, 1262, 1160, 1090 cm^{-1}. High resolution mass spectrum: Calcd. for $C_6H_6N_8$: 190.07154; Found: 190.07157. For 1,6-Diamino-benzo[1,2-d:4,5-d']bistriazole (**63**): mp 271-273°C as a light-tan solid from ethanol: ^{1}H NMR (250 MHz, d_6-DMSO) δ 8.59 (d, 1H, _J_ = 1Hz), 7.96 (d, 1H, _J_ = 1Hz), 7.09 (s, 4H); ^{13}C NMR(d_6-DMSO) δ 143.36, 139.98, 138.87, 132.72, 104.63, 91.08; mass spectrum, _m_/_e_ (relative intensity) 190 (2), 184 (6), 175 (17), 160 (74), 147 (30), 132 (35), 118 (26), 105 (20), 90 (39), 85 (33), 77 (58), 52 (100); IR (KBr) 3280, 3170, 1600, 1260, 970, 840 cm^{-1}. High resolution mass spectrum: Calcd. for $C_6H_6N_8$: 190.07154; Found: 190.07194. For 1-Amino-benzo[1,2-d:4,5-d']bistriazole (**64**): mp > 400°C as a light-tan solid from ethanol: ^{1}H NMR (250 MHz, d_6-DMSO) δ 8.10 (d, 1H, *J* =1Hz), 7.65 (d, 1H, *J* = 1Hz), 6.83 (s, 2H); ^{13}C NMR (d_6-DMSO) δ 146.19, 144.96, 142.18, 130.54, 101.60, 90.66; mass spectrum (not available because of the high melting point of the product); IR (KBr) 3250, 1620, 1313, 1282, 1180, 1120, 875, 847, 805 cm^{-1}.

6. **O-(2,4-Dinitrophenyl)hydroxylamine (57).** The following procedure is an improvement on the method of Tamura.[32c] The reaction using the same procedure and scale as described by Tamura, *et*. *al*., always gave starting material. Consequently, a modified procedure was developed which is quite different in terms of material balance and reaction time. To a stirred solution of ethyl O-(2,4-dinitrophenyl)acetohydroxamate[32c] (3 g, 11.15 mmol) in dioxane (30 mL) was added 70% of perchloric acid (20 mL, 223 mmol) at 25°C over 10 min. Stirring was continued at room temperature for 20 h and the mixture was then poured into ice water to give a yellow solid which was filtered and washed with water. Recrystallization from ethanol afforded 1.45 g (65%) of **57** as pale yellow needles; mp 112-113°C (lit.[32c] mp 112-113°C); ^{1}H NMR ($CDCl_3$) δ 8.7 (d, *J* = 3 Hz, 1H), 8.4 (dd, *J* = 10 and 3 Hz), 7.9 (d, *J* = 10 Hz, 1H), 6.9

(broad s, 2H, $-NH_2$).

7. Amination of benzo[1,2-d:4,5-d']bistriazole with O-(2,-4-dinitrophenyl)hydroxylamine. To a solution of 6 g (37.5 mmol) of benzobistriazole **39** in 160 mL of dry dimethylformamide under Ar was added 3.3 g (2.2 equiv.) of 60% sodium hydride oil dispersion (NaH was freed of mineral oil by washing with dry hexane) for a period of 5 min. The mixture was then stirred at 90-100°C for 1 h. After cooling, to room temperature, 14.93 g (75 mmol) of O-(2,4-dinitrophenyl)-hydroxylamine in 120 mL of dry DMF was added over 30 min. The mixture was stirred at room temperature for 1 h, then poured into 700 mL of dry ether. The precipitated yellow solid was filtered and the filtrate was concentrated under reduced pressure to afford 8.3 g of a red oil consisting of aminated products contaminated with DMF. An aqueous potassium hydroxide solution (12.6 g in 100 mL H_2O) was added to the oil and the mixture was stirred at 70°C for 1 h. After cooling the product was obtained by continuous extraction with ether for 72 h. The ether extract was evaporated to afford a mixture of three isomeric bis-adducts in a ratio 54:9:37 of compounds **40:41:63**. Several runs on this scale gave yields varying from 1.86 g to 4.6 g (26-65%). After extraction, the resulting basic solution was neutralized with 10% aqueous hydrochloric acid to give mono-aminated products which were recycled.

8. 1,4,5,8-Tetramethyl-1,4,5,8-tetrahydroanthracene-1,4:5,-8-diendoxide (73). This is a representative oxidation procedure for the use of DABT **40** as a diaryne equivalent. To a mixture of 0.13 g (0.684 mmol) of DABT and 0.657 g (6.842 mmol) of 2,5-dimethylfuran in 100 mL of dry THF at room temperature was added in portions 0.667 g (1.5 mmol) of lead tetraacetate (LTA) in 30 mL of dry tetrahydrofuran (THF) over a period of 30 min. After 10 min additional stirring, the lead diacetate was filtered, the filtrate was diluted with 500 mL of water and extracted three times with 100-mL portions of methylene chloride. The combined extracts were washed with saturated $NaHCO_3$ solution, saturated NaCl solution and dried over $MgSO_4$. Removal of the solvent and chromatography of the remaining solid on activated alumina with 1:1 chloroform:hexane gave 0.147 g (81%) of **73** as a mixture of two isomers in the ratio of 19:81 (determined by integrating the peaks at δ 6.78 and 6.76 in the 250 MHz ^1H NMR spectrum); white solid, mp 229°C (decomposition). The isomer mixture had the following spectral properties: ^1H NMR (250 MHz, $CDCl_3$) δ 6.96 (s, aromatic), 6.78 (s, minor, vinyl), 6.76 (s, major, vinyl), 1.87 (s, major, methyl), 1.86 (s, minor, methyl); ^{13}C NMR ($CDCl_3$) δ 151.14, 147.26 (major), 147.43 (minor), 110.62 (major), 110.32 (minor), 88.74, 15.33; mass spectrum, _m_/_e_ (relative intensity) 266 (5), 240 (9), 214 (7), 197 (33), 181 (18), 165 (13), 43 (100); IR (KBr) 3065, 2980, 2935, 1440, 1385, 1305, 1290, 1240, 1135 cm^{-1}.

9. 1,4,5,8-Tetrahydroanthracene-1,4:5,8-diendoxide (71). In a procedure similar to that used for **73**, reaction of **40** (0.2 g, 1.052 mmol) with excess furan (0.716 g, 10.52 mmol) in dry THF (50 mL) and LTA (1.03 g, 2.32 mmol) gave a crude reaction mixture. Flash chromatography of this crude product over slica gel, eluting with chloroform, gave 0.147 g (80%) of **71** as a mixture of two isomers. Separation of the isomers was not attempted. The 250 MHz proton NMR spectrum clearly indicated the presence of two isomers in the ratio of 77:23 (determined by integrating the peaks at δ 7.20 and 7.19); white solid, mp 196-203°C (lit.[21d] syn, mp 191-193°C, anti, mp 245°C). The isomer mixture had the following spectral properties: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.20 (s, major, aromatic H), 7.19 (s, minor, aromatic H), 7.02 (s, 4H), 5.63 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 147.82, 143.56 (minor), 143.40 (major), 114.10 (major), 113.85 (minor), 82.36; mass spectrum, m/e (relative intensity) 210 (41), 153 (100), 184 (28), 128 (22); IR (KBr) 3095, 3030, 1440, 1335, 1293, 1155, 995, 860, 750 cm^{-1}.

In this experiment when 2.1 mmol of furan was used under otherwise similar conditions, the yield of bis-adduct decreased to 79%.

The reaction was also repeated as follows: To a stirred suspension of 2.57 g (5.79 mmol) of LTA and 1.8 g (26.47 mmol) of furan in 100 mL of dry THF at room temperature under argon, was added 0.5 g (2.631 mmol) of **40** suspended in the same solvent (50 mL) over 30 min (upon addition no evolution of N_2 was observed). After additional stirring for 1 h, 5 mL of ethylene glycol was added prior to addition of water (500 mL). Filtration and drying gave 0.5 g of unreacted **40** (quantitative recovery).

10. **1,4,5,8-Tetramethyl-1,4,5,8-tetrahydroanthracene-1,4:5,-8-diendoxide (73) from 41.** In a procedure similar to that used for the preparation of **73** from **40**, reaction of 1,7-di-amino-benzo[1,2-d:4,5-d']bistriazole **41** (0.31 g, 1.63 mmol) with 2,5-dimethylfuran (0.35 g, 3.64 mmol) in dry THF (100 mL) with LTA (1.59 g, 3.58 mmol) gave a crude product. Chromatography of this crude product over silica gel using 1:1 chloroform:ether as eluent provided 0.35 g (80%) of bis-adduct **73** as a mixture of the syn and anti isomers, ratio 19/81 (determined by integrating the peaks at δ 6.78 and 6.76 in the ^{1}H NMR spectrum), identical with the independently synthesized material from 1,5-diamino-benzo[1,2-d:-4,5-d']bistriazole **40**; mp 229°C (decomposition), white solid; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.96 (s, 2H), 6.78 (s, minor), 6.76 (s, major), 1.87 (s, major), 1.86 (s, minor, methyl).

11. **1,4,5,8-Tetramethylanthracene (75).** A solution of **73** (0.7 g, 2.63 mmol) in 70 mL of absolute ethanol containing 0.03 g of 10% palladium on charcoal was hydrogenated at 60 psi and room temperature over 2 h. The mixture was filtered and 10 mL of concentrated hydrochloric acid was added to the colorless filtrate. The mixture was refluxed for 1 h, cooled, poured into 200 mL of water and extracted

twice with 50 mL of methylene chloride. The combined organic extracts were washed twice with 50 mL of saturated sodium bicarbonate solution and dried over magnesium sulfate. Removal of the solvent under reduced pressure gave crude product which was recrystallized from ethyl acetate to afford pure **75** (0.5 g 83%): mp 220°C [lit.[38] 221-222°C]; ^{1}H NMR ($CDCl_3$)δ 8.53 (s, 2H), 7.15 (s, 4H), 2.73 (s, 12H); mass spectrum, m/e (relative intensity) 234 (100), 219 (35), 202 (13), 178 (3), 117 (1), 40 (18).

12. **Bis-(N-methyl)-2,3,6,7-tetramethyl-1,4,5,8-tetraphenyl-1,4,5,8-tetrahydroanthracene-1,4:5,8-bisimine (80).** In a procedure similar to that used for **73**, reaction of **40** (0.267 g, 1.4 mmol) with 2,5-diphenyl-1,3,4-trimethylpyrrole[39] (0.73 g, 2.8 mmol) in dry THF (60 mL) and LTA (1.37 g, 3.08 mmol) gave, after workup, a grey residue. Chromatography of this crude product over silica gel using 2:3 chloroform:benzene as eluent gave 0.64 g (77%) of a pure isomer (**80**) which was recrystallized from ethyl acetate/hexane; white crystals, mp 273-275°C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.6-7.2(m, 22H), 1.8 (s, 12H), 1.6 (s, 6H); ^{13}C NMR ($CDCl_3$) δ130.52, 130.06, 130.02, 129.04, 128.35, 128.02, 127.72, 31.47, 29.66, 12.70; mass spectrum, m/e (relative intensity) 596 (2), 542 (1), 424 (2), 118 (100), 56 (33); IR (KBr) 3065, 3035, 2940, 2860, 1600, 1495, 1450, 1295, 1155 cm^{-1}. Anal. Calcd. for $C_{44}H_{40}N_2$: C, 88.55; H, 6.76; N, 4.69. Found: C, 88.23; H, 6.63; N, 4.58.

13. Reaction of 40 with 2,3-bis(methylene)-bicyclo[2.2.1]-heptane (83)[40]. In a procedure similar to that used for **73**, reaction of **40** (0.28 g, 1.47 mmol) with 2,3-bis(methylene)-bicyclo[2.2.1]heptane[40] (0.39 g, 3.25 mmol) suspended in 100 mL of dry THF with lead tetraacetate (1.5 g, 3.38 mmol) gave a grey residue. Recrystallization of the crude product from ethyl acetate/hexane furnished 0.43 g (93%) of **83** as a mixture of the syn and anti isomers, mp 245-250°C, white solid: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.56 (s) and 7.43 (s), (minor), 6.96 (s, major), 3.35 (s, 8H), 2.70 (m, 4H), 1.80-0.9 (m, 12H); mass spectrum, m/e (relative intensity) 314 (31), 286 (13), 253 (10), 245 (6), 229 (6), 217 (19), 179 (13), 129 (12), 115 (23); IR (KBr) 2942, 2855, 2810, 1428, 1277, 1100 cm^{-1}. High resolution mass spectrum: Calcd. for $C_{24}H_{26}$: 314.20344; Found: 314.20368.

14. Tetraethyl 1,4,5,8-tetrahydroanthracene-1,4:5,8-diendoxide-2,3,6,7-tetracarboxylate (87). In a procedure similar to that used for **73**, reaction of **40** (0.68 g, 3.57 mmol) with diethyl 3,4-furandicarboxylate[43] (1.52 g, 7.14 mmol) in dry THF (200 mL) and LTA (3.4 g, 7.67 mmol) gave a yellow solid. Chromatography of the crude product on silica gel with 1:1 ethyl acetate:petroleum ether gave 0.71 g (40%) of a single bis-adduct (**87**); mp 188-190°C (after recrystallization from ethyl acetate); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.45 (s, 2H), 5.90 (s, 4H), 4.30 (q, 8H, J = 7 Hz), 1,35 (t, 12H, J = 7Hz); ^{13}C NMR ($CDCl_3$) δ 162.50, 151.31, 146.52, 115.76, 85.18, 61.54, 14.07; mass spectrum, m/e (relative intensity) 498 (20), 425 (7), 381 (51), 350 (91), 328 (30), 254 (100), 226 (45), 158 (27), 139 (27); IR (KBr) 2983, 1695, 1628, 1465, 1442, 1395, 1290, 1215, 1125 cm^{-1}. High resolution mass spectrum: Calcd. for $C_{26}H_{26}O_{10}$: 498.15258. Found: 498.15282.

15. **Tetraethyl 1,4,5,8-tetramethyl-1,4,5,8,-tetrahydroanthracene-1,4:5,8-diendoxide-2,3,6,7-tetracarboxylate (89).** In a procedure similar to that used for **73** reaction of **40** (0.65 g, 3.42 mmol) with diethyl 2,5-dimethylfuran-3,4-dicarboxylate[44] (1.642 g, 6.84 mmol) in dry THF (100 mL) and LTA (3.34 g, 7.52 mmol) gave a yellow residue. Flash chromatography of this crude product over silica gel with 1:1 chloroform:hexane as eluent gave 1.26 g (67%) of one isomeric bis-adduct (**89**). An analytical sample was obtained by recrystallization from ethyl acetate; colorless needles, mp 233-236°C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.19 (s, 2H), 4.18 (q, 8H, J = 7 Hz), 1.95 (s, 12H), 1.29 (t, 12H, J = 7 Hz); ^{13}C NMR ($CDCl_3$) δ 163.00, 153.14, 149.81, 112.91, 112.32, 61.36, 61.24, 14.02; mass spectrum, m/e (relative intensity) 554 (10), 512 (9), 466 (8), 378 (41), 310 (5), 296 (28), 267 (9), 214 (16), 43 (100); IR (KBr) 2990, 2940, 1700, 1628, 1445, 1385, 1370, 1310, 1260, 1145 cm^{-1}. Anal. Calcd. for $C_{30}H_{34}O_{10}$: C, 64.97; H, 6.18. Found: C, 64.86; H, 6.15.

16. Dimethyl 1,4,5,8-tetrahydroanthracene-1,4:5,8-diendoxide-1,5-dicarboxylate (91). In a procedure similar to that used for **73**, reaction of **40** (1.0 g, 5.26 mmol) with methyl 2-furoate[43] (1.46 g, 11.6 mmol) in dry THF (100 mL) and LTA (5.13 g, 11.6 mmol) gave a crude product which was triturated with pentane (10 mL) followed by ether (20 mL). The residue was then chromatographed over silica gel (1:3 ethyl acetate:hexane) to give 0.8 g (47%) of a pure product (**91**). Recrystallization from ethyl acetate gave an analytical sample; white crystals, mp 240-242°C, ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.35 (s, 2H), 7.10 (s, vinyl H), 7.08 (s, vinyl H), 5.74 (s, bridgehead H), 4.07 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 168.05, 147.07, 144.05, 142.84, 113.96, 96.11, 82.47, 66.05, 52.82; mass spectrum, *m/e* (relative intensity) 326 (29), 300 (25), 274 (15), 239 (25), 213 (100), 179 (34), 152 (43), 126 (15); IR (KBr) 3130, 3095, 3040, 2960, 1760, 1445, 1350, 1200, 1150 cm^{-1}. *Anal*. Calcd. for $C_{18}H_{14}O_6$: C, 66.26; H, 4.32. Found: C, 66.23; H, 4.40.

17. Aromatization of dimethyl 1,4,5,8-tetrahydroanthracene-1,4:5,8-diendoxide-1,5-dicarboxylate (91). Diepoxide **91** (0.21 g, 0.648 mmol) dissolved in ethanol (50 mL) was hydrogenated in the presence of 10% Pd/C (20 mg) for 2 h and the catalyst was filtered. The resulting solution was refluxed with conc. HCl (3 mL) for 12 h and cooled to room temperature. The reaction mixture was poured into water (500 mL), extracted with methylene chloride (3 X 50 mL), washed with saturated aqueous sodium bicarbonate solution (3 X 100 mL), dried ($MgSO_4$) and concentrated in vacuo to yield 0.22 g (96%) of the transesterified product **93**. The diethyl ester **93** (0.22 g, 0.614 mmol) was treated with conc. HCl (3 mL) in acetic anhydride (30 mL) and refluxed for 2 h to afford 0.17 g (81%) of diethyl anthracene-1,5-dicarboxylate **94** as a yellow solid: mp 185°C [lit.[46] 185°C); 250 MHz ^1H NMR ($CDCl_3$) δ 9.67 (s, 2 H), 8.31 (m, 2H), 7.50 (m, 47), 4.53 (q, 4 H, *J* = 7 Hz), 1.51 (t, 6 H, *J* = 7 Hz).

18. Dimethyl 2,3-diphenyl-3-hydroxy-2,3-dihydrofuran-4,5-dicarboxylate (97). Benzoin (8.60 g, 40.5 mmol) and 6.9 g (48.6 mmol) of dimethyl acetylenedicarboxylate were heated at reflux for 20 h in 150 mL of acetone containing 5 g of potassium carbonate. The mixture was cooled, poured onto ice, and extracted with methylene chloride. The mixture was dried and the solvent evaporated to yield 6.2 g (40%) of crude solid which was recrystallized from methanol; white crystals, mp 116°C (lit.[47] 116-117°C); ^1H NMR ($CDCl_3$) δ 7.4-7.0 (m, 10H), 4.0 (s, 3H), 3.6 (s, 3H), 3.0 (s, 1H).

19. Dimethyl 4,5-diphenylfuran-2,3-dicarboxylate (98). The dihydrofuran **97** (5 g, 14.1 mmol) from above was refluxed for 1 h in 200 mL of methanol containing 1 mL of conc. sulfuric acid and the mixture was poured onto ice and extracted three times with 30-mL portions of methylene chloride. The combined extracts were washed twice with

50-mL portions of saturated sodium bicarbonate solution, once with 50 mL of saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Removal of the solvent yielded 4.25 g (85%) of **98** which was recrystallized from methanol, white crystals, mp 87-89°C (lit.[47] 87-89°C); ^{1}H NMR ($CDCl_3$) δ 7.39-7.29 (m, 10H), 3.95 (s, 3H), 3.77 (s, 3H).

20. Tetramethyl 3,4,7,8-tetraphenyl-1,4,5,8-tetrahydroanthracene-1,4:5,8-diendoxide-1,2,5,6-tetracarboxylate (99). The procedure was similar to that used for **73** except that the reaction was carried out at reflux. Reaction of **40** (0.4 g, 2.1 mmol) with dimethyl 4,5-diphenylfuran-2,3-dicarboxylate47 (1.41 g, 4.2 mmol) in dry THF (100 mL) and LTA (2.05 g, 4.62 mmol) gave a crude product. Recrystallization from chloroform afforded 1.22 g (78%) of one isomeric bis-adduct (**99**) as colorless needles, mp 283-287°C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.11 (s, 2H), 7.45-7.1 (m, 20H), 3.97 (s, 6H), 3.61 (s, 6H); ^{13}C NMR (not available because of poor solubility); mass spectrum, m/e (relative intensity) 746 (trace), 586 (5), 426 (28), 129 (29), 105 (100); IR (KBr) 3060, 2960, 1775 (C=O), 1725 (C=O), 1445, 1343, 1205, 1165, 1029 cm^{-1}. Anal. Calcd. for $C_{46}H_{34}O_{10}$: C, 73.99; H, 4,59. Found: C, 73.79; H, 4.70.

In this experiment when the reaction was carried out at room temperature, no trace of bis-adduct was observed and the diene used as the trapping agent was recovered quantitatively.

21. 2,6-Dibromo-1,4,5,8-tetrahydroanthracene-1,4:5,8-diendoxide (101). In a procedure similar to that used for **73**, reaction of **40** (0.92 g, 4.842 mmol) with 3-bromofuran[43] (1.565 g, 10.6 mmol) in dry THF (100 mL) and LTA (5.15 g, 11.6 mmol) gave, after the usual workup, a grey residue. Recrystallization of this crude product from chloroform afforded 1,23 g (69%) of a single bis-adduct; white crystals, mp 115°C (decomposition); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.32 (s, 2H), 6.96 (d, 2H, $\underline{J}$ = 2 Hz), 5.69 (broad s, 2H), 5.38 (d, 2H, $\underline{J}$ = 2 Hz); ^{13}C NMR (not available because of the poor solubility of the product); mass spectrum, $\underline{m}/\underline{e}$ (relative intensity) 368 (20), 289 (7), 287 (6), 262 (14), 180 (37), 152 (100), 126 (16); IR (KBr) 3090, 3020, 1573, 1335, 1237, 1210, 1122, 1028, 985 cm^{-1}. Anal. Calcd. for $C_{14}H_8Br_2O_2$: C, 45.69; H, 2.19. Found: C, 45.55; H, 2.27.

22. Bis-[2-Methyl-3-phenyl-2,3-dihydro]benzo[1,2-d:4,5-d']diisoxazole (107). In a procedure similar to that used for **73**, reaction of **40** (0.504 g, 2.653 mmol) with N-methyl-α-phenylnitrone[49] (0.717 g, 5.306 mmol) in dry THF (100 mL) and LTA (2.6 g, 5.86 mmol) gave a yellow solid. This solid was flash chromatographed on silica gel (3:1 ethyl acetate:hexane), yielding one pure bis-adduct (**107**), 0.83 g, 91%). An analytical sample was obtained by preparative TLC on silica gel (1:1 ethyl acetate:hexane); white crystals, mp 142-143°C; ^{1}H NMR (250 mHz, $CDCl_3$) δ 7.38 – 7.33 (m, phenyl 10H), 6.42 (s, central aromatic 2H), 5.04 (s, benzylic 2H), 2.94 (s, N-methyl 6H); ^{13}C NMR ($CDCl_3$) δ 151.05, 129.88

(overlap), 128.62, 128.26, 127.82, 103.53, 77.00, 45.94; mass spectrum, m/e (relative intensity) 344 (100), 329 (31), 314 (83), 286 (24), 267 (49), 115 (63); IR (KBr) 3095, 3040, 2965, 2880, 2830, 1460, 1340, 1165, 1145 cm^{-1}. Anal. Calcd for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.79; H, 5.85; N, 8.10.

23. **N-Methyl-α-2,4,6-trimethylphenylnitrone (108).** Freshly distilled mesitylaldehyde (10 g, 67.56 mmol) was added to a 250-mL round-bottomed flask containing N-methylhydroxylamine hydrochloride (7.05, 8.44 mmol) in methylene chloride (150 mL). Sodium bicarbonate (20 g, 238 mmol) was added to the flask, and the reaction mixture was refluxed for 12 h. When the mixture cooled, the sodium bicarbonate was filtered and washed with methylene chloride, and the solvent was removed at reduced pressure to yield 11 g (92%) of crude product **(108)**. Recrystallization from ethyl acetate gave pure product: mp 172-173°C: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.50 (s, vinyl, 1 H), 6.84 (s, aromatic, 2 H), 3.82 (s, $N\text{-}CH_3$, 3H), 2.24 (s, 3 H), 2.26 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 138.82, 136.99, 135.08, 127.93, 125.46, 52.77, 20.71, 19.36; mass spectrum, m/e (relative intensity) 177 (9), 162 (100), 145 (24), 115 (10); IR (KBr) 3080, 2910, 1570, 1440, 1410, 1395, 1370, 1180, 1038 cm^{-1}. Anal. Calcd. for $C_{11}H_{15}NO$: C, 132.12; H, 15.12; N, 14.01. Found: C, 74.41 ; H, 8.78; N, 7.81 .

24. **Bis-[2-Methyl-3-(2',4',6'-trimethylphenyl)-2,3-dihydro]-benzo[1,2-d:4,5-d']diisoxazole (109).** In a procedure similar

to that used for **73**, reaction of **40** (0.227 g, 1.194 mmol) with N-methyl-α-(2,4,6-trimethylphenyl)-nitrone **108** (0.42 g, 2.388 mmol) in dry THF (50 mL) and LTA (1.16 g, 2.616 mmol) gave a crude product which was flash chromatographed on silica gel (3:2 ether:chloroform) to provide 0.40 g (78%) of **109** (single isomer); white solid, mp 239-241°C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.85 (s, mesityl 4H), 6.14 (s, central aromatic 2H), 5.66 (s, benzylic 2H), 2.96 (s, N-methyl 6H), 2.30 (broad s, 12H), 2.27 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 151.22, 141.70, 139.05, 138.05, 130.12, 130.09, 129.17, 101.38, 72.59, 46.45, 20,83; mass spectrum, m/e (relative intensity) 428 (100), 413 (10), 384 (84), 309 (19), 160 (3), 133 (21); IR (KBr) 3010, 2960, 2920, 2860, 1610, 1475, 1440, 1315, 1160 cm^{-1}. High resolution mass spectrum: Calcd. for $C_{28}H_{32}N_2O_2$: 428.24636; Found: 428.23901.

25. Attempted synthesis of 1,4-dimethyl-1,4,5,8-tetrahydroanthracene-1,4:5,8-diendoxide (110). To a stirred mixture of **40** (0.29 g, 1.5 mmol) and 2,5-dimethylfuran (0.1447 g, 1.5 mmol) in 75 mL of dry tetrahydrofuran was added in portions LTA (0.665 g, 1.5 mmol) suspended in 30 mL of THF at room temperature for a period of 30 min. Upon completion of the addition of LTA, furan (0.102 g, 1.5 mmol) was added to the reaction mixture followed by addition of LTA (0.665 g, 1.5 mmol) in 30 mL of dry THF over 30 min. The reaction mixture was stirred for an additional 10 min, and the lead diacetate was filtered. The filtrate was diluted with 500 mL of water and extracted with three

100-mL portions of chloroform. The combined extracts were washed once with 50 mL of saturated sodium bicarbonate solution and dried over anhydrous magnesium sulfate. Removal of the solvent in vacuo afforded a yellow oil which was chromatographed on a silica gel using 2:1 chloroform:benzene as eluent. The first fraction, 0.12 g was 1,4,5,8-tetramethyl-1,4,5,8-tetrahydroanthracene-1,4:5,8-diendoxide **(73)**. The second fraction, 0.11 g was 1,4,5,8-tetrahydroanthracene-1,4:5,8-diendoxide **(71)**.

26. Reaction of 40 with one equivalent of 2,5-dimethylfuran and one equivalent of lead tetraacetate (LTA). To a stirred mixture of **40** (0.37 g, 1.947 mmol) and 2,5-dimethylfuran (0.187 g, 1.947 mmol) in 100 mL of dry THF at room temperature was added in portions LTA (0.86 g, 1.947 mmol) suspended in dry THF (20 mL) over 30 min. After 10 min additional stirring, lead diacetate was removed by filtration. The filtrate was diluted with 500 mL of water and extracted with three 280-mL portions of chloroform. The combined extracts were washed once with saturated aqueous sodium bicarbonate solution and dried over anhydrous magnesium sulfate. Removal of the solvent gave a crude product which was chromatographed on silica gel using 1:1 chloroform:ether as eluent to afford 0.18 g (70%) of **73**: mp 229°C (decomp) ^1H NMR (250 MHz, $CDCl_3$) δ 6.96 (s, aromatic), 6.78 (s, minor, vinyl), 6.76 (s, major, vinyl), 1.87 (s, major, methyl), 1.86 (s, minor, methyl).

27. Attempted reaction of 1-amino-benzo[1,2-d:4,5-d']-bistriazole 64, with 2,5-dimethylfuran and lead tetraacetate. To a stirred mixture of 1-amino-benzo[1,2-d:4,5-d']-bistriazole **64** (0.3 g, 1.71 mmol) and 2,5-dimethylfuran (0.8 g, 8.32 mmol) in 150 mL of dry THF at reflux under argon was added lead tetraacetate (1.67 g, 1.71 mmol) in portions over 30 min. After the usual work-up, removal of the solvent left a tan residue shown by ^{1}H NMR to be unreacted **64**.

28. 1,3,3,4,7,8-Hexamethyl-5,6-bis(Z,Z-cyanomethylene)-bicyclo[2.2.2]oct-7-en-2-one (116). To a mixture of 0.62 g (3.263 mmol) of 1,6-diamino-benzo [1,2-d:4,5-d']bistriazole, **63**, and 0.58 g (3.258 mmol) of 2,3,4,5,6,6-hexamethylcyclohexa-2,4-dienone **9** in 100 mL of dry tetrahydrofuran (THF) at room temperature was added in portions 3.2 g (7.21 mmol) of lead tetraacetate (LTA) in 50 mL of dry THF over a period of 30 min. After 5 min additional stirring, the lead diacetate was filtered, the filtrate was diluted with 500 mL of water and extracted three times with 100-mL portions of methylene chloride. The combined extracts were washed with saturated aqueous sodium bicarbonate solution, saturated aqueous sodium chloride solution and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and the residue was chromatographed on silica gel using 3:1 chloroform:hexane as eluent to afford 0.74 g (81%) of **116** as a white solid, mp 368-369°C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.66 (s, 1H, vinyl), 5.62 (s, 1H, vinyl), 1.77 (s, 3H, *J* = 1Hz), 1.70 (s, 3H, *J* = 1Hz), 1.46 (s, 3H), 1.41 (s, 3H), 1.09 (s, 3H), 0.89 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 199.50 (C=O), 161.28, 155.75, 139.52, 129.98, 116.54, 115.87, 98.06, 96.13 (six vinyl and two nitrile carbons), 60.06, 52.24, 45.71 (three quaternary carbons), 23.58 (overlap), 14.25, 13.90, 11.99, 11.62 (six methyl carbons); mass spectrum, *m/e* (relative intensity) 280 (trace), 210 (100, M^+-dimethylketene), 237 (1), 195 (17), 183 (9), 168 (10), 153 (4); IR (KBr) 3025, 2970, 2930, 2870, 2215 (CN), 1740 (C=O), 1590, 1440, 1385, 1270 cm^{-1}. High resolution mass spectrum: Calcd. for $C_{18}H_{20}N_2O$: 280.1575; Found: 280.1582.

29. Reaction of 1,6-diamino-benzo[1,2-d:4,5-d']bistriazole 63 with two equivalents of lead tetraacetate. To a stirred mixture of 1,6-diamino-benzo[1,2-d:4,5-d']bistriazole **63** (0.56 g, 2.95 mmol) in 100 mL of dry THF under argon was added lead tetraacetate (2.9 g, 6.5 mmol) in portions over 30 min. After the usual workup, removal of the solvent gave only 0.17 g of a polymeric oil.

30. Reaction of 1,5-diamino-benzo[1,2-d:4,5-d']bistriazole 40 with one equivalent of lead tetraacetate. Lead tetraacetate (0.7 g, 1.58 mmol) in 30 mL of dry THF was added over 20 min in portions to a stirred suspension of **40** (0.3 g, 1.58 mmol) in 50 mL THF under argon at room temperature. The solvent was removed under reduced pressure and washing of the brown residue with water left only a polymeric powder. No desired product could be isolated from the residue.

31. **Reaction of 1,5-diamino-benzo[1,2-d:4,5-d']bistriazole 40 with lead tetraacetate in the presence of 1,1-dimethoxyethylene.** Lead tetraacetate (3.1 g, 6.95 mmol) in 50 mL of dry THF was added over 30 min in portions to a stirred suspension of **40** (0.6 g, 3.16 mmol) and 1,1-dimethoxyethylene[53] (0.62 g, 6.95 mmol) in 100 mL THF under argon at room temperature. Lead diacetate formed was removed by filtration. A work up sample of the reaction mixture indicated the presence of the unreacted olefin (0.57 g, 95% recovery).

32. **1,2,3,4,5,6,7,8-Octaphenylanthracene (125).** In a procedure similar to that used for **73**, reaction of **40** (0.018 g, 0.0947 mmol) with 1,2,3,4-tetraphenylcyclopentadienone (0.0728 g, 0.190 mmol) in refluxing THF (300 mL) and LTA (0.093 g, 0.21 mmol) gave a crude product. Recrystallization from benzene gave 0.041 g (56%) of **125** as a yellow solid, mp 415-417°C; ^{1}H NMR (250 MHz, d_6-DMSO, 110°C) δ 7.33 (s, 2H), 7.1-6.7 (m, 40H); mass spectrum, <u>m</u>/<u>e</u> (relative intensity) 786 (71), 105 (9), 44 (100); IR (KBr) 3080, 3055, 3030, 1595, 1490, 1443, 1032 cm^{-1}. High resolution mass spectrum. Calcd for $C_{62}H_{42}$: 786.3284. Found: 786.33130

33. **Tetramethyl 2,3,6,7-tetraphenylanthracene-1,4,5,8-tetracarboxylate (128).** In a procedure similar to that used for **73**, reaction of **40** (0.2 g, 1.052 mmol) with 2,5-methoxycarbonyl-3,4-diphenylcyclopentadienone[54] (0.732 g, 2.10 mmol) in dry THF (50 mL) and LTA (1.026 g, 2.31 mmol) gave a grey product. Flash chromatography over silica

gel eluting with 2:1 chloroform:hexane yielded 0.70 g (93%) of **128** which was recrystallized from ethyl acetate to give yellow crystals, mp 375-376°C; ^{1}H NMR (250 MHz, $CDCl_3$) δ8.55 (s, 2H), 7.25-7.07 (m, 20H), 3.65 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 168.75, 138.37, 138.13, 133.37, 130.40, 129.99, 128.34, 126.66, 52.11; mass spectrum, m/e (relative intensity) 714 (100), 683 (1), 619 (3), 504 (5), 476 (8), 325 (48), 237 (38); IR (KBr) 3060, 3025, 2950, 1721, 1434, 1360, 1226, 1092, 1041 cm^{-1}. Anal. Calcd. for $C_{46}H_{34}O_8$: C, 77.30; H, 4.79. Found: C, 77.33; H, 4.88.

34. Bis-(N-methyl)-1,2,3,4,5,6,7,8-octaphenyl-1,4,5,8-tetrahydroanthracene-1,4:5,8-bisimine (130). In a procedure similar to that used for **73**, reaction of **40** (0.3078 g, 1.62 mmol) with N-methyl-2,3,4,5-tetraphenylpyrrole[40] (1.25 g, 3.24 mmol) in dry THF (100 mL) and LTA (1.58 g, 3,56 mmol) gave a yellow product which was recrystallized from benzene to yield 1.2 g (88%) of a single isomer (**130**); white solid, mp 205-207°C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.8-6.6 (m), 2.12 (broad s); ^{13}C NMR ($CDCl_3$) δ 134.58, 131.37, 130.98, 128.46, 128.07, 127.66, 127.31, 127.03, 126.96, 126.85, 126.62, 77.14, 31.46; mass spectrum, m/e (relative intensity) 844 (M^+, not shown), 399 (3), 385 (8), 178 (100); IR (KBr) 3060, 3030, 2950, 1605, 1485, 1443, 1325, 1290, 1155 cm^{-1}. Anal. Calcd for $C_{64}H_{48}N_2$: C, 90.96; H, 5.72; N, 3.31. Found: C, 90.85; H, 5.70; N, 3.25.

35. 1,4,5,8-Tetraphenyl-1,4,5,8-tetrahydroanthracene-1,4:5,-8-diendoxide (133). In a procedure similar to that used for **73**, reaction of **40** (0.293 g, 1.54 mmol) with 2,5-diphenylfuran (0.678 g, 3.08 mmol) in dry THF (100 mL) and LTA (1.50 g, 3.38 mmol) gave a crude product. Preparative TLC on silica gel using 4:1 benzene:hexane as the eluent yielded 0.59 g (75%) of **133** as a pale yellow solid. Although the melting point was fairly sharp, the ^{13}C NMR analysis showed some minor extraneous peaks; mp 264-265°C; ^1H NMR (250 MHz, $CDCl_3$) δ 7.67-7.25 (m, 22H), 6.74 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 151.02, 146.24, 144.49, 135.61, 128.70, 126.93, 113.42, 93.53; mass spectrum, *m/e* (relative intensity) 514 (100), 498 (18), 105 (18); IR (KBr) 3035, 1605, 1495, 1450, 1425, 1350, 1105, 985 cm^{-1}. *Anal*. Calcd. for $C_{38}H_{26}O_2$: C, 88.69; H, 5.09. Found: C, 88.58; H, 5.08.

36. 5,7,12,14-Tetraphenyl-5,7,12,14-tetrahydropentacene-5,-14:7,12-diendoxide (140). In a procedure similar to that used for **73**, reaction of **40** (0.097 g, 0.51 mmol) with 1,3-diphenylisobenzofuran (0.276 g, 1.02 mmol) in THF (40 mL) and LTA (0.5 g , 1.12 mmol) gave a crude product which was recrystallized from ethyl acetate/hexane to yield 0.28 g (88%) of a pure product (**140**); white crystals, mp 306-308°C; ^1H NMR (250 MHz, $CDCl_3$) δ 8.2-6.85 (m); ^{13}C NMR ($CDCl_3$) δ 149.22, 134.85, 128.80, 128.43, 126.61, 125.68, 120.36, 113.49, 113.29, 90.50; mass spectrum, *m/e* (relative intensity) 614 (41), 493 (19), 404 (45), 105 (100), 77 (15); IR (KBr) 3065, 3040, 1600, 1495, 1450, 1425, 1340, 1312 cm^{-1}. Anal. Calcd. for $C_{46}H_{30}O_2$: C, 89.88, H, 4.92. Found: C, 89.76; H, 4.85.

37. **5,7,12,14-Tetraphenylpentacene (141)**. A dry 500 mL three-necked flask, oven-dried, equipped with a rubber septum, a magnetic stirring bar, a dropping funnel, and a reflux condenser connected to a bubbler, was under argon. The flask was covered with aluminum foil to avoid light. To a suspension of 9.0 mL (excess) of titanium tetrachloride in 200 mL of freshly distilled tetrahydrofuran at 0°C was added 10.0 g of zinc powder (excess). The steel grey suspension was heated to reflux, and a solution of bis-epoxide (**140**) (1.8 g, 2.931 mmol) in 50 mL of THF was added dropwise over 10 min. The mixture was refluxed for 16 h, then cooled to room temperature, and poured into dilute hydrochloric acid. The resulting deep-blue mixture was extracted twice with 100-mL portions of methylene chloride. The combined extracts were washed three times with 100-mL portions of saturated aqueous sodium bicarbonate solution, dried over anhydrous magnesium sulfate, and concentrated in vacuo to afford the crude product (all the work-up was performed in a dark hood as quickly as possible). This crude product was triturated with ethanol (20 mL) and filtered to give 1.38 g (81%) of **141** as a violet solid, mp 410-411°C (lit.[56] 411°C); ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.21 (s, 2H), 7.68-7.64 (AA', 4H), 7.43-7.26 (m, 20H), 7.18-7.13 (BB', 4H); ^{13}C NMR ($CDCl_3$) δ 138.72, 131.28, 130.31,129.11, 128.78, 128.08, 127.09, 125.87, 124.80, 124.60; mass spectrum, m/e (relative

intensity) 582 (100), 507 (31), 426 (13), 303 (14), 291 (85), 253 (87), 244 (48), 231 (19), 214 (98), 207 (36)

38. Dimethyl 5,7,12,14-tetraphenyl-6,13-dihydro-6,13-ethenopentacene-5,16-dicarboxylate (151). A 250-mL three-necked flask was fitted with a septum, a magnetic stirring bar, a dropping funnel, and a condenser topped by an argon bubbler connection. The flask was covered with aluminum foil up to the necks to avoid light. To a stirred solution of 0.644 g (1.107 mmol) of 5,7,12,14-tetraphenylpentacene (**141**) in 50 mL of dry THF was added 0.157 g (1.107 mmol) of dimethyl acetylenedicarboxylate in 50 mL of THF through a dropping funnel over 10 min. The resulting solution was refluxed for 5 h, then cooled to room temperature. The reaction mixture was poured into water (200 mL) and the cloudy aqueous layer was extracted three times with 30-mL portions of methylene chloride. The combined extracts were washed twice with 50-mL portions of a saturated aqueous sodium bicarbonate solution, once with a saturated aqueous sodium chloride solution and dried over anhydrous magnesium sulfate. After removal of the solvent, the grey solid was flash chromatographed on a silica gel column and eluted with 1:1 chloroform:benzene to give 0.68 g (85%) of **151** as a white solid. An analytical sample was recrystallized from ethanol, mp 375-376°C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.5 (AA', 4H), 7.4-7.2 (m, 20H), 7.13 (BB', 4H), 5.58 (s, 2H), 3.74 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 146.90, 130.14, 137.02, 130.93, 130.52, 130.40, 128.16, 127.94, 127.19, 126.60, 125.68, 52.06, 47.12; mass spectrum, m/e (relative intensity) 724 (100), 605 (45), 582 (52), 302 (78), 263 (48), 250 (20), 213 (22); IR (KBr) 3050, 3020, 2940, 1715 (C=O), 1630, 1592, 1485, 1432, 1370, 1325, 1260, 1230 cm^{-1}. Anal. Calcd. for $C_{52}H_{36}O_4$: C, 86.17; H, 5.00. Found: C, 85.94; H, 5.15.

39. 5,7,12,14-Tetraphenyl-6,13-dihydro-6,13-ethanopentacene-15,16-dicarboxylic anhydride (153). This Diels-Alder adduct was prepared by the reaction of 5,7,12,14-tetraphenyl pentacene **141** (0.484 g, 0.8314 mmol) and maleic anhydride **152** (0.0815 g, 0.8314 mmol) in dry THF as in the preparation of Diels-Alder adduct **151**. The crude product was triturated with ethanol (2 X 20 mL) to give 0.26 g (46%) of **153** as a white solid. The melting point was checked in a sealed capillary tube. At 75°C, the compound turned slowly to blue and at 200 °C, complete blue solution was formed. It seems that the compound undergoes a retro Diels-Alder reaction on heating. ^1H NMR (250 MHz, $CDCl_3$) δ 7.45-6.95 (m, 28H), 5.06 (d, *J* = 1.2 Hz, 2H), 3.52 (d, *J* = 1.2 Hz, 2H); ^{13}C NMR (not available because of poor solubility); mass spectrum, m/e (relative intensity) 680 (not shown), 582 (25), 507 (3), 426 (2), 291 (26), 253 (15), 244 (20), 213 (14), 44 (100); IR (KBr) 3050, 3020, 1766, 1490, 1440, 1373, 1225, 1070, 1030, 925 cm^{-1}.

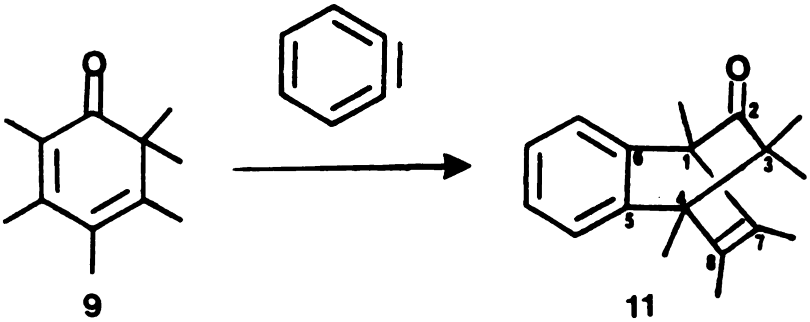
PART II. ACID-CATALYZED AND PHOTOCHEMICAL REARRANGEMENTS OF NOVEL KETONES

Introduction

In part II of this thesis, the structure determination of adduct **102** (page 48), obtained from the reaction of DABT-LTA and 2,3,4,5,6,6-hexamethylcyclohexa-2,4-dien-1-one, is presented. Also, the acid-catalyzed and photochemical rearrangements of this and a related ketone and epoxy ketone are described.

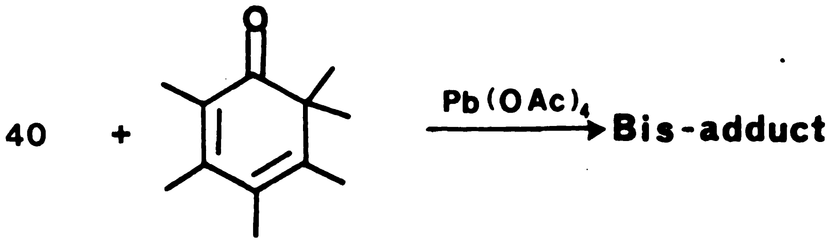
Results and Discussion

A. Structure of the Bis-adduct Obtained From the Reaction of Hexamethyl-2,4-cyclohexadienone 9 and DABTLTA. Hart and Gray prepared the adduct 11[16] by the reaction of 2,3,4,5,-6,6-hexamethylcyclohexa-2,4-dien-1-one 9[60] with benzyne generated from benzene diazonium 2-carboxylate. The ^1H NMR spectrum of this adduct showed two methyl groups at δ 0.47 and 1.06 (syn and anti-3-methyls), a six-proton signal at δ 1.62 (bridgehead methyls), and two mutually coupled (*J* = 1 Hz) methyl signals (allylic methyl) at δ 1.82 and 1.74.



9 **11**

Dienone **9** was subjected to reaction with **40** and LTA to give an analogous bis-adduct **102**, (79% yield), mp 338°C (decomp), which appeared to be one of the four possible regioisomers (**154-157**) as shown. Compound **102** gave the correct analysis and its 250 MHz ^1H NMR spectrum showed a sharp singlet for the two aromatic protons at δ 7.00, two homoallylic methyl signals (*J* = 1 Hz) at δ 1.78 and 1.69, and four methyl singlets at δ 1.67, 1.62, 1.07 and



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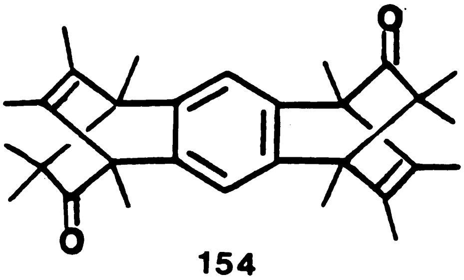

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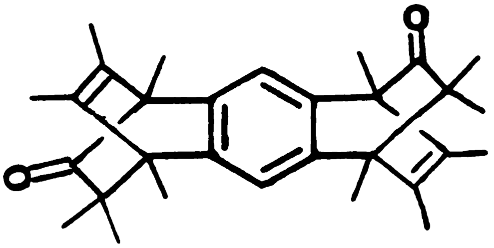

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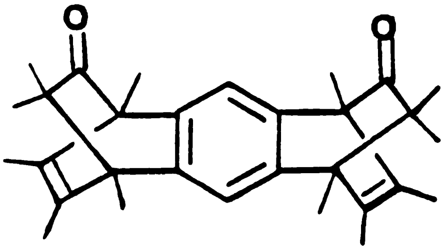

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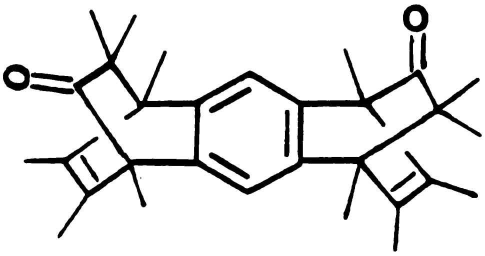
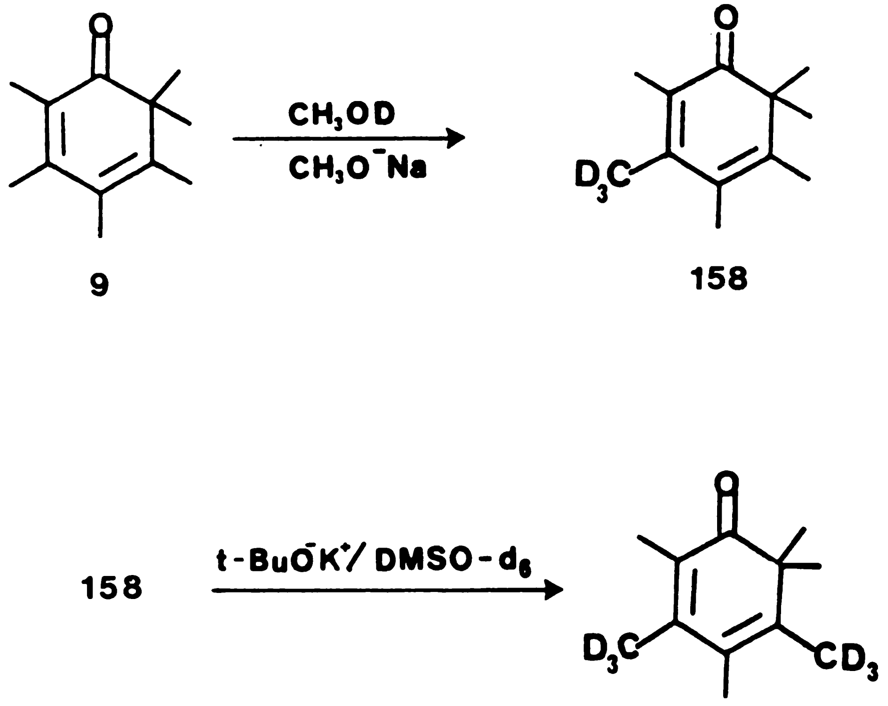


157

0.49. On the basis of the ^{1}H NMR data, two posssible structures, **156** and **157** can be excluded because they would be expected to show two different aromatic proton signals. The ^{13}C NMR spectrum showed fifteen bands, also consistent with either structure **154** or **155**. The infrared spectrum had a carbonyl band at 1710 cm^{-1} and a strong carbon-carbon double bond absorption at 1600 cm^{-1}. Unfortunately, these spectral data do not afford enough information to tell whether the bis-adduct is **154** or **155**. From the viewpoint of product development control, structure **154** is preferred since the molecule may have a natural tendency to reduce its dipole moment. The ultimate structure proof for the bis-adduct must be provided by a single crystal X-ray diffraction study which is in progress. For convenience, structure **154** will be used in this discussion.

In connection with the NMR methyl peak assignment of the bis-adduct, it was useful to synthesize trideutero-**9**, labeled at C-3 **(158)** and hexadeutero-**9**, labeled at C-3 and C-5 **(159)**. These labeled dienones were prepared according to Hart and coworkers as shown below.[64]



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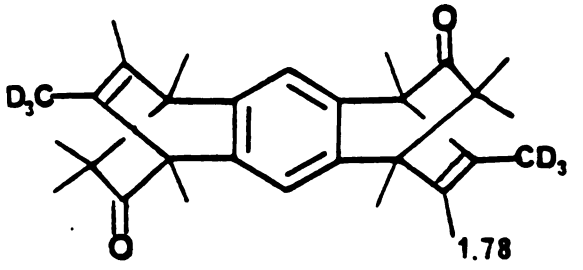
158

158

Reaction of dienones, **158** and **159** separately with DABT-LTA provided the corresponding bis-adducts **160** and **161**. The 250 MHz ^{1}H NMR spectrum of the $\underline{d}_6$-bis-adduct **160** was identical with that of **154** except that the methyl proton signal at δ 1.69 was absent and the peak at 1.78 was unsplit. The $\underline{d}_{12}$-bis-adduct **161** had a singlet for the two aromatic protons at δ 7.00 and four sharp methyl singlets at δ 1.78, 1.67, 1.07 and 0.49 in its 250 MHz ^{1}H NMR spectrum. Consequently, the ^{1}H NMR signals of **154** were assigned as indicated in the figure.



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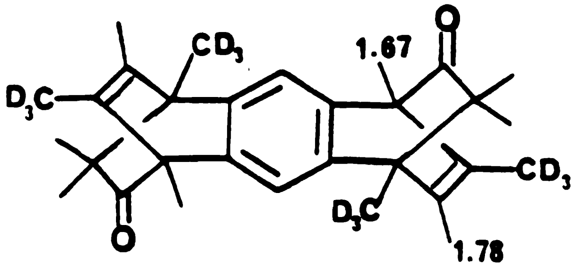

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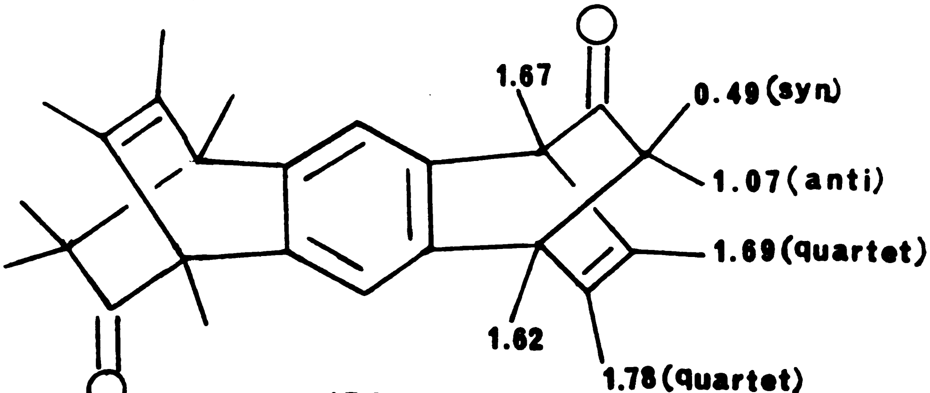
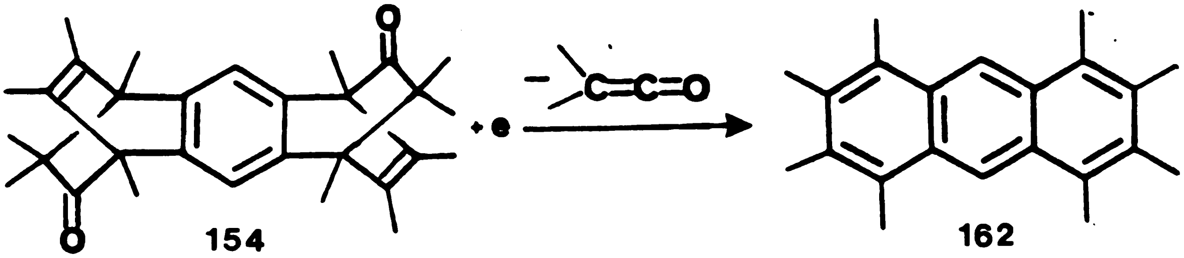


154

The mass spectrum of **154** showed a small parent peak at m/e 430 (relative intensity 1), a weak fragmentation peak at m/e 360 (M^+-dimethylketene) and a base peak at m/e 290 (M^+-two dimethylketenes). In fact, the mass spectrum of **154** was very similar to that of compound **162**[65] indicating that it easily loses two dimethylketene species on electron impact.



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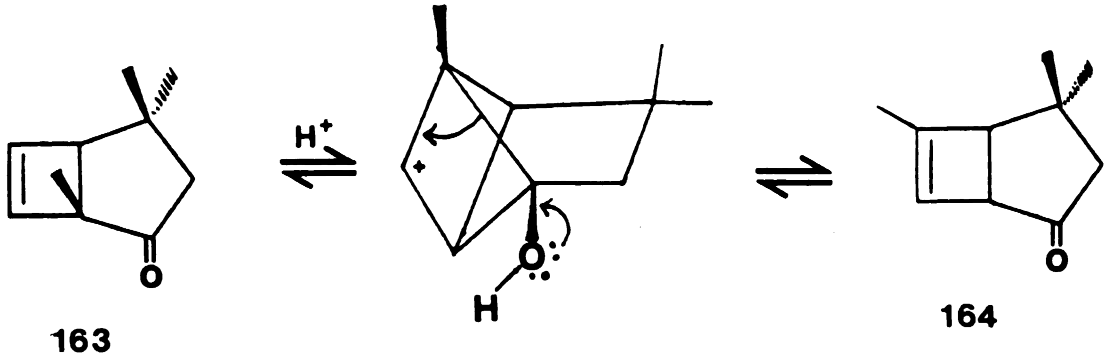
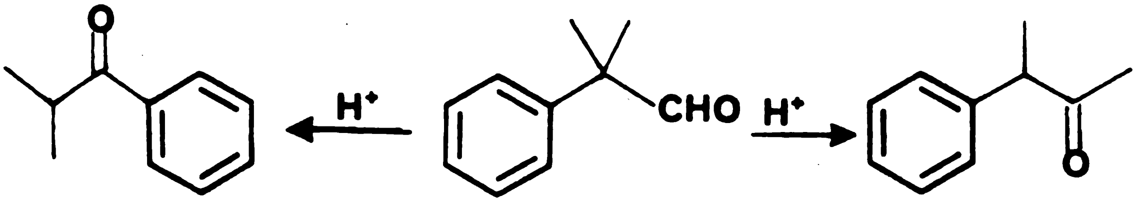
162

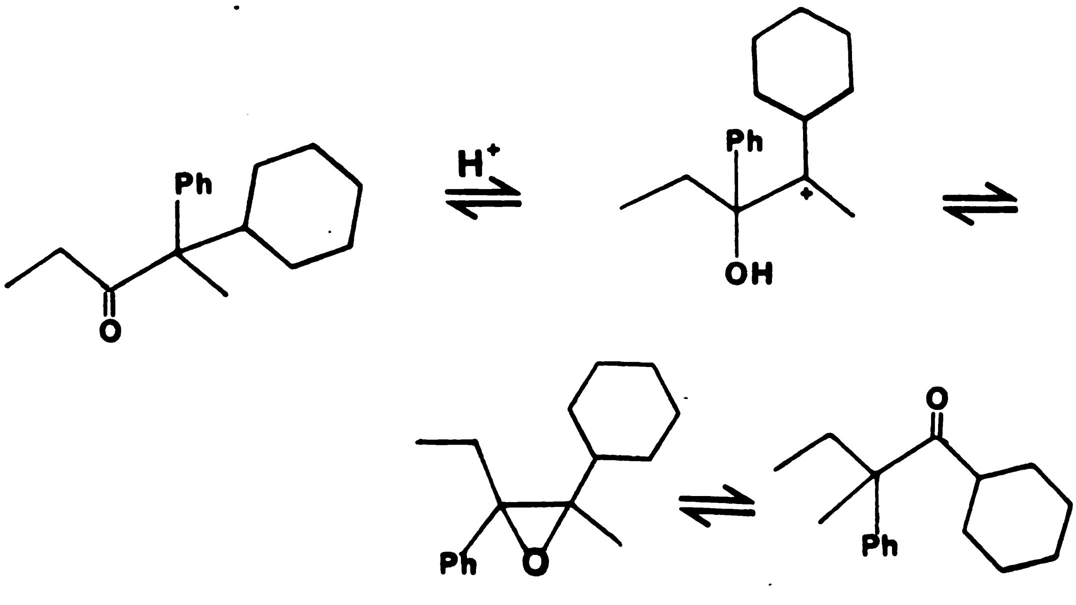
B. Acid-catalyzed Rearrangement of 1,3,3,4,7,8,10,12,12,13-16,17-Dodecamethyl-benzo[1,2-e:4,5-e']bisbicyclo[2.2.2]oct-5,7-diene-2,11-dione (154). The rearrangement of , -unsaturated ketones in acid[66] has considerable potential for the synthesis of unusual bi- and tricyclic ring systems. In most examples described thus far, however, the double bond is present in a relatively strained cyclobutene ring. For example, the isomerization **163** ⟶ **164** was reported to be nearly quantitative; the mixture resulting from heating **163** in benzene containing TsOH contained 92.5% of **164** and 7.5% of recovered **163**[67]. These data reflect that **163** and **164** are equilibrated by acid and the equilibrium mixture contains



> 90% of **164**. The greater stability of **164** may result from the removal of a 1,3-methyl-methyl interaction.

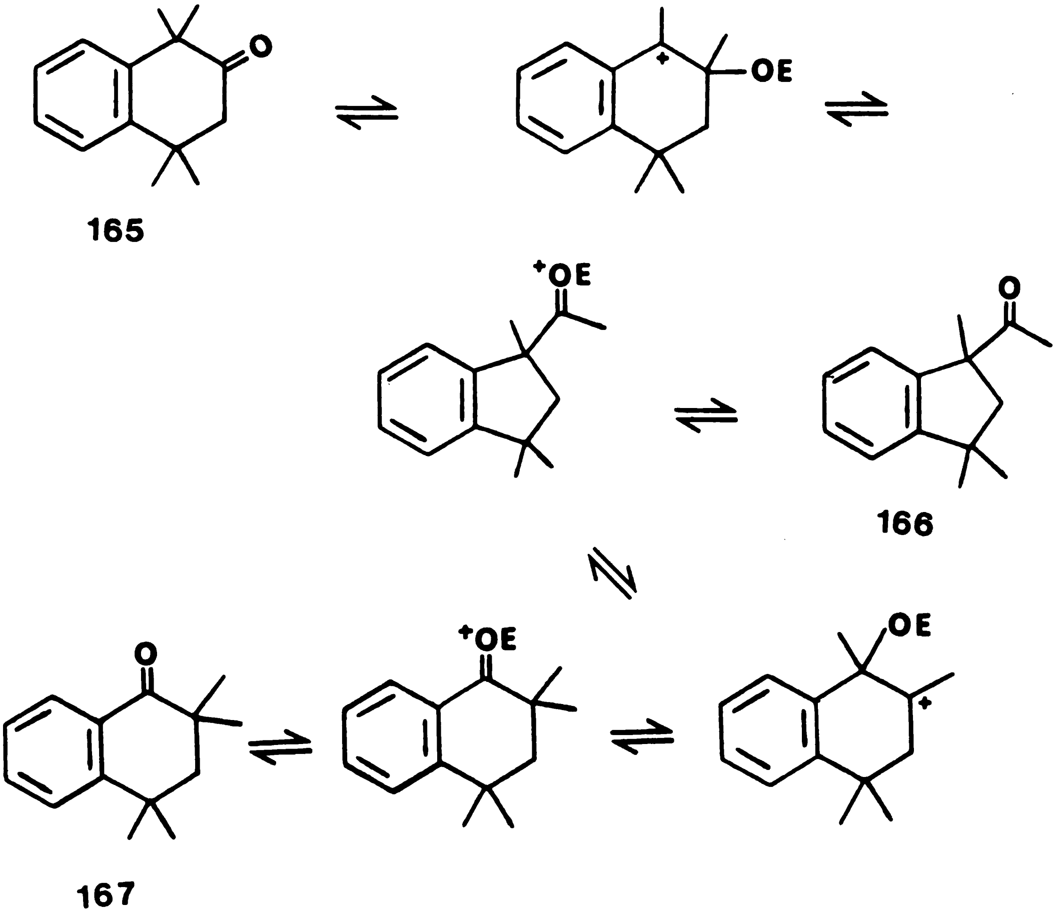
When the β, γ unsaturation is incorporated into an aromatic ring, aryl and/or alkyl migrations may be observed, as shown below.[68-69] The examples here are illustrative; numerous other examples are presented in Fry's review.[70]



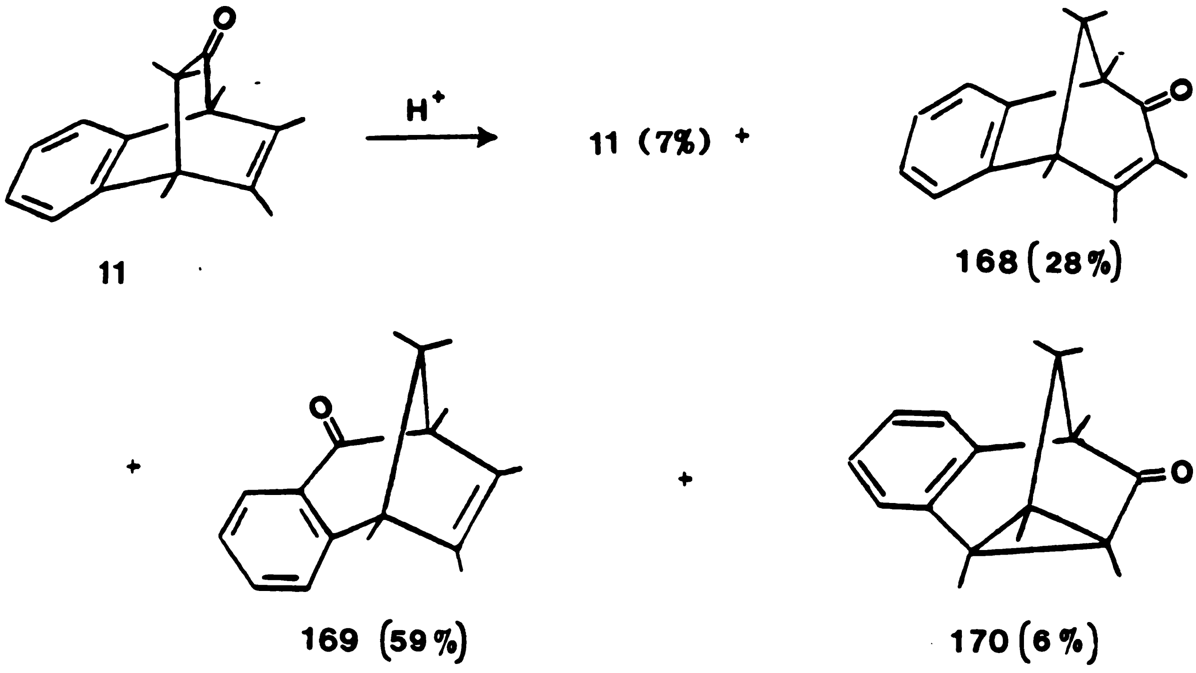


The tetralone **165** is converted into **166** by the action of Lewis acids such as aluminum chloride, ferric chloride, and hydrogen fluoride. Ketone **166** undergoes further isomerization to yield **167**. The course of these changes is outlined in Scheme 6.[71]

Scheme 6



Hart and Love discovered a more complex series of isomerizations of β,γ-unsaturated ketones contained in bicyclo[2.2.2]- and bicyclo[3.2.1]octane systems.[72] For example, when ketone **11** was refluxed with trifluoroacetic acid (TFA) for several hours, an equilibrium mixture of **11** and **168-170** was obtained in the amounts shown. A possible mechanism



11

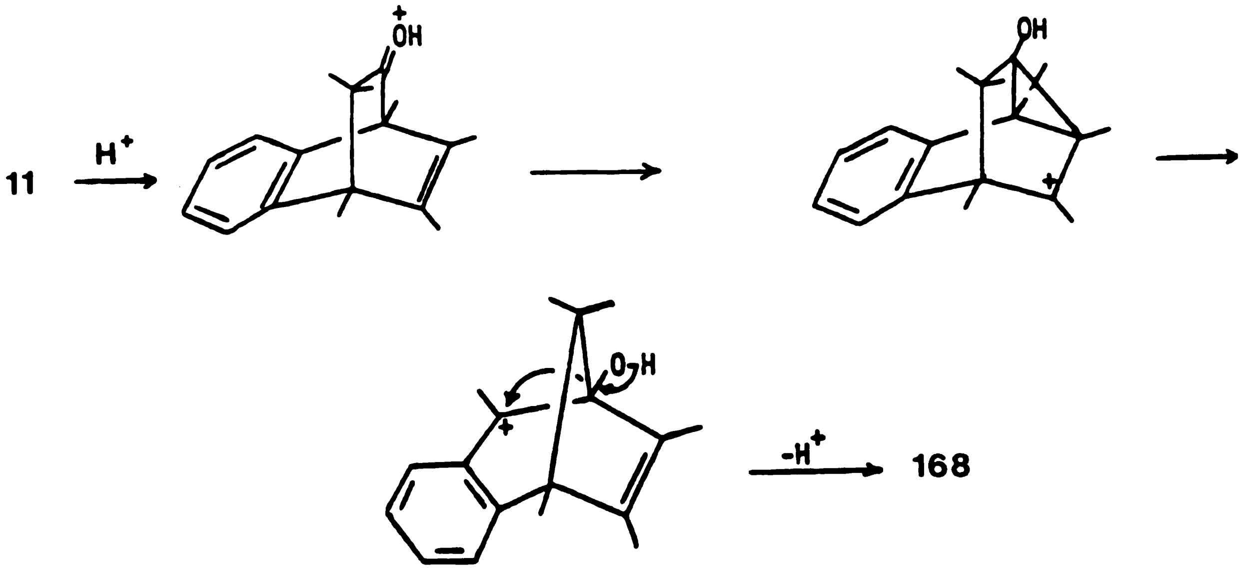
168 (28%)

169 (59%)

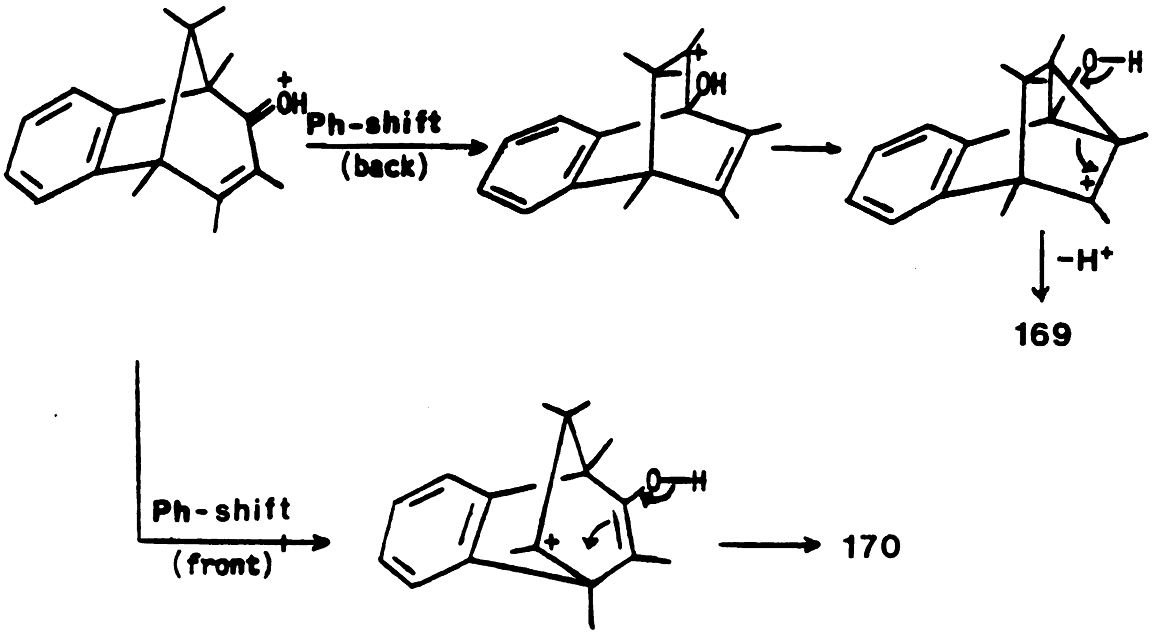
170 (6%)

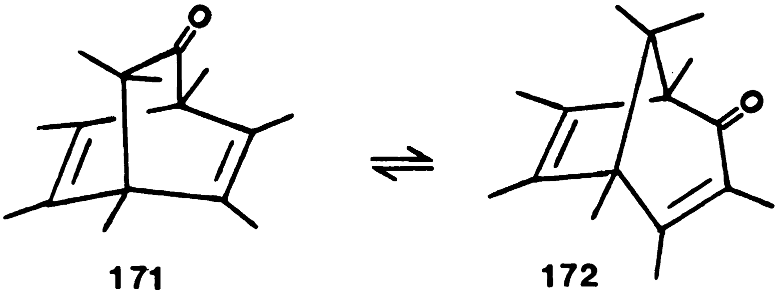
for the isomerization which explains the formation of **168** before **169** is shown in Schemes 7 and 8. Isomerization of **11** to **168** involves vinyl, alkyl and aryl migrations. The acid-catalyzed interconversion of **171** and **172** occurs similarly.

<u>Scheme 7</u>



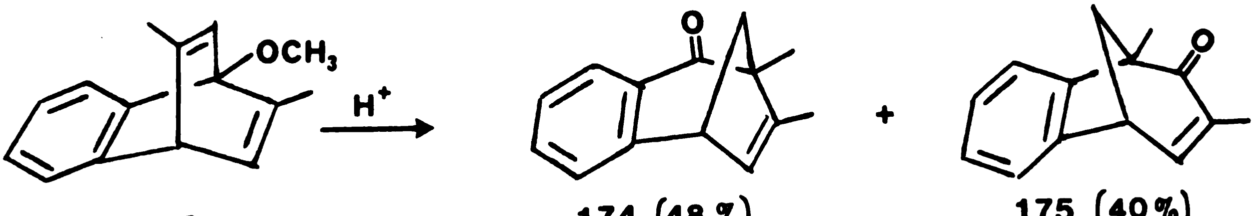
Scheme 8





171 **172**

The closely related rearrangement of **173** to **174** and **175** was also reported.[73]

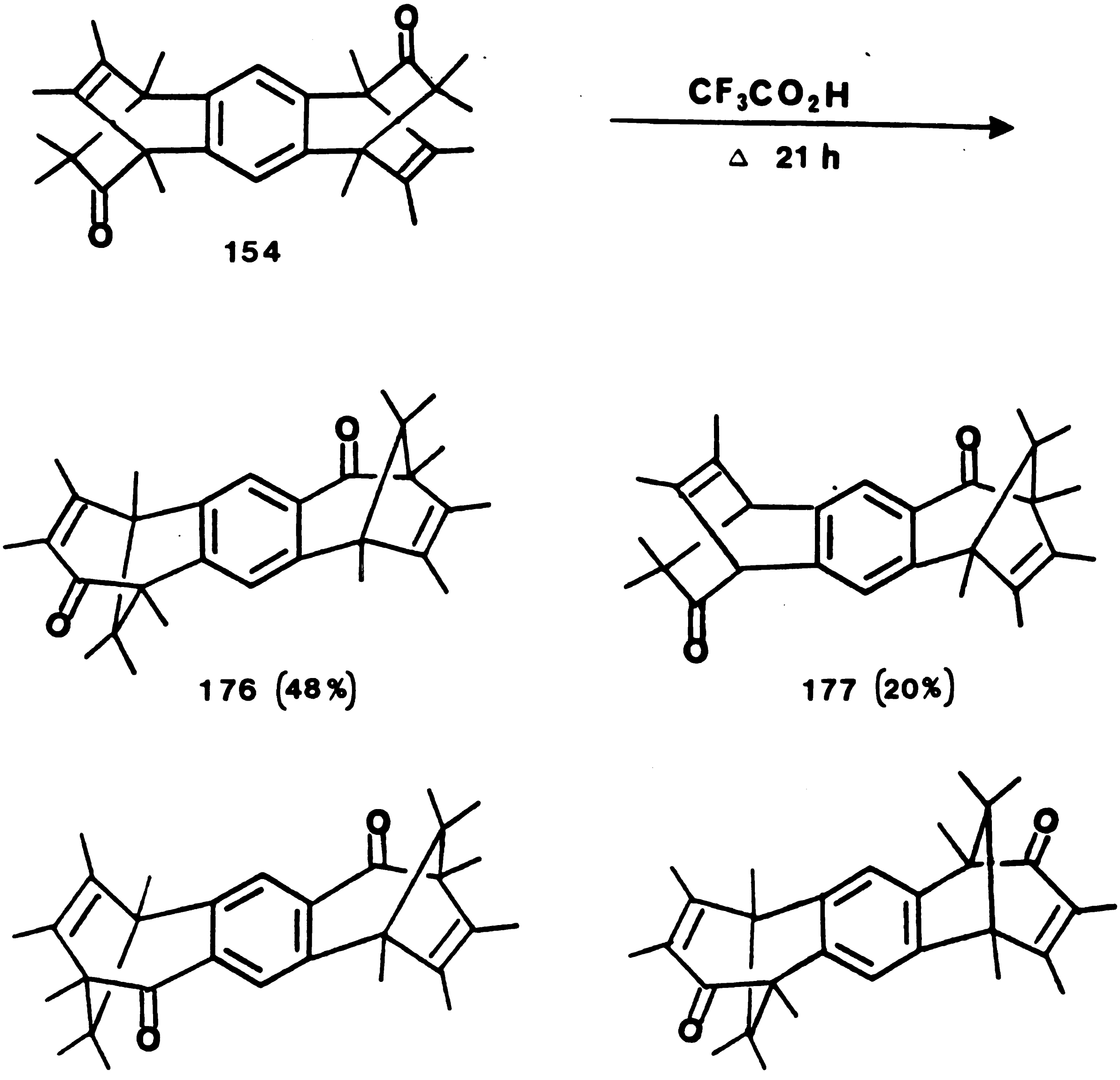


173 **174 (48 %)** **175 (40%)**

Since diketone **154** was readily available from the bis--aryne studies (p. 104) it was thought of interest to study its acid-catalyzed rearrangement. This ketone is the first molecule in that contains the same β,γ-unsaturated ketone moieties twice, and thus the outcome of the rearrangement might be quite interesting.

The acid-catalyzed rearrangement of ketone **154** in neat TFA afforded after 21 h an equilibrium mixture of four isomeric ketones (**176-179**), with some minor unknowns (8%). These structures have been arbitrarily numbered in what is thought to be the order of their formation during the reaction. The ratio of isomers was obtained from integration of the aromatic region (δ8-6.7) of the crude quenched sample. Tables 7 and 8 list the NMR spectra (^{1}H and ^{13}C) of each of these ketones. All methyl group signals in Table 7 appear as sharp singlets with the exception of those labeled with an asterisk; these show a small (ca. 1 Hz) splitting typical of adjacent methyl groups on a carbon-carbon double bonds. It turned out that the diketones **176** and **177**, with no symmetry, were predominant when equilibrium was established.

The structure determination of ketones **176-179** follows from their spectra and deuterium labeling experiments when necessary. Both ketones **178** and **179** have a center of inversion (point group Ci) whereas ketones **176** and **177** do not. Thus, it is very clear from the ^{1}H NMR spectra whether the ketone is symmetric or not since there will be only one



154

176 (48%)

177 (20%)

178 (15%)

179 (9%)

Table 7. ^{1}H NMR spectra of diketones (**154, 176-179**).

Compound	Aromatic	Methyl	mp(°C)
154	7.00	1.78*,1.69*,1.67	338(decomp)
		1.62,1.07,0.49	
176	7.64	1.88*,1.61*,1.44(overlap)	256-257
	6.90	1.37(overlap)	
		1.23,1.14,1.01(overlap)	
		0.78,0.71	
177	7.88	1.53,1.46,1.43	248-249
	6.83	1.30,1.25,1.22	
		1.17,1.15,1.03	
		0.98,0.72,0.41	
178	7.77	1.45*,1.44*,1.30	313-314
		1.16,1.03,0.73	
179	6.74	1.86*1.61,1.31	335-336
		1.29,0.99,0.77	

Table 8. ^{13}C NMR spectra of diketones (**154**, **176-179**).

Compound	Ketone	Aromatic and Vinyl	Quaternary	Methyl
154	199.51	143.16, 140.34	58.42, 50.42	24.14, 23.54
		138.28 132.00	45.19	15.30, 13.08
		115.40		12.56 12.18
176	198.39	157.95, 149.93	66.52, 64.46	21.72, 21.15
	197.39	149.34, 148.04	62.32, 57.33	17.92, 16.74
		147.61, 131.45	56.47, 55.48	16.36, 13.26
		129.38, 125.45		12.50, 11.34
		119.77, 118.70		(overlap)
				10.66, 10.06,
				9.76
177	197.21	147.66, 146.84	66.47, 57.29	22.96, 21.66
	191.25	142.28, 136.78	55.36, 45.13	17.88, 17.26
		131.32, 130.86	42.25, 42.00	13.66, 13.03
		129.23, 128.80		11.29, 10.00
		122.53, 117.03		9.92, 9.73
				7.72, 5.49

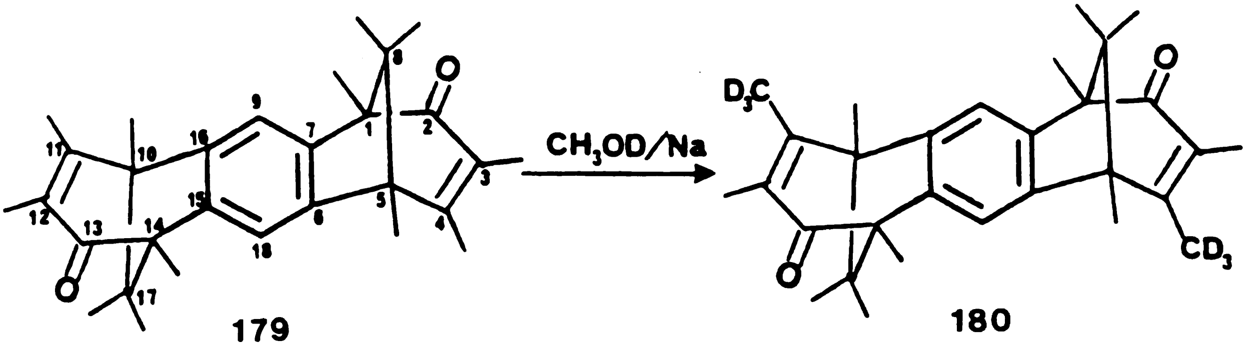
Table 8. ^{13}C NMR spectra of diketones (**154**, **176-179**) continued.

Compound	**Ketone**	**Aromatic and Vinyl**	**Quaternary**	**Methyl**
178	197.00	148.34, 147.22	66.77, 57.21	21.57, 17.98
		132.96, 130.84	56.19	12.35, 11.40
		121.90		10.01, 9.75
179	199.36	157.30, 150.29	63.59, 62.34	21.26, 16.89
		143.64, 125.10	55.47	16.40, 13.29
		116.93		11.34 (overlap)

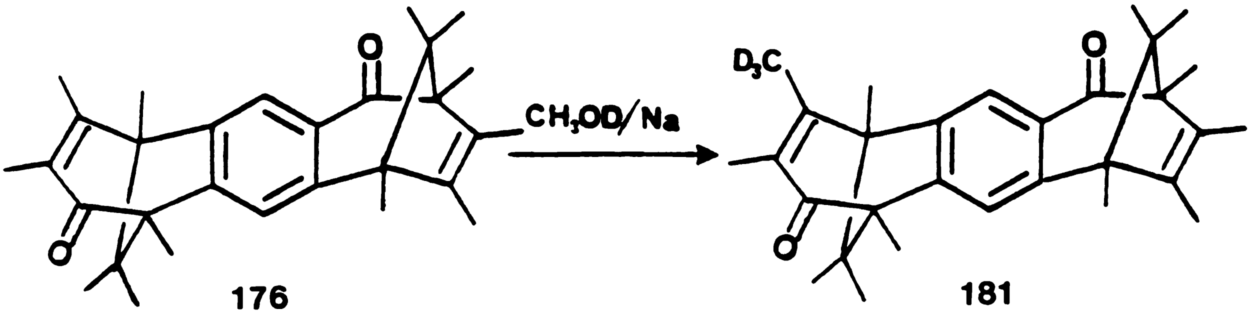
band for the aromatic protons if the structure is symmetric. The chemical shifts of the aromatic protons in **178** and **179** should be quite different from one another. Apparently, the protons in **178** are substantially deshielded by the carbonyl group alpha to the benzene ring.

The 250 MHz ^{1}H NMR spectrum of **178** showed a sharp singlet for the two aromatic protons at δ 7.77, two coupled allylic methyl groups (δ 1.45, 1.44; $\underline{J}$ = 1 Hz) and four other methyl singlets. The ^{13}C spectrum of **178** had fifteen signals as required by symmetry. The infrared spectrum of **178** showed carbonyl absorptions at 1670 cm^{-1} (KBr). The enone **178** is yellow, with an absorption maximum at 239 nm (ϵ=2100).

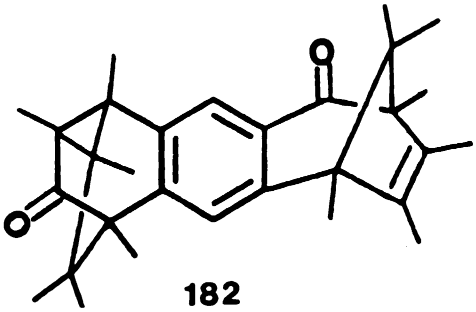
The infrared spectrum of **179** showed the expected carbonyl band at 1650 cm^{-1} (lower frequency than **178**) and the ultraviolet spectrum, with the maximum at 240 nm (ϵ=2200), was also consistent with the structure. The aromatic proton signal in the ^{1}H NMR spectrum of **179** can be compared with that of **178**. Since the signal occurs at higher field in **179** (δ 6.74) than in **178** (δ 7.77), it was concluded that the carbonyl group in **179** is not conjugated with the aromatic ring. Since compound **179** is a conjugated enone, base-catalyzed labeling of **179** should occur only at the C-4 and C-11 methyls. Treatment of **179** at room temperature with CH_3OD and approximately one equivalent of sodium gave the same dienone **180**; in this case, the C-4 and C-11 allylic methyls were labeled as judged by the absence of the peak at δ 1.86. Also, as expected the peak at δ 1.61 had sharpened to a singlet.



The structure differentiation of **176** from **177** was mainly based on their infrared spectra and labeling experiments. The infrared spectrum of **176** had a strong absorption at 1655 cm^{-1} due to two conjugated carbonyl groups. On the other hand, compound **177** showed two carbonyl bands at 1720 and 1670 cm^{-1}, respectively. Enone **176**, when treated with Na/CH$_3$OD, gave the trideuterio compound **181** which lacked the low field methyl signal at δ 1.88.

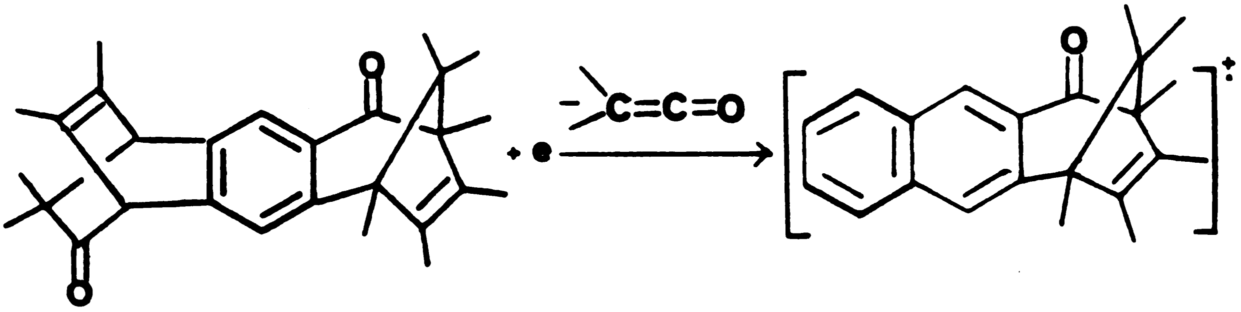


It may be suggested that compound **182** is a possible structure which can be assigned instead of **177**. In order



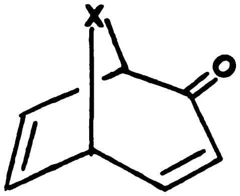
182

to assign the structure **177** with certainty, it was felt necessary to examine its spectra, especially ^{13}C and mass spectrum, more closely. The ^{13}C NMR spectrum of **177** had ten aromatic and vinyl and six quaternary carbon signals confirming structure **177** . Further evidence supporting structure **177** came from its mass spectrum. It showed a parent peak at *m/e* 430, a base peak at *m/e* 415 (M^+-methyl) and a major fragmentation peak at *m/e* 360 (M^+-dimethylketene). Loss of a ketene moiety was found to be typical for this type of structure as discussed in the previous chapter.



The same equilibrium mixture was obtained when each of the rearranged ketones was separately subjected to the isomerization conditions. Since the same equilibrium mixture was obtained from all four ketones (**176-179**), the steps must be reversible.

C. Photoisomerization of 1,3,4,5,8,8,10,11,12,14,17,17-Dodecamethyl benzo[1,2-f:4,5-f']bisbicyclo[3.2.1]oct-3,11-dien-2,-14-dione (179). Bicyclo[3.2.1]octadienones of type **183** have been shown to photoisomerize to ketene **184**. The ketenes were detected by low-temperature infrared spectroscopy, and in all but the first example by trapping with a nucleophile. In the absence of a nucleophile, ketenes **184** recyclize to **183** or dimerize.[75]



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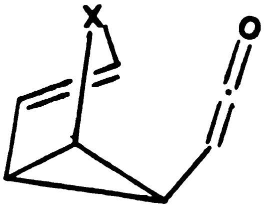
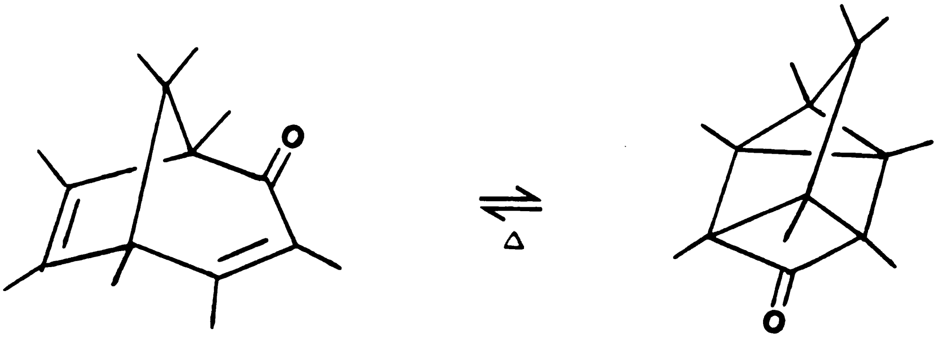


184

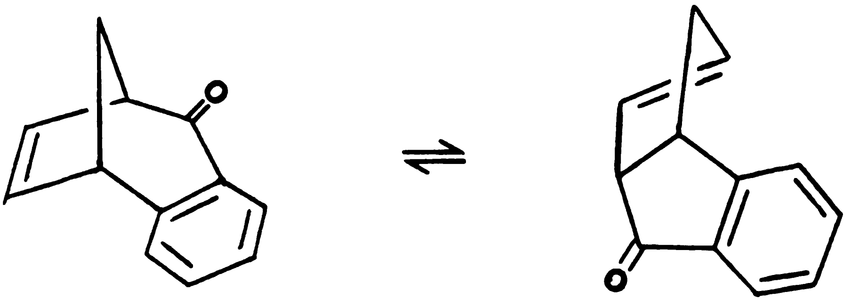
X = has been an electron pair,[74] or a CH_2, CH=CH,[75] o-C_6H_4, or EtO_2CNNCO_2Et[75] group)

Hart and Love demonstrated that ketene **184** (X = CH_2), when completely substituted with methyl groups, reacts differently from its unsubstituted analogs.[77] It neither reacts with nucleophiles nor recyclizes to 183, but undergoes a facile intramolecular [2 + 2] cycloaddition. Thus, irradiation of **185** (1% solution in methanol, Pyrex) gave the tetracyclic structure **186** in 100% yield. The photoproduct **186** isomerizes thermally to **185** in carbon tetrachloride at 100°C with a half-life of 50 min.



185 **186**

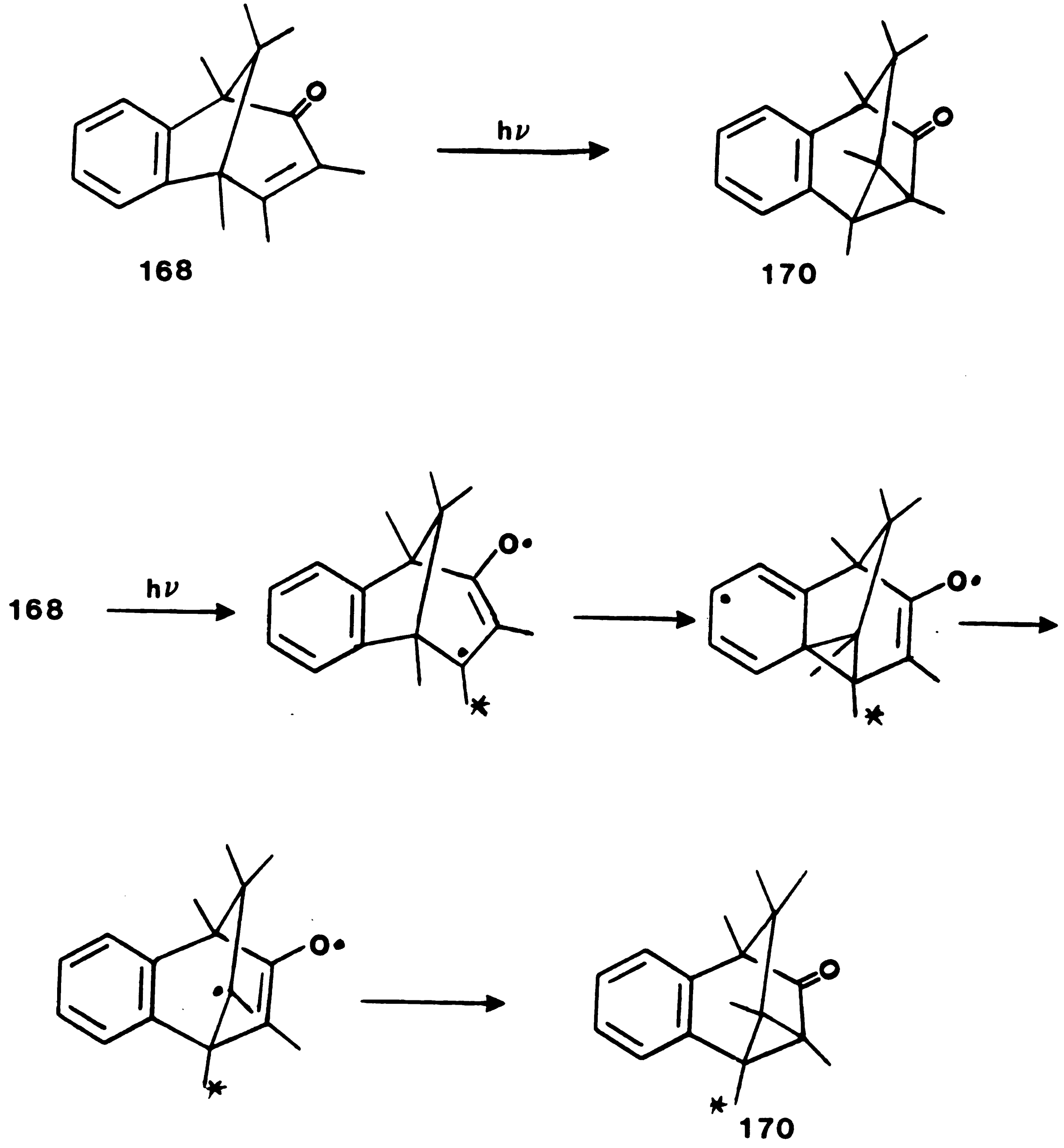
However, the corresponding 3,4-benzooctadienones **187** were shown to undergo reversible 1,3-acyl shifts (**187** $\rightleftharpoons$ **188**).[75] The other possible (i.e., 7,8-)benzoderivatives of **187** underwent a facile photoisomerization.[79] Ketones of the general structure **168** can be regarded as 4-arylcyclohexenones, compounds whose photochemistry has been extensively studied.[80-81]



187 **188**

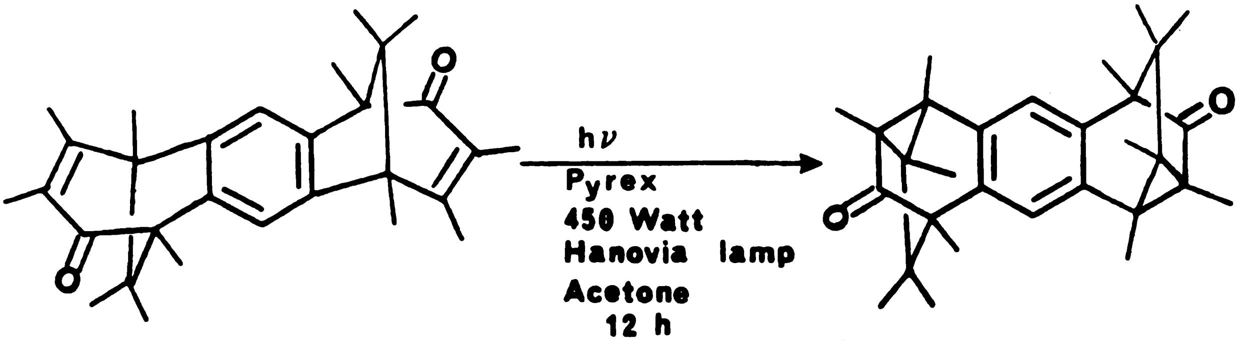
Rearrangement of **168** to **170** was studied with labeled **168** (the label is designated by an asterisk in the mechanistic scheme 9 shown below) and concluded to be an aryl migration mechanism.

Scheme 9



In a continued effort to explore the scope of the photoisomerization reaction described, as well as the synthesis of the interesting ring system which it generates, compound **179** was investigated.

A degassed solution of **179** in spectroscopic grade acetone, on irradiation for 12 h through a Pyrex filter using a 450 watt Hanovia lamp, gave virtually pure photoproduct **189** contaminated with less than 2% of starting dienone **179**. However, when the reaction was monitored by ^{1}H NMR after 3 h, only partial rearrangement (< 20%) occurred. The infrared spectrum of **189** showed the carbonyl absorption at 1715 cm^{-1}, whereas the starting dienone **179** had the band at 1650 cm^{-1}. The 250 MHz ^{1}H NMR spectrum had a singlet for the two aromatic protons at δ 6.89 and six methyl singlets at δ1.48, 1.28, 1.19, 1.14, 0.96 and 0.34. The peak at δ 0.34 was assigned to the syn methyl of the gem-dimethyl group and the signal was shifted to higher field compared to the corresponding ones (0.41 — 0.77) of its isomers (**154**, **176-179**). This is probably due to the shielding effect



179 **189**

of the adjacent methyl group in the cyclopropane ring. The ^{13}C NMR spectrum had a peak for the carbonyl carbon at δ 199.03, three aromatic carbon peaks at δ 136.87, 136.12 and 117.59, five quaternary carbon peaks at δ 54.70, 45.32, 42.07, 39.96 and 35.97 and six methyl peaks at δ 23.00, 17.65, 13.13, 9.96, 7.83, and 5.60.

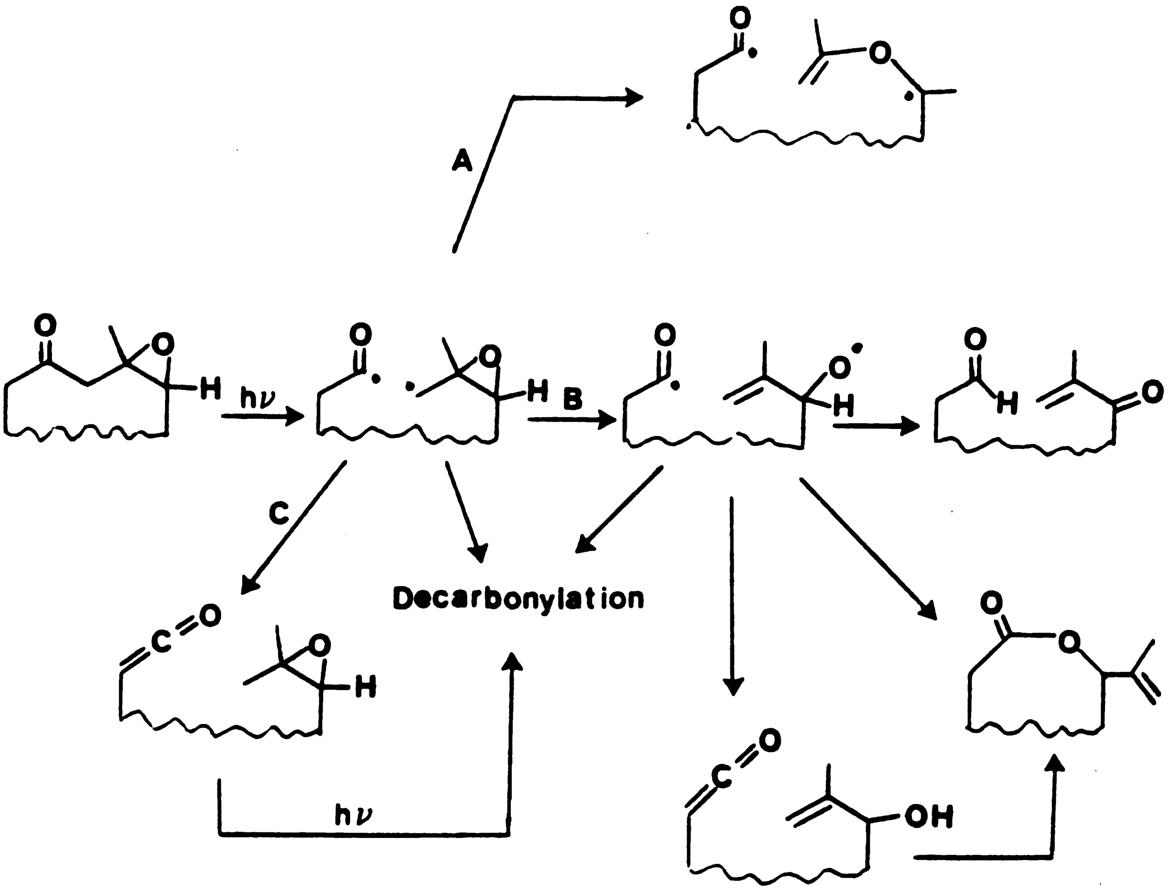
It was suspected that the dienone **179** on irradiation might lead to complicated products unlike its mono-analog **168** since chromophores of new species generated would require different energies for further conversion. Photoisomerization of general structure **168** appears to be quite interesting in affording a single product in excellent yield.

D. Photodecarbonylation of syn-7,8-syn-16,17-diepoxy-1,3,3,4,7,8,10,12,12,13,16,17-dodecamethyl-benzo[1,2-e:4,5-e'] bisbicyclo[2.2.2]oct-2,11-dione (199).

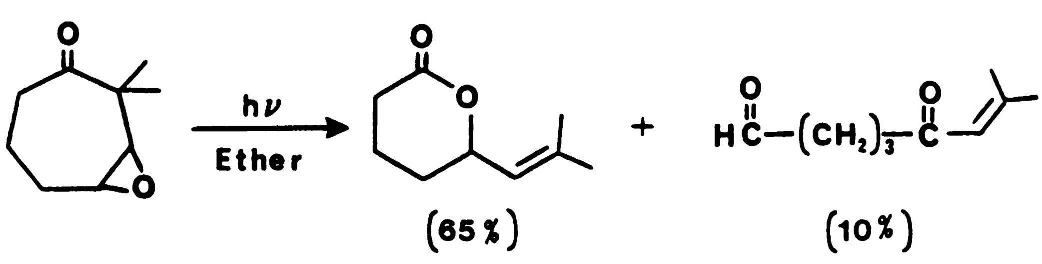
Literature Background

When an epoxy function is located β, γ to a carbonyl group, a Norrish type I mechanism satisfactorily rationalizes the photoproducts. The chemistry of the initially-formed acyl alkyl diradical is dominated by cleavage of the β-carbon oxygen bond; the resulting acyl alkoxy diradical undergoes competitive reactions shown in Scheme 10.[85]

Scheme 10



There are two routes for lactone formation in path B, direct closure of the acyl alkoxy diradical or disproportionation to a hydroxy ketene followed by intramolecular trapping. For example:[83]

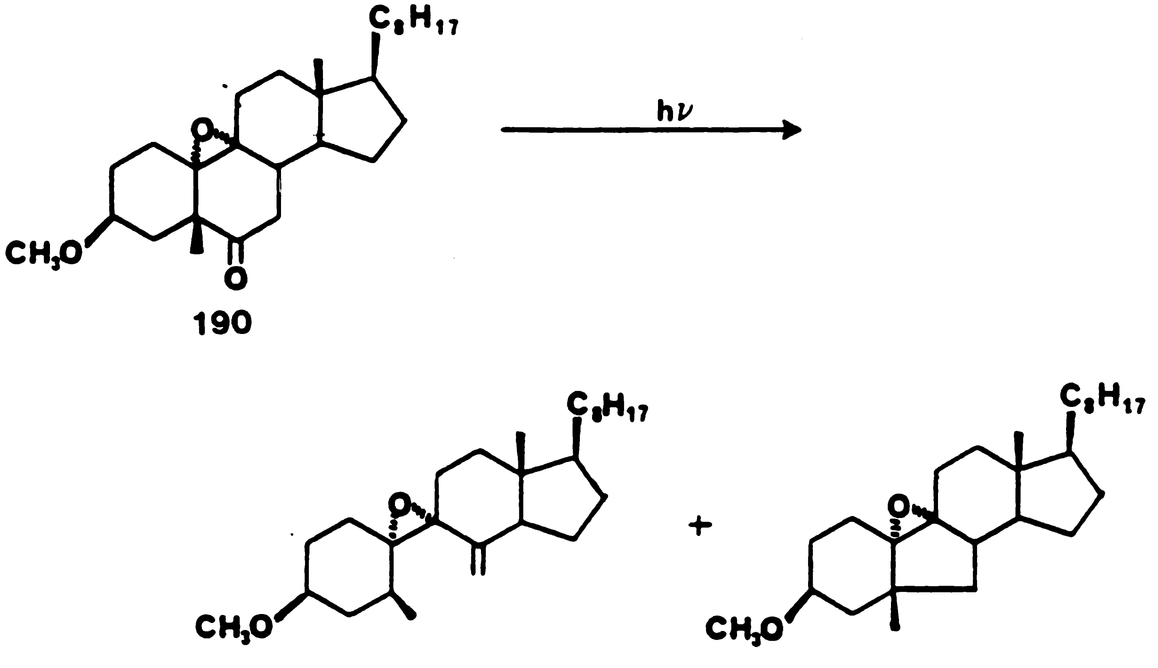


An attempt to understand the A vs. B competition has been made by comparison of the behavior of two diastereomeric β,γ-epoxy ketones.[84] The observation was that only β-oxygen-carbon bond breaking occurs.[84]

In addition, we note the possibility that disproportionation of the acyl alkyl diradical could be a source of decarbonylation product.

Since the present work involves photodecarbonylation of β,γ-diepoxy ketones, literature survey follows on that topic.

Chambers and Marples have investigated the photodecarbonylation of a steroidal β-,γ-epoxy ketone.[85] Irradiation of an ethereal solution of the 9α,10α-epoxy-6-ketone **190** in the absence of oxygen resulted in the formation of unsaturated epoxide **191** (20%) and B-nor epoxide **192** (3%), and several minor products.

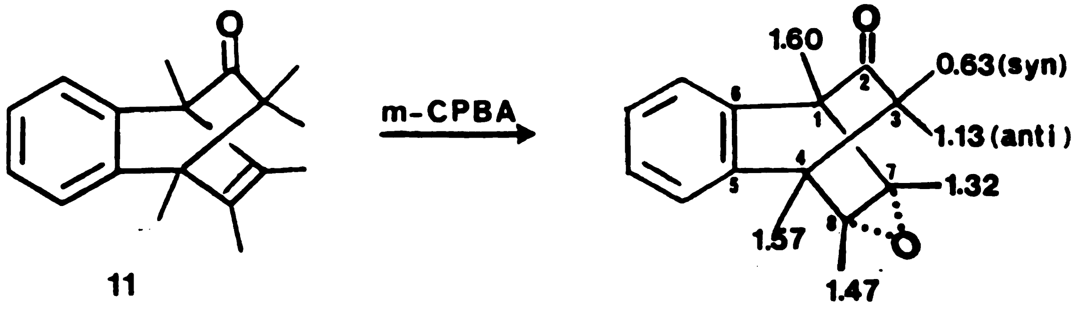


190

191 **192**

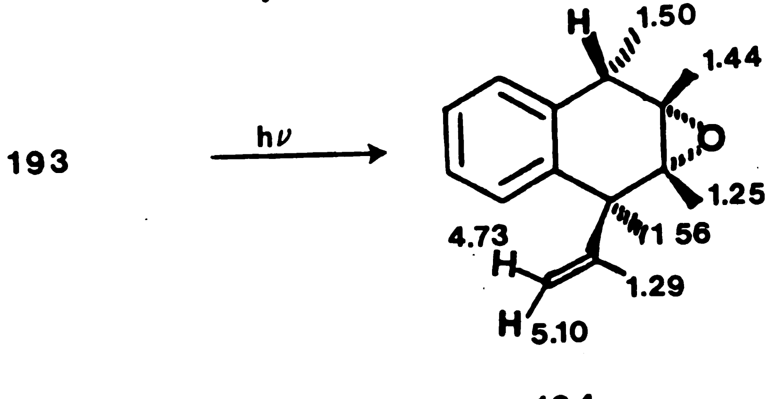
Hart and coworkers have studied the photochemistry of a family of β,γ-epoxy ketones which also undergo photodecarbonylation to provide unsaturated epoxides.[86] These reactions proceeded in high chemical yield and by a mechanism clearly different from that reported by Chambers and Marples for the decarbonylation of **190**.

Treatment of hexamethylbenzobicyclo[2.2.2]octadienone **11** with m-chloroperbenzoic acid gave the endo epoxy ketone **193**. The geometry of the epoxide oxygen was established as endo from ^{1}H NMR chemical shifts, and the difference in chemical shifts, of the methyls at C-7 and C-8.[86]



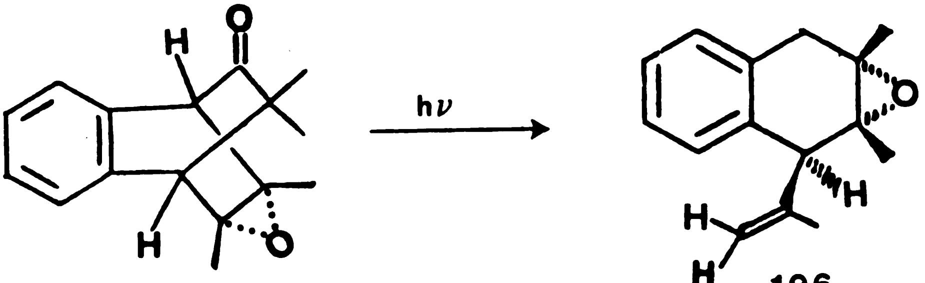
11 **193**

Irradiation of an ether solution of **193** through a Corex filter with a Hanovia L 450-W lamp afforded unsaturated epoxide **194** in ca. 95% yield.



194

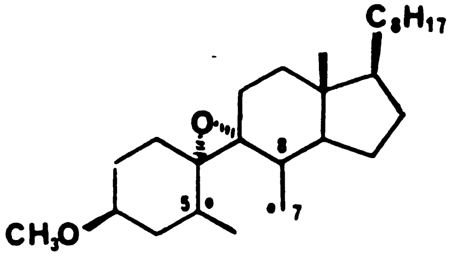
An analogous photodecarbonylation occurs with the tetramethylepoxy ketone **195** to give **196** in 75% yield. However, irradiation of acetone solutions of epoxy ketone **193** or



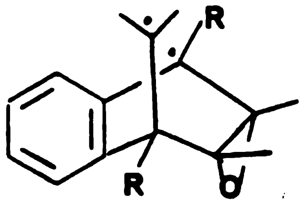
195 **196**

195 through Pyrex resulted in a much slower rate of disappearance of the epoxy ketone, and the formation of complex reaction mixtures.

Chambers and Marples have concluded from labeling studies that the diradical **197** provides **191** by two hydrogen migrations, C-7 ⟶ C-5 and C-8 ⟶ C-7 (overall a formal 1,4-hydrogen shift), which may be consecutive in this order or synchronous.[85] However, this mechanism does not account for the formation of **194** from **193** and **196** from **195**. Ostensibly, **194** and **196** result from diradical **198** following formal



197

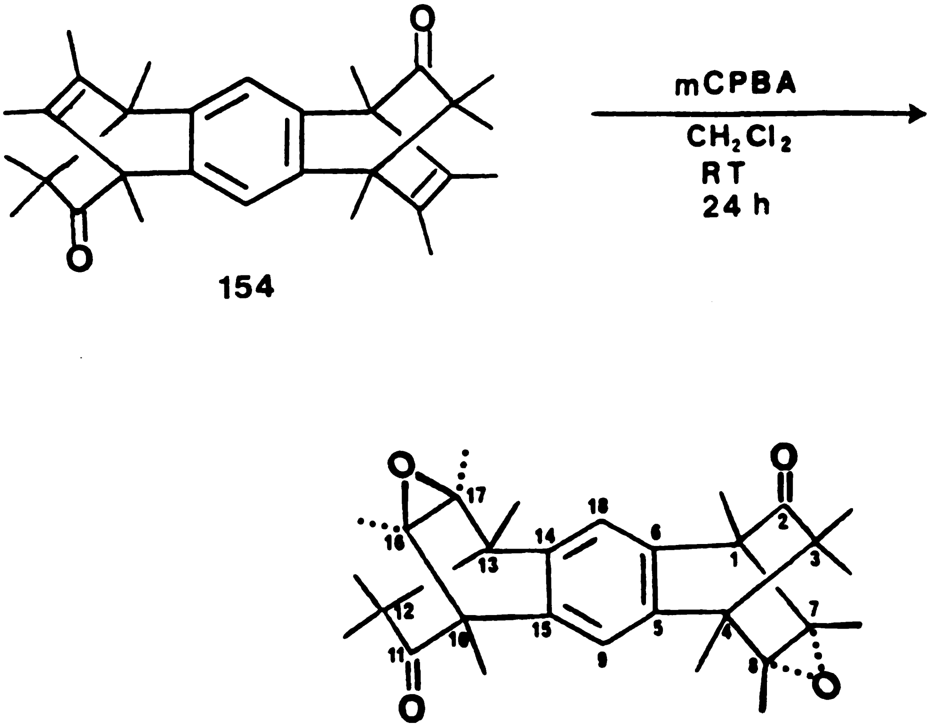


198

1,6-hydrogen shifts. Thus it is apparent that the Chambers and Marples mechanism is not an exclusive route for the photodecarbonylation of β,γ-epoxy ketones.

Results and Discussion

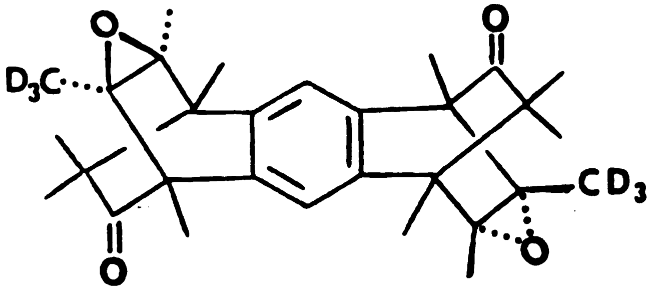
We have studied the photochemistry of symmetrical β,γ-di-epoxy ketone **199**, which was readily prepared (mp 308-309°C, 85% yield) by the reaction of **154** and m-chloroperbenzoic acid. The 250 MHz ^{1}H NMR spectrum of **199** consisted of a



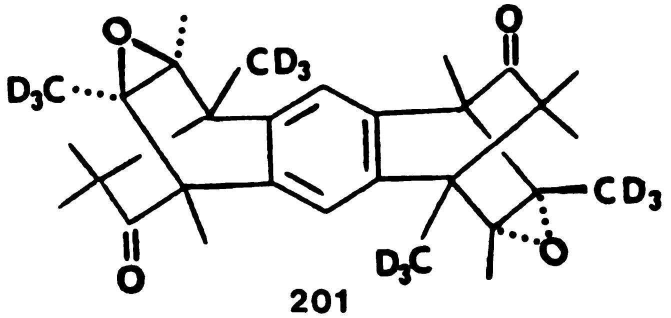
154

199

singlet at 6.90 for the two aromatic protons and six methyl singlets at δ 1.62, 1.56, 1.44, 1.32, 1.16 and 0.65, indicating it was a single isomer. The ^{13}C NMR spectrum showed a peak for the carbonyl carbon at δ 194.21, three aromatic carbon signals at δ 140.63, 133.64, and 116.99 and five quaternary carbon signals at δ 62.71, 59.36, 57.06, 48.49, and 47.12 and six methyl carbon peaks at δ 24.35, 22.54, 15.98, 13.21, 12.50 and 11.92, as required by its Ci symmetry. The infrared spectrum of **199** showed a strong carbonyl band at 1720 cm^{-1}. Deuterated analogs (**200** and **201**) of **199** were prepared in a similar fashion from the corresponding diketones (**160** and **161**).

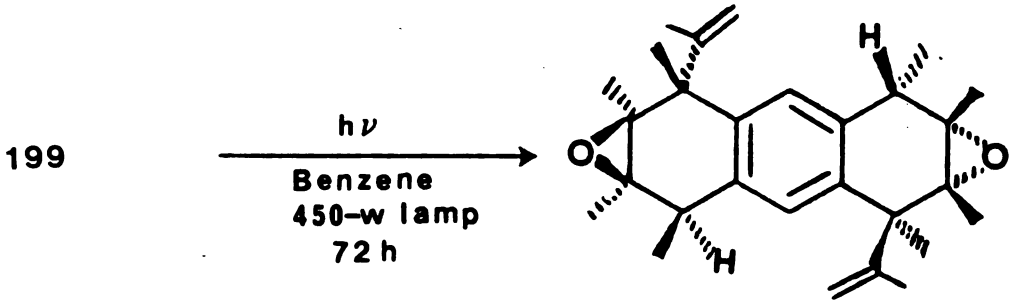


200



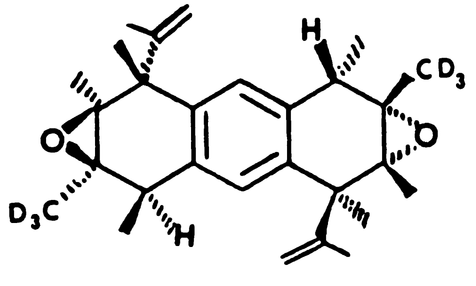
201

A 72 h irradiation of a benzene solution of **199** through Pyrex (Hanovia 450-W lamp) gave unsaturated epoxide **202** in quantitative yield. The 250 MHz ^{1}H NMR spectrum of **202** (mp 222-223°C) showed a singlet at δ 6.94 for the aromatic

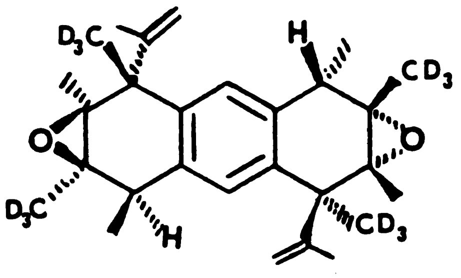


202

protons, two vinyl multiplets at δ 5.09 and 4.79, a quartet at δ 2.98 ($\underline{J}$ = 7 Hz) for the benzylic protons, a doublet at δ 1.41 for the benzylic methyls, and four methyl singlets at δ 1.56, 1.45 and 1.28 (overlap), as expected from the assigned structure. The infrared spectrum of **202** showed no carbonyl absorption. When **200** (labeled with CD_3 at C_7 and C_{16}) was irradiated, the methyl signal at δ 1.45 was absent in the NMR spectrum of the product **203**. When **201** (labeled with CD_3 at C_4, C_7, C_{13} and C_{16}) was used, the signals at δ 1.45 and 1.56 were absent in the ^{1}H NMR of the product **204**. This evidence permited an unambiguous

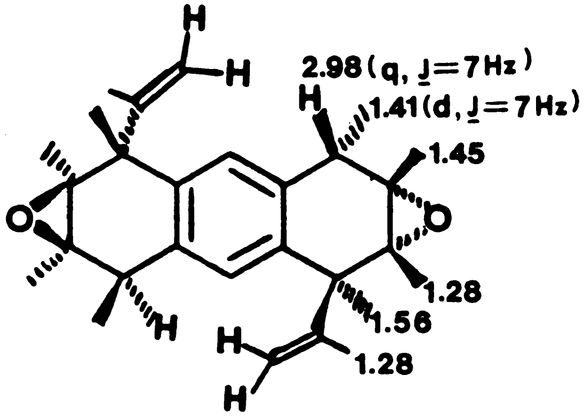


203



204

assignment of structures **202** to the photoproduct from **199**.



The photoproducts obtained from **199-201** are readily accounted for by the earlier mechanism proposed by Hart and coworkers.

Experimental

1. **1,3,3,4,7,8,10,12,12,13,16,17-Dodecamethyl-benzo[1,2-e:4,5-e']bisbicyclo[2.2.2]oct-7,16-dien-2,11-dione (154).** In a procedure similar to that used for **73**, reaction of **40** (1.1 g, 5.78 mmol) with 2,3,4,5,6,6-hexamethyl-cyclohexa-2,4-dien-1-one (2.06 g, 11.57 mmol) in dry THF (200 mL) and LTA (5.65 g, 12.73 mmol) gave a yellow residue which was flash chromatographed over silica gel (1:1 ethyl acetate:hexane) to afford 1.95 g (79%) of a single bis-adduct. An analytical sample was obtained by recrystallization from ethanol, mp 338°C (decomposition); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.00 (s, aromatic, 2H), 1.78 (d, C_8 and C_{17}-CH_3, _J_ = 1 Hz, 6H), 1.69 (d, C_7 and C_{16}-CH_3, _J_ = 1 Hz, 6H), 1.67 (s, C_1 and C_{10}—CH_3, 6H), 1.62 (s, C_4 and C_{13}-CH_3, 6H), 1.07 (s, C_3 and C_{12}-CH_3, anti, 6H), 0.49 (s, C_3 and C_{12}—CH_3, syn, 6H); ^{13}C NMR ($CDCl_3$) δ 195.51 (C=O), 143.16, 140.34, 138.28, 132.00, 115.40 (three aromatic and two vinyl C), 58.42, 50.42, 45.19 (three quaternary C), 24.14, 23.54, 15.30, 13.08, 12.56, 12.18 (six methyl C); mass spectrum, _m/e_ (relative intensity) 430 (1), 360 (10, M^+-dimethylketene), 290 (100, M^+-two dimethylketene), 275 (9), 260 (3), 215 (1), 70 (23); IR (KBr) 2980, 2940, 1710, 1600, 1585, 1460, 1440, 1386, 1265 cm^{-1}. _Anal_. Calcd. for $C_{30}H_{38}O_2$: C, 83.67; H, 8.89. Found: C, 83.59; H, 8.79.

2. **2,4,5,6,6-Pentamethyl-3-methyl-d_3-2,4-cyclohexadienone (158).**[64] 2,3,4,5,6,6-Hexamethyl-2,4-cyclohexadienone (4g) was dissolved in 20 mL of methanol-d containing ~0.3 g of sodium. Monitoring the solution by examination of its NMR spectrum showed that the methyl signal at δ 2.05 disappeared in less than 10 min at room temperature. No further change in the NMR spectrum occurred after several hours. The trideuterio dienone was isolated by pouring the solution into 400 mL of methylene chloride and washing with three 25-mL portions of ice water. Any residual base was removed with solid CO_2. The solution was dried over $MgSO_4$ and concentrated to a yellow oil, which was purified by distillation on a spinning-band column, yielding 3.3 g (83%) of **158**, bp 82-84°C (1.7 mm Hg) (lit.[64] 100-105°C at 2 mm Hg). A forerun boiling at a lower temperature was rejected. ^1H NMR (250 MHz, $CDCl_3$) δ 1.86 (s, 6H), 1.85 (s, 3H), 1.11 (s, 6H).

3. **2,4,6,6-Tetramethyl-3,5-dimethyl-d_6-2,4-cyclohexadienone (159).** C_3-Trideuterated dienone (2.3 g) was added to a solution of 0.68 g of potassium t-butoxide in 12 mL of dimethyl sulfoxide-d_6. The NMR spectrum of the solution changed during 6 h at room temperature. The red-brown solution was poured into 600 mL of methylene chloride and worked up in the usual way. The product was purified by distillation on a spinning-band column to yield 2.0 g (87%) of **159**, 68-70°C (0.2 mm Hg). ^1H NMR (250 MHz, $CDCl_3$) δ 1.87 (s, allylic methyl, 3H), 1.83 (s, allylic methyl, 3H),

1.13 (s, gem-dimethyl, 6H).

4. 1,3,3,4,8,10,12,12,13,17-Decamethyl-7,16-dimethyl-d_6-benzo[1,2-e:4,5-e']bisbicyclo[2.2.2]oct-7,16-dien-2,11-dione (160). In a procedure similar to that used for **73**, reaction of **40** (0.2 g, 1.05 mmol) with 2,4,5,6,6-pentamethyl-3-methyl-d_3-2,4-cyclohexadienone (0.381 g, 2.1 mmol) in dry THF (40 mL) and LTA (0.886 g, 2.2 mmol) gave a yellow solid. Recrystallization of this crude product from ethyl acetate afforded 0.33 g (76%) of a pure isomer; white needles, mp 331°C (decomposition); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.00 (s, aromatic 2H), 1.78 (s, C_8 and C_{17}-CH_3), 1.67 (s, C_1 and C_{10}-CH_3), 1.62 (s, C_4 and C_{13}-CH_3), 1.07 (s, C_3 and C_{12}-CH_3, anti, 6H), 0.49 (s, C_3 and C_{12}-CH_3, syn 6H); mass spectrum (CI), m/e (relative intensity) 436 (91), 435 (100), 364 (19), 295 (7), 281 (8). High resolution mass spectrum: Calcd. for $C_{30}H_{32}D_6O_2$: 436.32483. Found: 436.32471.

5. 1,3,3,8,10,12,12,17-Octamethyl-4,7,13,16-tetramethyl-d_{12}-benzo[1,2-e:4,5-d']bisbicyclo[2.2.2]oct-7,16-dien-2,11-dione (161). In a procedure similar to that used for **73**, reaction of **40** (0.030 g, 0.1578 mmol) with 2,4,6,6-tetramethyl-3,5-dimethyl-d_6-2,4-cyclohexadienone (0.058 g, 0.3157 mmol) in dry THF (25 mL) and LTA (0.154 g, 0.347 mmol) gave a grey solid. Recrystallization of the crude product from ethyl acetate yielded 0.051 g (75%) of a pure isomer; white needles, mp 327°C (decomposition); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.00 (s, aromatic 2H), 1.78 (s, C_8 and C_{17}-CH_3), 1.67

(s, C_1 and C_{10}-CH_3, 6H), 1.07 (s, C_3 and C_{12}-CH_3, anti, 6H), 0.49 (s, C_3 and C_{12}-CH_3, syn, 6H); mass spectrum, m/e (relative intensity) 442 (M^+, trace), 372 (8, M^+-dimethylketene), 302 (100, M^+-two dimethylketene), 70 (29). High resolution mass spectrum: Calcd. for $C_{30}H_{26}D_{12}O_2$: 442.36249. Found: 442.36263.

6. Acid-catalyzed rearrangement of ketone 154. Ketone **154** (500 mg) was refluxed in neat TFA (50 mL) for 21 h and cooled to room temperature. The reaction mixture was poured into ice water and then extracted with three 100-mL portions of methylene chloride. The combined extracts were washed with three 50-mL portions of saturated aqueous sodium bicarbonate solution, dried over anhydrous magnesium sulfate and evaporated to dryness to provide rearranged products (**176-179**) and some unknowns. The ratio of isomers (**176**:**177**:**178**:**179**:48:20:15:9) was determined from integration of the aromatic region (δ 8~6.7). The crude product mixture was chromatographed on a silica gel preparative TLC plate with 4:1 chloroform:hexane (five developments) to afford 69.5 mg of **178**, 38 mg of **179**, 207.5 mg of **176** and 90 mg of **179** along with some unknown products. Analytical samples of **176** through **179** were obtained by recrystallization from ethanol. For 1,5,6,7,8,8,10,11,12,14,17,17-Dodecamethyl-benzo [1,2-c:4,5-f']bisbicyclo[3.2.1]oct-6,11-dien-2,13-dione **(176)**: mp 256-257°C, white solid; ^1H NMR (250 MHz, $CDCl_3$) δ 7.64 (s, 1H), 6.90 (s, 1H), 1.88 (d, J = 1Hz, 3H), 1.61 (d, J = 1Hz, 3H), 1.44 (s, overlap, 6H), 1.37 (s, overlap, 6H), 1.23 (s, 3H), 1.14 (s, 3H), 1.01 (s, overlap, 6H), 0.78

(s, 3H), 0.71 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 198.39 (C=O), 197.39 (C=O), 157.95, 149.93, 149.34, 148.04, 147.61, 131.45, 129.38, 125.45, 119.77, 118.70 (ten aromatic and vinyl C), 66.52, 64.46, 62.32, 57.33, 56.47, 55.48 (six quaternary C), 21.72, 21.15, 17.92, 16.74, 16.36, 13.26, 12.50, 11.34 (overlap), 10.66, 10.06, 9.76 (twelve methyl C); mass spectrum m/e (relative intensity) 430 (23), 415 (100), 387 (4), 360 (3), 345 (5), 237 (3), 179 (3), 165 (4); IR (KBr) 2970, 2930, 2887, 1655 (C=O), 1600, 1430, 1380, 1280, 1213, 1195 cm^{-1}; UV ($CHCl_3$) λ_{max} 246 nm (ϵ=2700). High resolution mass spectrum: Calcd. for $C_{30}H_{38}O_2$: 430.28716; Found: 430.28717. For 1,5,6,7,8,8,10,11,11,13,16,17-Dodecamethylbenzo[1,2-c:4,5-e']bicyclo[3.2.1]oct-bicyclo[2.2.2]oct-6,16-dien-2,12-dione (**177**): mp 248-249°C; ^1H NMR (250 MHz, $CDCl_3$) δ 7.88 (s, 1H), 6.83 (s, 1H), 1.53 (s, 3H), 1.46 (s, 3H), 1.43 (s, 3h), 1.30 (s, 3H), 1.25 (s, 3H), 1.22 (s, 3H), 1.17 (s, 3H), 1.15 (s, 3H), 1.03 (s, 3H), 0.98 (s, 3H), 0.72 (s, 3H), 0.41 (s, 3H); ^{13}C NMR ($CDCl_3$) δ197.21(C=O), 191.25 (C=O), 147.66, 146.84, 142.28, 136.78, 131.32, 130.86, 129.23, 128.80, 122.53, 117.03 (ten aromatic and vinyl C), 66.47, 57.29, 55.36, 45.13, 42.25, 42.00 (six quaternary C), 22.96, 21.66, 17.88, 17.26, 13.66, 13.03, 11.29, 10.00, 9.92, 9.73, 7.72, 5.49 (twelve methyl C); mass spectrum, m/e (relative intensity) 430 (28), 415 (100), 360 (16), 330 (4), 275 (6), 149 (28); IR (KBr) 2968, 2930, 1720 (C=O), 1670 (C=O), 1598, 1450, 1380, 1260, 1210 cm^{-1}. High resolution mass spectrum: Calcd. for

$C_{30}H_{38}O_2$: 430.28716; Found: 430.28701. For 1,5,6,7,8,8,10-11,12,13,17,17-Dodecamethyl-benzo[1,2-c:4,5-c']bisbicyclo[3.2.1]oct-6,11-dien-2,14-dione (**178**): mp 313-314°C, yellow crystals; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.77 (s, 2H) 1.45 (s, *J* = 1, 6H), 1.44 (s, *J* = 1, 6H), 1.30 (s, 6H), 1.16 (s, 6H), 1.03 (s, 6H), 0.73 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 197.00 (C=O), 148.34, 147.22, 132.96, 130.84, 121.90 (five aromatic and vinyl C), 66.77, 57.21, 56.19 (three quaternary C), 21.57, 17.98, 12.35, 11.40, 10.01, 9.75 (six methyl C); mass spectrum, *m/e* (relative intensity) 430 (17), 415 (100), 385 (1), 200 (22); IR (KBr) 2986, 2930, 2875, 1670 (C=O), 1440, 1400, 1376, 1272, 1185, 1158 cm^{-1}; UV ($CDCl_3$) λ_{max} 239 nm (ϵ= 2100). High resolution mass spectrum: Calcd. for $C_{30}H_{38}O_2$: 430.28716; Found: 430.28717. For 1,3,4,5,8,8-10,11,12,14,17,17-Dodecamethyl-benzo[1,2-f:4,5-f']bisbicyclo-[3.2.1]oct-3,11-dien-2,13-dione (**179**): mp 335-336°C, white solid; ^{1}H NMR 250 MHz, $CDCl_3$) δ 6.74 (s, 2H), 1.86 (d, *J* = 1, 6H), 1.61 (d, *J* = 1, 6H), 1.31 (s, 6H), 1.29 (s, 6H), 0.99 (s, 6H), 0.77 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 199.36 (C=O), 157.30, 150.29, 143.64, 125.10, 116.93 (five aromatic and vinyl C), 63.59, 62.34, 55.47 (three quaternary C), 21.26, 16.89, 16.40, 13.29, 11.34 (overlap) (six methyl C); mass spectrum, *m/e* (relative intensity) 430 (100), 415 (78), 387 (18), 361 (10), 265 (7), 251 (3), 97 (84); IR (KBr) 3010, 2985, 2930, 2875, 1650 (C=O), 1615, 1385, 1320, 1305, 1228 cm^{-1}; UV ($CHCl_3$) λ_{max} 240 nm (ϵ =2200). High resolution mass spectrum: Calcd. for

$C_{30}H_{38}O_2$: 430.28716; Found: 430.29749.

7. **1,3,5,8,8,10,12,14,17,17-Decamethyl-4,11-dimethyl-d_6-benzo[1,2-f:4,5-f']bisbicyclo[3.2.1]oct-3,11-dien-2,13-dione (180).** The dienone **179** (15 mg) was dissolved in 20 mL of methanol-d containing 0.1 g of sodium and refluxed for 30 h and cooled. The hexadeutero dienone was isolated by pouring the solution into 100 mL of methylene chloride and washing twice with 25 mL of water. Any residual base was removed with solid CO_2. Removal of the solvent in vacuo yielded 14 mg (93%) of pure hexadeutero dienone **180**. ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.74 (s, 2H), 1.61 (s, 6H), 1.31 (s, 6H), 1.29 (s, 6H), 0.99 (s, 6H), 0.77 (s, 6H).

8. **1,5,6,7,8,8,10,12,14,17,17-Undecamethyl-11-methyl-d_3-benzo[1,2-c:4,5-f']bisbicyclo[3.2.1]oct-6,11-dien-2,13-dione (181).** In a procedure similar to that used for **180**, reaction of **176** (13 mg) with 0.1 g of sodium in 20 mL of methanol-d gave after work-up pure trideutero dienone. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.64 (s, 1H), 6.90 (s, 1H), 1.61 (s, 3H), 1.44 (s, overlap, 6H), 1.37 (s, overlap, 6H), 1.23 (s, 3H), 1.14 (s, 3H), 1.01 (s, overlap, 6H), 0.78 (s, 3H), 0.71 (s, 3H).

9. **The equilibration of ketone 178 in TFA.** A 20 mg sample of ketone **178** was refluxed for 21 h in neat TFA and quenched using the procedure outlined in general quenching studies to afford 19 mg of a pale yellow solid. The ^{1}H NMR spectrum of the sample was similar to that of a sample from the

rearrangement (21 h reflux) of **154** in TFA.

10. Photoisomerization of 1,3,4,5,8,8,10,11,12,14,17,17-dodecamethyl-benzo[1,2-f:4,5-f']bisbicyclo[3.2.1]oct-3,11-dien-2,13-dione (179). A degassed solution of **179** (20 mg) in 20 mL of spectroscopic grade acetone was irradiated through a pyrex filter using a 450 watt Hanovia lamp for 21h. Removal of the solvent in vacuo gave essentially pure photoproduct **191** contaminated with less than 2% of starting dienone **179**; mp 367°C (decomposition), white solid; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.89 (s, 2H), 1.48 (s, 6H), 1.28 (s, 6H), 1.19 (s, 6H), 1.14 (s, 6H), 0.96 (s, 6H), 0.34 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 199.03 (C=O), 136.87, 136.12, 117.59 (three aromatic C), 54.70, 45.32, 42.07, 39.96, 35.97 (five quaternary C), 23.00, 17.65, 13.13, 9.96, 7.83, 5.60 (six methyl C); mass spectrum, m/e (relative intensity) 430 (100), 415 (84), 387 (16), 361 (12), 333 (11), 303 (10), 275 (8), 245 (9), 205 (3), 97 (57); IR (KBr) 2975, 2921, 1715, (C=O), 1460, 1387, 1323, 1270, 1048, 985 cm^{-1}; High resolution mass spectrum: Calcd. for $C_{30}H_{38}O_2$: 430.28716; Found: 430.28701.

11. Syn-7,8-syn-16,17-diepoxy-1,3,3,4,7,8,10,12,12,13,16,17-dodecamethyl-benzo[1,2-e:4,5-e']bisbicyclo[2,2,2]oct-2,11-dione (199). A solution of 0.23 g (1.33 mmol) of 85% m-chloroperbenzoic acid in 10 mL of methylene chloride was added during 10 min to an ice-cold stirred solution of 0.22 g (0.511 mmol) of **154** in 20 mL of methylene chloride. Stirring was continued in an ice bath for 1 h and at room temperature for an additional 24 h. Excess peracid was destroyed by the addition of 10% sodium sulfite until a test with starch-iodide paper was negative. The reaction mixture was washed three times with 50 mL of 5% sodium bicarbonate solution, twice with 50 mL of water, and once with 50 mL of saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. Removal of the solvent provided a crude product which was recrystallized from ethanol to yield of 0.2 g (85%) of a single isomer **(199)** as white needles: mp 308-309°C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.90 (s, aromatic, 2H), 1.62 (s, C_1 and C_{10}—CH_3, 6H), 1.56 (s, C_4 and C_{13}-CH_3, 6H), 1.44 (s, C_8 and C_{17}-CH_3, 6H), 1.32 (s, C_7 and C_{16}-CH_3, 6H), 1.16 (s, C_3 and C_{12}-CH_3, anti, 6H), 0.65 (s, C_3 and C_{12}-CH_3, syn, 6H); ^{13}C NMR ($CDCl_3$) δ 194.21, (C=O), 140.63, 133.64, 116.99 (three aromatic C), 62.71, 59.36, 57.06, 48.49, 47.12, (five quaternary C), 24.35, 22.54, 15.98, 13.21, 12.50, 11.92 (six methyl C); mass spectrum, <u>m</u>/<u>e</u> (relative intensity) 462 (7), 392 (8), 349 (20), 263 (36), 251 (13), 236 (22), 221 (11), 206 (8), 43 (100); IR (KBr) 2975, 1720, 1463, 1380, 1260, 1093, 1010, 873 cm^{-1}; UV ($CHCl_3$) λ_{max} 236 (ϵ=1600). High resolution mass spectrum: Calcd. for $C_{30}H_{38}O_4$: 462.2770; Found: 462.2778.

12. **Syn-7,8-syn-16,17-diepoxy-1,3,3,4,8,10,12,12,13,17-decamethyl-7,16-dimethyl- d_6 -benzo[1,2-e:4,5-e']bisbicyclo[2.2.2]-oct-2,11-dione (200).** In a procedure similar to that used for **199**, reaction of **160** (0.098 g, 0.224 mmol) with 85% m-chloroperbenzoic acid gave a crude product which was

recrystallized from ethanol to yield 0.089 g (85%) of a single isomer **(200)** as white needles: mp 308-309°C; ^1H NMR (250 MHz, $CDCl_3$) δ 6.90 (s, aromatic, 2H), 1.62 (s, C_1 and C_{10}-CH_3, 6H), 1.56 (s, C_4 and C_{13}-CH_3 6H), 1.44 (s, C_8 and C_{17}-CH_3, 6H), 1.16 (s, C_3 and C_{12}-CH_3, anti, 6H), 0.65 (s, C_3 and C_{12}-CH_3, syn, 6H); mass spectrum, m/e (relative intensity) 468 (trace), 397 (6), 352 (22), 293 (10), 265 (30), 251 (27), 239 (39), 97 (23), 43 (100). High resolution mass spectrum: Calcd for $C_{30}H_{32}D_6O_4$: 468.31465. Found: 468.31390.

13. **Syn-7,8-syn-16-17-diepoxy-1,3,3,8,10,12,12,17-octamethyl-4,7,13,16-tetramethyl-d_{12}-benzo[1,2-e:4,5-e']bisbicyclo[2.2.2]-oct-2,11-dione (201).** In a procedure similar to that used for **199**, reaction of **161** (0.024 g, 0.0542 mmol) with 85% m-chloroperbenzoic acid gave a crude product which was recrystallized from ethanol to yield 0.021 g (85%) of a single isomer **(201)** as white needles: mp 308-309°C; ^1H NMR (250 MHz, $CDCl_3$) δ 6.90 (s, aromatic 2H), 1.62 (s, C_1 and C_{10}-CH_3, 6H), 1.44 (s, C_8 and C_{17}-CH_3, 6H), 1.16 (s, C_3 and C_{12}-CH_3, anti, 6H), 0.65 (s, C_3 and C_{12}-CH_3, syn, 6H); mass spectrum, m/e (relative intensity) 474 (trace), 403 (3), 358 (9), 288 (16), 271 (14), 244 (17), 70 (22), 43 (100). High resolution mass spectrum: Calcd for $C_{30}H_{26}D_{12}O_4$: 474.35232; Found: 474.3522.

14. **Photolysis of 199.** A solution of 20 mg of **199** in 20 mL of benzene was irradiated at room temperature with a

450-watt Hanovia lamp through a Pyrex filter. Monitoring the photolysis by 250 MHz ^1H NMR after 12 h irradiation showed a significant decrease in the concentration of **199** and a progressive increase in the concentration of photoproducts (two sets of vinyl peaks at δ 5.11, 4.81 (minor) and δ 5.09, 4.79 in the 250 MHz ^1H NMR). Examination of the photolysis by 250 MHz ^1H NMR after irradiation for 72 h indicated the presence of only a single photoproduct **202** which was recrystallized from ethylacetate: mp 222-223°C; ^1H NMR (250 MHz, $CDCl_3$) δ 6.94 (s, 2H), 5.09 (m, 2H), 4.79 (m, 2H), 2.98 (q, _J_ = 7Hz, 2H), 1.56 (s, 6H), 1.45 (s, 6H), 1.41 (d, _J_ = 7 Hz, 6H), 1.28 (s, 12H);mass spectrum, _m/e_ (relative intensity) 406 (2), 363 (3), 149 (16), 95 (17), 43 (100); IR (KBr) 3094, 2981, 2947, 1512, 1464, 1380, 1266 cm^{-1}. High resolution mass spectrum: Calcd. for $C_{28}H_{38}O_2$: 406.28716; Found: 406,28735.

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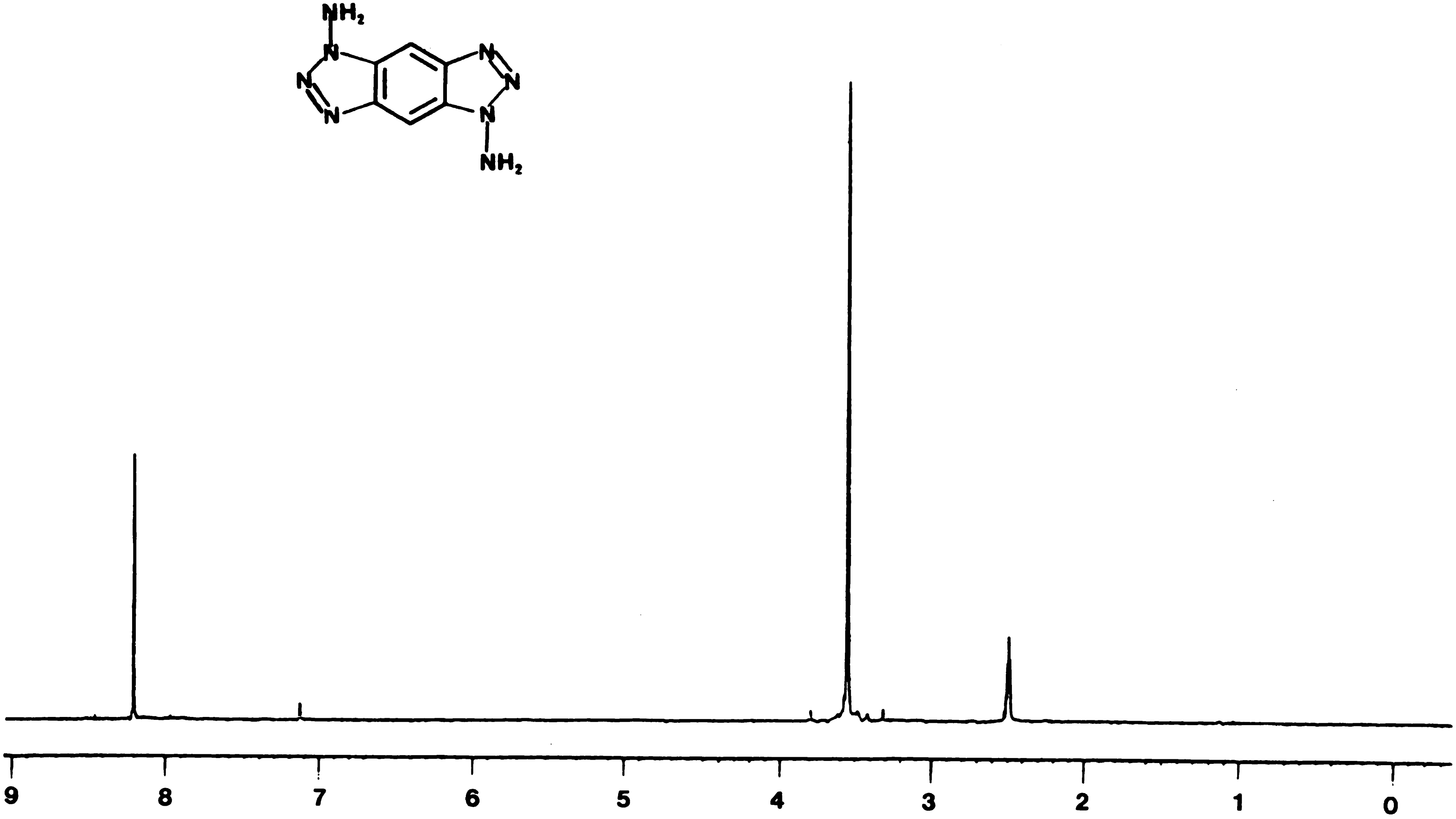
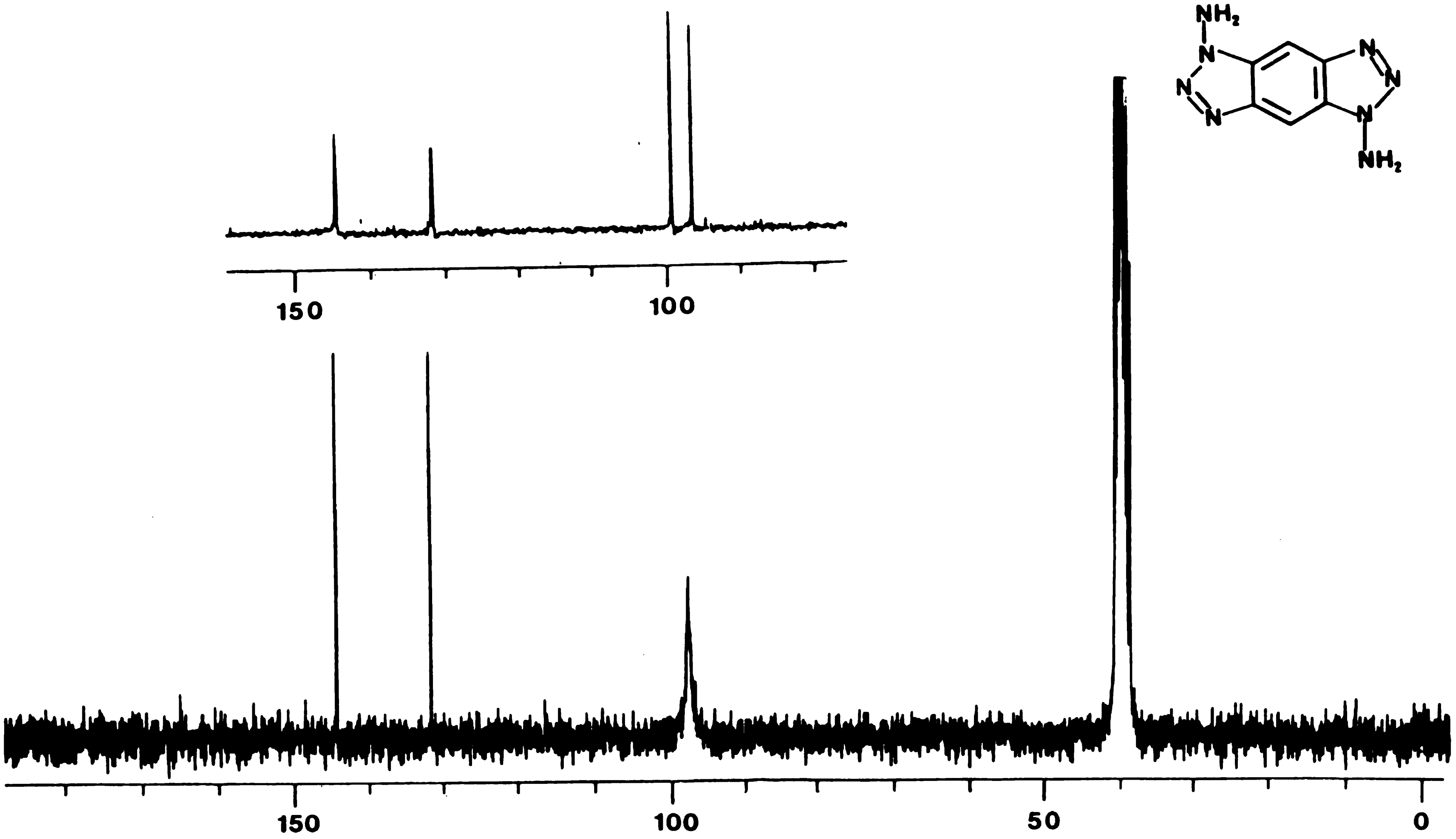
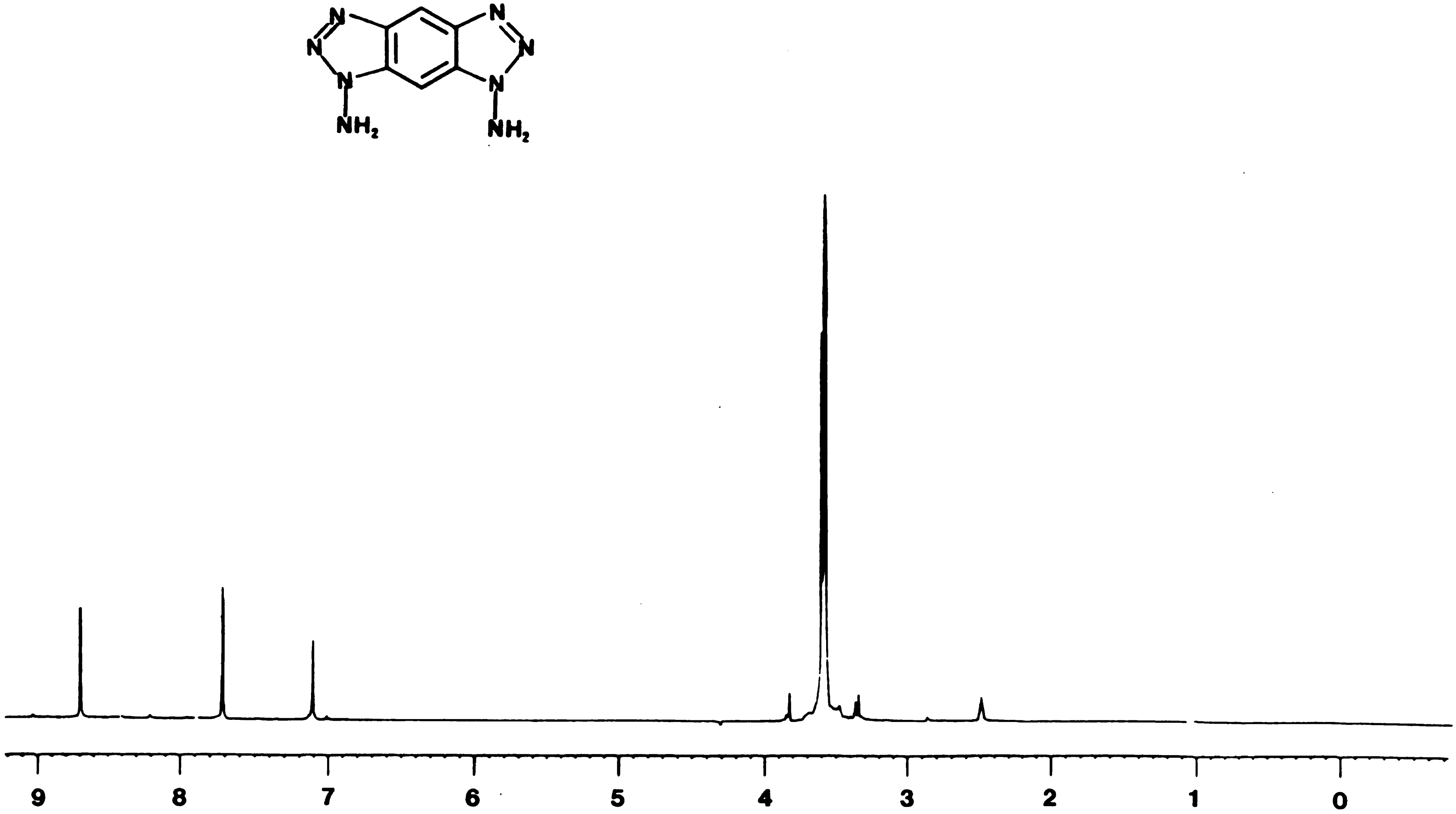


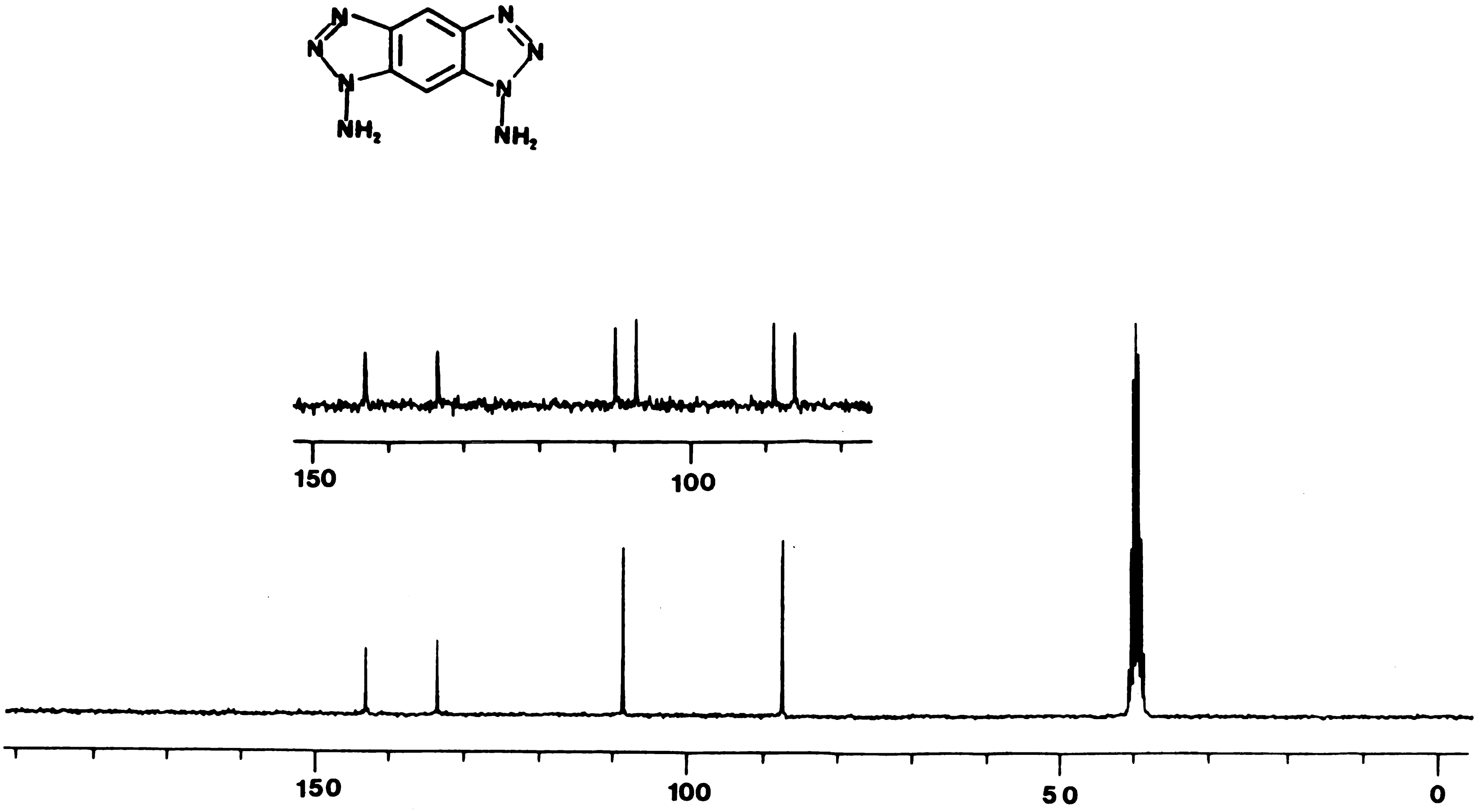
1. 250 MHz ^{1}H NMR of 1,5-Diamino-benzo[1,2-d:4,5-d']bistriazole (DABT) (40).



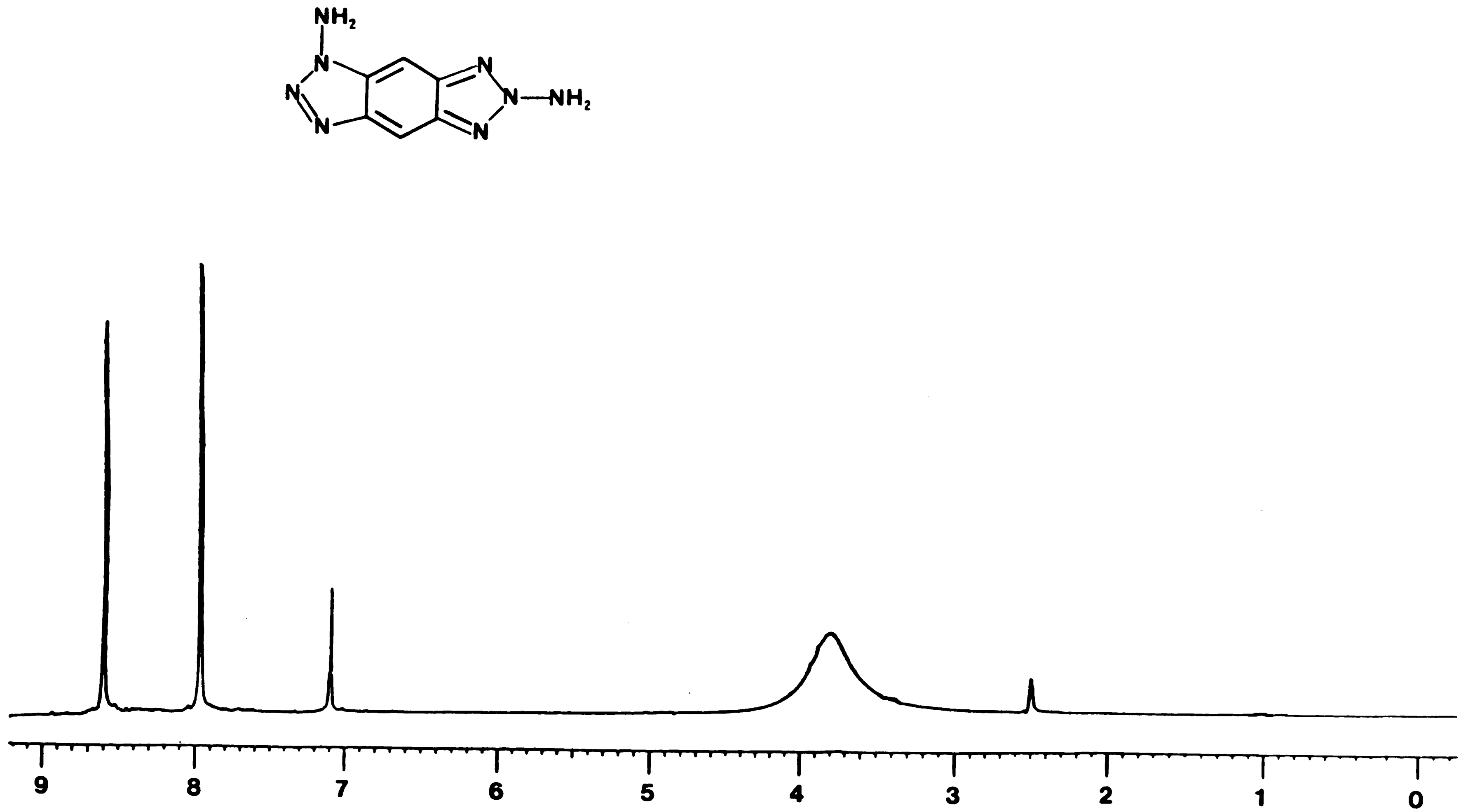
2. ^{13}C NMR of 1,5-Diamino-benzo[1,2-d:4,5-d']bistriazole (DABT) (40).



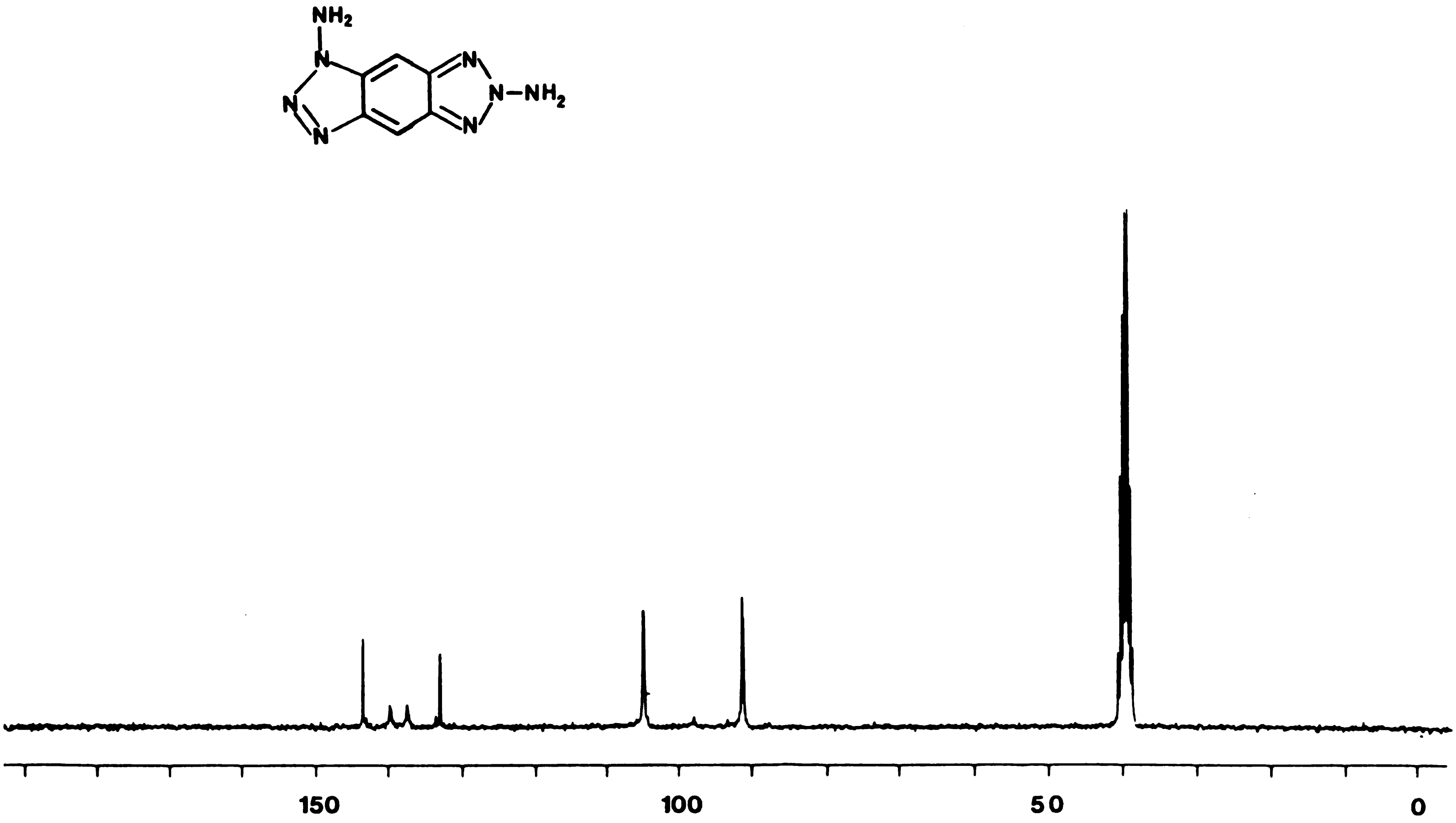
3. 250 MHz ^{1}H NMR of 1,7-Diamino-benzo[1,2-d:4,5-d']bistriazole (41).



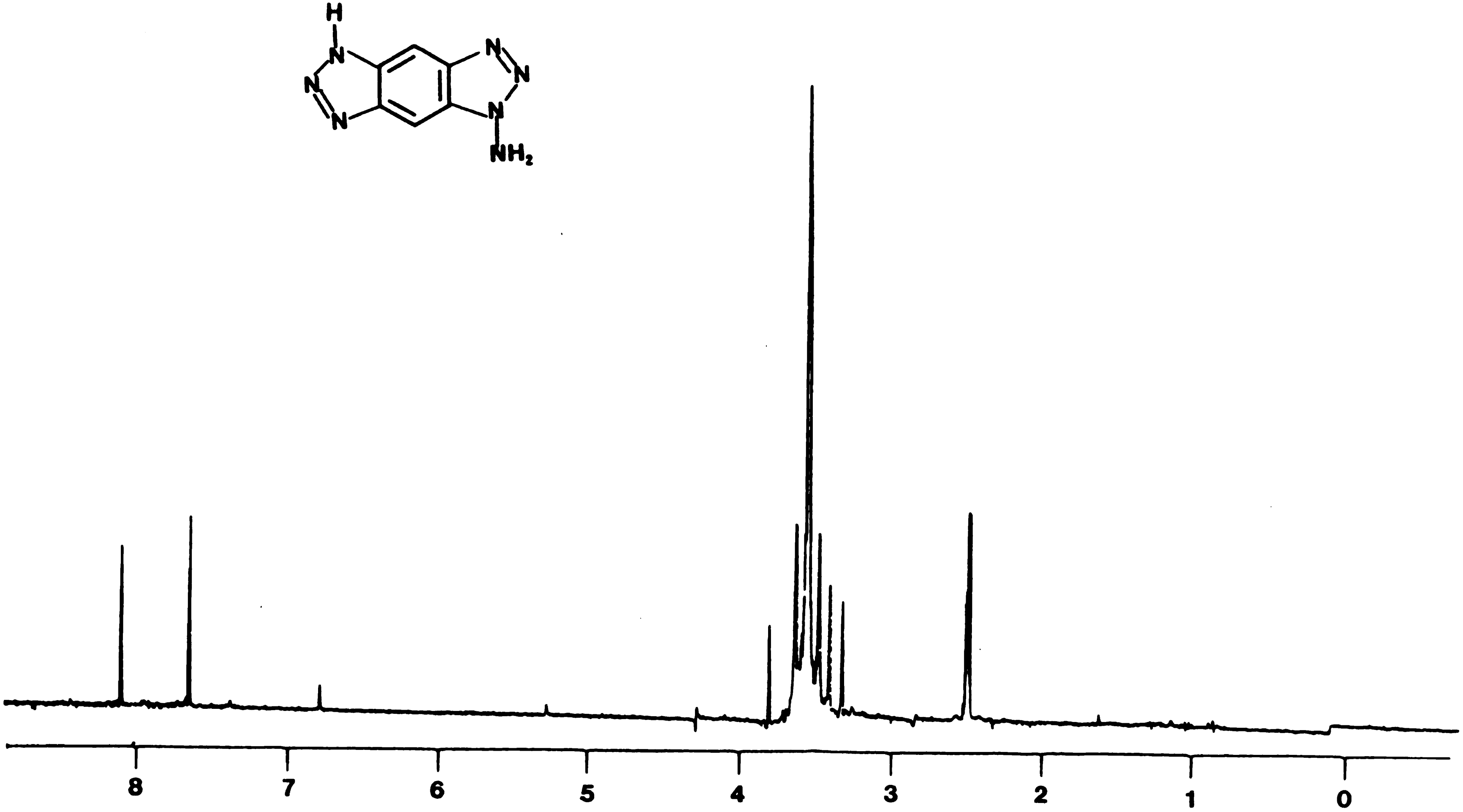
4. ^{13}C NMR of 1,7-Diamino-benzo[1,2-d:4,5-d']bistriazole (**41**).



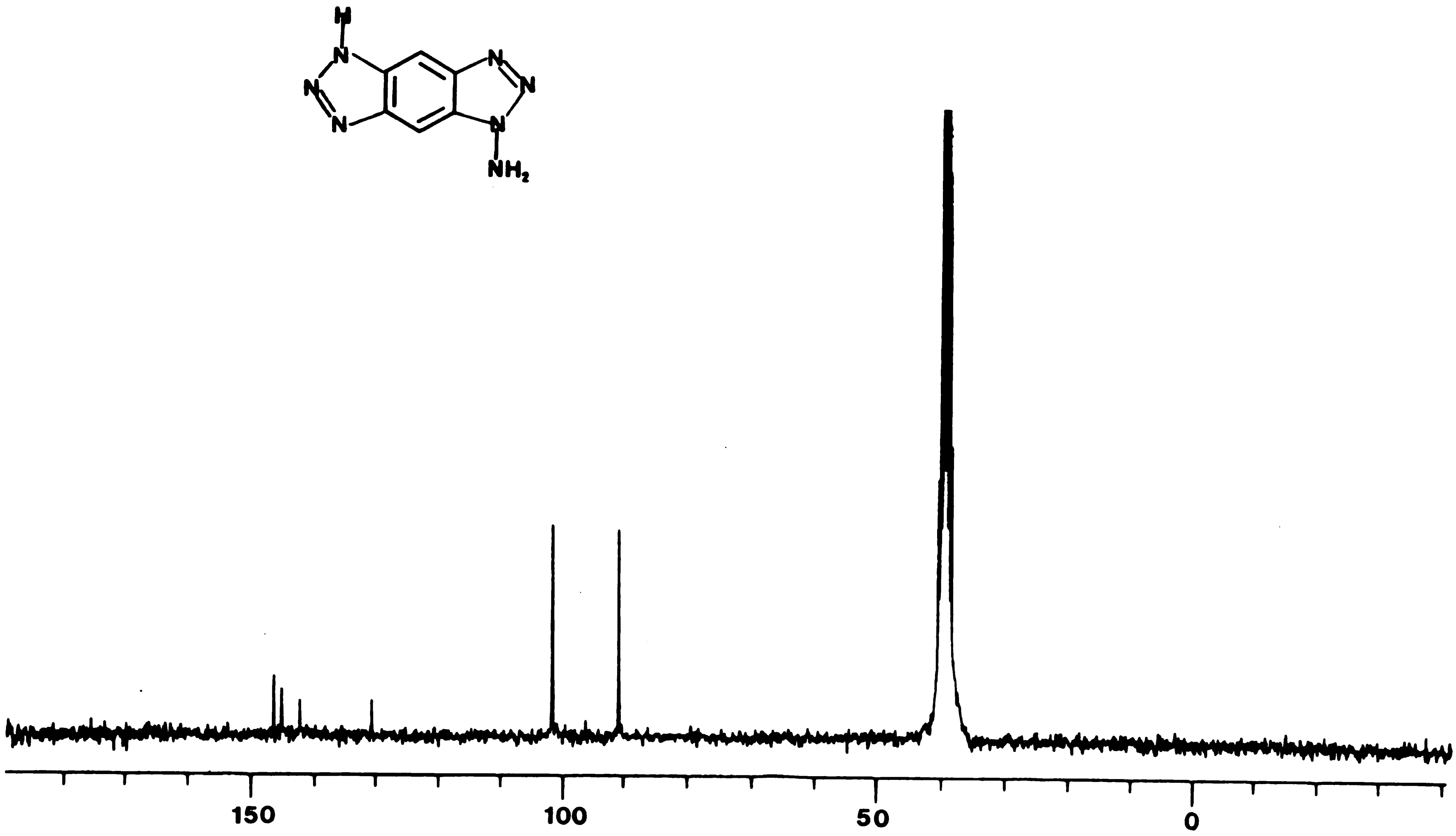
5. 250 MHz ^{1}H NMR of 1,6-Diamino-benzo[1,2-d:4,5-d']bistriazole (**63**).



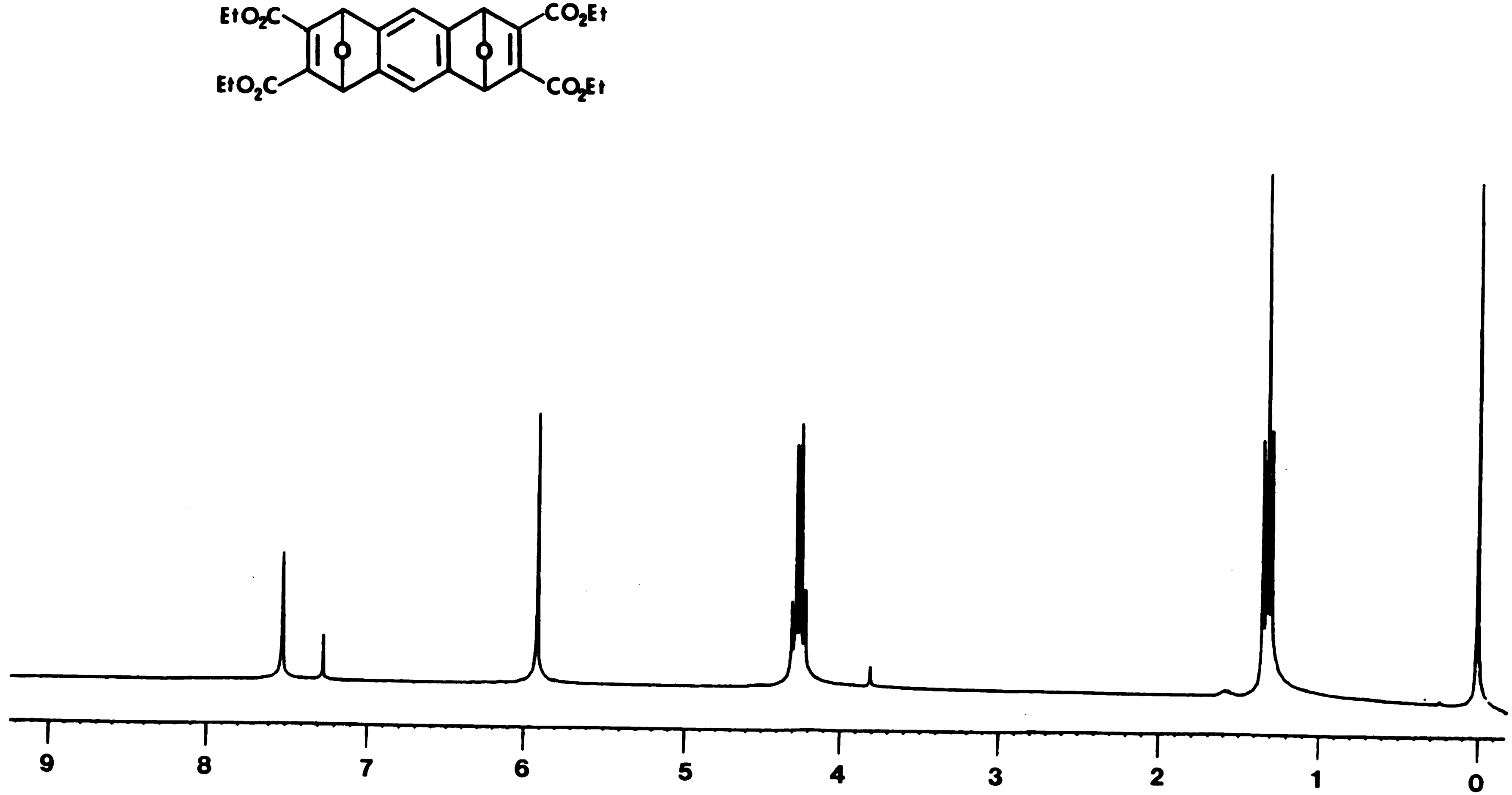
6. ^{13}C NMR of 1,6-Diamino-benzo[1,2-d:4,5-d']bistriazole (63).



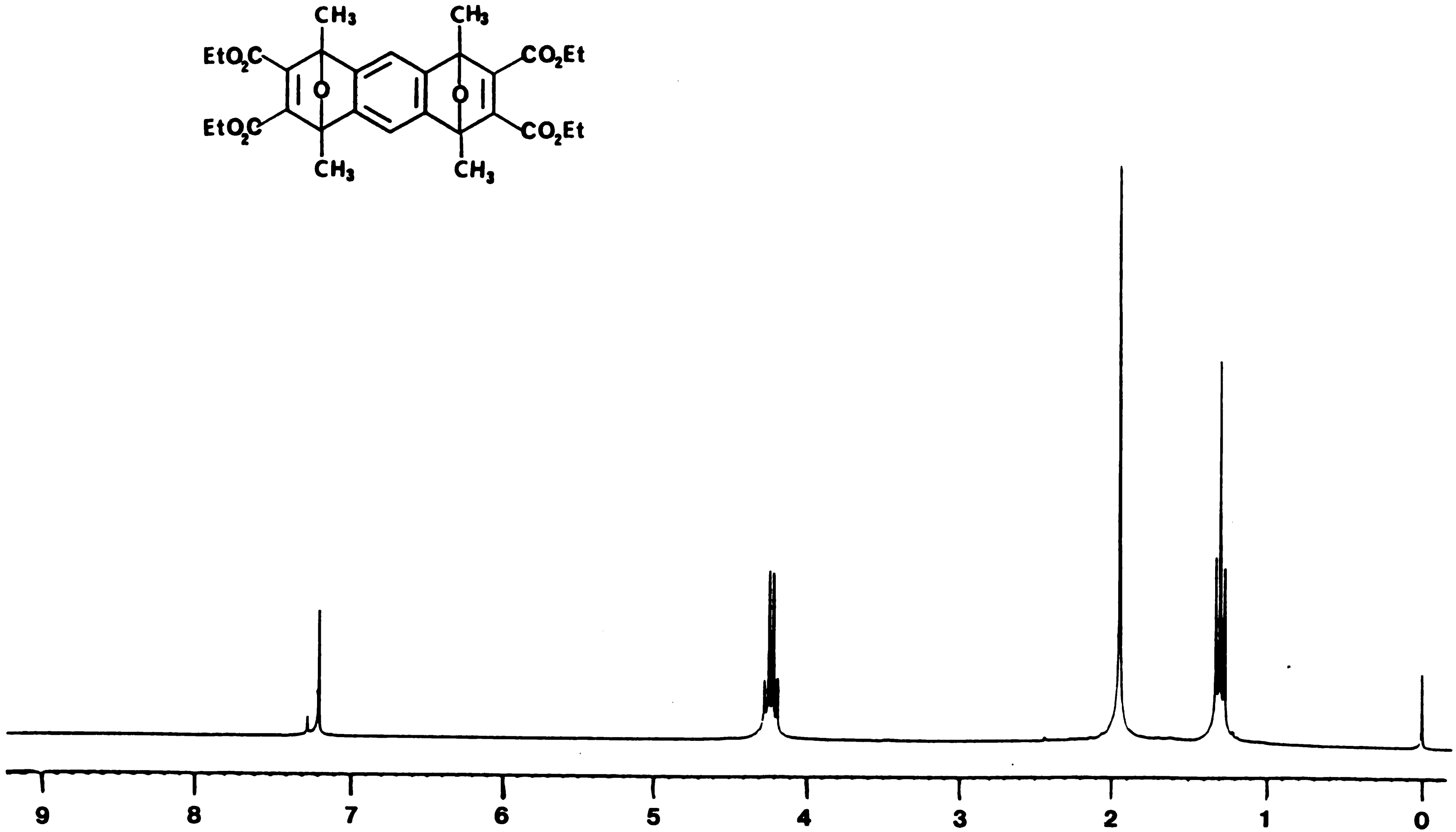
7. 250 MHz ^{1}H NMR of 1-Amino-benzo[1,2-d:4,5-d']bistriazole (**64**).



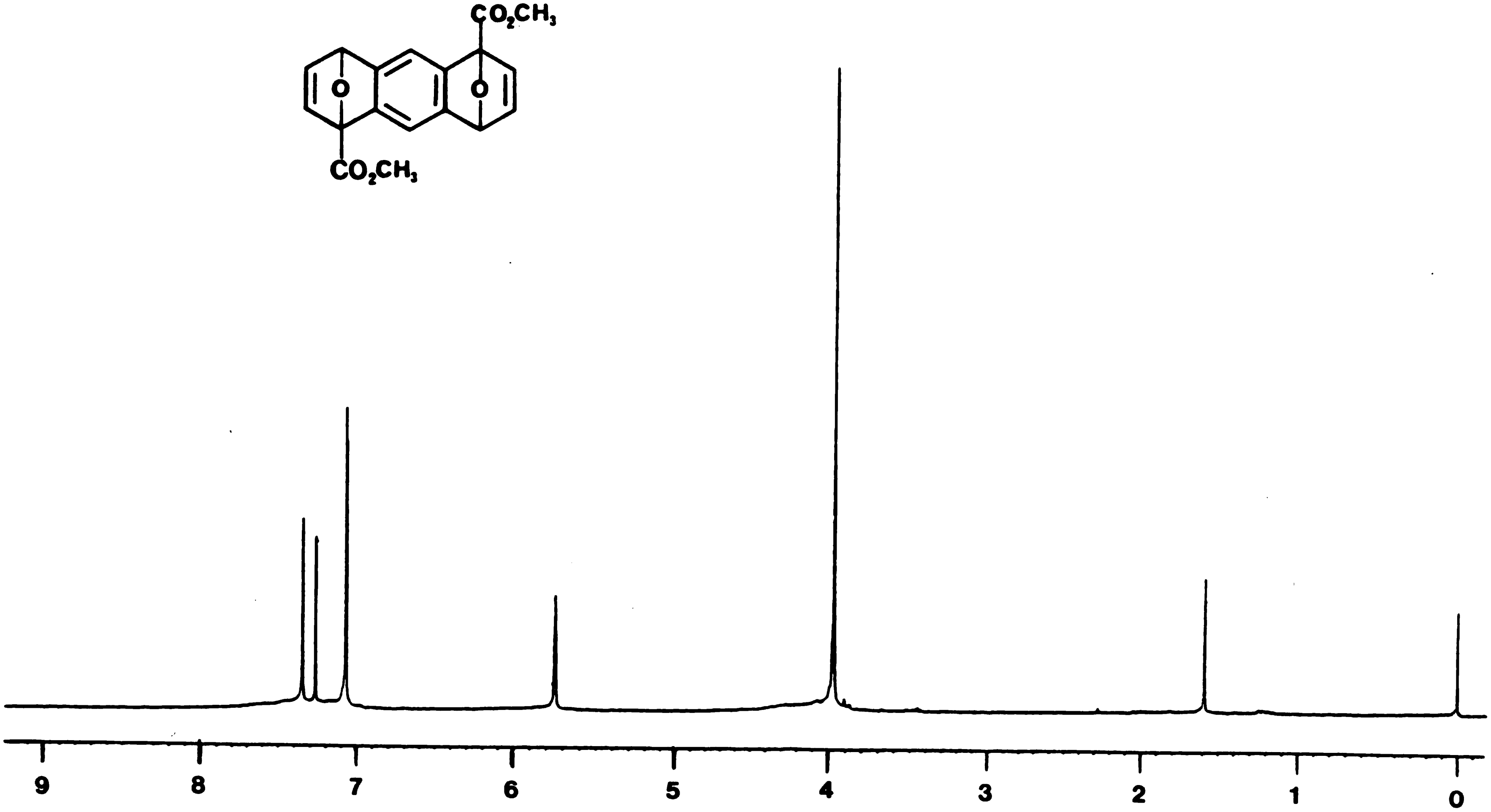
8. ^{13}C NMR of 1-Amino-benzo[1,2-d:4,5-d']bistriazole (**64**).



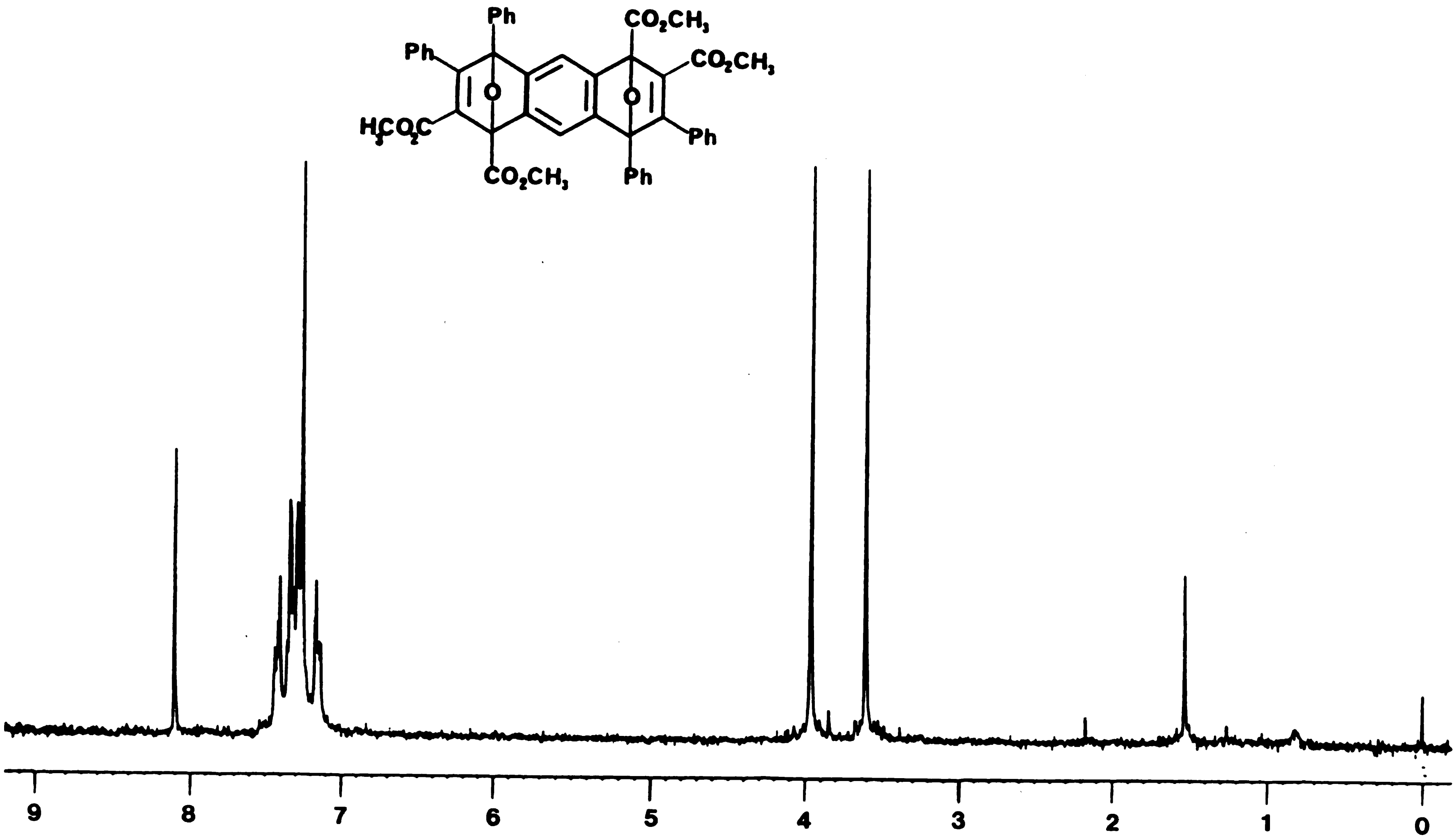
9. 250 ^{1}H NMR of Tetraethyl 1,4,5,8-tetrahydroanthracene-1,4:5,8-diendoxide-2,3,6,7-tetracarboxylate (**87**).



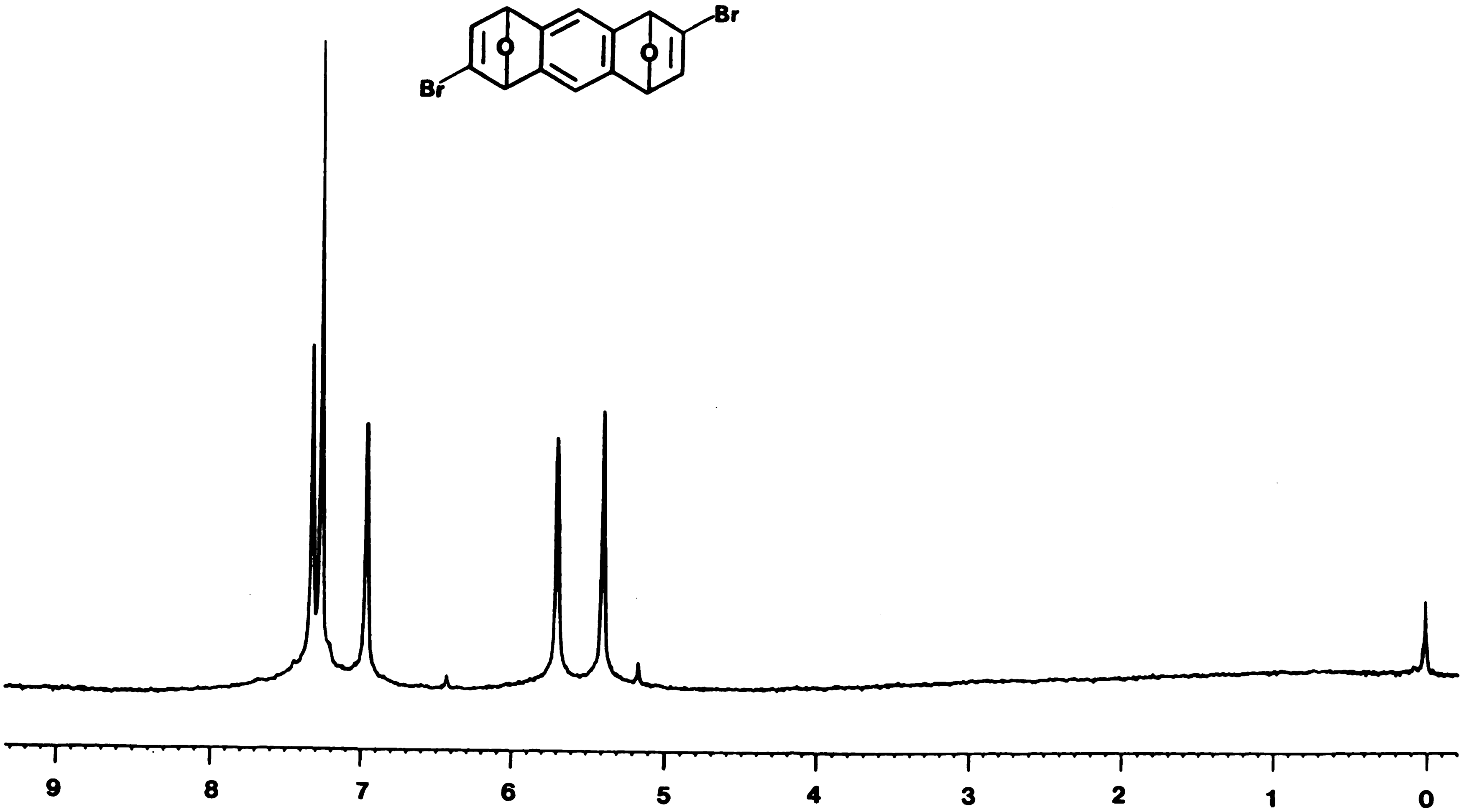
10. 250 MHz ^{1}H NMR of Tetraethyl 1,4,5,8-tetramethyl-1,4,5,8-tetrahydroanthracene-1,4:5,8-diendoxide-2,3,6,7,-tetracarboxylate (**89**).



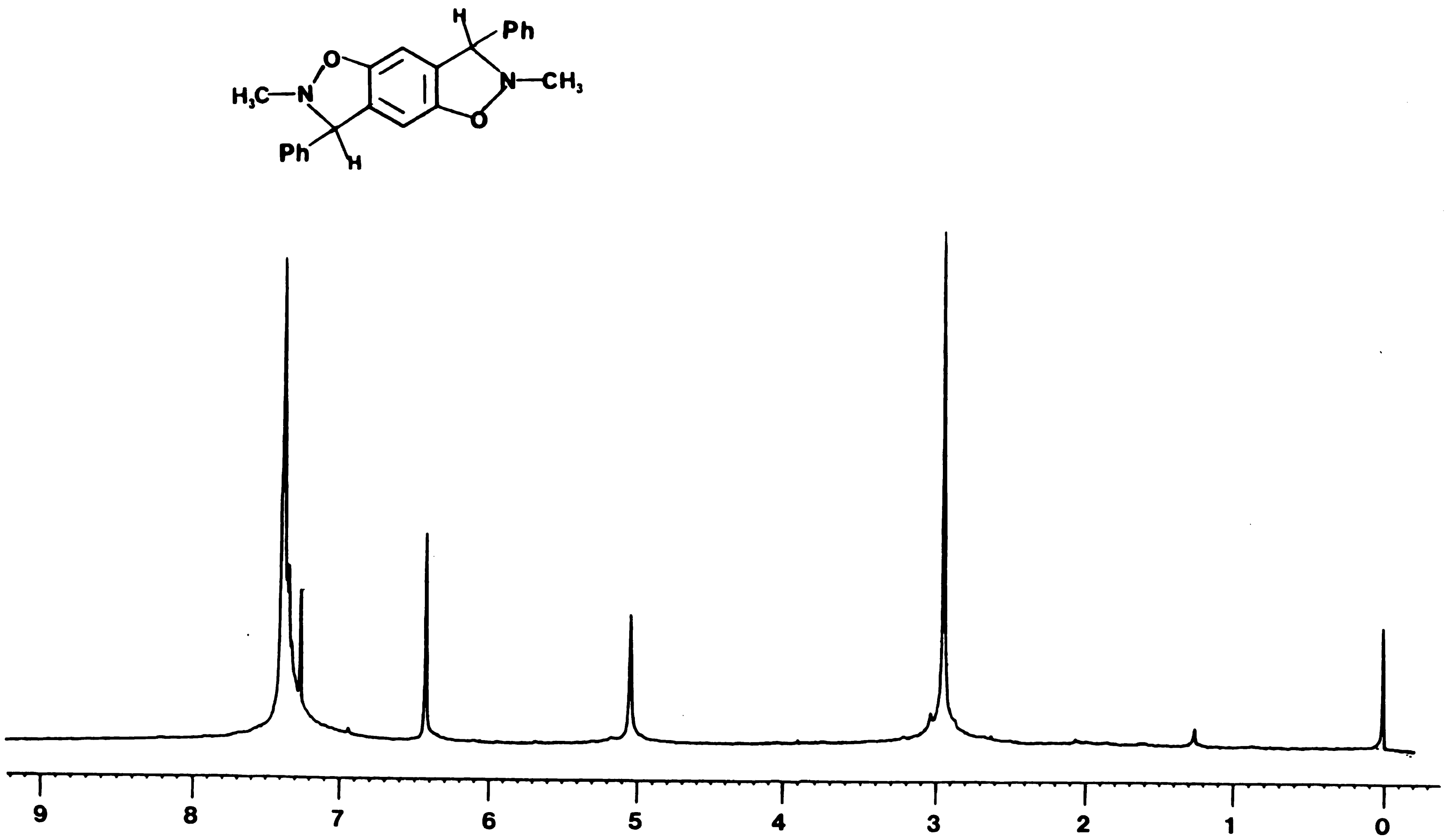
11. 250 MHz ^{1}H NMR of Dimethyl 1,4,5,8-tetrahydroanthracene-1,4:5,8-diendoxide-1,5-dicarboxylate (**91**).



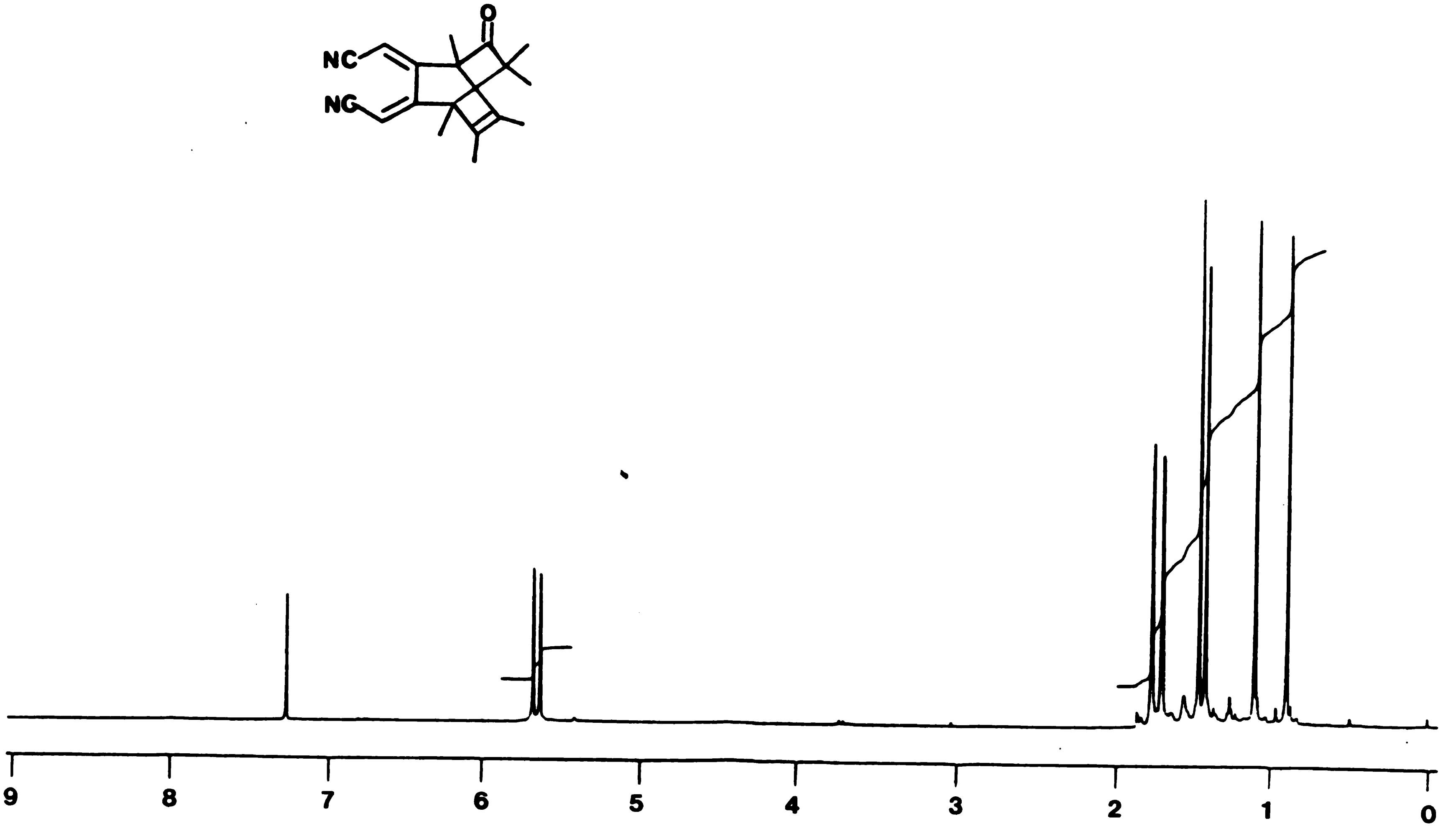
12. 250 MHz ^1H NMR of Tetramethyl 3,4,7,8-tetraphenyl-1,4,5,8-tetrahydroanthracene-1,4:5,8-diendoxide-1,2,5,6-tetracarboxylate (99).



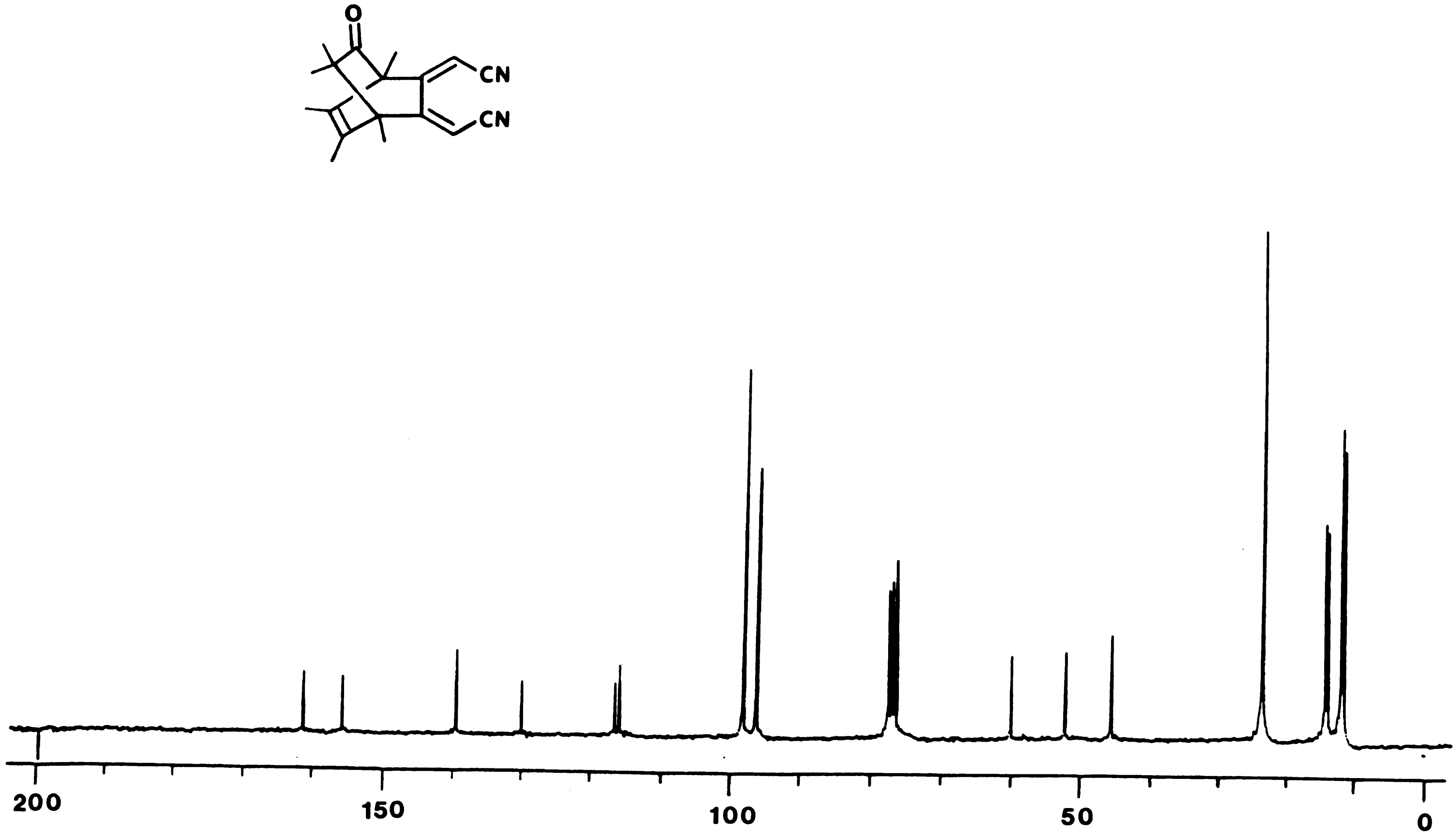
13. 250 MHz ^{1}H NMR of 2,6-Dibromo-1,4,5,8-tetrahydroanthracene-1,4:5,8-diendoxide (**101**).



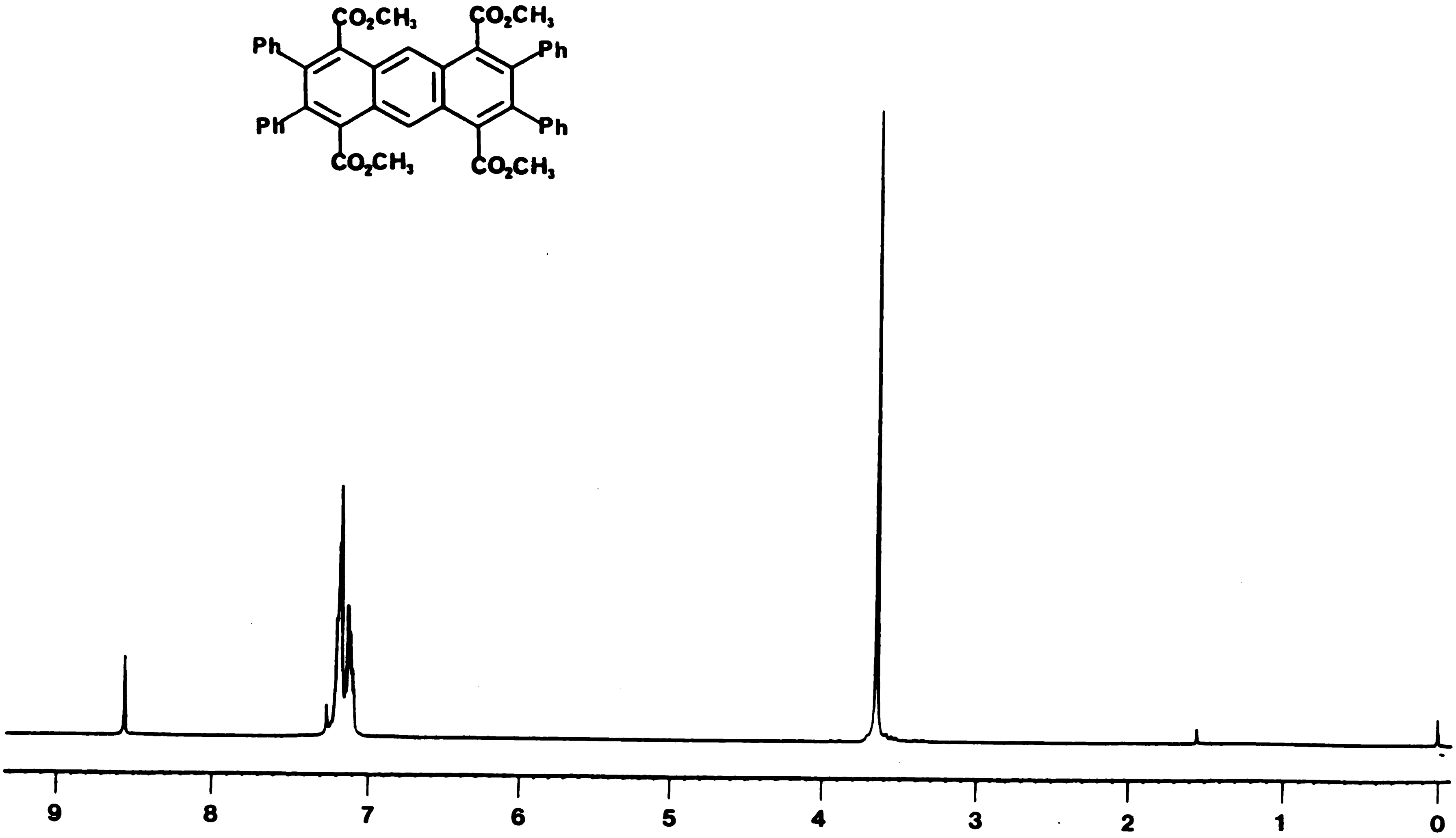
14. 250 MHz ^{1}H NMR of Bis-[2-methyl-3-phenyl-2,3-dihydro]benzo[1,2-d:4,5-d']diisoxazole (107).



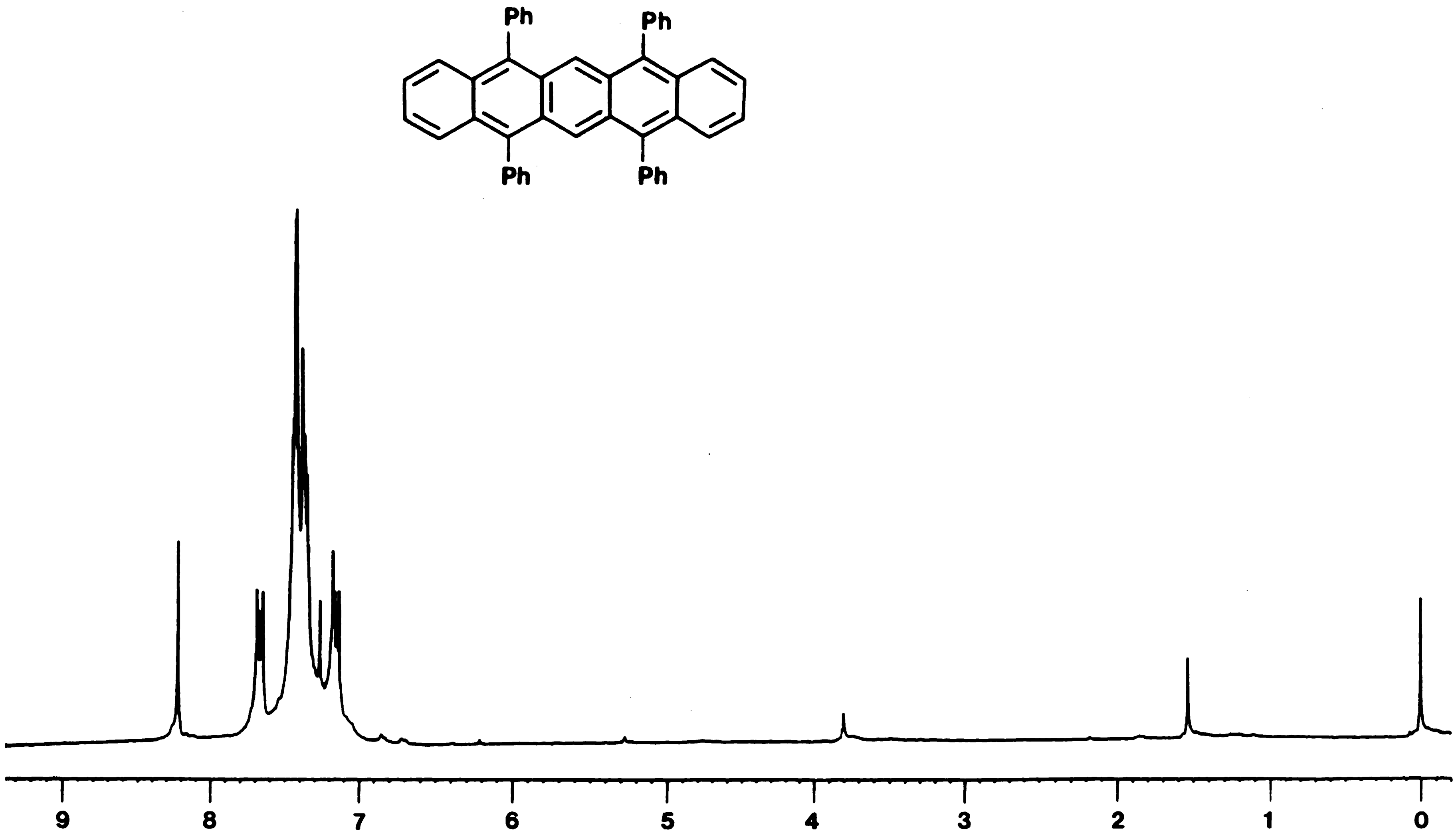
15. 250 MHz ^{1}H NMR of 1,3,3,4,7,8-Hexamethyl-5,6-bis(Z,Z-cyanomethylene)-bicyclo[2.2.2]oct-7-en-2-one (**116**).



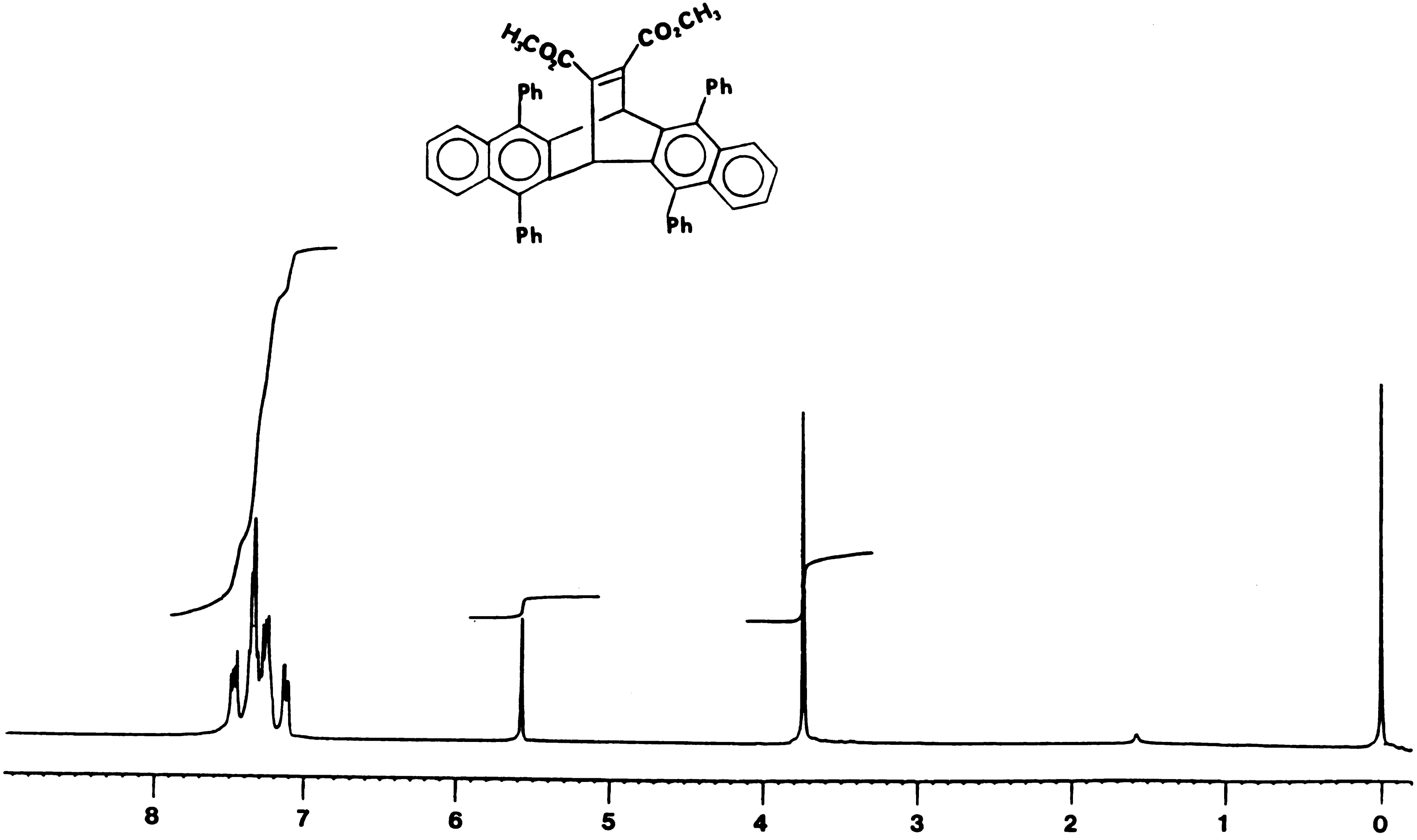
16. ^{13}C NMR of 1,3,3,4,7,8-Hexamethyl-5,6-bis(Z,Z-cyanomethylene)-bicyclo[2.2.2]oct-7-en-2-one (**116**).



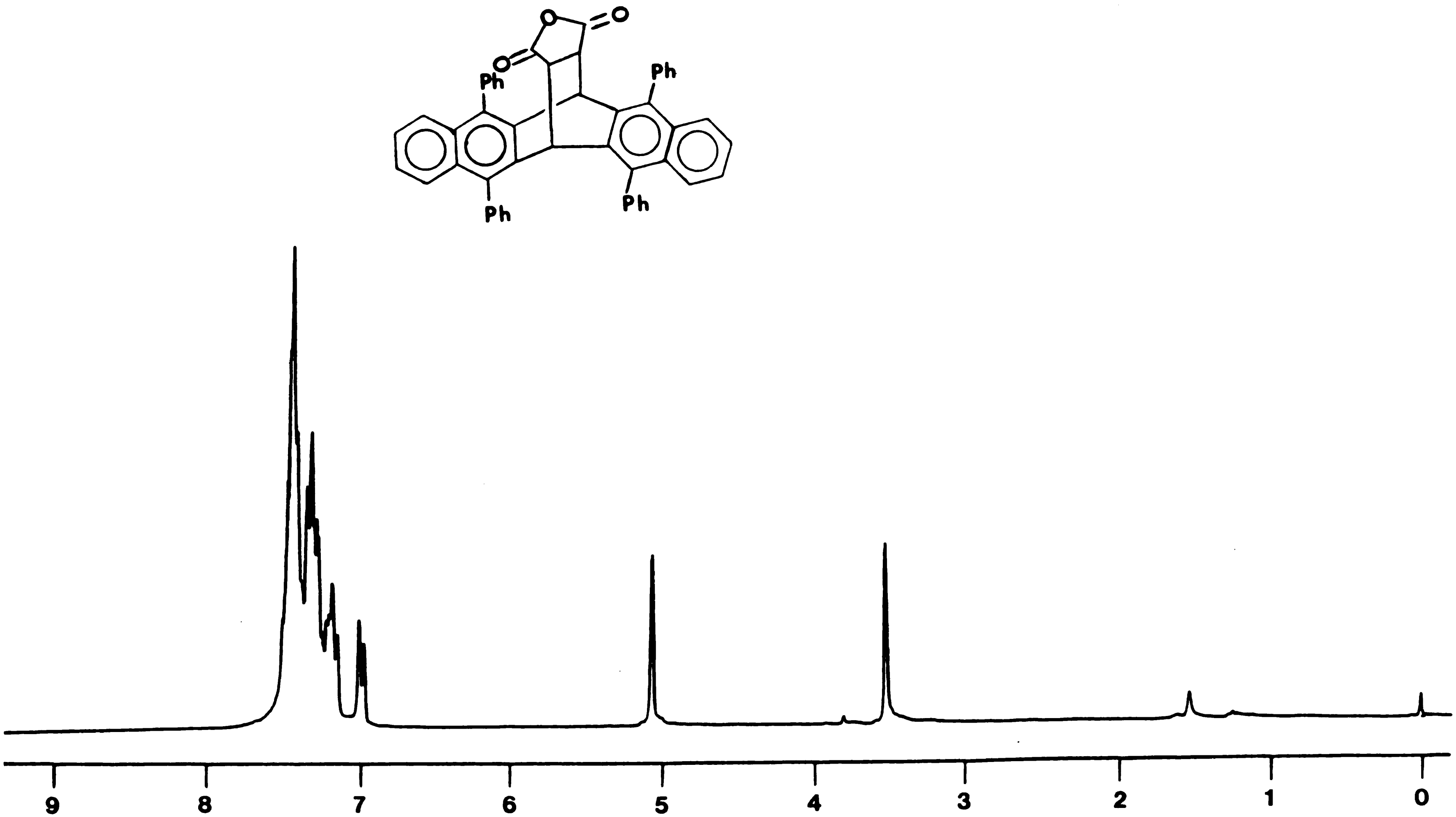
17. 250 MHz ^{1}H NMR of tetramethyl 2,3,6,7-tetraphenylanthracene-1,4,5,8-tetracarboxylate (**128**).



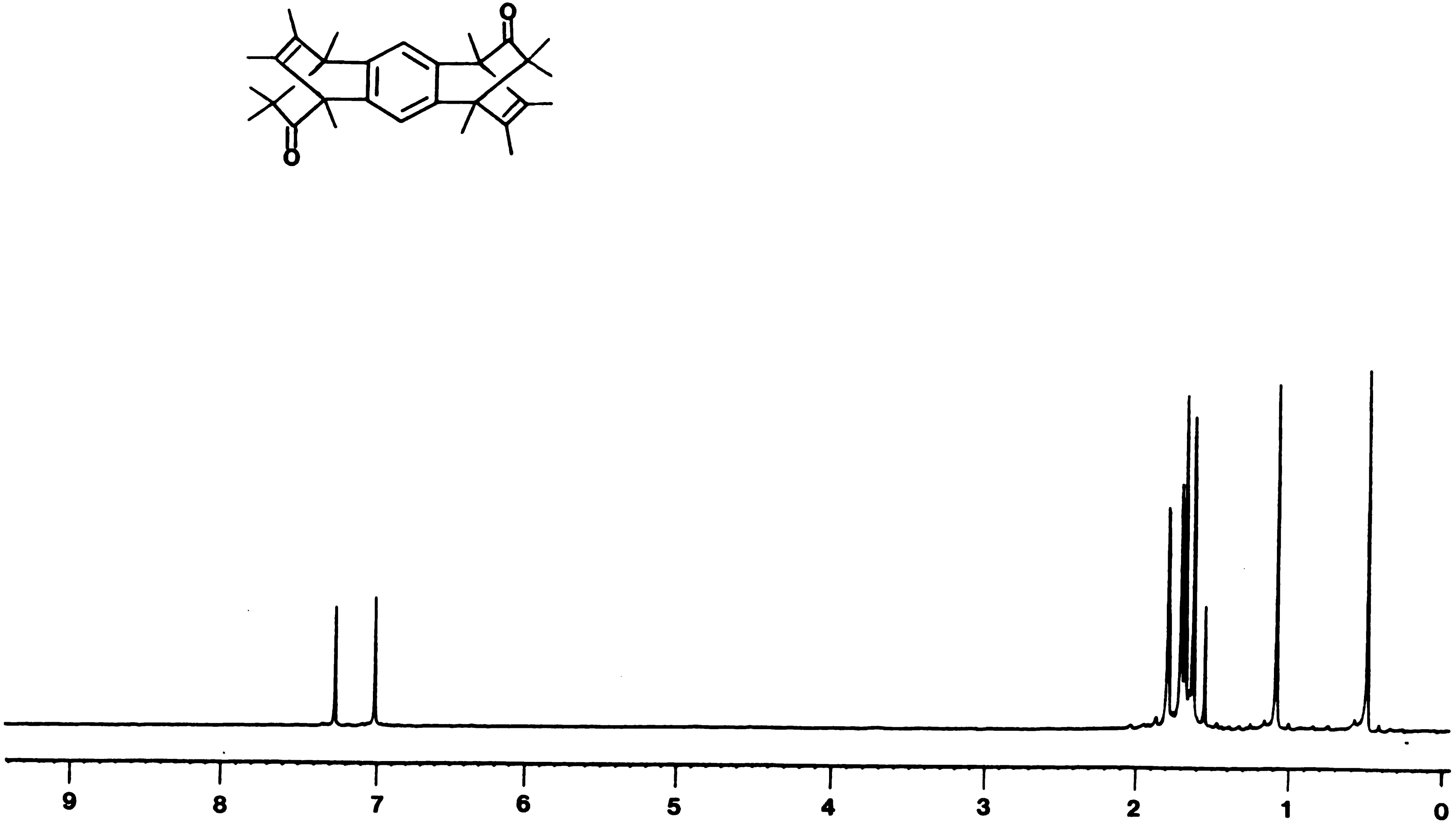
18. 250 MHz ^1H NMR of 5,7,12,14-Tetraphenylpentacene (**141**).



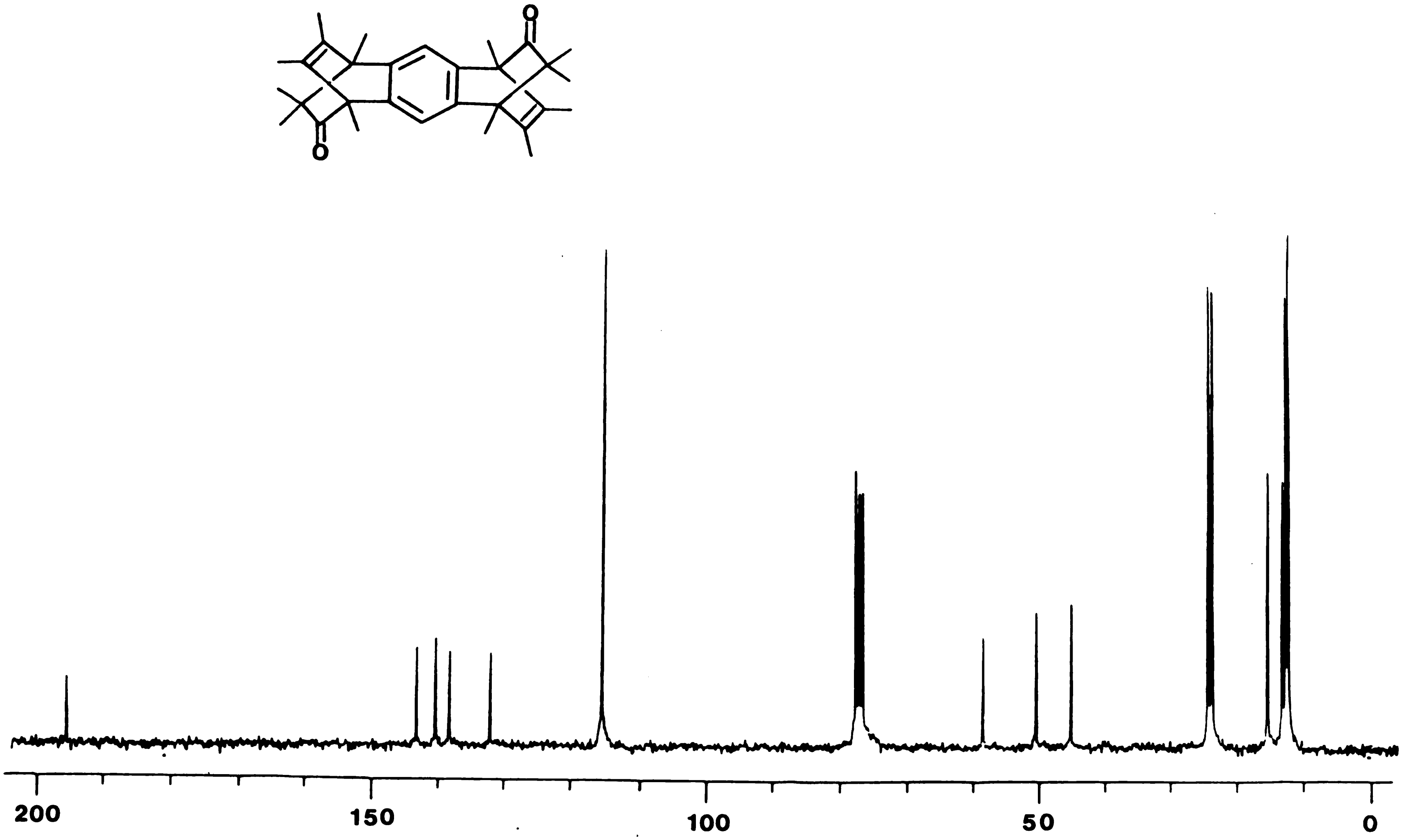
19. 250 MHz ^{1}H NMR of Dimethyl 5,7,12,14-tetraphenyl-6,13-dihydro-6,13-ethenopentacene-15-16-dicarboxylate (151).



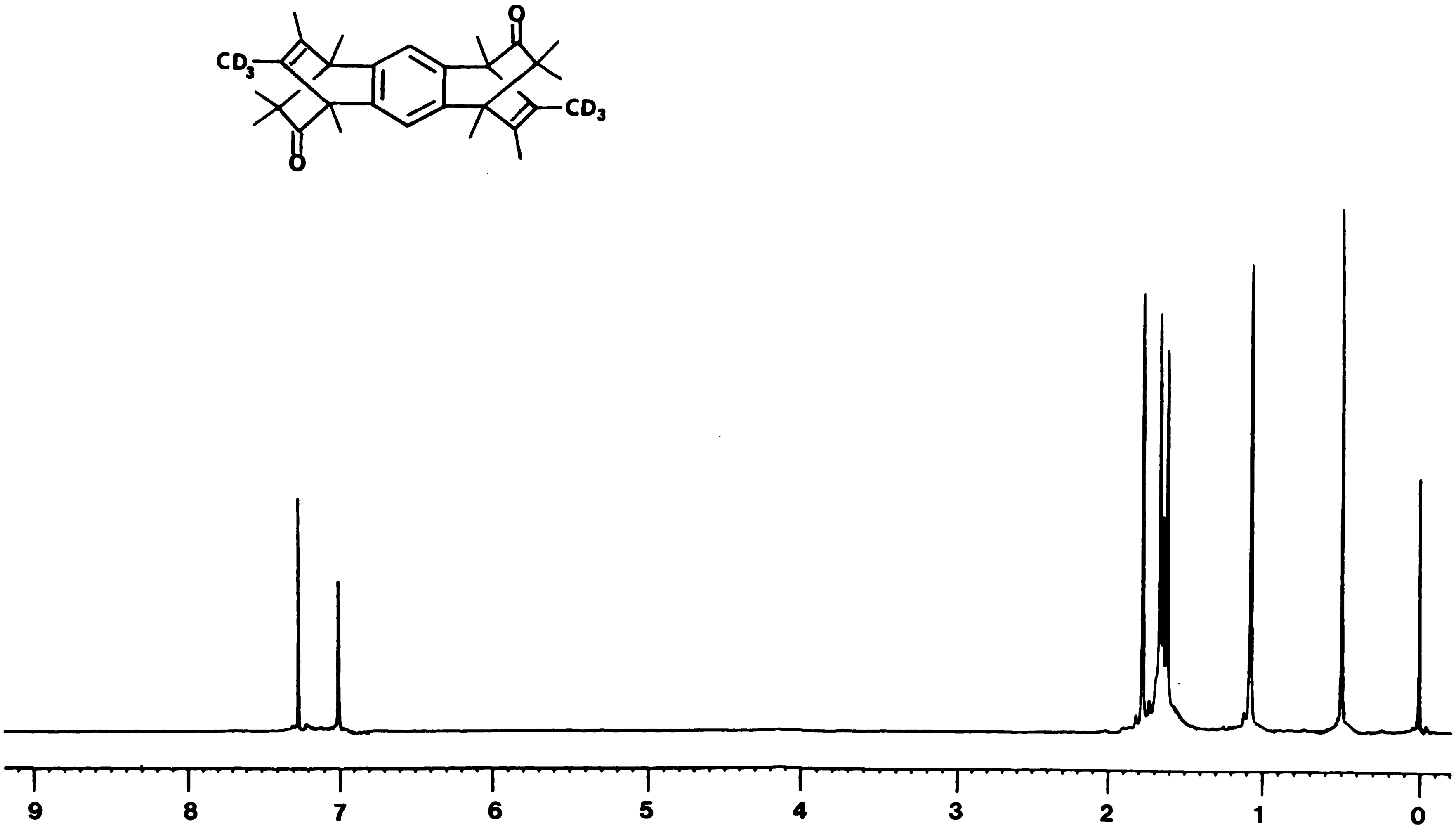
20. 250 MHz ^{1}H NMR of 5,7,12,14-Tetraphenyl-6,13-dihydro-6,13-ethanopentacene-15,16-dicarboxylic anhydride (**153**).



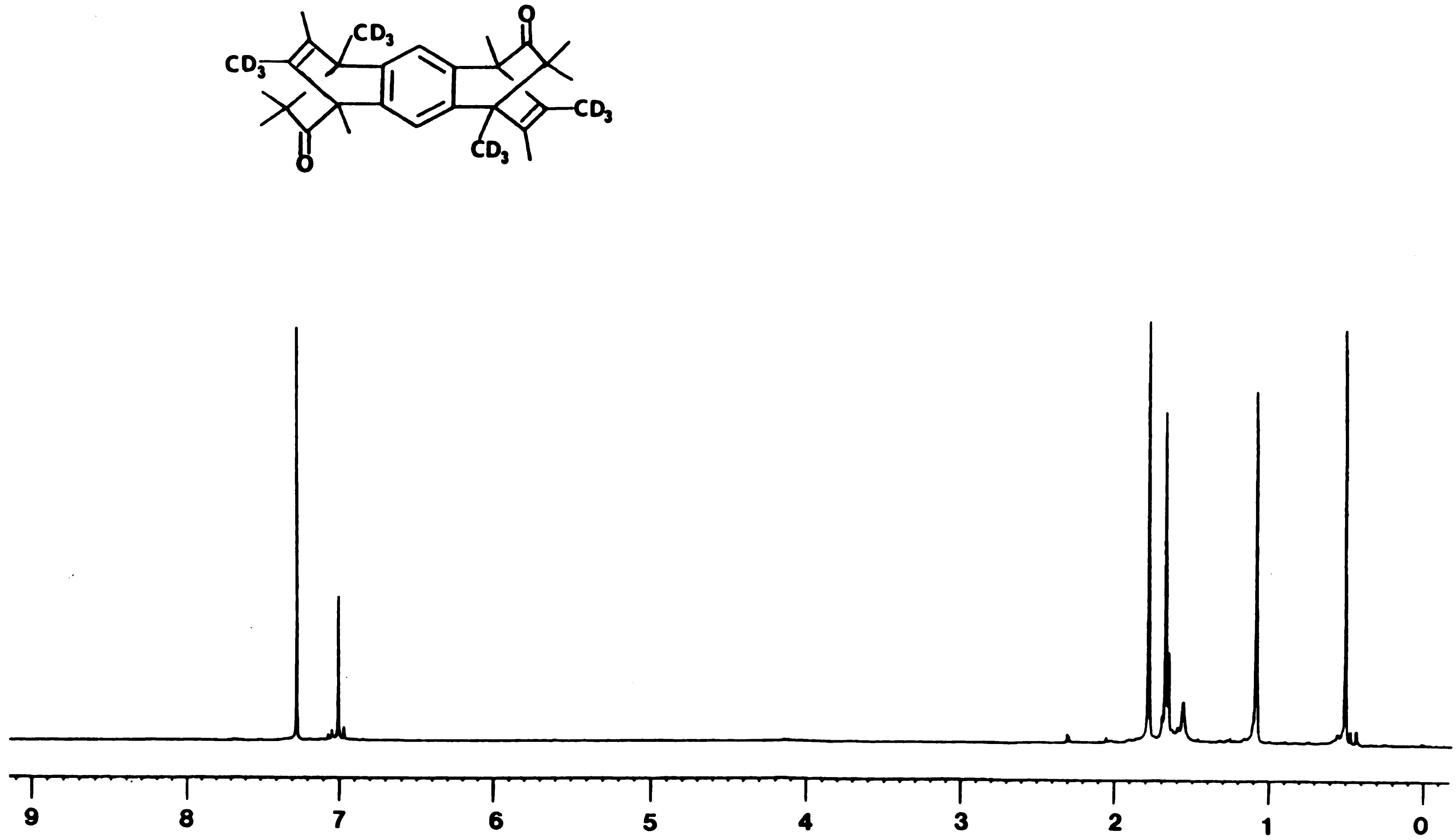
21. 250 MHz ^1H NMR of 1,3,3,4,7,8,10,12,12,13,16,17-Dodecamethyl-benzo[1,2-e:4,5-e']bis-bicyclo[2.2.2]oct-7,16-dien-2,11-dione (**154**).



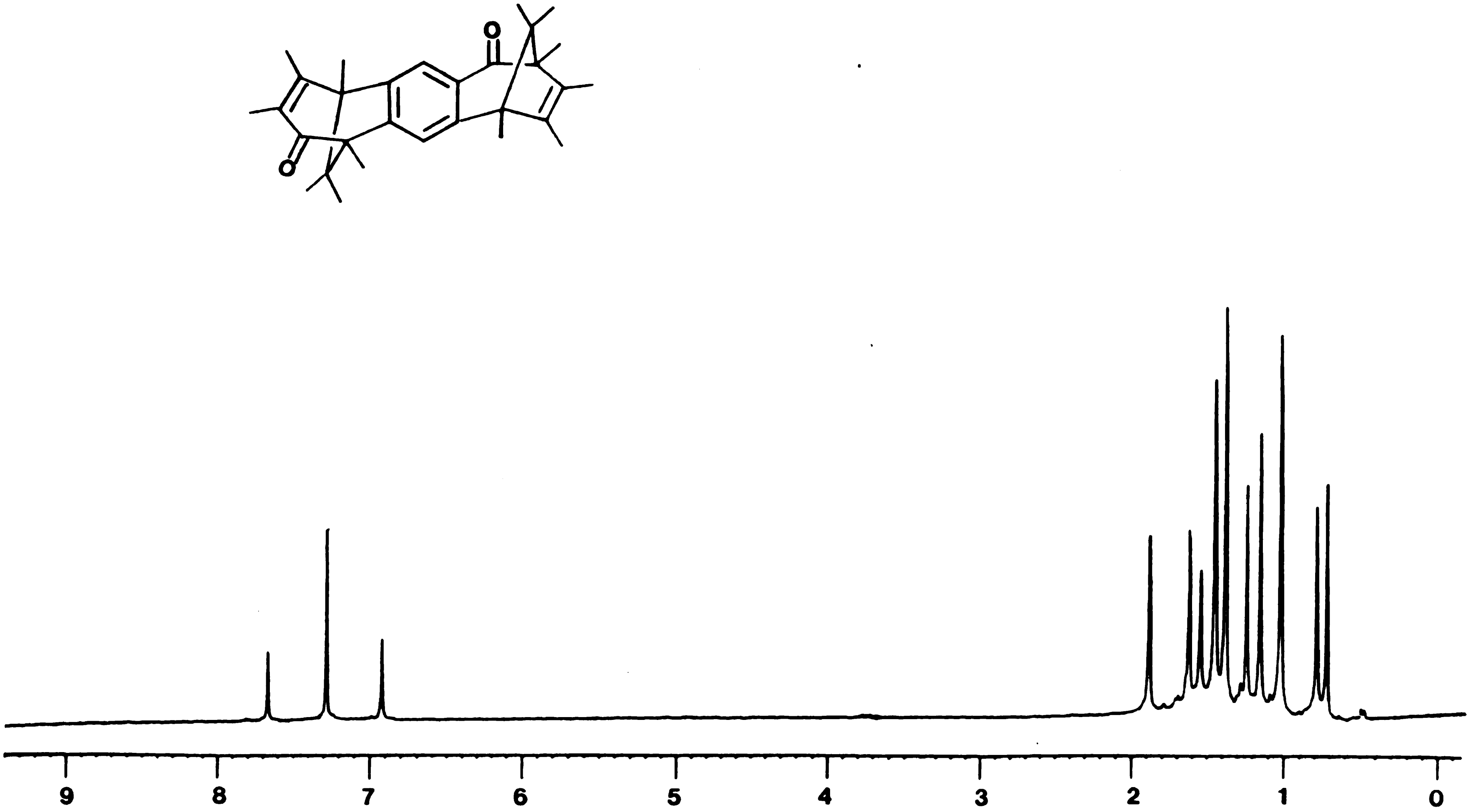
22. ^{13}C NMR of 1,3,3,4,7,8,10,12,12,13,16,17-Dodecamethyl-benzo[1,2-e:4,5-e']bisbicyclo [2.2.2]oct-7,16-dien-2,11-dione (**154**).



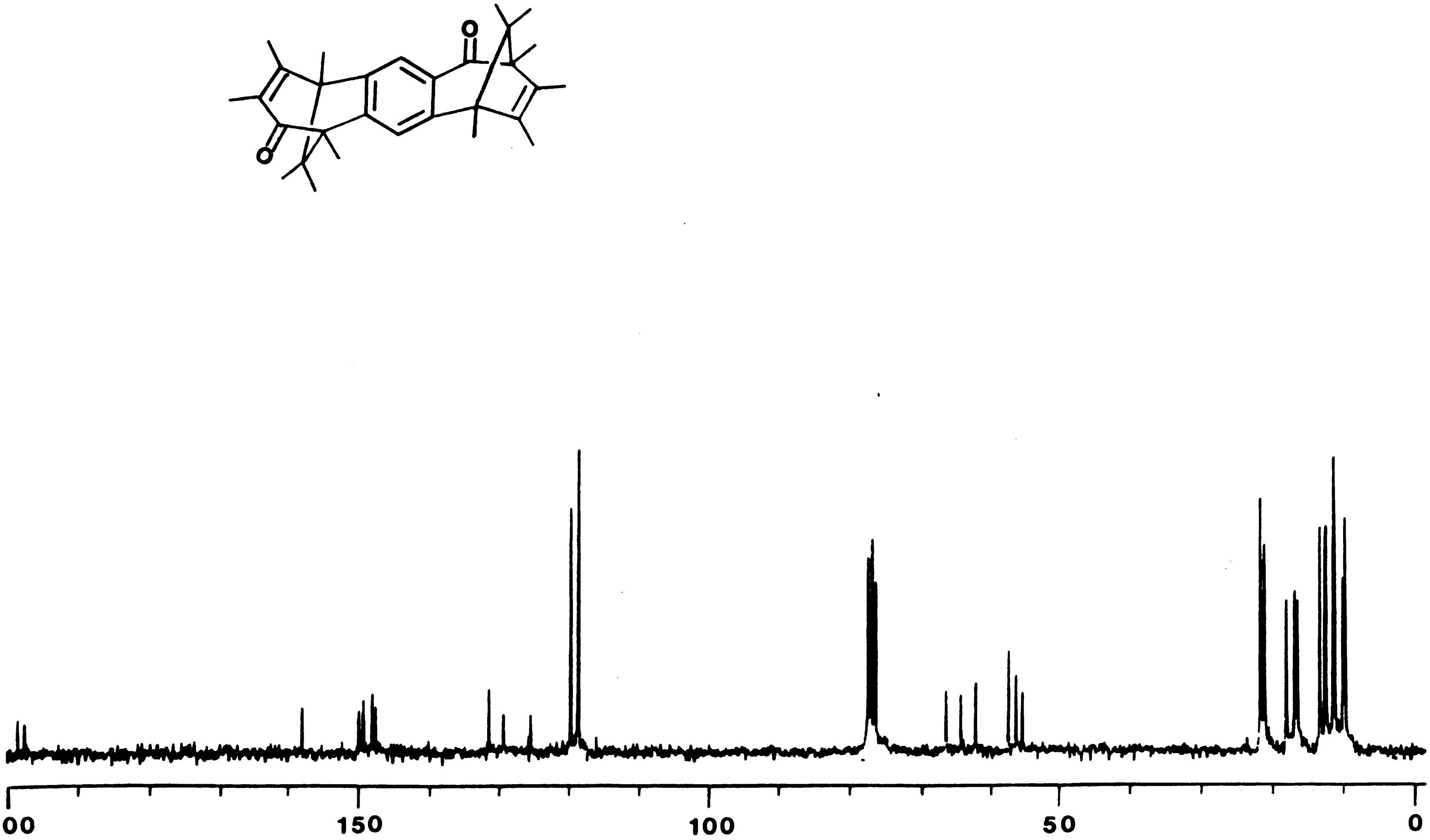
23. 250 MHz ^{1}H NMR of 1,3,3,4,8,10,12,12,13,17-Decamethyl-7,16-dimethyl-d_6-benzo [1,2-e:4,5-e']bisbicyclo[2.2.2]oct-7,16-dien-2,11-dione (**160**).



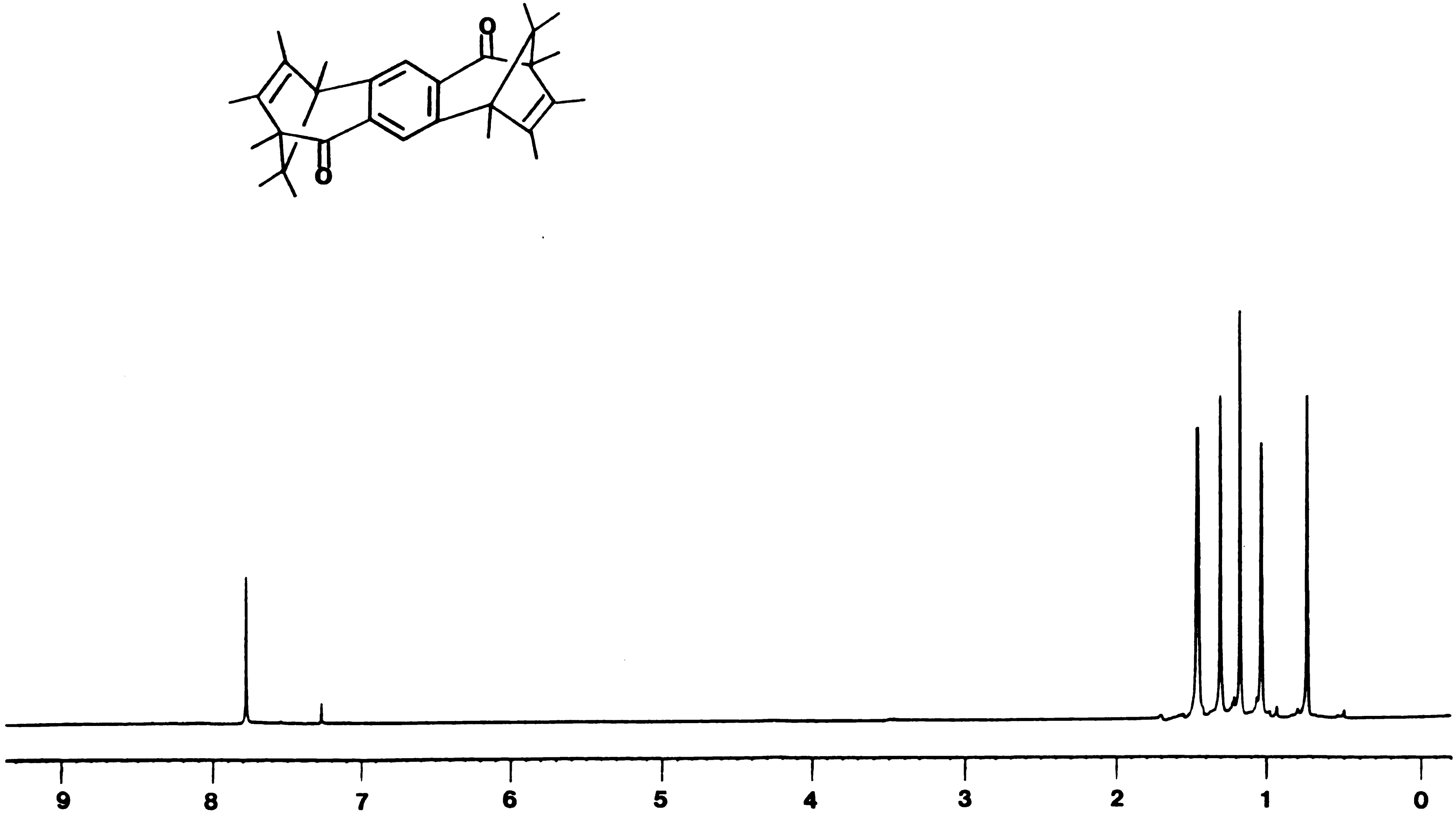
24. 250 MHz ^{1}H NMR of 1,3,3,8,10,12,12,17-Octamethyl-4,7,13,16-tetramethyl-d_{12}-benzo [1,2-e:4,5-e']bisbicyclo[2.2.2]oct-7,16-dien-2,11-dione (**161**).



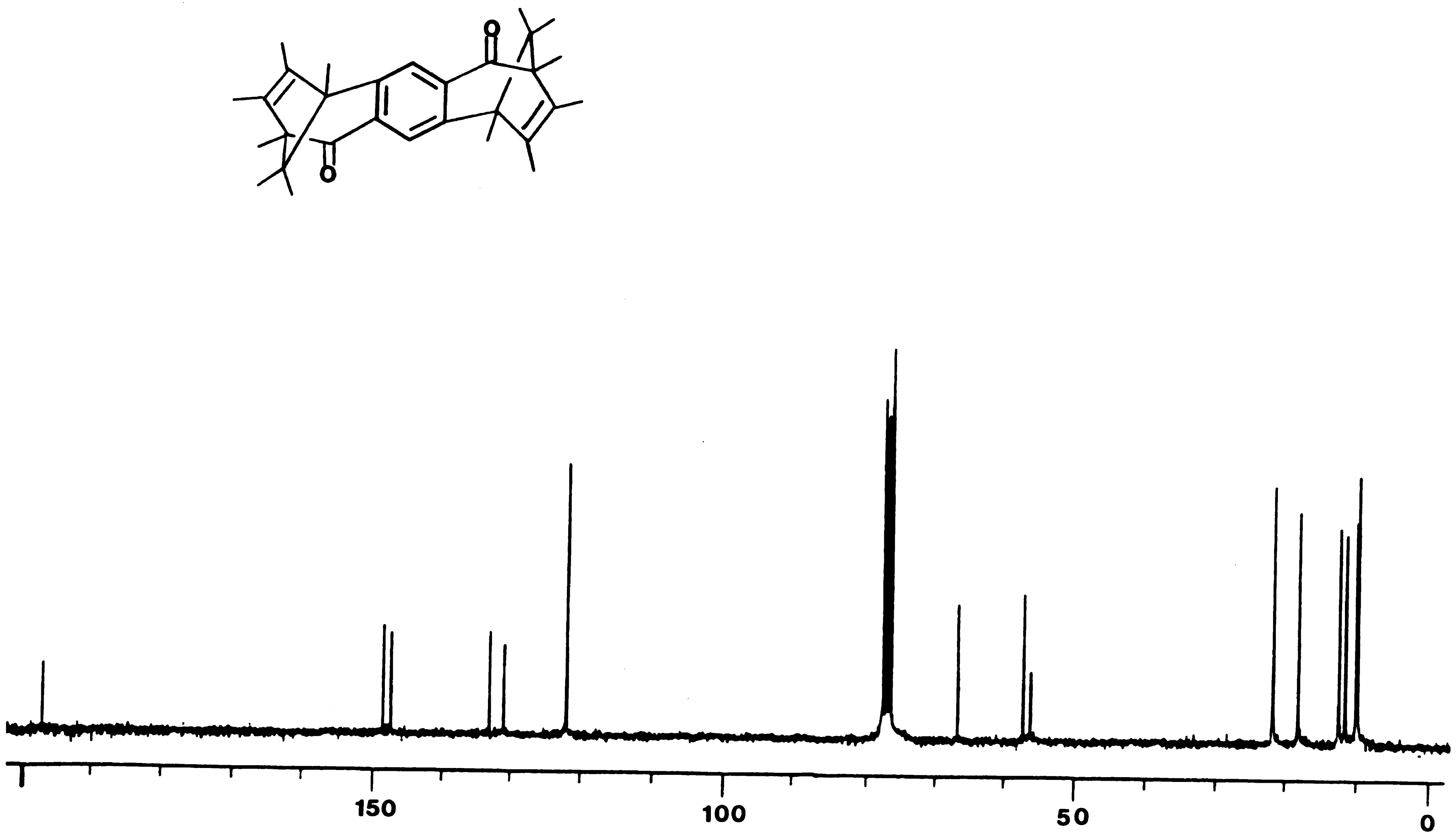
25. 250 MHz ^{1}H NMR of 1,5,6,7,8,8,10,11,12,14,17,17-Dodecamethyl-benzo[1,2-c:4,5-f']bis-bicyclo[3.2.1]oct-6,11-dien-2,13-dione (**176**).



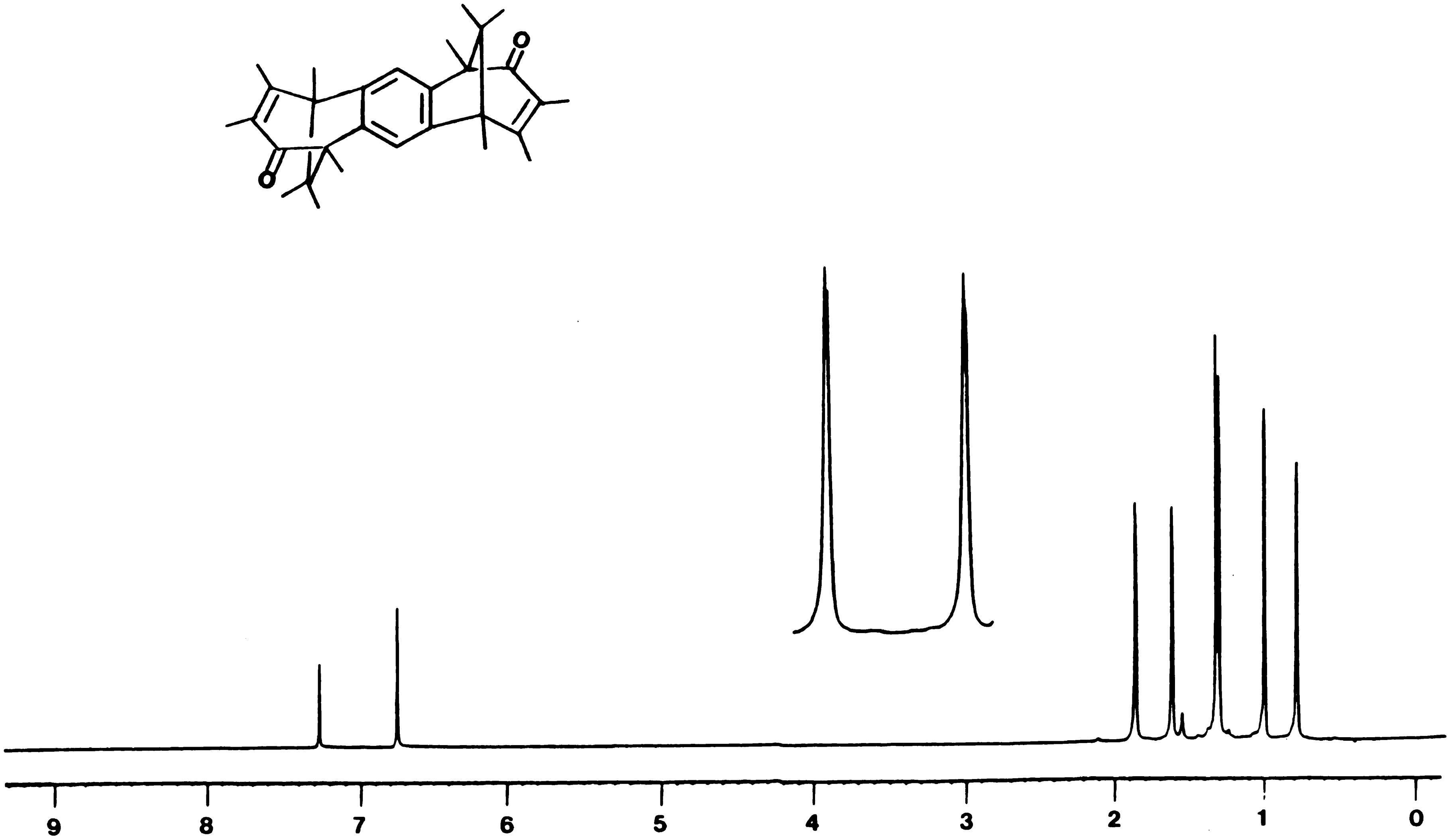
26. ^{13}C NMR of 1,5,6,7,8,8,10,11,12,14,17,17-Dodecamethyl-benzo[1,2-c:4,5-f']bisbicyclo [3.2.1]oct-6,11-dien-2,13-dione (**176**).



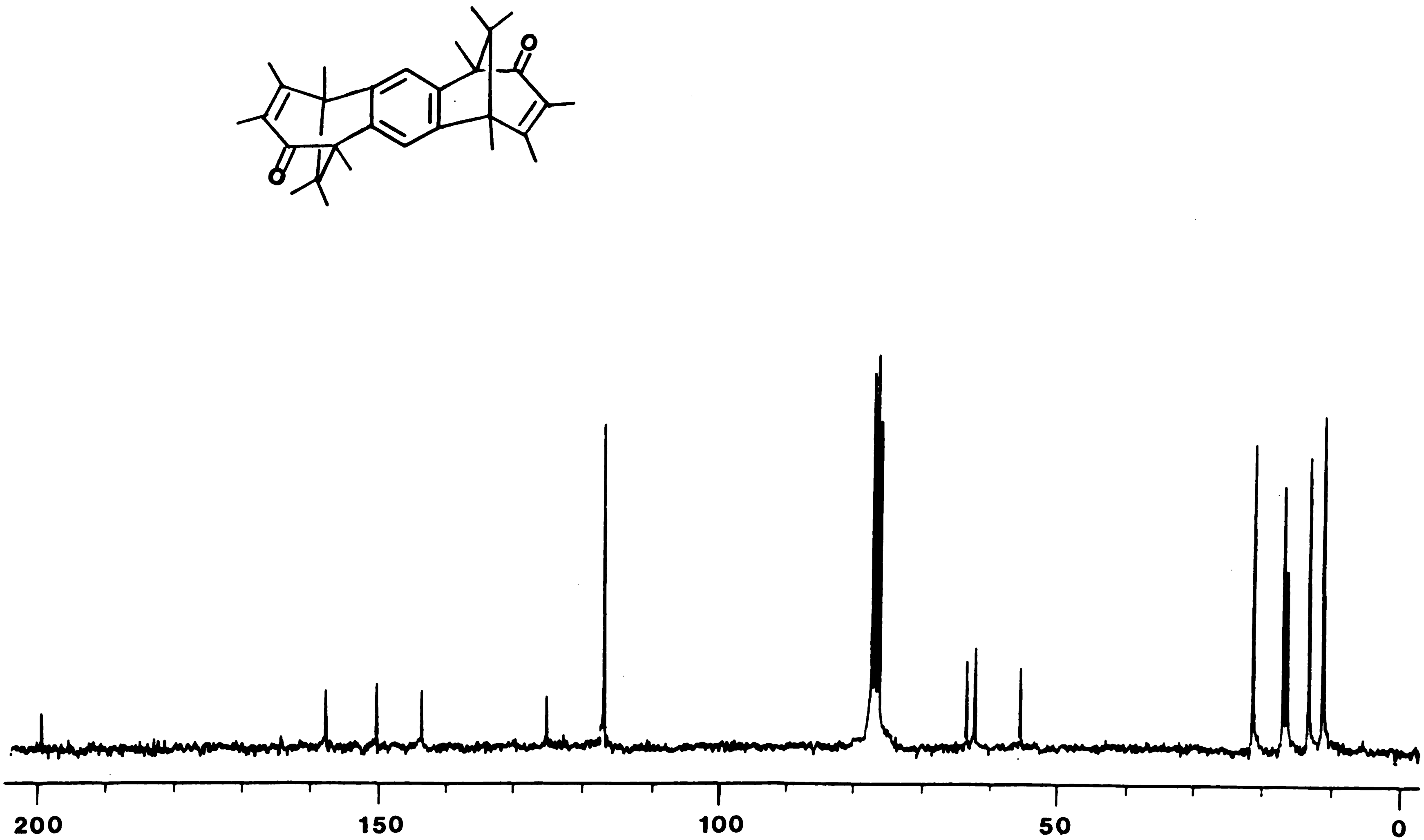
27. 250 MNz ^{1}H NMR of 1,5,6,7,8,8,10,11,12,13,17,17-Dodecamethyl-benzo[1,2-c:4,5-c'] bisbicyclo[3.2.1]oct-6,11-dien-2,14-dione (**178**).



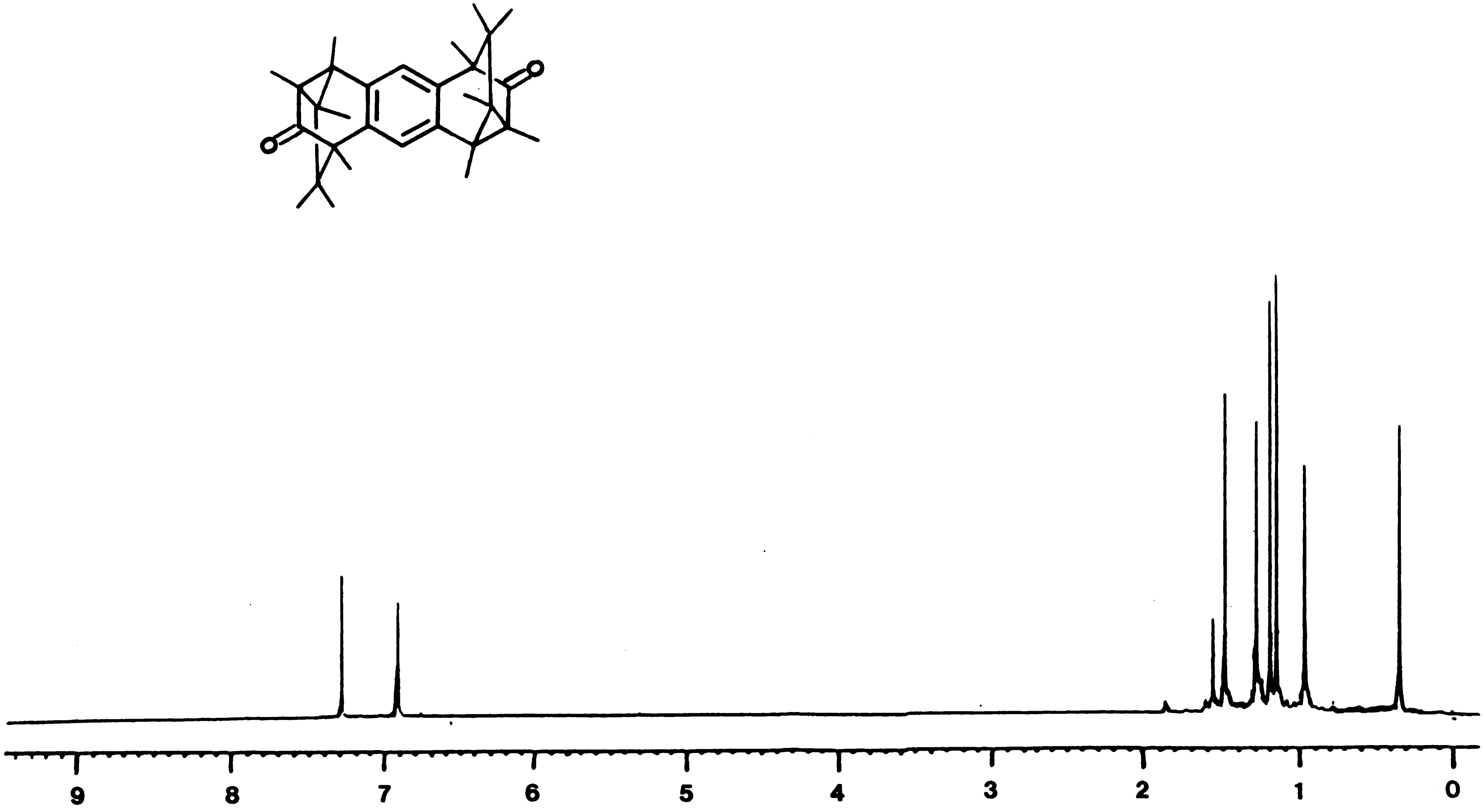
28. ^{13}C NMR of 1,5,6,7,8,8,10,11,12,13,17,17-Dodecamethyl-benzo[1,2-c:4,5-c']bisbicyclo [3.2.1]oct-6,11-dien-2,14-dione (**178**).



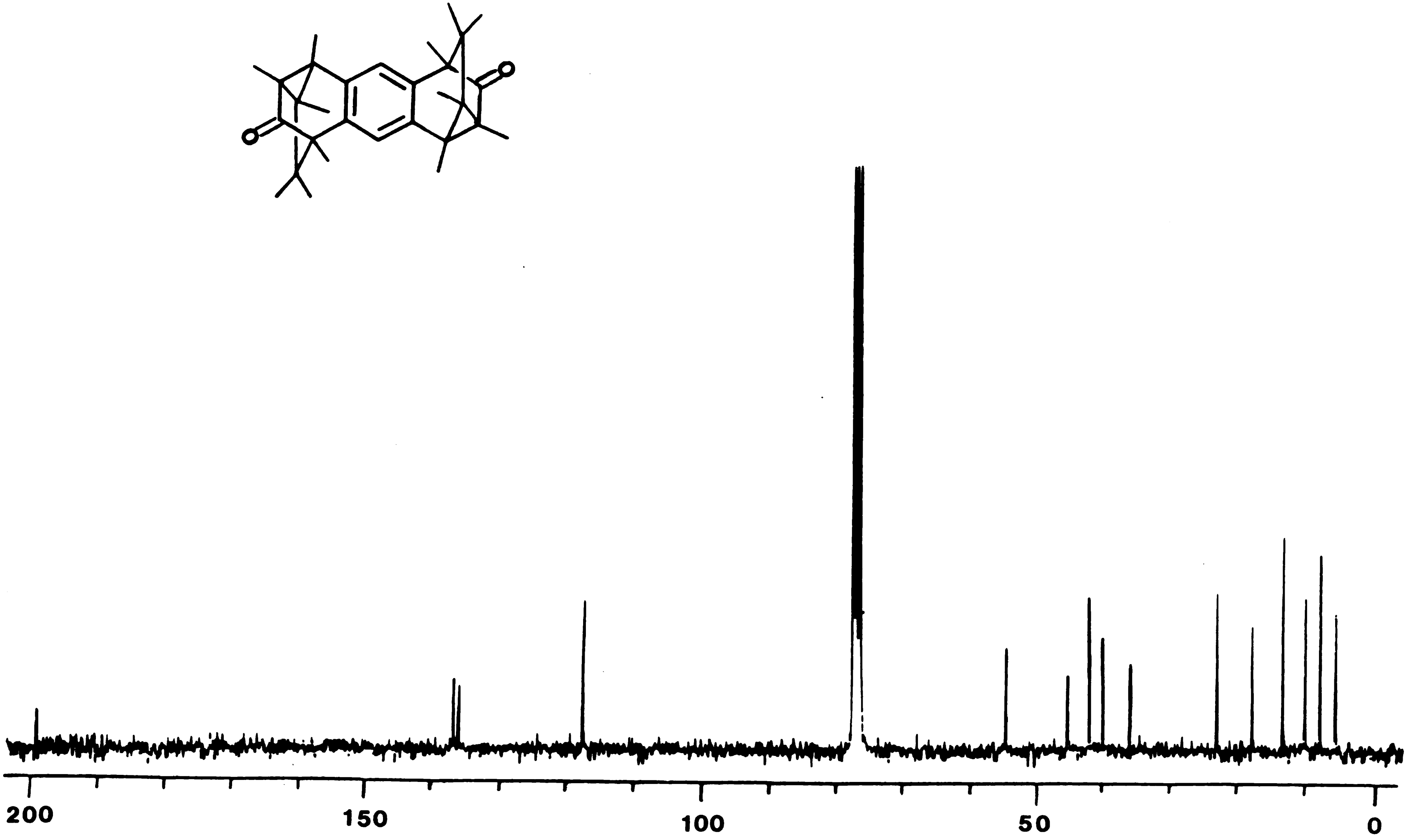
29. 250 MHz ^{1}H NMR 1,3,4,5,8,8,10,11,12,14,17,17-Dodecamethyl-benzo[1,2-f:4,5-f']bisbicyclo[3.2.1]oct-3,11-dien-2,13-dione (**179**).



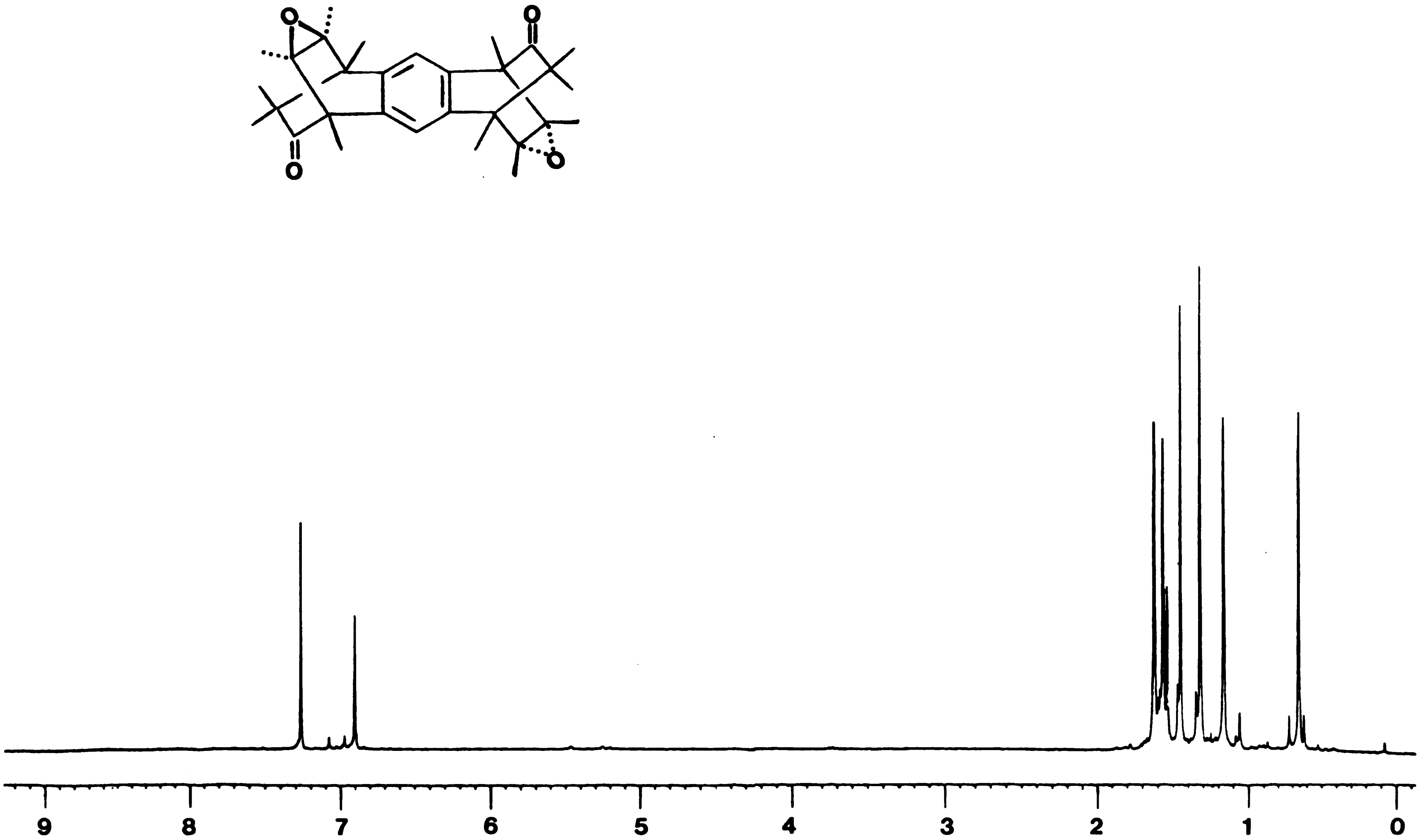
30. ^{13}C NMR 1,3,4,5,8,8,10,11,12,14,17,17-Dodecamethyl-benzo[1,2-f:4,5-f']bisbicyclo [3.2.1]oct-3,11-dien-2,13-dione (**179**).



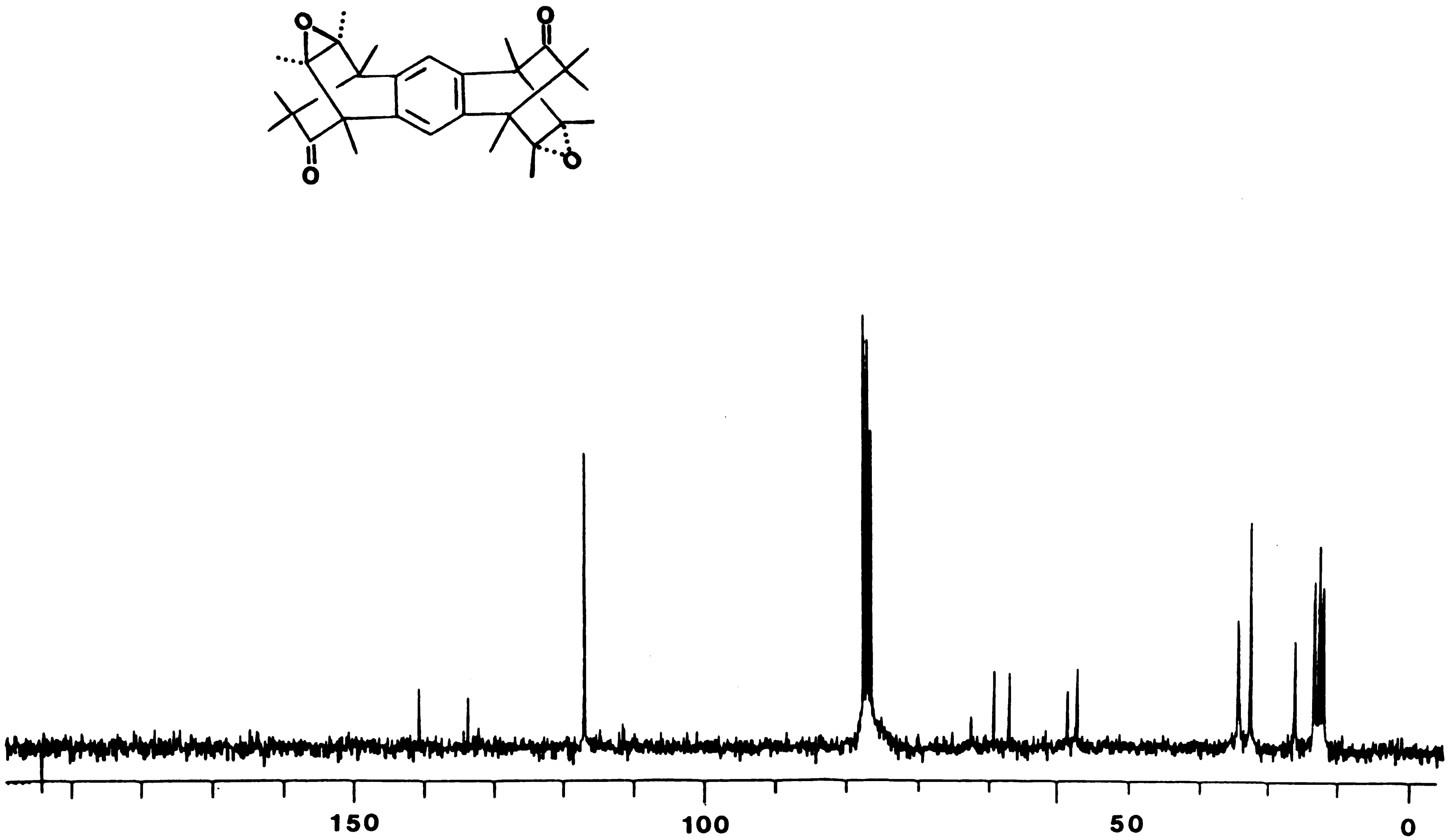
31. 250 MHz ^{1}H NMR of ketone **189**.



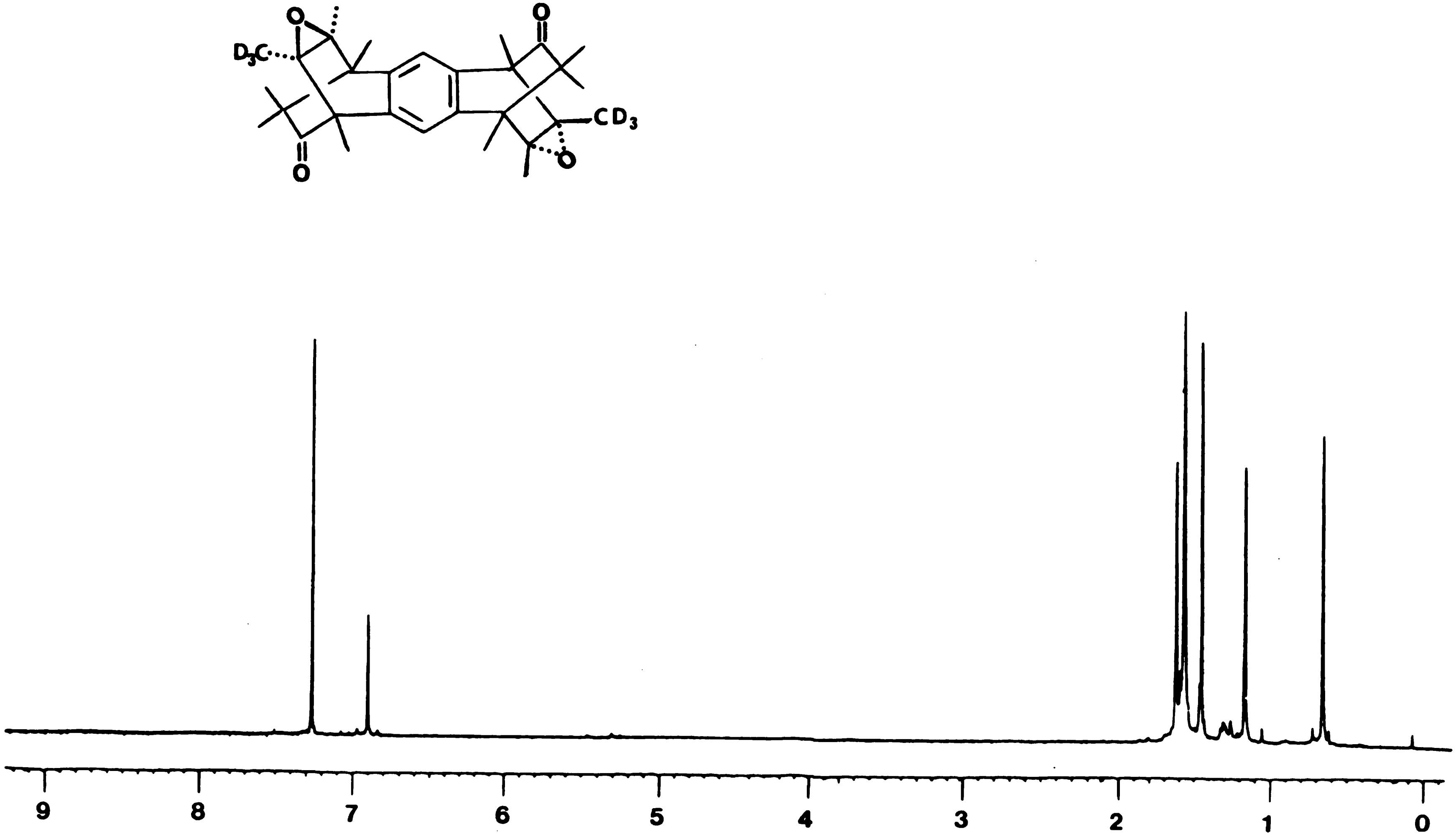
32. ^{13}C NMR of ketone **189**.



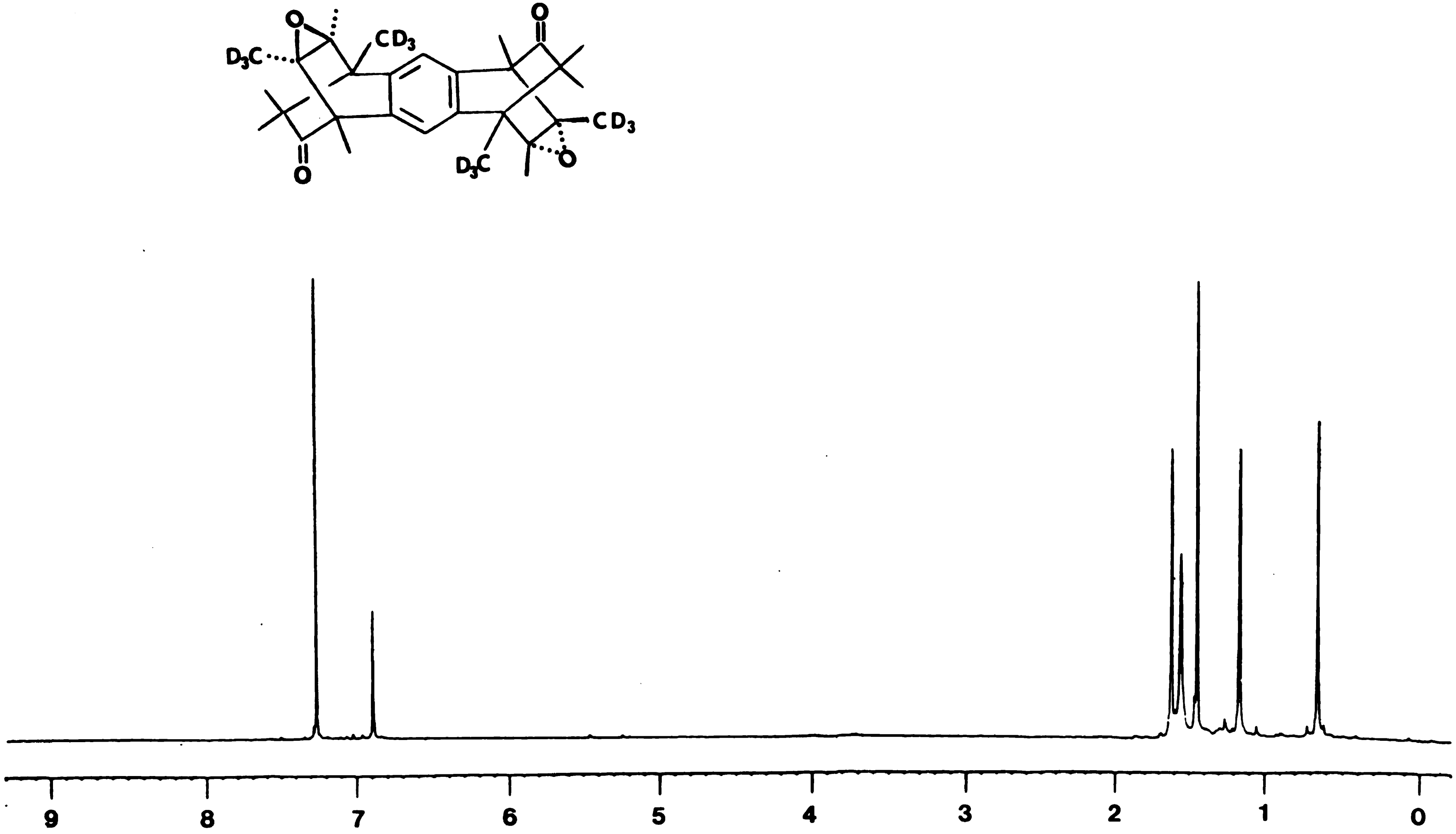
33. 250 MHz ^1H NMR of epoxy ketone 199.



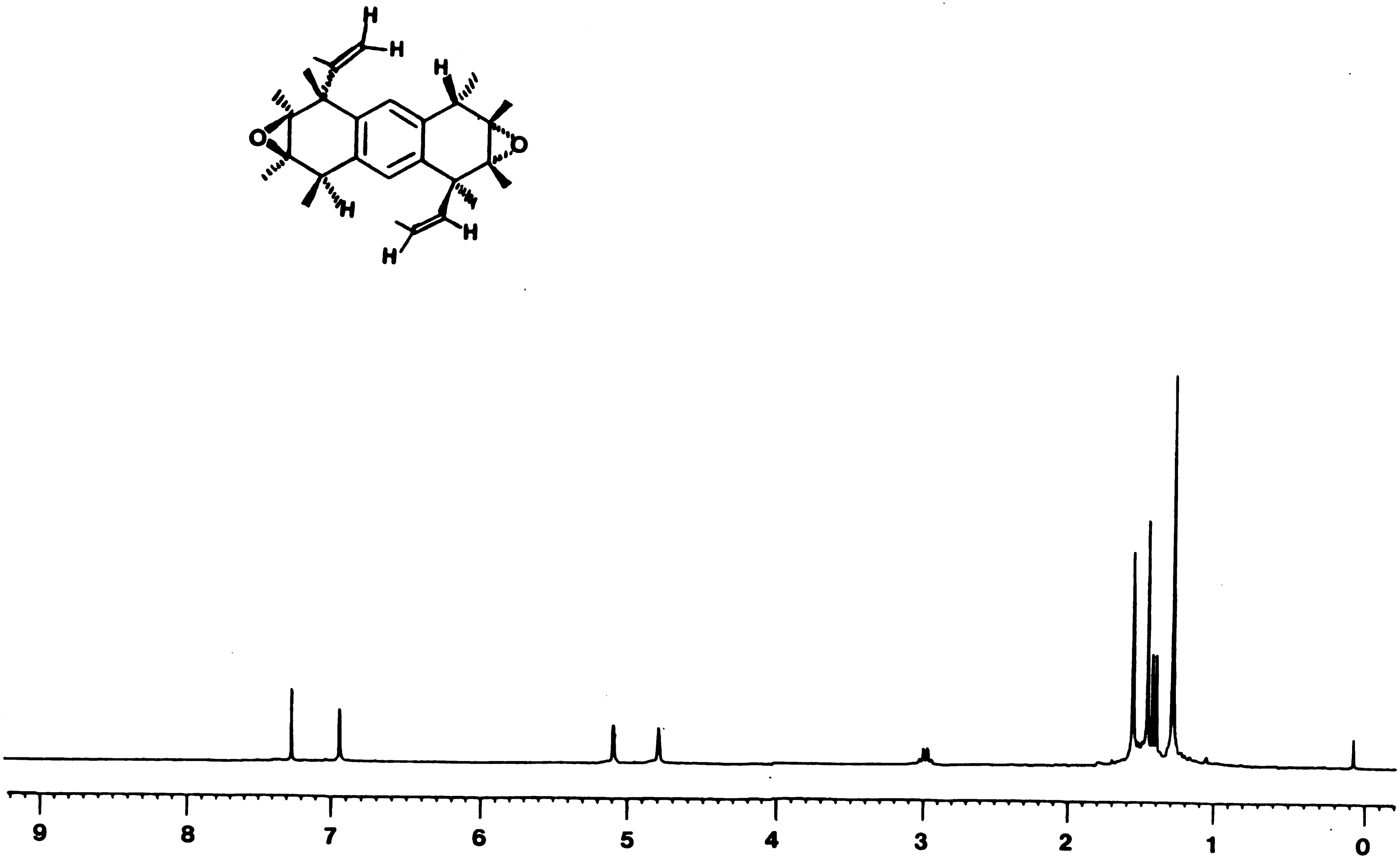
34. ^{13}C NMR of epoxy ketone **199**.



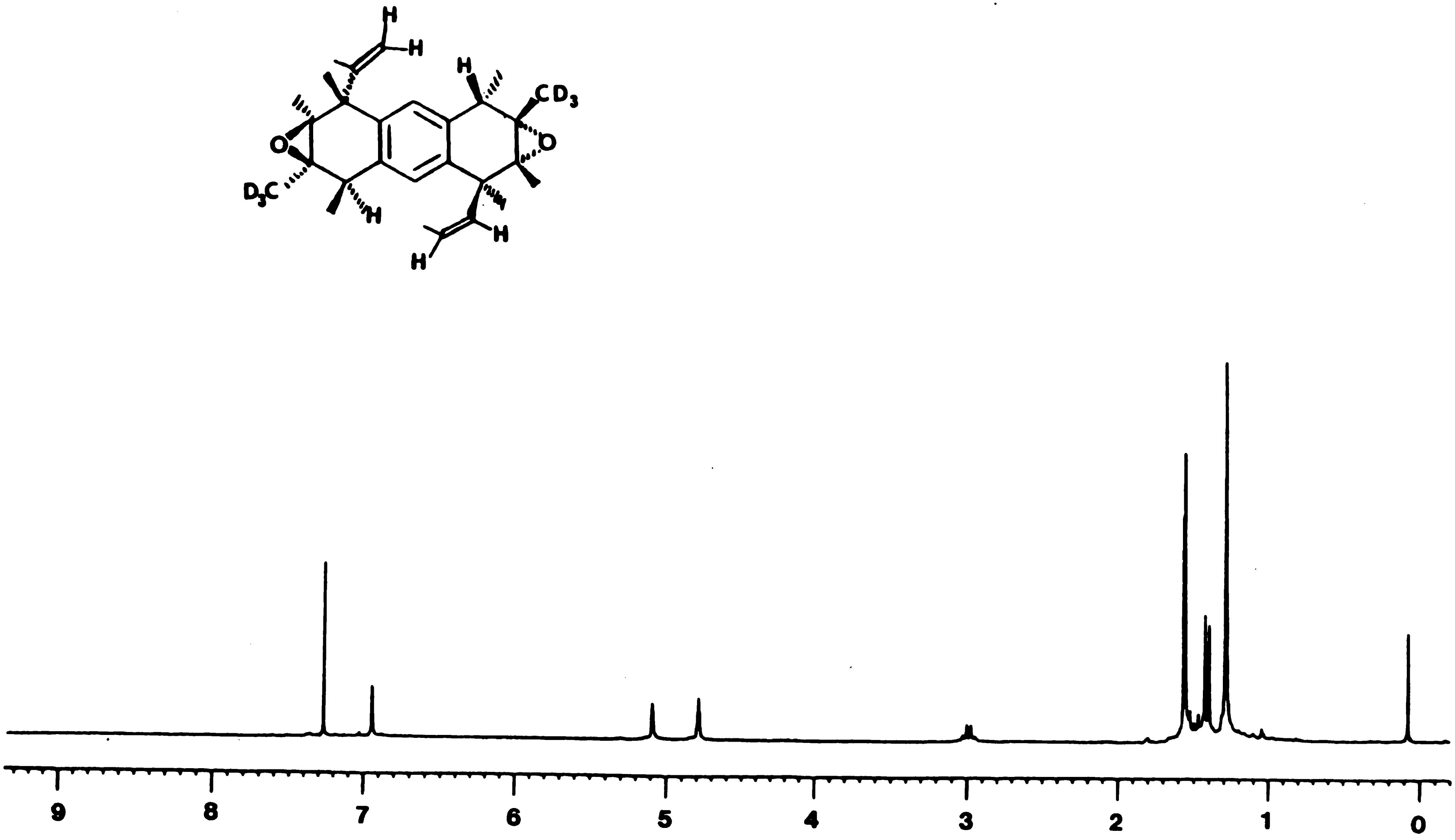
35. 250 MHz ^{1}H NMR of epoxy ketone **200**.



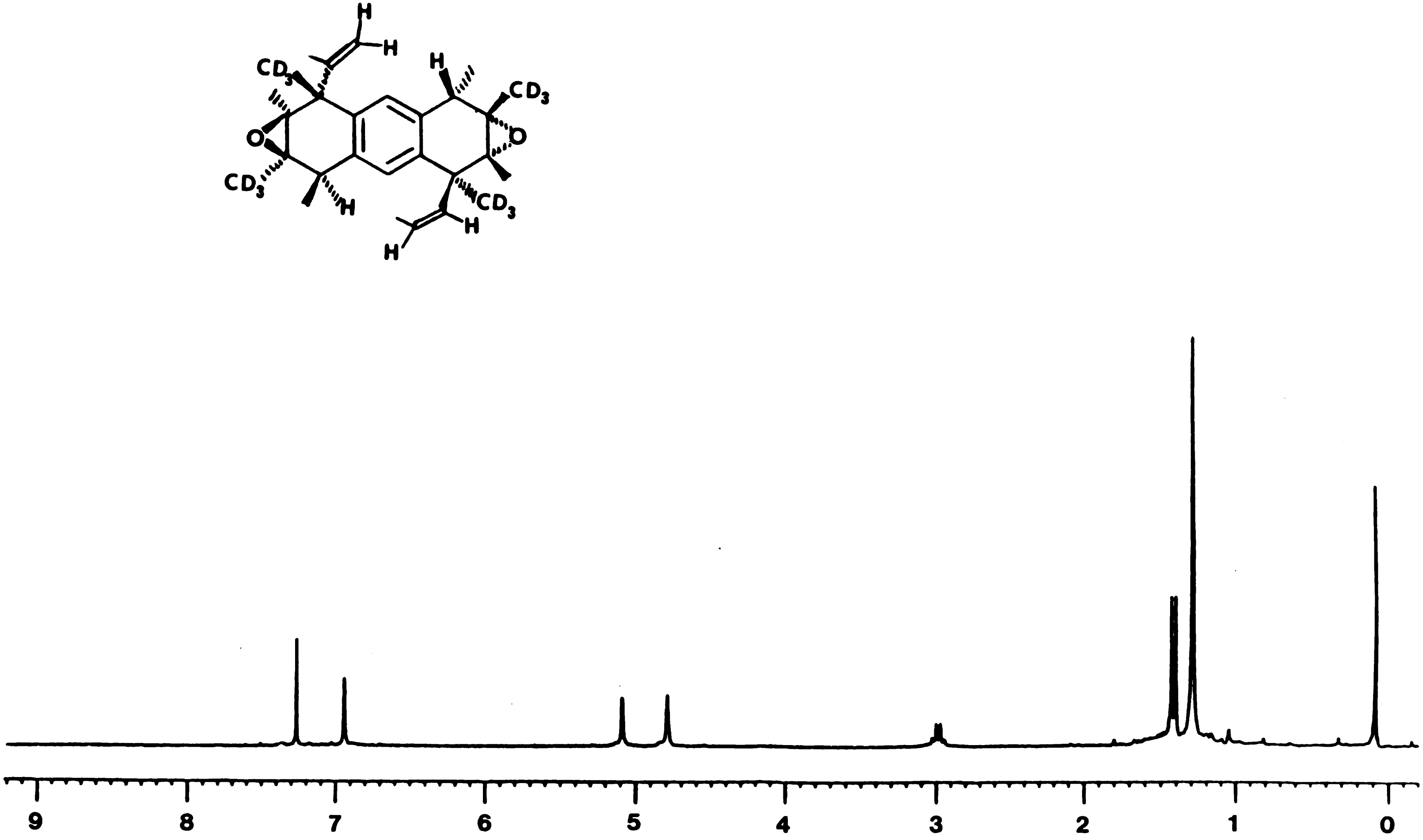
36. 250 MHz ^{1}H NMR of epoxy ketone 201.



37. 250 MHz ^{1}H NMR of epoxide **202**.



38. 250 MHz ^{1}H NMR of epoxide **203**.



39. 250 MHz ^{1}H NMR of epoxide **204**.