Studies on the Reaction of Alkynes with Iron Carbonyl Reagents and Applications of Cyclobutenediones in Organic Synthesis

A Thesis

Submitted for the Degree of

DOCTOR OF PHILOSOPHY

By

AMERE MUKKANTI

SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD
HYDERABAD 500 046
INDIA

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Dedicated to

the Almighty and

My Grand Mother

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School of Chemistry
University of Hyderabad
Central University P. O.
Hyderabad 500 046
India

Statement

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the School of Chemistry, University of Hyderabad, Hyderabad, under the supervision of **Professor M. Periasamy.**

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

AMERE MUKKANTI

School of Chemistry
University of Hyderabad
Central University P. O.
Hyderabad 500 046
India

Certificate

Certified that the work embodied in this thesis entitled '**Studies on the Reaction of Alkynes with Iron Carbonyl Reagents and Applications of Cyclobutenediones in Organic Synthesis**' has been carried out by Mr. AMERE MUKKANTI, under my supervision and the same has not been submitted elsewhere for a Degree.

M. Periasamy

PROFESSOR M. PERIASAMY
(THESIS SUPERVISOR)

M. Periasamy 28/8/04

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SCHOOL OF CHEMISTRY

Dean
School of Chemistry
University of Hyderabad
Hyderabad-500 046, India

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I close with thanks giving to the Almighty for the showers of blessing during the hour of trial

AMERE MUKKANTI

ABBREVIATIONS

Ac	:	acetyl
aq.	:	aqueous
Ar	:	aryl
Bu	:	butyl
Bn	:	benzyl
Cat.	:	catalyst
DABCO	:	1,4-diazabicyclo[2.2.2]octane
DCM	:	dichloromethane
DMSO	:	dimethyl sulphoxide
dr	:	diastereomeric ratio
E	:	electrophile
EI	:	electron impact
Et	:	ethyl
EtOAc	:	ethyl acetate
Eq. or eq.	:	equation
equiv.	:	equivalent
i	:	iso
L	:	ligand
i-Pr	:	isopropyl
liq.	:	liquid
LVT	:	low valent titanium
Me	:	methyl
mp	:	melting point
M	:	metal
n	:	primary

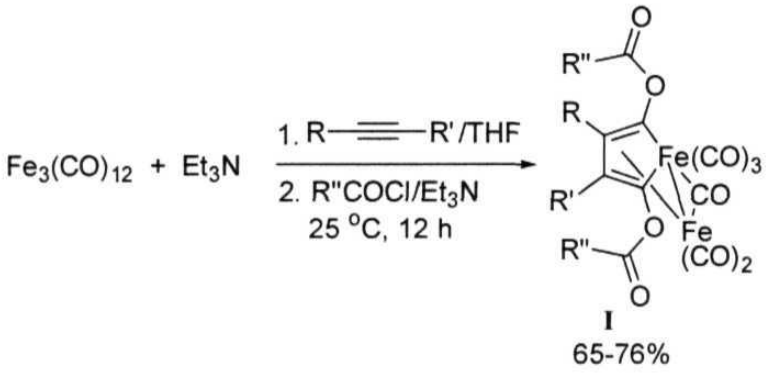
Nu	:	nucleophile
o	:	ortho
ORTEP	:	oak ridge thermal ellipsoid plot
Ph	:	phenyl
Py	:	pyridine
R	:	alkyl
rt	:	room temperature
THF	:	tetrahydrofuran
TMEDA	:	tetramethylethylenediamine
TMS	:	tetramethylsilane
TMSCl	:	trimethylsilyl chloride
X	:	halide

Abstract

This thesis describes **Studies on the Reaction of Alkynes with Iron Carbonyl Reagents and Applications of Cyclobutenediones in Organic Synthesis**. It comprises of three chapters 1) Introduction 2) Results and Discussion and 3) Experimental Section along with references. The work described in this thesis is exploratory in nature and is arranged in the order the investigations were executed.

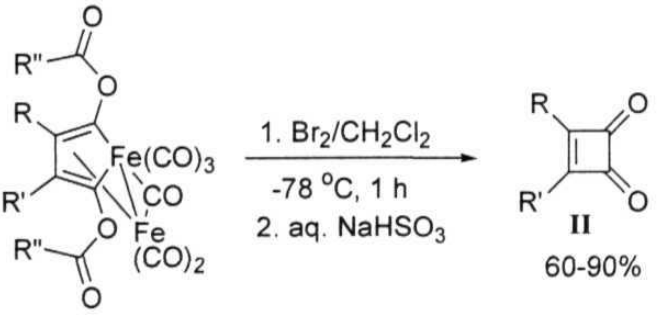
The first chapter describes a brief review on the methods of preparation of a wide-range of cyclobutenedione derivatives *via* cycloadditions, using transition metal reagents and from simple cyclobutenediones. Also, a concise survey of synthetic applications of cyclobutenediones is described.

The second chapter deals with results and discussion of the studies undertaken towards the preparation of cyclobutenediones using iron carbonyl and $TiCl_4$/Zn/CO reagent systems. The reactions of 3,4-diphenyl-3-cyclobutene-1,2-dione with the organotitanium reagents is also discussed. It was observed that the addition of Et_3N and acid chlorides to the alkyne-iron carbonyl complex, formed in the reaction of $Fe_3(CO)_{12}$, Et_3N and alkyne in THF, leads to the formation of the acyloxyferrole complex **I** in good yields 65-76% (eq. 1). The structure of the acyloxyferrole complex **I** was identified by single crystal X-ray analysis.



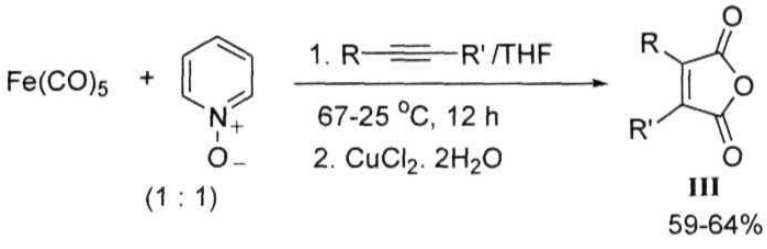
--- eq.1

These acyloxyferrole complexes are readily transformed to the corresponding cyclobutenediones in moderate to good yields using bromine (eq. 2). Probable reaction pathways and the intermediates that may be involved in the formation of acyloxyferrole complexes as well as cyclobutenediones are discussed.



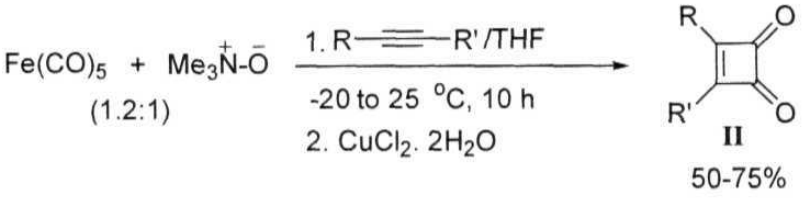
--- Eq. 2

We have found that the reaction of alkynes with $Fe(CO)_5$ in the presence of pyridine *N*-oxide (1:1 ratio) at 70 °C gives the corresponding maleic anhydride derivatives after $CuCl_2.2H_2O$ oxidation (eq. 3). Whereas the use of in 2:1 ratio of $Fe(CO)_5$ and pyridine *N*-oxide led to the formation of a mixture of 2,5-and 2,6-disubstituted benzoquinones (60% yield).



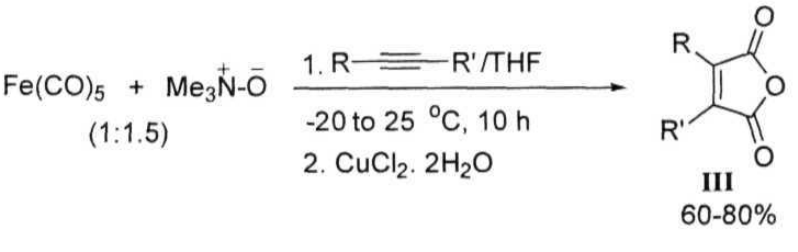
--- Eq. 3

Interestingly, the "$Fe(CO)_4$" species prepared under mild conditions using the $Fe(CO)_5/Me_3NO$ reagent system in 1.2:1 ratio, reacts with alkynes at 25 °C to give the corresponding cyclobutenediones in moderate to good yields (50-75%) after $CuCl_2.2H_2O$ oxidation (eq. 4).



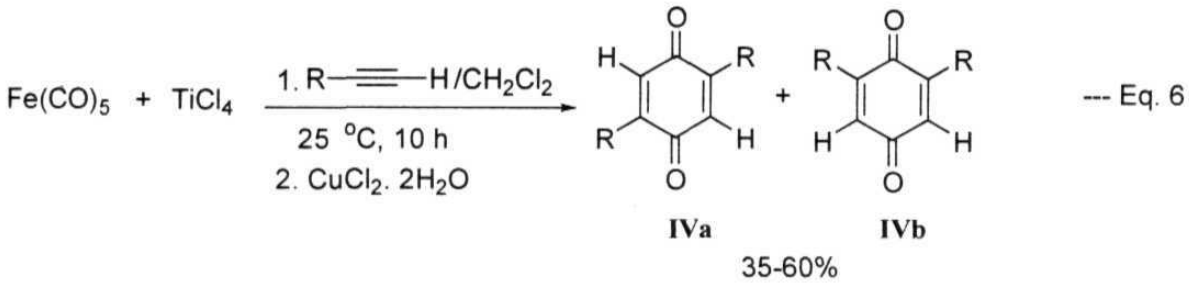
--- Eq. 4

In the runs using $Fe(CO)_5/Me_3NO$ in 1:1.5 ratio, the corresponding cyclic anhydrides were obtained in good yields along with traces of cyclobutenediones (3-5%) after $CuCl_2.2H_2O$ oxidation (eq. 5).



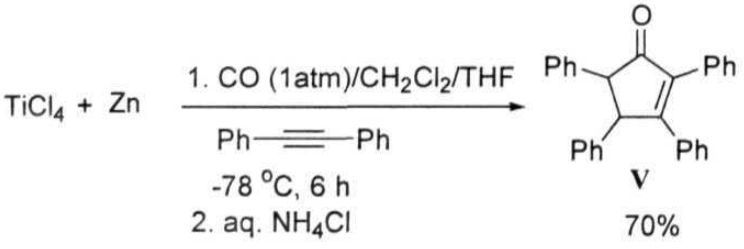
--- Eq. 5

We have explored the possibility of generating reactive iron carbonyl species from $Fe(CO)_5$ using $TiCl_4$ for synthetic applications. It was observed that the addition of $TiCl_4$ to a mixture of $Fe(CO)_5$/alkyne at 25 °C in dichloromethane gives a mixture of benzoquinones after $CuCl_2.2H_2O$ oxidation (35-60%) (eq. 6). Several 1-alkynes were converted to the corresponding 2,5-and 2,6-dialkylbenzoquinones.

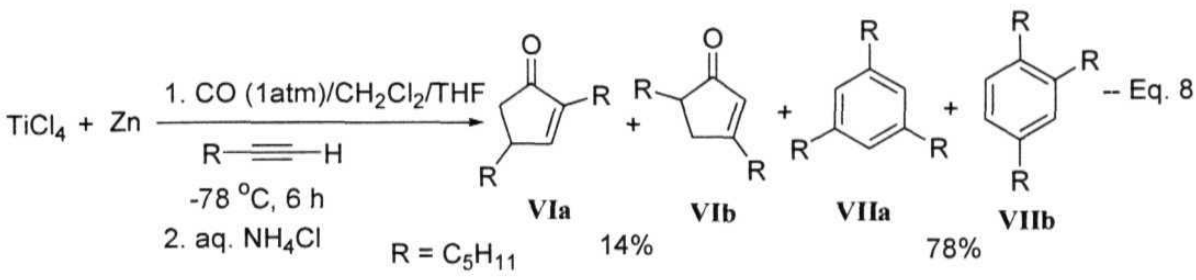


--- Eq. 6

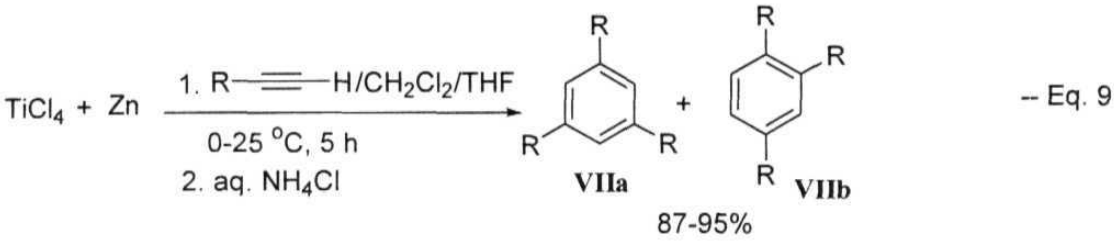
Carbonylation of alkynes were also studied using the $TiCl_4$/Zn/CO reagent system. Cyclopentenone **V** was obtained in 70% yield in a run with diphenylacetylene (eq. 7). The structure of **V** was identified by single crystal X-ray analysis. The use of 1-alkynes under the same conditions gave the corresponding trisubstituted benzenes (78%) as major product besides the corresponding cyclopentenones (14%) (eq. 8).



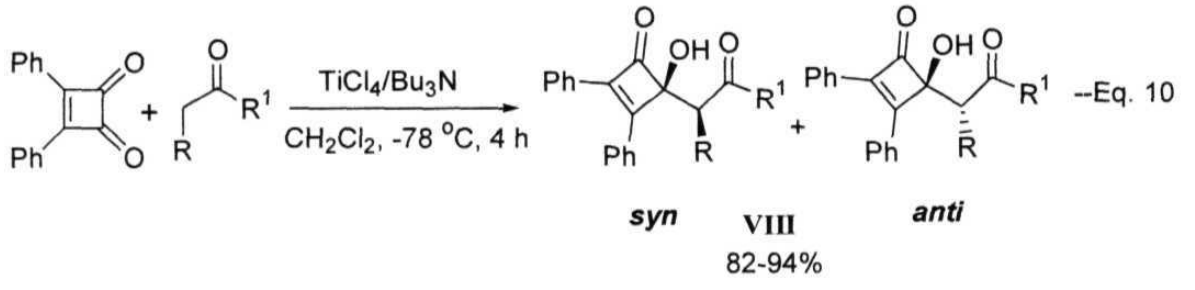
--- Eq. 7



In runs, without using CO, a mixture of 1,3,5- and 1,2,4-trisubstituted benzenes **VIIa** and **VIIb** were obtained (eq. 9).



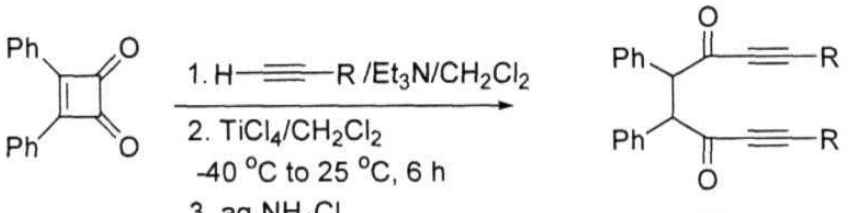
We have also examined the reactivity of cyclobutenediones with organotitanium reagents. It was observed that the reaction of 3,4-diphenyl-3-cyclobutene-1,2-dione with the titanium enolates, generated *in situ* using ketones and $TiCl_4/Bu_3N$ at –78 °C gave the corresponding 4-hydroxy-4-substituted-2-cyclobutenones **VIII** (eq. 10). The stereochemistry of the aldol adduct **VIII** was confirmed by single crystal X-ray analysis.



VIII
82-94%

--Eq. 10

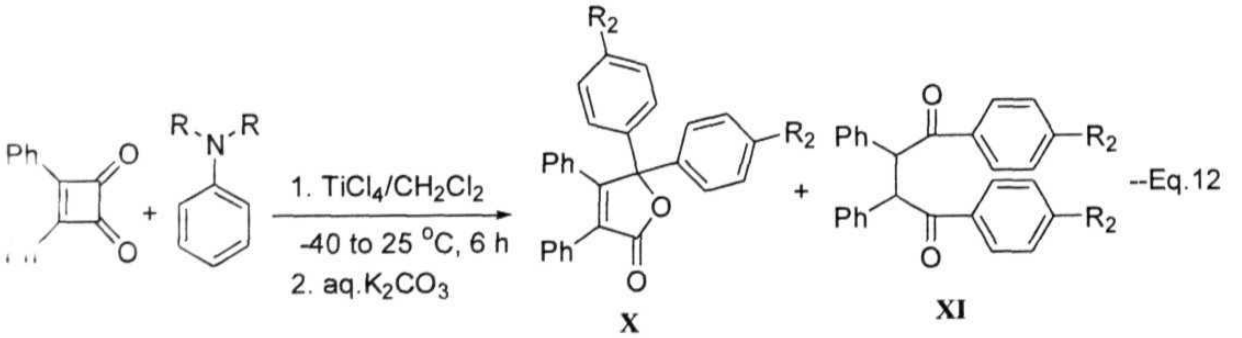
We have observed that the reaction of alkynyltitanium species with 3,4-diphenyl-3-cyclobutene-1,2-dione gave the corresponding 1,8-disubstituted-4,5-diphenyl-1,7-octadiyne-3,6-dione albeit in low yields **IX** (eq. 11).



IX
15-21%
dl:meso

--- Eq. 11

Interestingly, aryltitanium species react with cyclobutenedione to afford butenolide **X** as the major product along with 1,4-diketone **XI** (eq. 12).

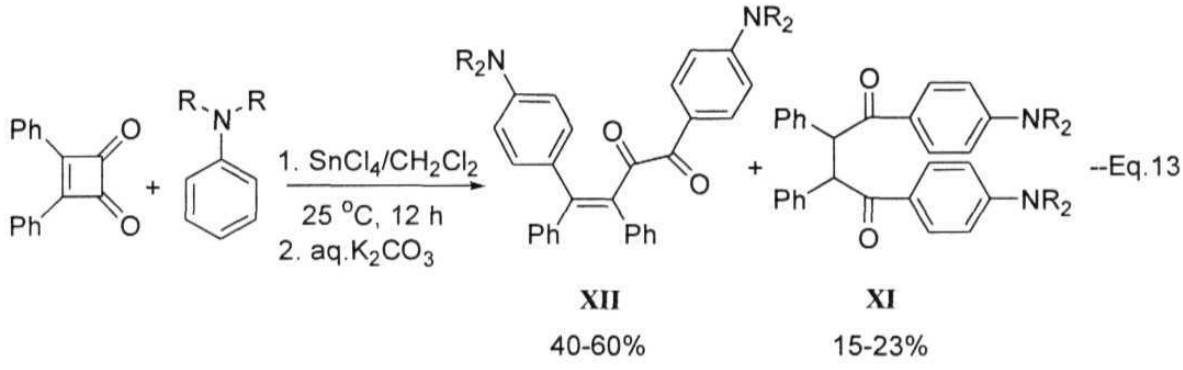


X
30-65%

XI
8-12%

--Eq.12

Whereas the reaction of *N,N*-dialkylarylamines with 3,4-diphenyl-3-cyclobutene-1,2-dione at room temperature in the presence of $SnCl_4$ led to a novel ring cleaved product 1,4-bis(4-diethylaminophenyl)-3,4-diphenyl-3-butene-1,2-dione **XII** along with a small amount of the 1,4 diketone **XI** (eq. 13). The structure of **XII** was identified by single crystal X-ray analysis.



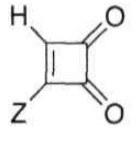
XII 40-60%

XI 15-23%

Mechanisms of these Lewis acid promoted reactions of cyclobutenediones are discussed.

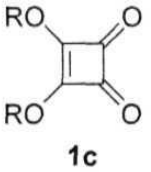
1. Introduction

Cyclobutenediones are considered as quinones of unstable cyclobutadienes because of their formal resemblance to cyclobutadienes by virtue of all sp^2 hybridised carbons in a four membered ring.[1] Phenylcyclobutenedione, was the first cyclobutenedione to be synthesized by *J. D. Roberts et al.*[1a] in 1955. The initial studies on cyclobutenediones were limited primarily to their unusual stability,[1] vinylogous behaviour[2] and aromaticity of their oxoanions.[3] Extraction of moniliformin **1a**, a fungal toxin, from *Fusarium moniliforme* by *Cole et al.*[4] led to the synthesis and testing of wide range of cyclobutenediones. Consequently, a number of biological and pharmaceutical applications of cyclobutenediones were discovered. For example, the di-*n*-butylsquarate **1c** (R = n-C_4H_9) is a potent allergen and has been used in the treatment of alopecia areata, and in immunotherapy for warts in children.[5,6] Squaric acid **1c** (R = H) itself is an inhibitor of glyoxylase I,[7] semisquaric acid **1b** is for pyruvate dehydrogenase and transketolase[8] and **1d** is inhibitor for PTPases (protein tyrosine phosphatases).[9]

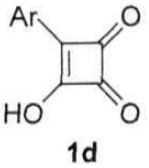


Z = KO **1a**

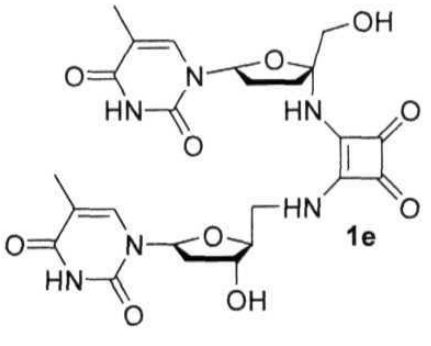
Z = HO **1b**



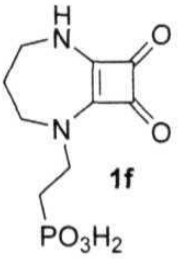
1c



1d



1e



1f

Recently, the diamide of squaric acid **1e** was used as a replacement for one of the phosphate diester linkages in an oligodeoxynucleotide,[10] while **1f** as antagonist of the NMDA (N-methyl-D-aspartate) receptor.[11] Also, some of the cyclobutenedione derivatives are useful as high-affinity ligands for exitatory amino acid receptors[12] and anion recognition systems.[13]

Extensive studies by *Liebeskind,*[14a] *Moore,*[14b-c] *and Paquette*[14d] have shown that cyclobutenediones are highly versatile starting materials for the synthesis of an array of multifunctional carbocyclic and heterocyclic compounds. Recently, squarate diamides have been used in the construction of chiral auxiliaries.[15] Also, cyclobutenedione derivatives (squaraines) are used as NLO materials[16] and photoconductors.[17] Accordingly, we have decided to explore the development of new methods for the synthesis of cyclobutenediones. A brief review of various methods reported for the synthesis of cyclobutenediones will be helpful for discussion.

1.1 Synthesis of Cyclobutenediones

1.1.1 Synthesis by Thermal or Photochemical Cycloadditions

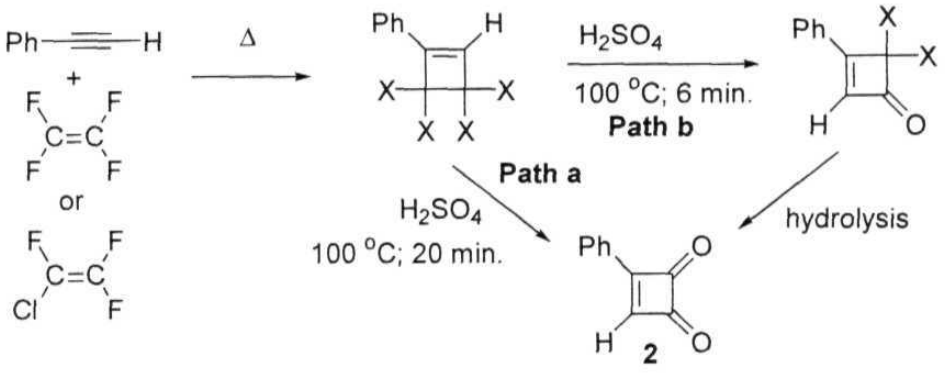
1.1.1.1 Cycloadditions Involving Alkynes

1.1.1.1.1 Addition of Alkynes to Tetrahaloalkenes

Cycloaddition reactions between fluoroalkenes and substituted acetylenes have proven to be of considerable value in the synthesis of cyclobutenediones.[18] For example,

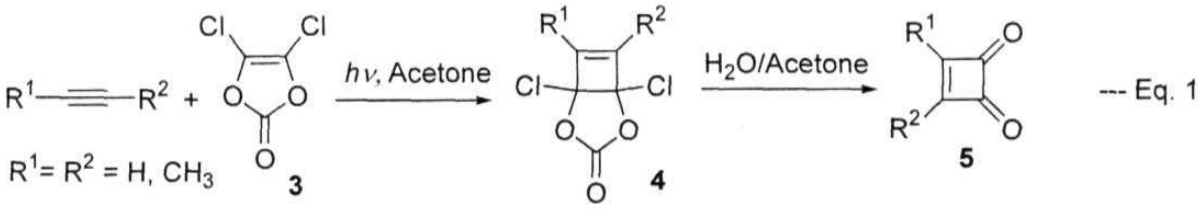
the first reported cyclobutenedione, i.e. phenylcyclobutenedione **2**, was prepared by cycloaddition of chlorotrifluoroethylene or tetrafluoroethylene to phenylacetylene to form tetrahalogenated phenylcyclobutene. The resulting tetrahalogenated phenylcyclobutene was subjected to acid hydrolysis either directly (**Path a**) or *via* dihalogenated phenylcyclobutenone (**Path b**) to provide cyclobutenediones (**Scheme 1**).[1a]

Scheme 1



1.1.1.1.2 Addition of Alkynes to Dichlorovinylene Carbonate

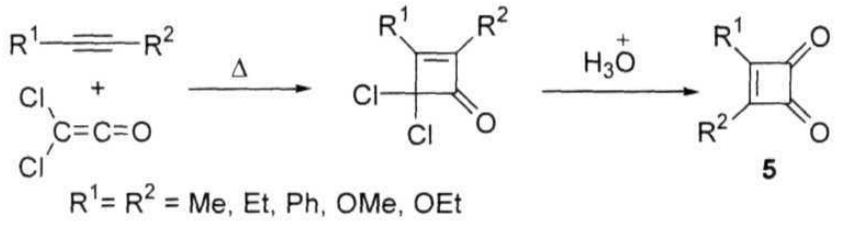
Irradiation of a mixture of dichlorovinylene carbonate (DCVC) **3** and alkyne in polar aprotic solvents like acetone or acetonitrile in the presence of photo-sensitizers gives cycloadduct **4** in poor yields 10-15%. Subsequent hydrolysis of adduct at 60 °C in 60% acetone/water yields the corresponding cyclobutenediones (eq. 1).[19]



--- Eq. 1

1.1.1.1.3 Addition of Alkynes to Ketenes

Thermal cycloaddition of alkynes to dichloroketene followed by acid hydrolysis of the resulting cylobutenone affords cyclobutenediones (eq. 2).[20]

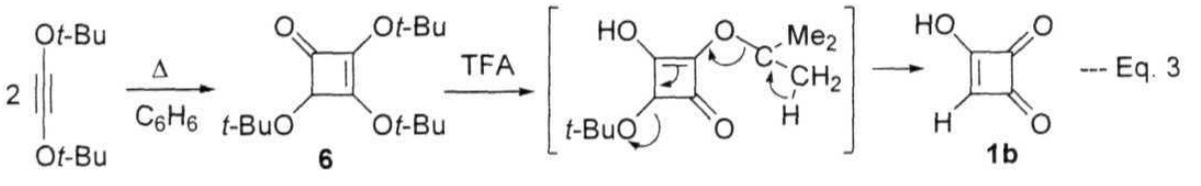


$R^1 = R^2$ = Me, Et, Ph, OMe, OEt

--- Eq. 2

1.1.1.1.4 Alkyne Dimerisation

3-Hydroxycyclobutene-1,2-dione (semisquaric acid) **1b**, the parent compound of the natural mycotoxin "moniliformin" has been synthesized by thermal dimerisation of di-*t*-butoxyethyne followed by solvolysis of **6** using trifluroacetic acid (eq. 3).[21]



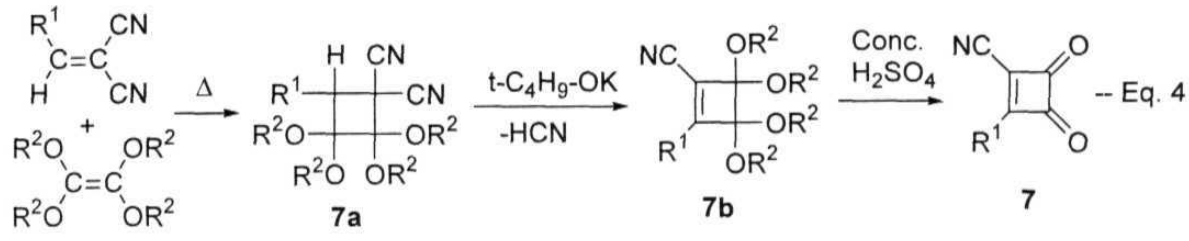
--- Eq. 3

1.1.1.2 Cycloadditions Involving Alkenes

1.1.1.2.1 Addition of Electron-rich Olefins to Electron-poor Olefins

Tetraalkoxy ethylene, an electron-rich olefin, adds on to electron-poor ethylene derivatives under thermal conditions to form 1,1,2,2-tetraalkoxy-3,3-dicyano-4-arylcyclobutene **7a**, which upon base catalysed elimination of HCN gives **7b**. The 3-

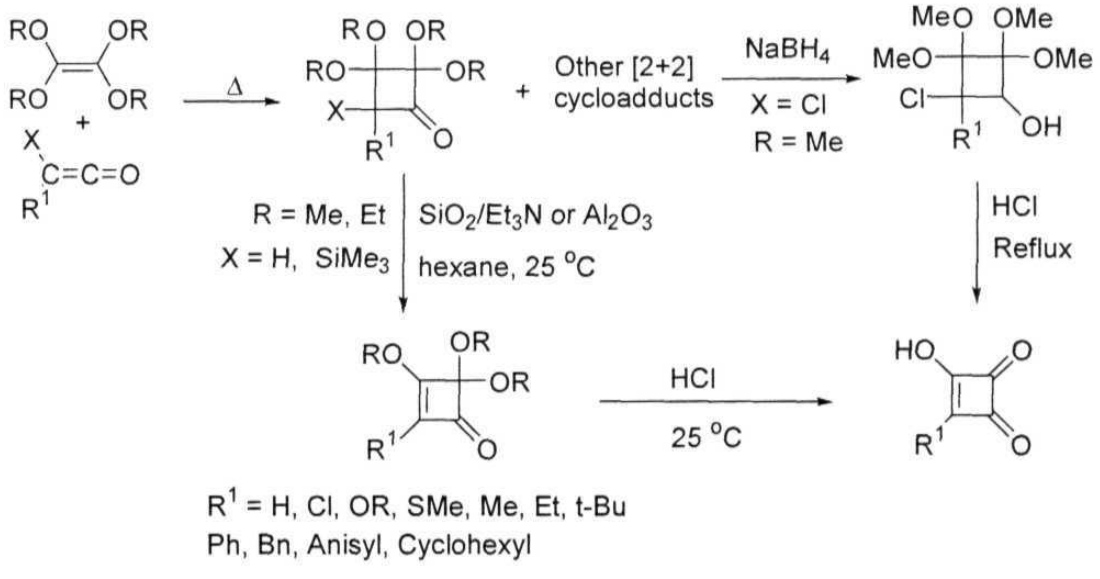
cyanocyclobutenedione **7** is obtained by hydrolysis of acetal groups using concentrated sulphuric acid at 25 °C (eq. 4).[22]



1.1.1.2.2 Addition of Electron-rich Olefins to Ketenes

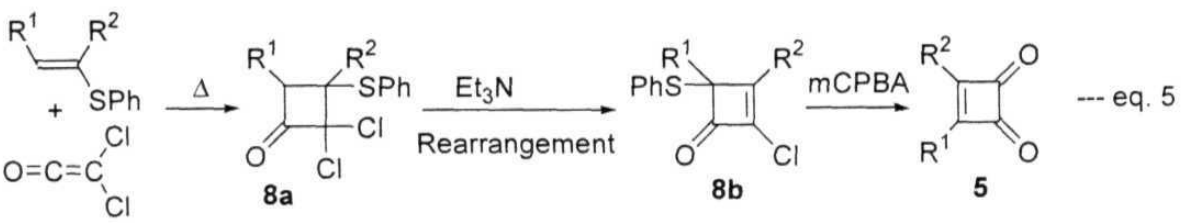
An improved synthesis of cyclobutenediones and derivatives of semi squaric acid was achieved by (2+2) cycloaddition of the tetraalkoxyethylenes with alkylketene,[23a] chloroketene,[23b] oxy ketene[23c] or trimethylsilyl ketene,[23d] produced *in situ* by triethylamine-promoted dehydrohalogenation of the corresponding acyl chlorides (**Scheme 2**).

Scheme 2



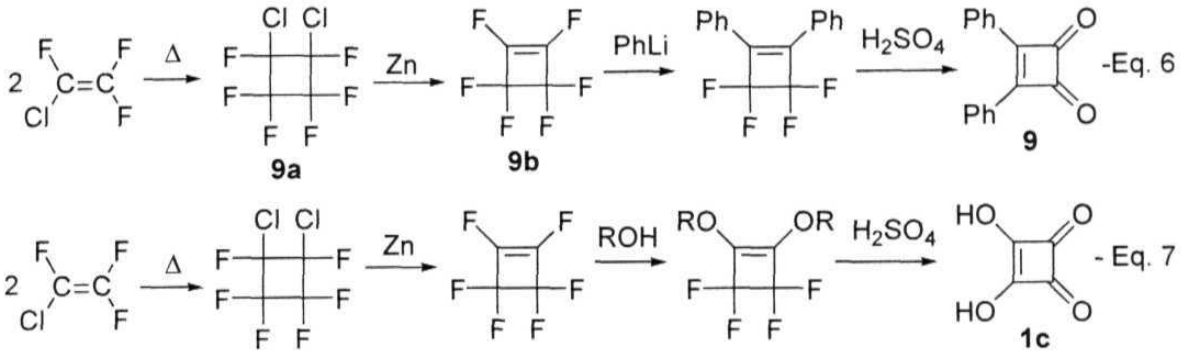
1.1.1.2.3 Addition of Thioenol Ethers to Ketenes

Recently, *Liebeskind et al.*[24] reported a relatively simple protocol for the synthesis of cyclic and acyclic cyclobutenediones starting from ketones (eq. 5). Phenylthioenol ethers, prepared from ketones undergo regiospecific [2+2] cycloaddition with dichloroketone to provide dichlorocyclobutanone **8a**, which upon Et_3N/CH_3CN treatment produces rearranged product **8b** through HCl elimination. Reaction of **8b** with m-chloroperbenzoic acid gives cyclobutenedione.



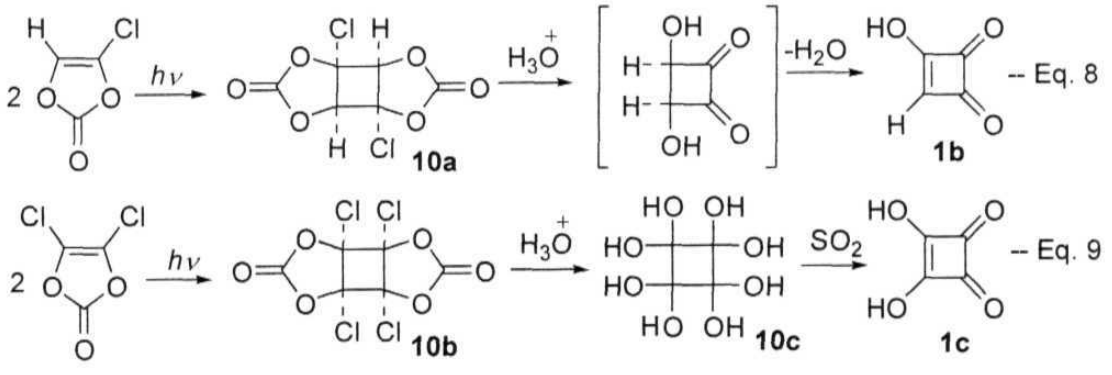
1.1.1.2.4 Cyclodimerisation of Tetrahaloethylenes

Heating of fluorinated ethylenes leads to stable cyclobutane rings **9a** in contrast to other halogenated olefins (chloro and bromo) which give polymerised products.[25] The cyclisation process is exclusively a "head to head"or "tail to tail" joining to form only one isomer. Dechlorination of **9a** with Zn affords cyclobutene **9b**, which upon further reaction with aryl lithium reagents provides 3,4-diarylcyclobutene-1,2-dione after hydrolysis (eq. 6). Squaric acid **1c** was first synthesized in 1959 by *Cohen et al.*[25a] following a similar procedure (eq. 7).



1.1.1.2.5 Cyclodimerisation of Chlorovinylene Carbonate

Both mono and dichlorovinylene carbonates undergo dimerisation upon irradiation in acetone solution to form cyclobutanes **10a** and **10b**, respectively. Hydrolysis of the adduct **10a** yields hydroxycyclobutenedione **1b**, whereas the **10b** gives octahydrocyclobutane **10c,** which on reaction with SO_2 yields squaric acid **1c** (eqs. 8 and 9).[26]

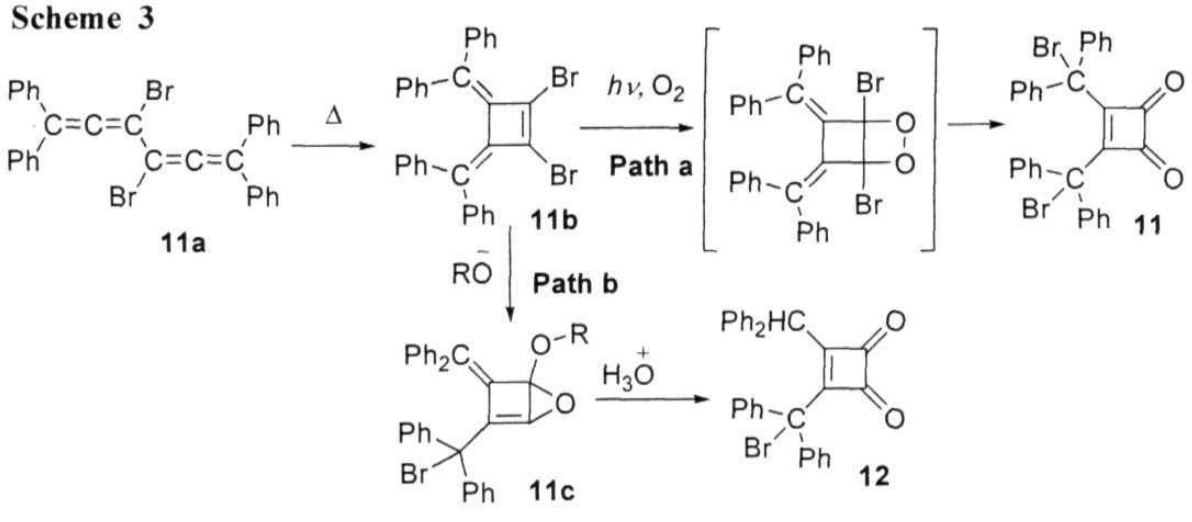


1.1.1.2.6 Intramolecular Cycloaddition of Olefins

Allenes of the type **11a** undergo intramolecular [2+2] cycloaddition under thermal conditions to form 1,2-dibromo-3,4-bis(diphenylmethylene)cyclobutene **11b** which on

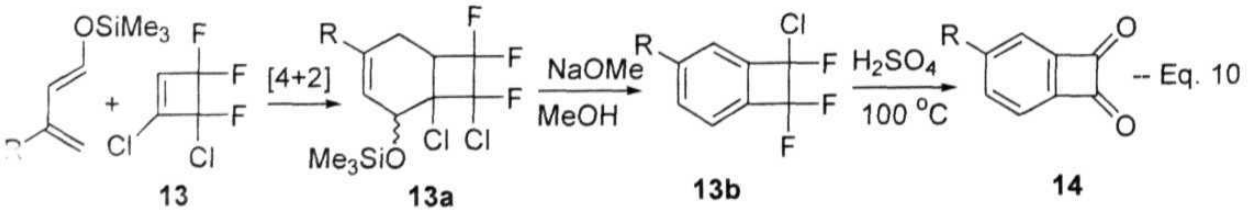
photo-oxidation affords 3,4-bis(bromodiphenylmethyl)cyclobutene-1,2-dione **11** (**Path a**) (**Scheme 3**). Alternatively, it can be converted to stable, isolable cyclobutene epoxide **11c** by refluxing with potassium alkoxide (**Path b**). Acid catalysed photochemical ring opening of **11c** gives 3-diphenylmethyl-4-bromodiphenylmethylcyclobutene1,2-dione **12** in quantitative yields.[27]

Scheme 3

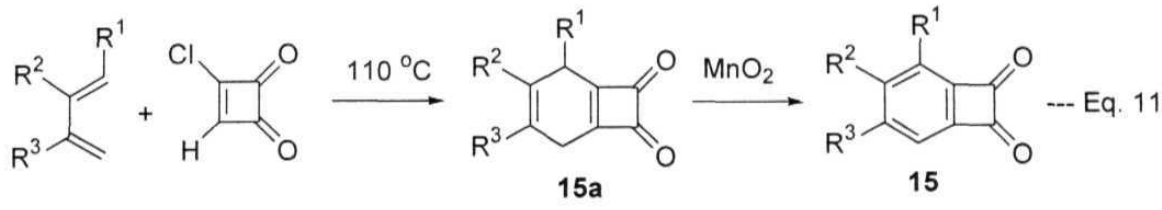


1.1.1.2.7 Addition of Dienes to Olefins

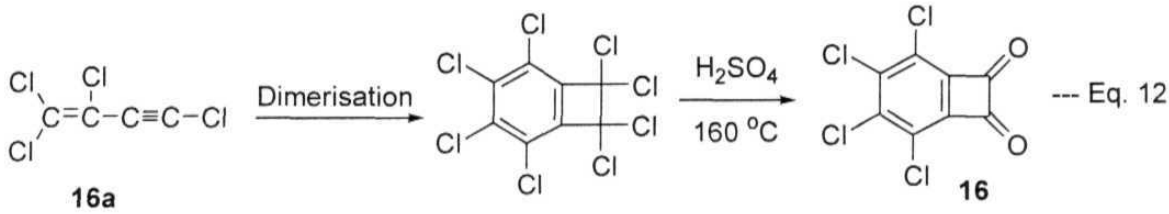
Substituted benzocyclobutenediones **14** have been prepared by utilizing Diels-Alder chemistry. Cycloaddition of trimethylsiloxy dienes to 1,4-dichloro-3,3,4-triflurocyclobutene **13** gives the cycloadduct **13a** that on aromatisation followed by acid hydrolysis gives benzocyclobutenediones (eq.10).[28]



Diels-Alder reaction of 3-chloro-3-cyclobutene-1,2,dione with dienes gives the adduct **15a**, which upon oxidation by active MnO_2 produces benzocyclobutenediones **15** (eq. 11).[29]

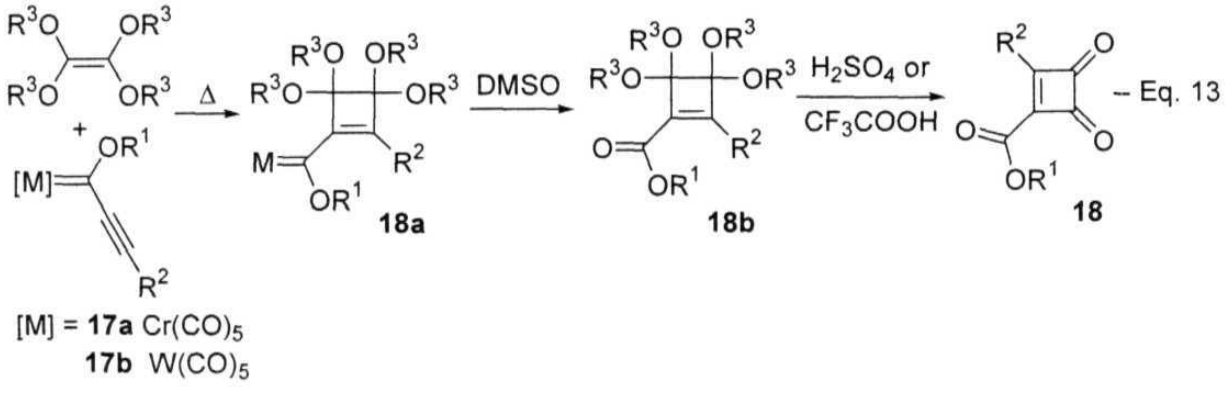


Similarly, tetrachlorobenzocyclobutenedione **16** has been prepared *via* dimerisation of polychlorinatedenyne **16a** followed by acid hydrolysis (eq. 12).[30]

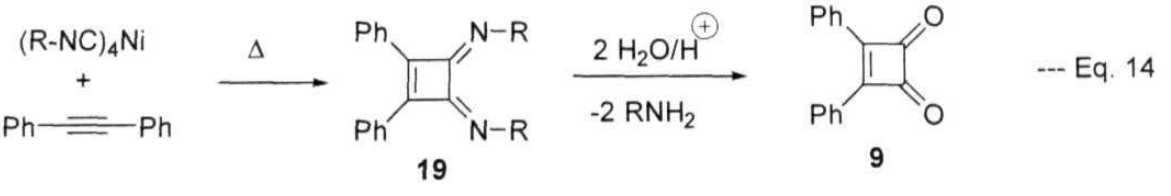


1.1.2 Cyclobutenediones *via* Transition Metal Complexes

Thermal reaction of alkynylalkoxycarbene complexes of chromium **17a** and tungsten **17b** with tetraalkoxyethylene affords good yields of [2+2] cycloadducts under mild conditions. The release of organic ligand from metal carbonyl was achieved by DMSO oxidation, and the resulting cyclobutene **18b** gives differently substituted cyclobutenediones **18** upon H_2SO_4 or CF_3COOH hydrolysis.[31]

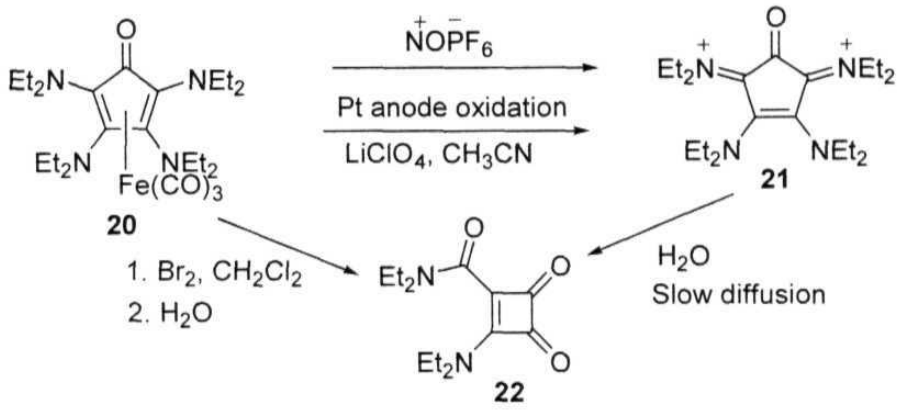


A novel cycloaddition of nickel complex to alkyne was reported. An equimolar ratio of tetrakis(arylisocynide)nickel and diphenylacetylene were refluxed in toluene to yield di-iminocyclobutene **19**, which upon aqueous HCl work up gave diphenylcyclobutenedione (eq. 14).[32]

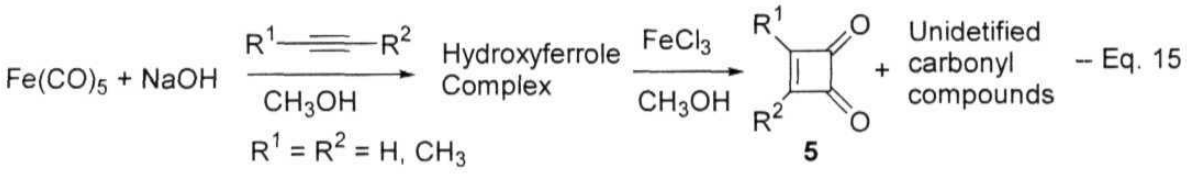


Oxidation of tetrakis(diethylamino)cyclopentadienone **20** with bromine and aqueous work up affords a novel cyclobutenedione with an interesting functionality **22**.[33] Dione has also been prepared *via* **21** by electrochemical or nitrosonium hexafluorophosphate oxidation (**Scheme 4**).[33]

Scheme 4

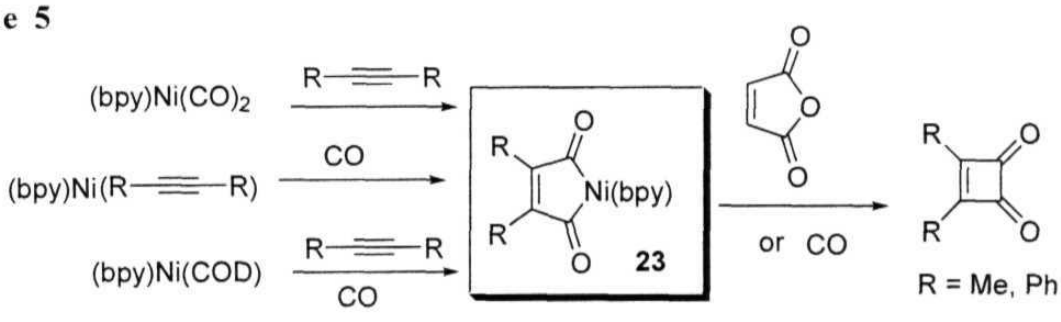


It was reported that the $FeCl_3$ oxidation of ferrole complex formed in the reaction of acetylene with an alkaline solution of $Fe(CO)_5$ leads to cyclobutenedione in low yield (eq. 15).[34]

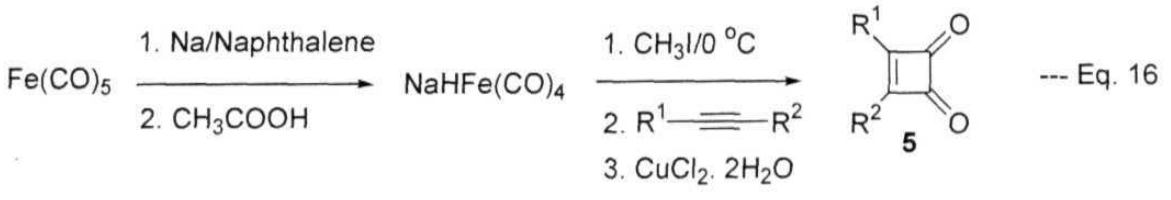


Herrera et al.[35] reported that the nickelacyclopentenediones **23**, prepared by reaction of $(bpy)Ni(CO)_2$ with alkyne in THF at 20 °C, affords cyclobutenediones with maleic anhydride or carbon monoxide (**Scheme 5**). Nickel complex **23** can also be obtained from the reaction of (bpy)Ni(alkyne) with molecular CO.[35a]

Scheme 5

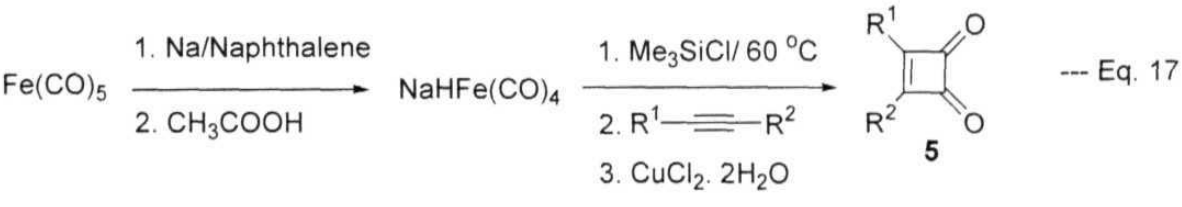


It was reported from this laboratory that the reaction of $NaHFe(CO)_4/CH_3I$ reage combination with alkynes at 60 °C gives the corresponding cyclobutenediones along w unsaturated carboxylic acids after $CuCl_2.2H_2O$ oxidation (eq. 16).[36a] Also, traces cyclobutenediones are obtained upon I_2 treatment of $NaHFe(CO)_4$ in the presence of methano



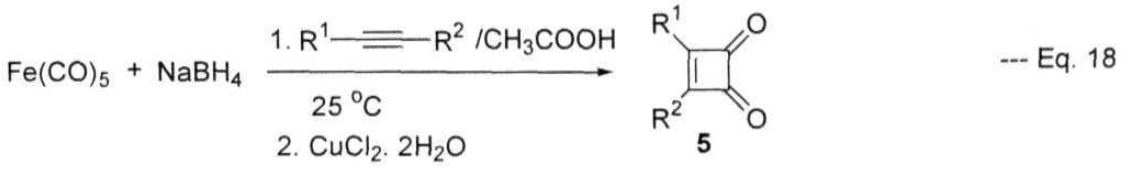
--- Eq. 16

It was found that the reagent, prepared using $NaHFe(CO)_4/Me_3SiCl$ at 60 °C, reaction with alkynes followed by $CuCl_2.2H_2O$ oxidation produced correspond cyclobutenedione (63%) as the only product (eq. 17).[36b]



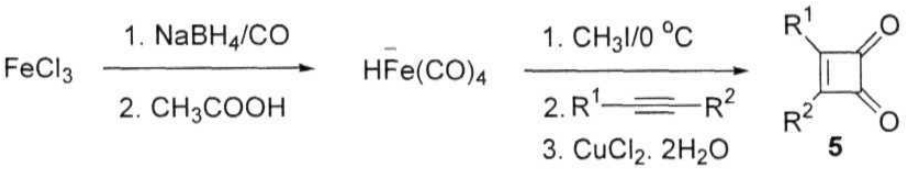
--- Eq. 17

Also, it was reported that the $[HFe_3(CO)_{11}]^-$ species, prepared *in situ* us $Fe(CO)_5/NaBH_4/CH_3COOH$, reacts with alkynes to give the corresponding cyclobutenedio in good yields (60-73%) after $CuCl_2.2H_2O$ oxidation (eq. 18).[37]



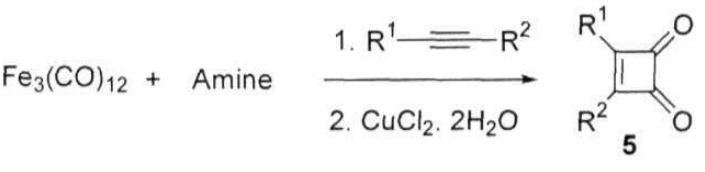
--- Eq. 18

Further, it was found that the iron carbonyl species, prepared by the reduction of $FeCl_3/NaBH_4$ in THF at 25 °C in the presence of CO reacts with alkynes at room temperature to give a complex that gives the corresponding cyclobutenediones after $CuCl_2.2H_2O$ oxidation (eq. 19).[38]



--- Eq. 19

Finally, coordinatively unsaturated iron carbonyl species, prepared using $Fe_3(CO)_{12}$/amine react with alkynes under ambient conditions to afford cyclobutenediones (eq. 20).[39]

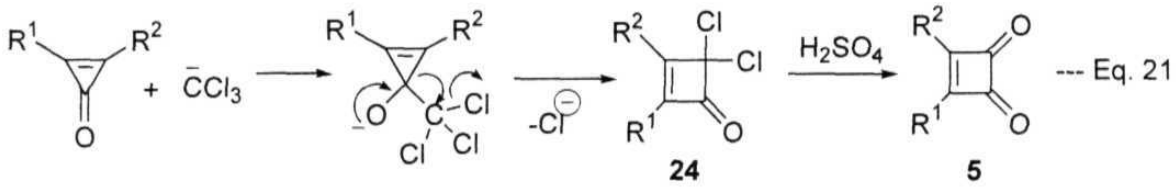


--- Eq. 20

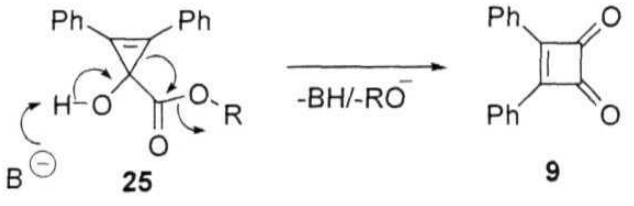
1.1.3 Cyclobutenediones from Cyclopropene Derivatives

Though, this is not a method of choice due to the difficulty associated with starting material preparation, cyclobutenediones could be obtained from cyclopropenones by ring expansion. Reaction of sodium trichloroacetate with dialkylcyclopropenone under thermal

conditions gives **5** *via* dichlorodialkylcyclobutenone **24** (eq. 21).[40] Similarly, base hydrolysis of **25** directly gives the corresponding cyclobutenedione (eq. 22).[41]



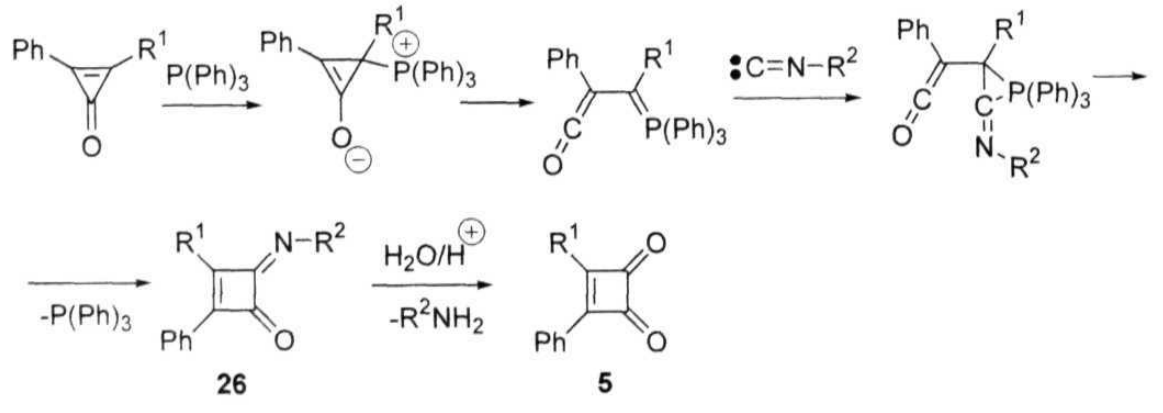
--- Eq. 21



--- Eq. 22

Also, it has been reported that isonitriles react with cyclopropenones to give cyclobutenedione in the presence of triphenylphosphine *via* iminocyclobutenone **26**.[42] The formation of **26** involves Michael addition of $P(Ph)_3$ to generate ketene-phosphorane followed by concerted rearrangement of P-C bonds as shown in **Scheme 6**.

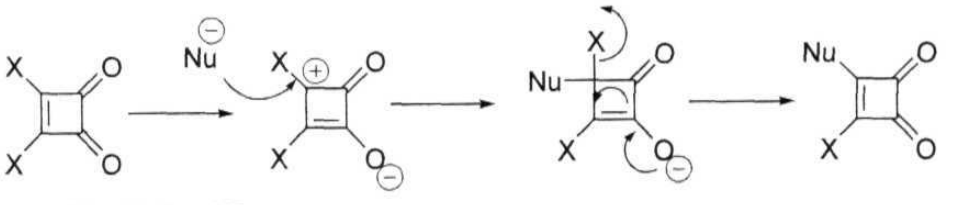
Scheme 6



1.1.4 Cyclobutenediones from Other Simple Cyclobutenediones

Synthesis of cyclobutenediones based on cycloaddition reactions is limited to either to squaric acid or aryl and simple alkyl derivatives. Hence, cyclobutenediones with a wide range of substituents have been synthesized from simple diones such as hydroxy, halo or alkoxy substituted cyclobutenediones by reacting with variety of carbon as well as hetero atom nucleophiles. The underlying principle in all these reactions is the vinylogous behaviour of cyclobutenediones i.e. hydroxy, halo and alkoxy cyclobutenediones show the reactivity similar to that of acid, acid chloride and ester, respectively (**Scheme 7**).[2]

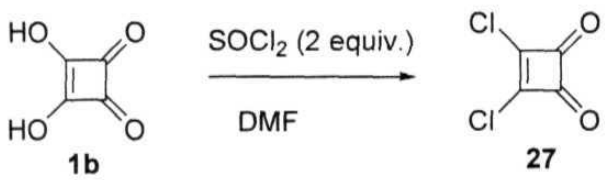
Scheme 7



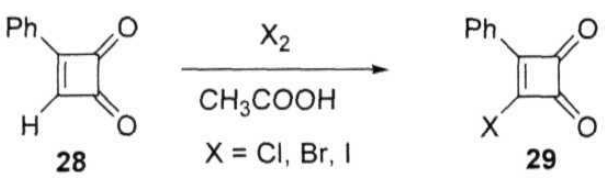
X = OH, Cl, Br, OR

1.1.4.1 Preparation of Halogen Derivatives of Cyclobutenedione

It has been reported that the reaction of squaric acid with $SOCl_2$ in the presence of DMF leads to the replacement of both the OH groups to form dichlorocyclobutenedione in good yields **27** (eq. 23).[43] Also, phenylcyclobutenedione is readily halogenated in glacial acetic acid (eq. 24).[1b]



--- Eq. 23

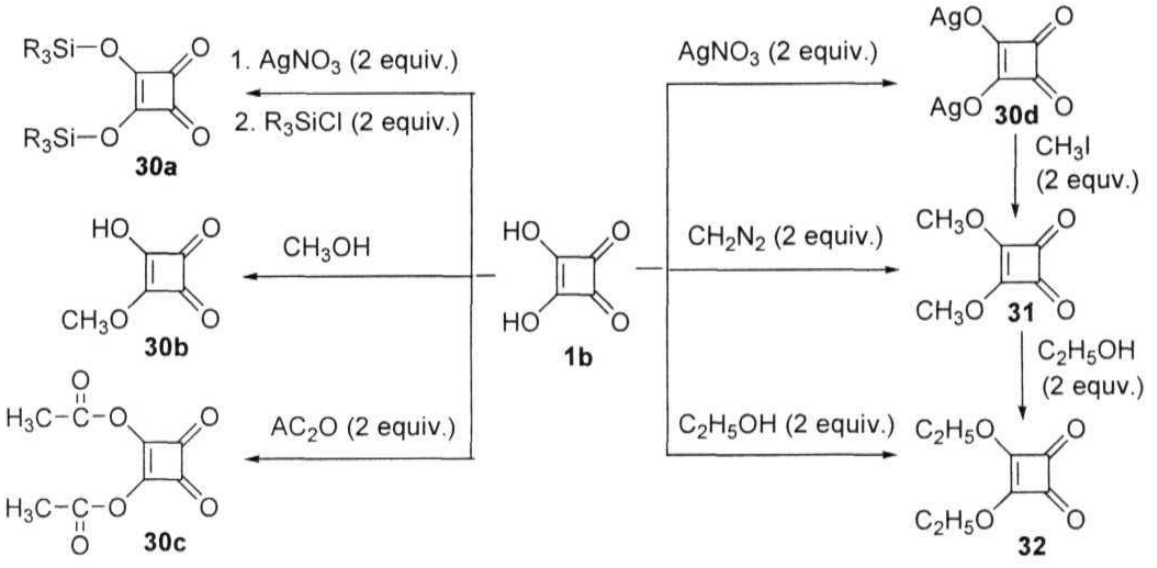


--- Eq. 24

1.1.4.2 Preparation of Alkoxy Derivatives of Cyclobutenedione

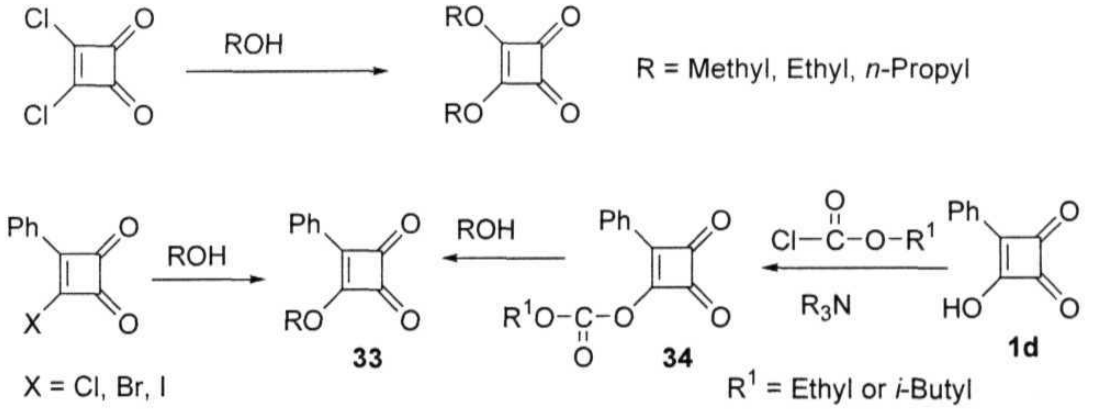
Alkoxy derivatives of cyclobutenedione, squaric acid esters, have been synthesized from squaric acid following different strategies as outlined in **Scheme 8**.[44] The chemical properties of squaric acid are mainly determined by its acid character and its reactivity is comparable to that of dicarboxylic acids. Ethyl or butyl alcohol treatment of squaric acid gives the corresponding diesters, whereas methanol gives monoester **30b**. However, dimethylsquarate was synthesized by the action of diazomethane on **1b** or by the reaction of methyl iodide with **30d**.

Scheme 8



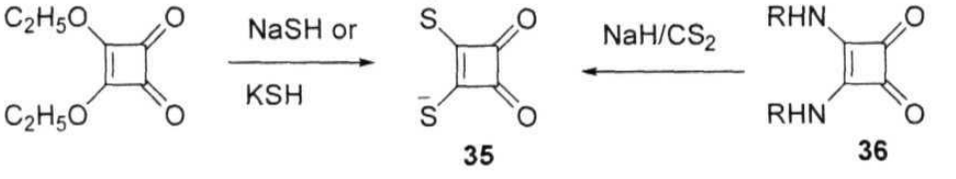
A similar reaction of halocyclobutenediones with alcohols give good yields of squaric acid esters (**Scheme 9**).[2b] As described later in this section, dialkoxy squarates are extensively used in the synthesis of a variety of cyclobutenediones.

Scheme 9

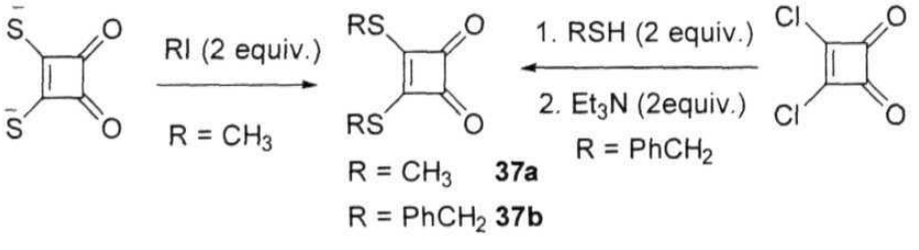


1.1.4.3 Preparation of Thionyl and Selenyl Derivatives of Cyclobutenedione

It was reported that the reaction of diethyl squarate with 2 equiv. of sodium or potassium hydrosulfide in alcohol gives the 1,2-dithiosquarate anion **35**,[45] which has also been prepared from squaric acid diamide **36** in low yield (eq. 25)[45]. Dithiosquarate anion is readily alkylated with CH_3I to give dithioester **37a**. Also, thioester **37b** has been synthesised by the reaction of benzylmercaptan and 3,4–dichloro-3-cyclobutene-1,2-dione in the presence of a base (eq. 26).[46]



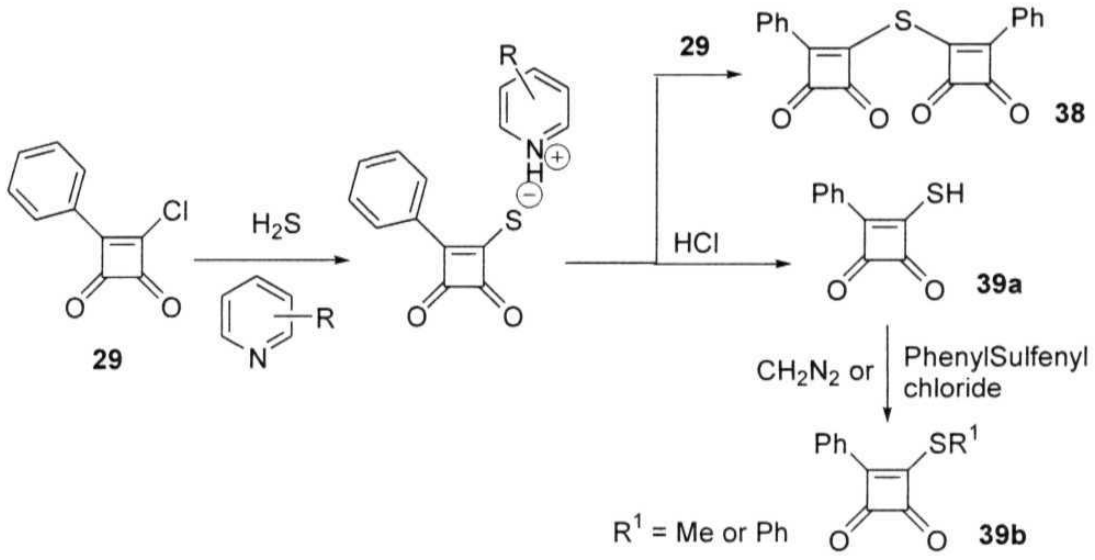
--- Eq 25



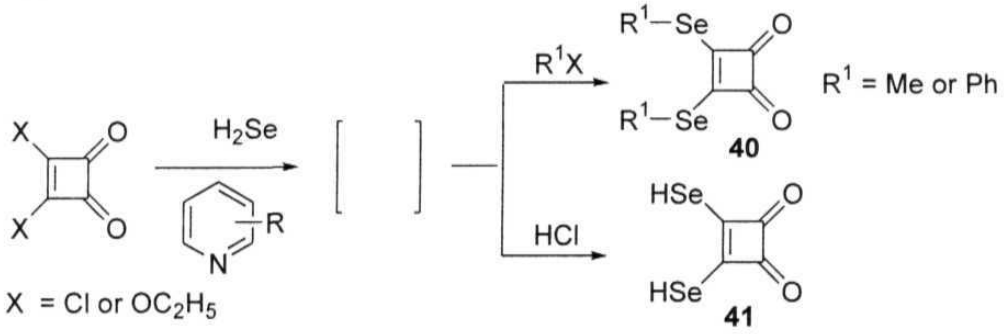
--- Eq 26

Similarly, the reaction of 3-chloro-4-phenyl-3-cyclobutene-1,2-dione **29** with pyridine saturated with hydrogen sulfide leads to thioether **38**. After acid work up, 3-mercapto-4-phenyl-3-cyclobutene1,2-dione **39a** was obtained, which could be converted to thioester **39b** with suitable reagents (**Scheme 10**).[47a] Similar reactivity was reported between hydrogen selenide and dichloro- or diethoxycyclobutenediones (**Scheme 11**).[47b]

Scheme 10



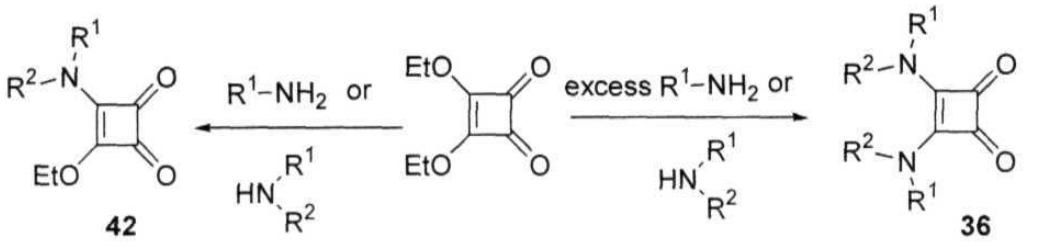
Scheme 11



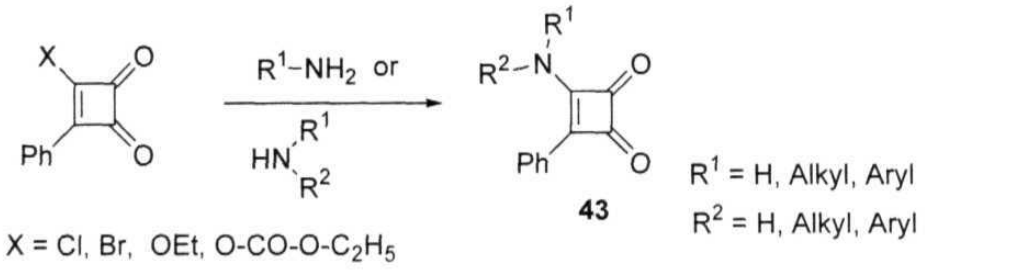
1.1.4.4 Preparation of Amine Derivatives of Cyclobutenedione

Amine derivatives of cyclobutenedione are known as amides of squaric acid. Reaction of slight excess of a primary or a secondary amine with dialkylsquarate in CH_3OH or CH_2Cl_2 at room temperature give monoamide monoester **42** in excellent yield.[48,44a] Diamides of squaric acid **36** are prepared under more basic conditions using

large excess of amine or by adding triethylamine (eq. 27). Also, halocyclobutenediones react with amines but provide amides in lower yields (eq. 28).[49]



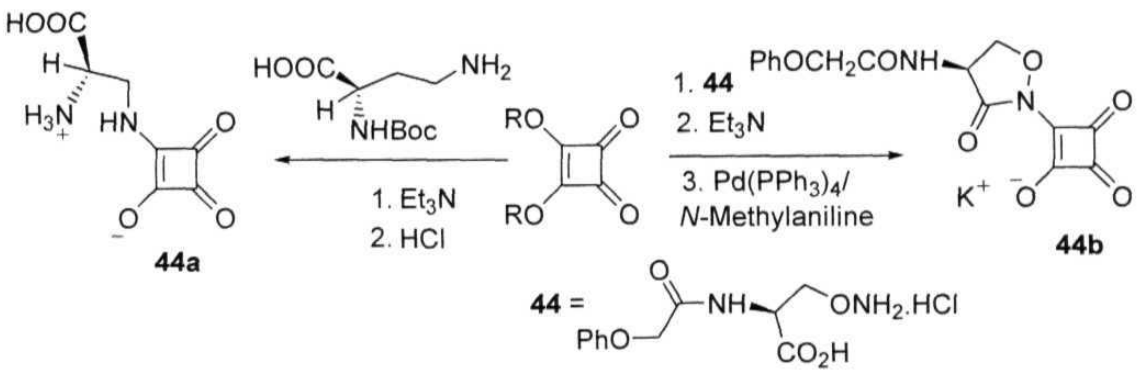
--- Eq. 27



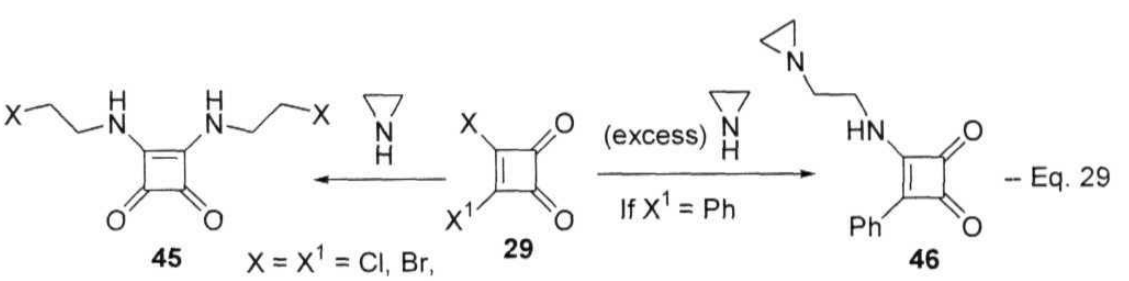
--- Eq. 28

This reaction could also be performed in a buffered solution (pH 7), which is appropriate for biopolymers. Hence, this controlled nucleophilic substitution forms the basis for the use of diethyl squarate as a coupling reagent to conjugate oligosaccharides to proteins or polyazamacrocycles.[50] Several biologically active and drug molecules such as **44a** and **44b** have been developed following similar method (**Scheme 12**).[51]

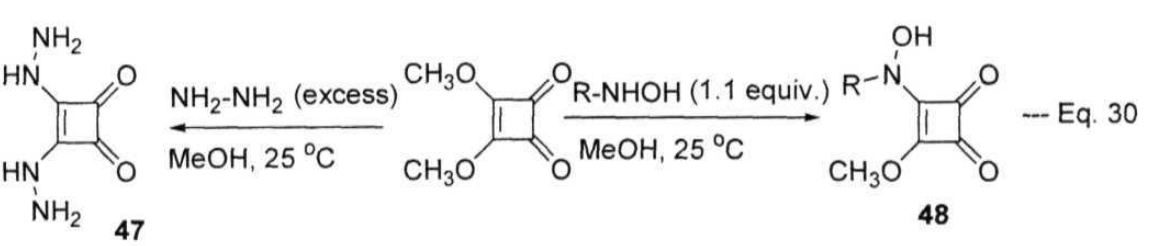
Scheme 12



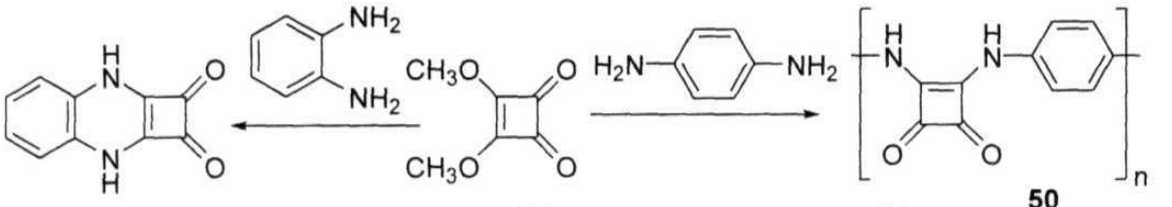
Also, it was found that aziridine reacts with dihalocyclobutenedione under suitable conditions to generate either 1,2–diamides **45** or (aziridinoethylamino)cyclobutenedione **46** (eq. 29).[52]



Dimethyl squarate reacts with hydrazine and hydroxylamines to form 3,4-dihydrazino-3-cyclobutene-1,2-dione **47** and *N*-hydroxylamide methylesters **48** respectively (eq.30).[2d,53]



Also, dimethyl squarate undergoes nucleophilic substitution reaction with *ortho* and *para*-phenylenediamine to provide **49** and **50** respectively.[2d]

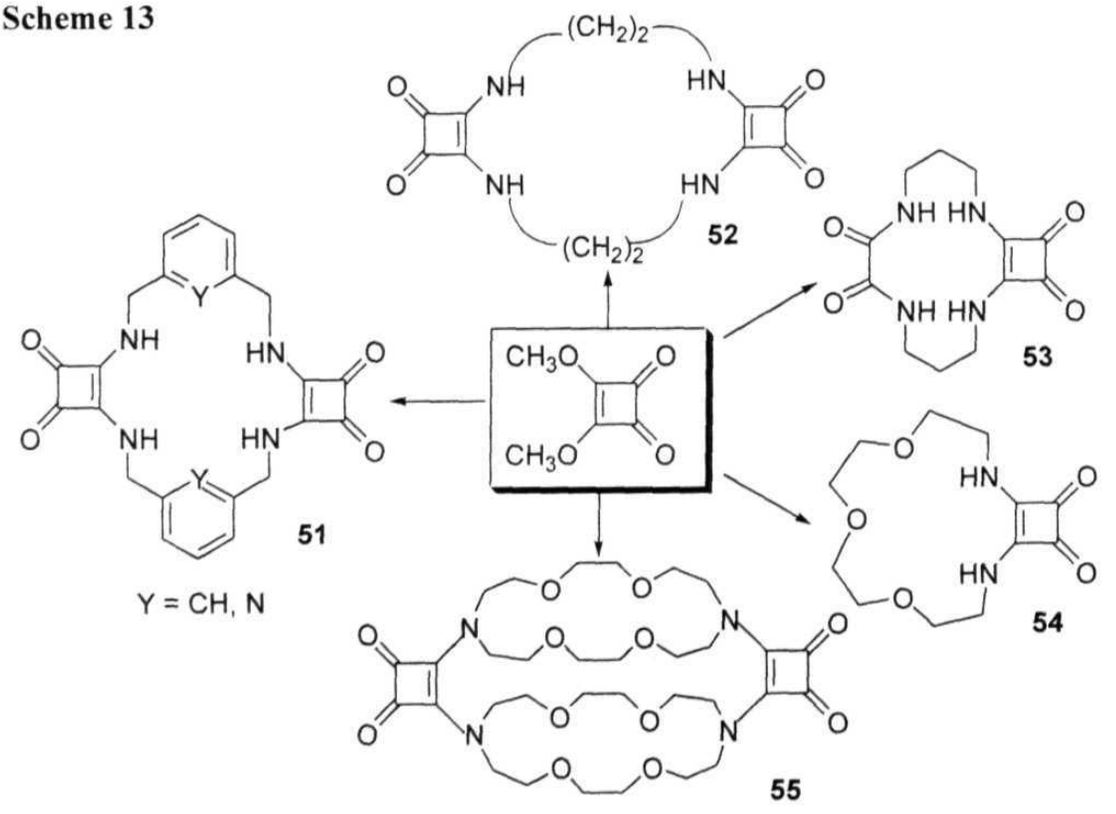


49 **31** **50**

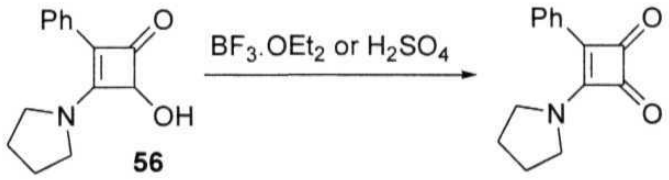
--- Eq. 31

Macrocyclic bridged squaric acid diamides of type **51-54** have been synthesised in good yields by the reaction of 1,ω-diamines with 1,2-dimethoxycyclobutenedione under high dilution conditions (**Scheme 13**).[54] Cryptands of type **55** are obtained from 1,2-dimethoxycyclobutenedione and monocyclic crown ether amines.

Scheme 13



Recently, it has been reported that $BF_3.Et_2O$ or H_2SO_4 induces oxidation of some 4-hydroxycyclobutenone **56** to furnish the corresponding cyclobutenediones (eq. 32).[55]

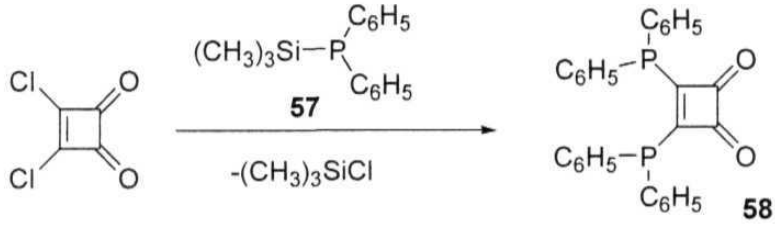


56

--- Eq. 32

1.1.4.5 Preparation of Phosphine Derivatives of Cyclobutenedione

1,2-Bis(diphenylphosphine)cyclobutenedione **58** was prepared by the reaction of dichlorocyclobutenedione with diphenyl(trimethylsilyl)phosphine **57** in ether at –78 °C. [56]

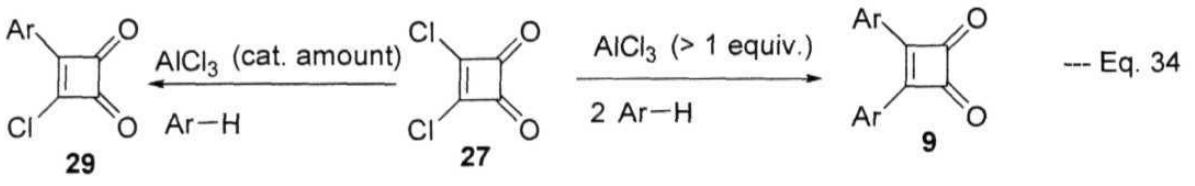


57 **58**

--- Eq. 33

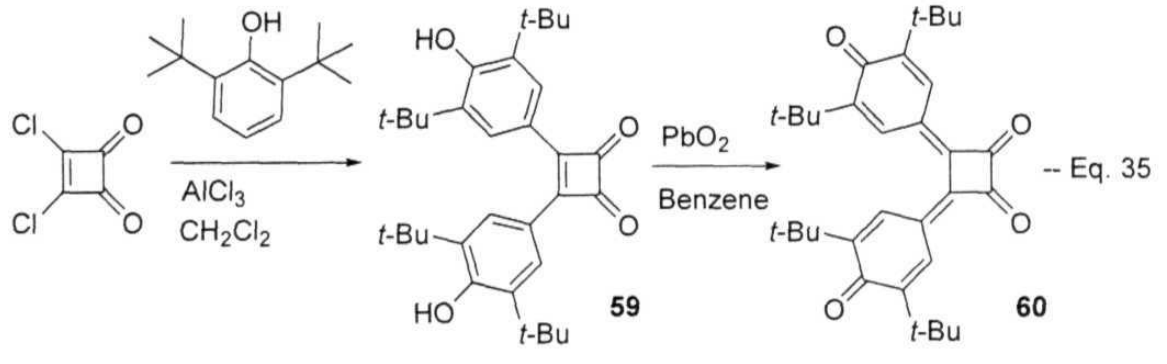
1.1.4.6 Preparation of Alkyl, Alkenyl, Alkynyl and Aryl Derivatives of Cyclobutenedione

Arylcyclobutenediones can be obtained by the reaction of halocyclobutenediones with arenes under Friedel-Craft acylation conditions. Dichlorocyclobutenedione **27** affords either mono **29** or diarylcyclobutenediones **9** depending upon the amount of catalyst ($AlCl_3$), the molar ratio of reactants and reaction conditions (eq. 34).[57,58]



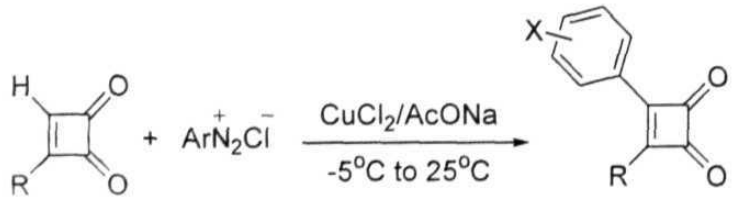
--- Eq. 34

A new class of cyclobutenediones containing quinoid rings have been prepared by Friedel-Crafts reaction (eq. 35). Reaction of 1,2-dichloro-3-cyclobutene-1,2-dione with $AlCl_3$ and 2,6-di*t*-butylphenol in refluxing dichloromethane yields **59**. Compound **59** is readily oxidized to 1,2-diquinocyclobutanedione **60** using PbO_2.[59]



-- Eq. 35

3-Amino-4-aryl- and 3-aryl-4-hydroxy-3-cyclobutene-1,2-diones have been obtained by the reaction of diazonium salt/cupric chloride, Meerwein arylation, with squaramides and semisquaric acid, respectively (eq. 36).[60]



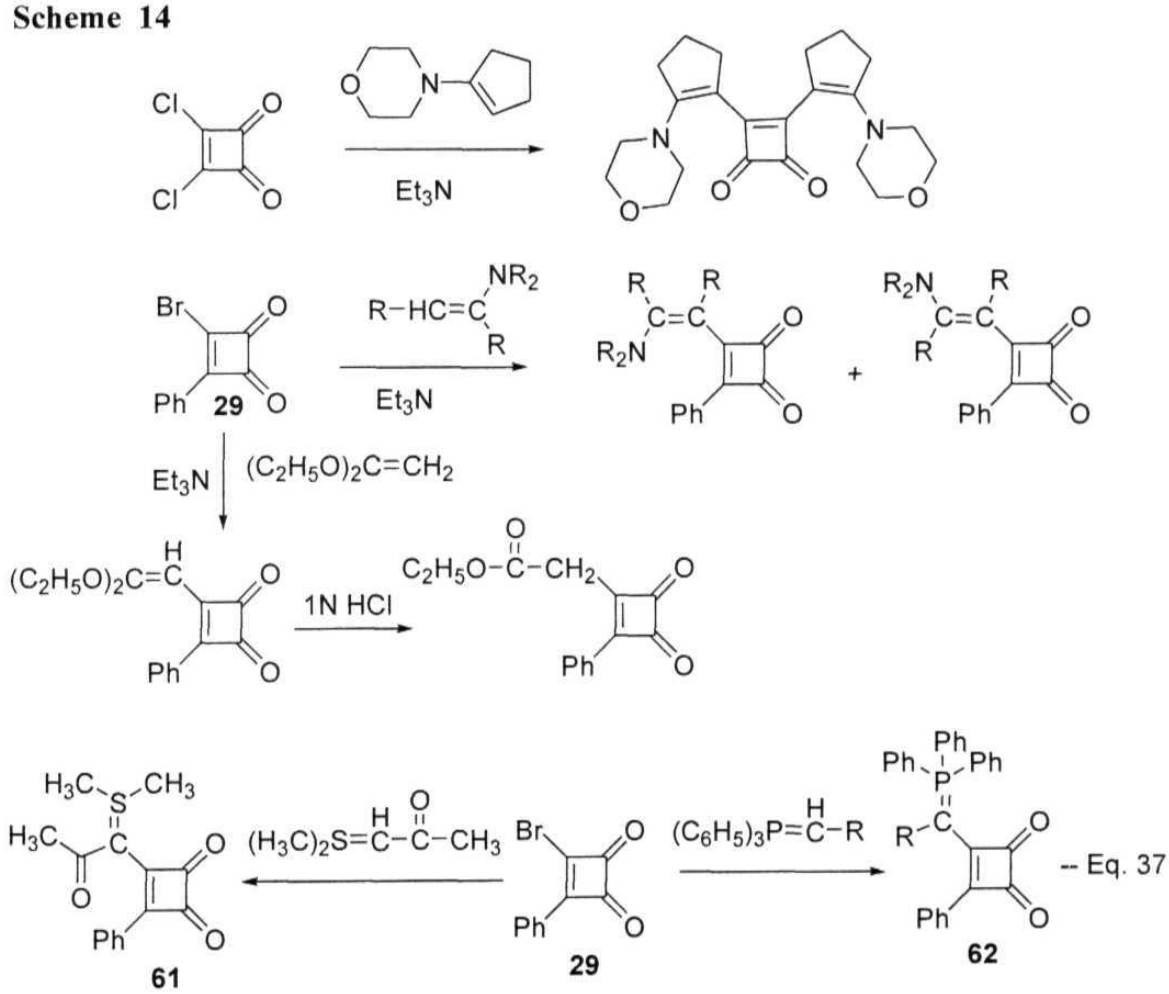
--- Eq. 36

R = NR'_2, OH

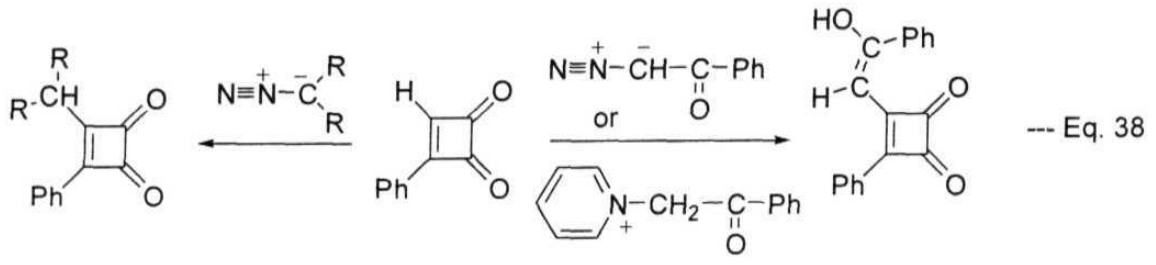
X = F, Cl, Br, Me, OMe, NO_2, COOH

Dichlorocyclobutenedione as well as bromophenylcyclobutenedione **29** condenses with electron rich olefins such as enamines, ketene acetals in the presence of triethylamine (**Scheme 14**).[61] Similarly, phosphrous and sulphur ylides react with **29** to generate cyclobutenediones with diverse substituents (eq. 37).[62]

Scheme 14



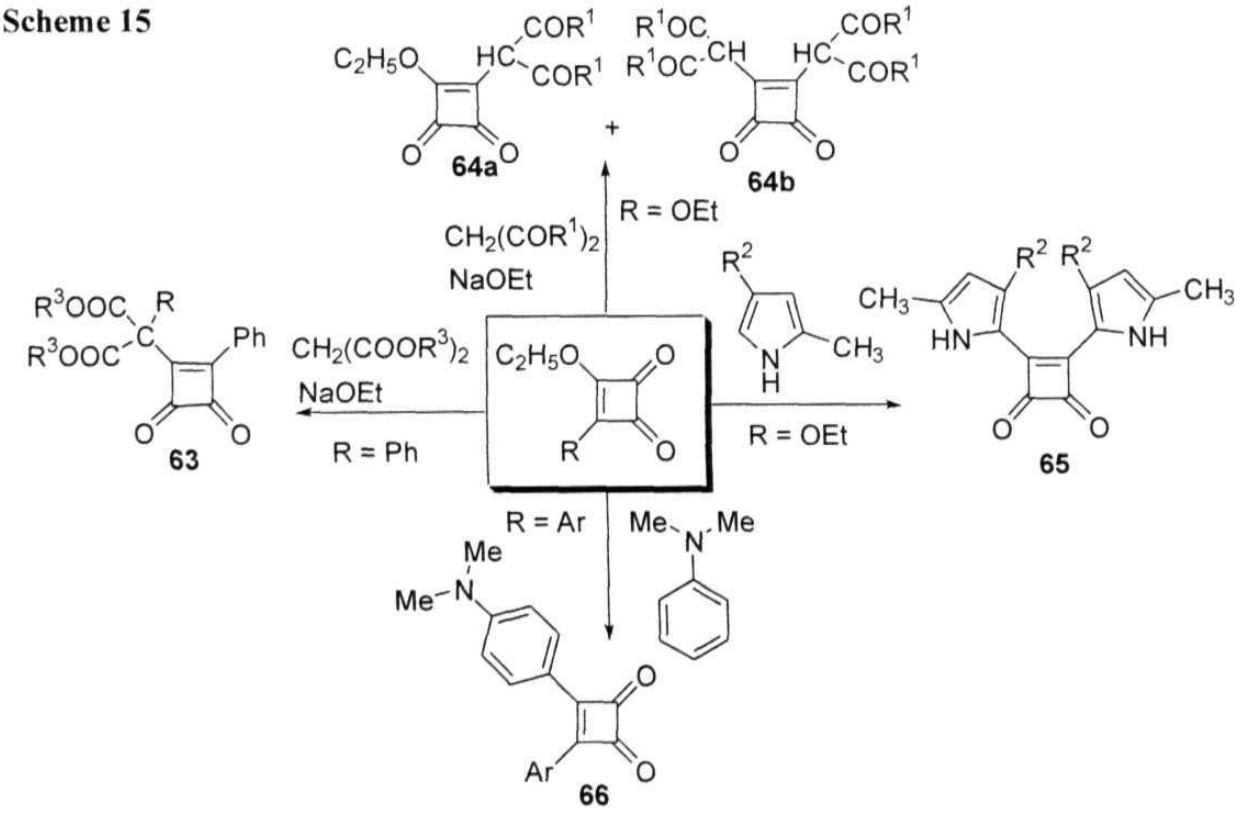
Alkyl and alkenyl derivatives of cyclobutenedione have been prepared by the reaction of diazoalkanes with phenylcyclobutenedione through an unusual nucleophilic substitution (eq. 38).[63]



--- Eq. 38

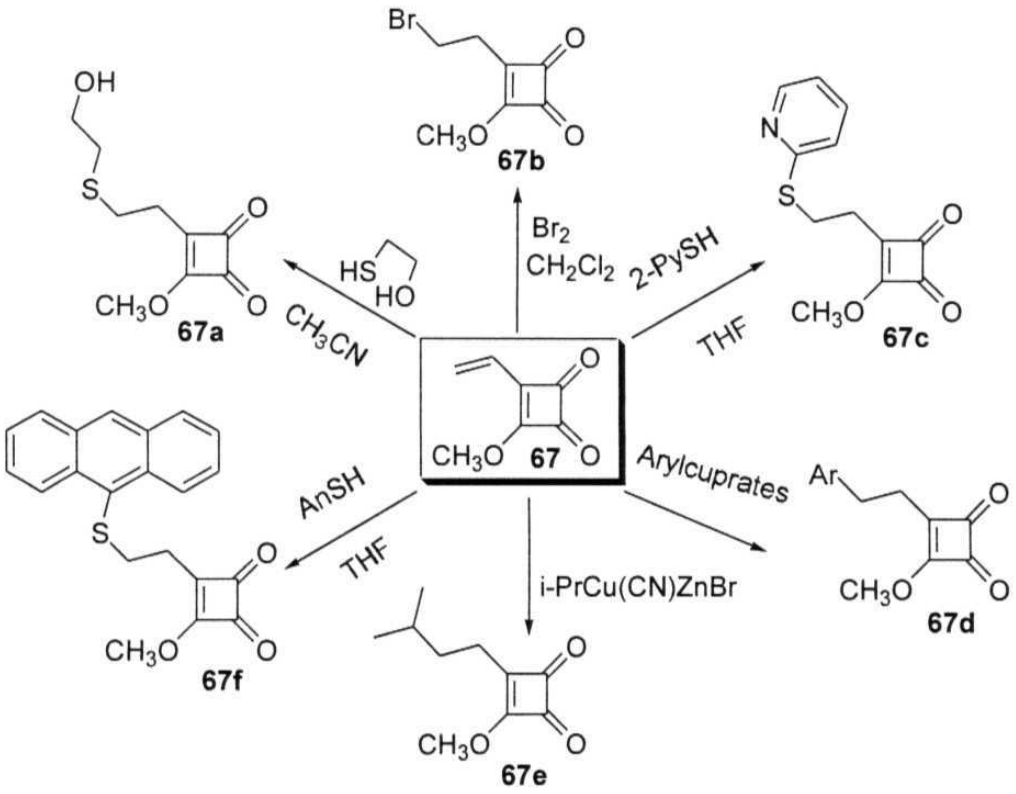
Functionalised cyclobutenediones were obtained by the reaction of squarates with compounds having acidic hydrogen on carbon atom in the presence of sodium alkoxide in alcoholic solution. For example, alkoxycyclobutenediones condense smoothly with diethylmalonoate and 1,3-diketones to afford **63** and **64** respectively.[64] Also, diethylsquarate condenses with 2-methylpyrrole in acetic anhydride to form dipyrrolyl cyclobutenedione **65** (**Scheme 15**).[65]

Scheme 15



3-Ethynyl-4-methoxycyclobutene-1,2-dione **67** was prepared by the addition of vinyllithium to dimethyl squarate followed by quenching of resulting alkoxide with trifluoroacetic anhydride. Compound **67** undergoes facile 1,6-addition of carbon and non carbon nucleophiles to form a variety of substituted cyclobutenediones (**Scheme16**).[66]

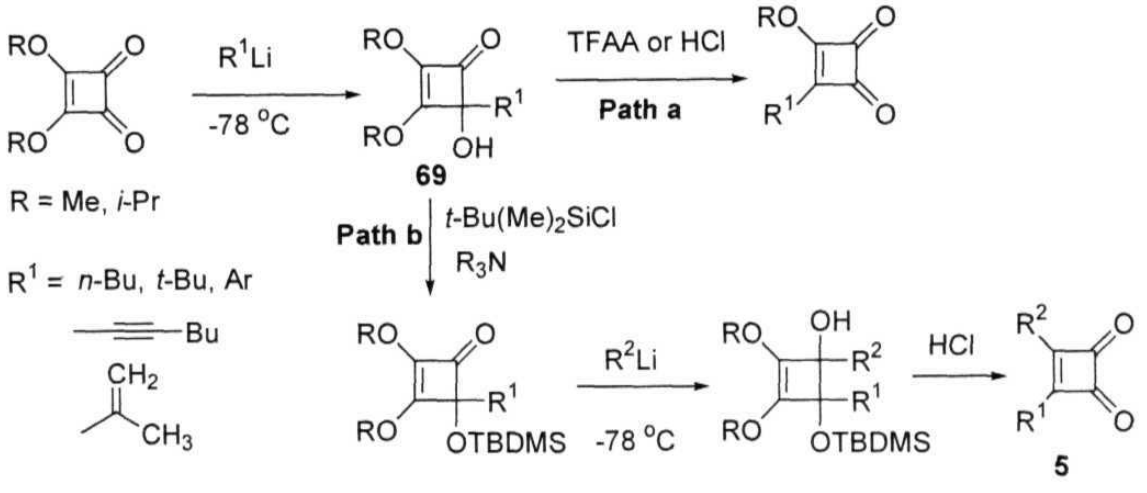
Scheme 16



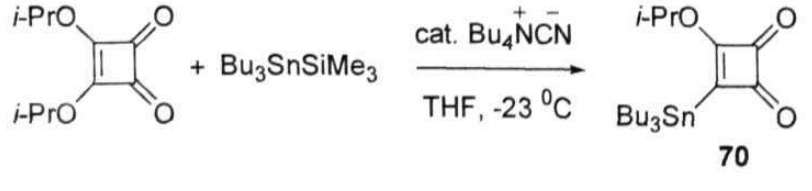
A few simple alkyl derivatives of cyclobutenediones are prepared by the reaction of diethylsquarate **32** with Grignard reagents. These reactions proceed in lower yields.[67] An efficient process was independently developed by *Moore*[68] and *Liebeskind*[69] *via* nucleophilic 1,2 addition of organolithium to dialkoxycyclobutenediones followed by hydrolysis of the resulting hydroxycyclobutenone **69** (**Scheme 17**). Also, differentially

disubstituted cyclobutenediones **5** obtained through step-wise addition of two different alkyllithium reagents (**Scheme 17, Path b**).[69]

Scheme 17



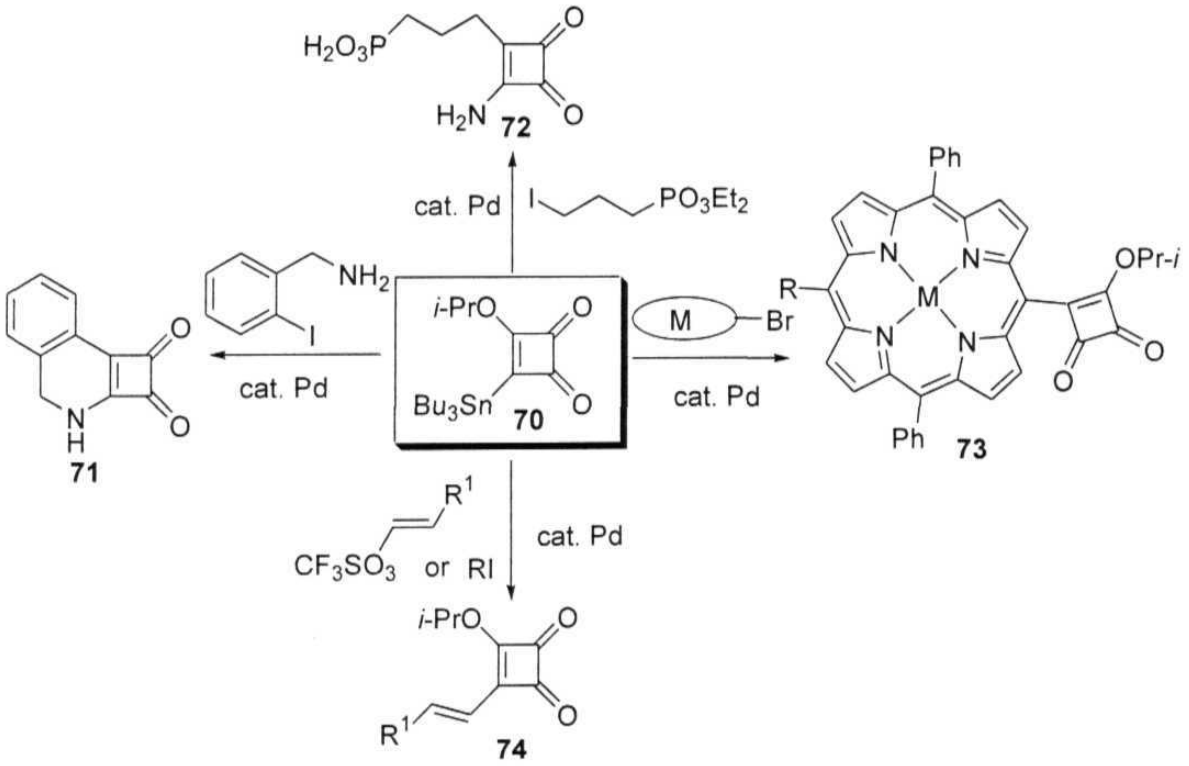
The methods which rely on the introduction of substituents on to cyclobutenedione core as organolithium nucleophiles are restricted to substituents that are compatible with strongly basic and nucleophilic conditions. *Liebeskind et al.*[70] developed a general method involving stable 3-stanylcyclobutenedione **70** which was readily prepared by the treatment of 3,4-diisopropoxy-3-cyclobutene-1,2-dione with n-$Bu_3SnSiMe_3$ in the presence of catalytic amount of cyanide ion (eq. 38).



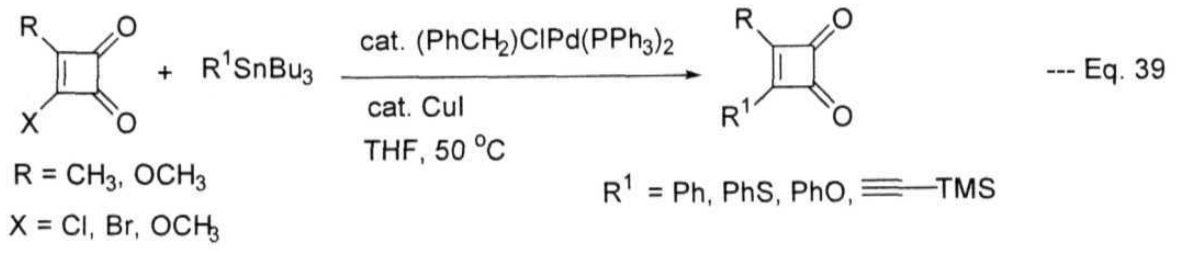
--- Eq. 38

Stanylcyclobutenedione **70** undergoes cross-coupling with organic iodides attached to sp^3, sp^2 and sp-hybridised carbon atoms and with vinyltrifluoromethanesulfonate esters in the presence of $PhCH_2ClPd(PPh_3)_2/CuI$ catalyst to provide a wide variety of substituted cyclobutenediones[71] including porphyrin derivatives **73** (**scheme 18**).[72]

Scheme 18

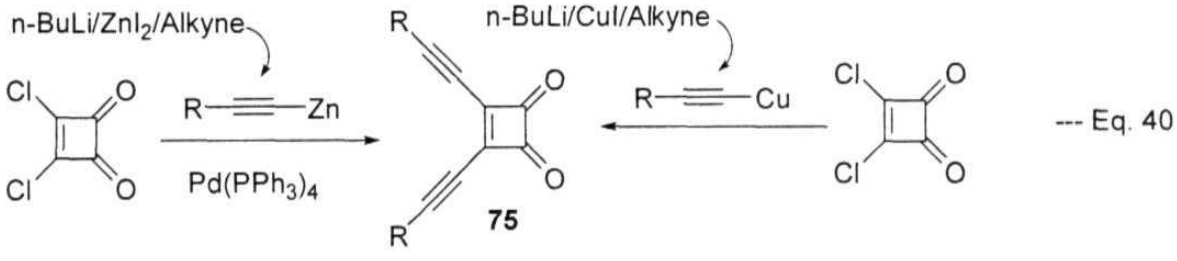


Also, a reverse reaction of above method has been reported (**Scheme 18**) in which cyclobutenediones act as halide partner of Stille cross-coupling, to give a broad array of substituted cyclobutenediones (eq. 39).[73]



--- Eq. 39

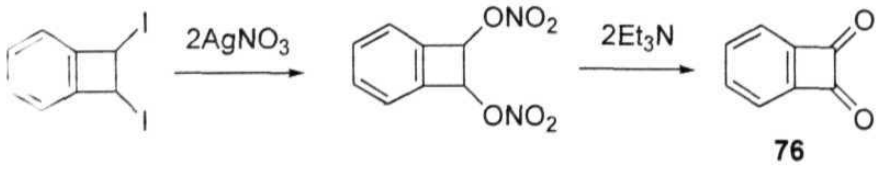
3,4-Dialkynyl-3-cyclobutene-1,2-diones **75** were synthesized by the reaction of 3,4-dichloro-3-cyclobutene-1,2-dione either with tri(*n*-butylstanyl)alkynes in the presence of catalytic amounts of $Pd(PPh_3)_4$ or with the soluble copper (I) acetylides (eq. 40).[74] Analogous method for the preparation of highly functionalized cyclobutenediones was developed by *Knochel et al.*[75] based on zinc-copper reagents.



--- Eq. 40

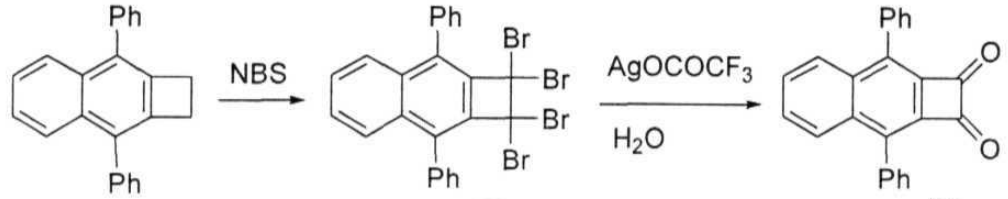
1.1.5 Synthesis of Benzocyclobutenediones

Benzocyclobutenedione **76** was first synthesized by *Cava et al.*[76] in 1957 using simple organic transformations from 1,2-diiodobenzocyclobutene as shown in (eq. 41).



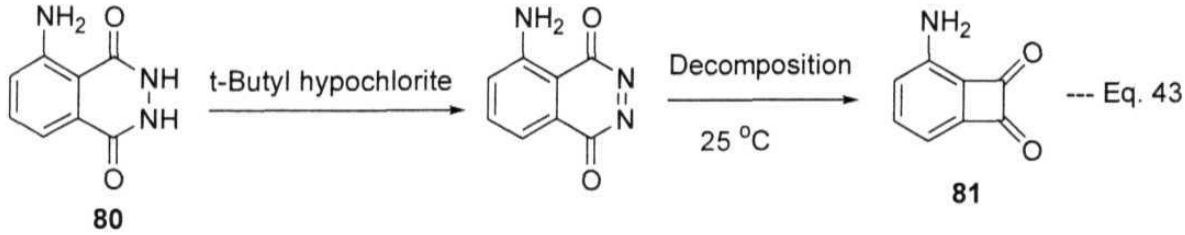
--- Eq. 41

Bromination of 3,8-diphenylnaphtho[b]cyclobutene **77** with NBS generates tetrabromoderivative **78** along with mixture of other bromides. The tetrabromide **78** reacts with silver trifluoroacetate and water to give 3,8-diphenylnaphtho[b]cyclobutene-1,2-dione **79** (eq. 42).[77]



--- Eq. 42

Also, 3-aminobenzocyclobutenedione **81** has been prepared *via* the oxidation of luminol **80** using *t*-butyl hypochlorite (eq. 43).[78]

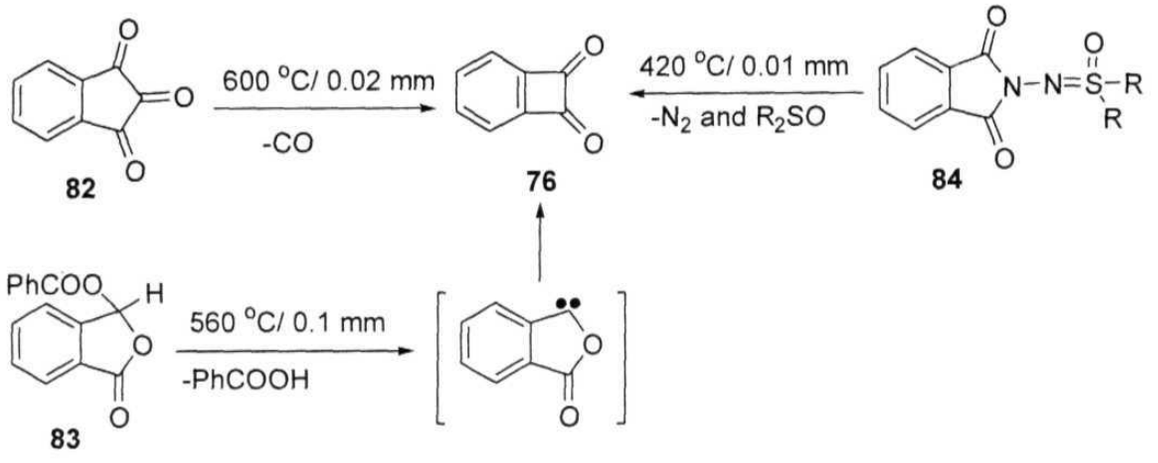


--- Eq. 43

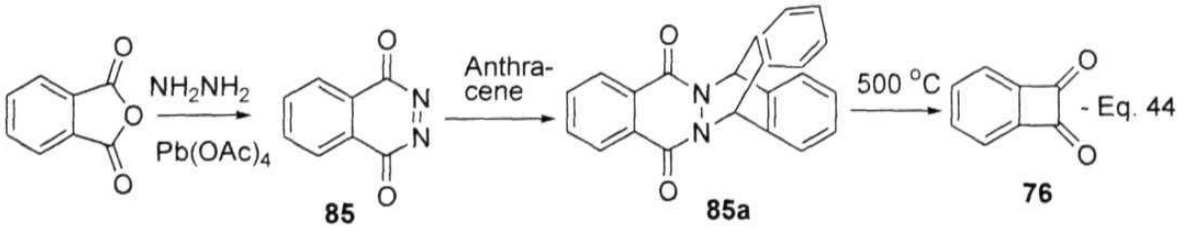
It has been reported that the vapour phase pyrolysis of indanetrione **82**,[79a] and 3-bezyloxyphthalide **83**[79b] give traces of benzocyclobutenedione **76**. Whereas

phthalamidodiphenylsulphoxide **84** gives benzocyclobutenedione in 35-70% yield under similar conditions (**Scheme 19**).[79c]

Scheme 19



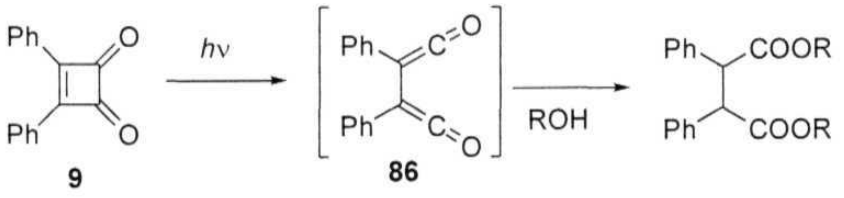
Synthesis of benzocyclobutenediones, on multi-gram scale, was achieved by flash vacuum pyrolysis of the Diels-Alder adducts of phthalazine-1,4-diones **85** with anthracene, cyclopentadiene[80] or indene[80] (eq. 44). Among these, anthracene adduct **85a** gives better yields.[81]



1.2 Synthetic Applications of Cyclobutenediones

1.2.1 Synthesis of Open Chain Compounds.

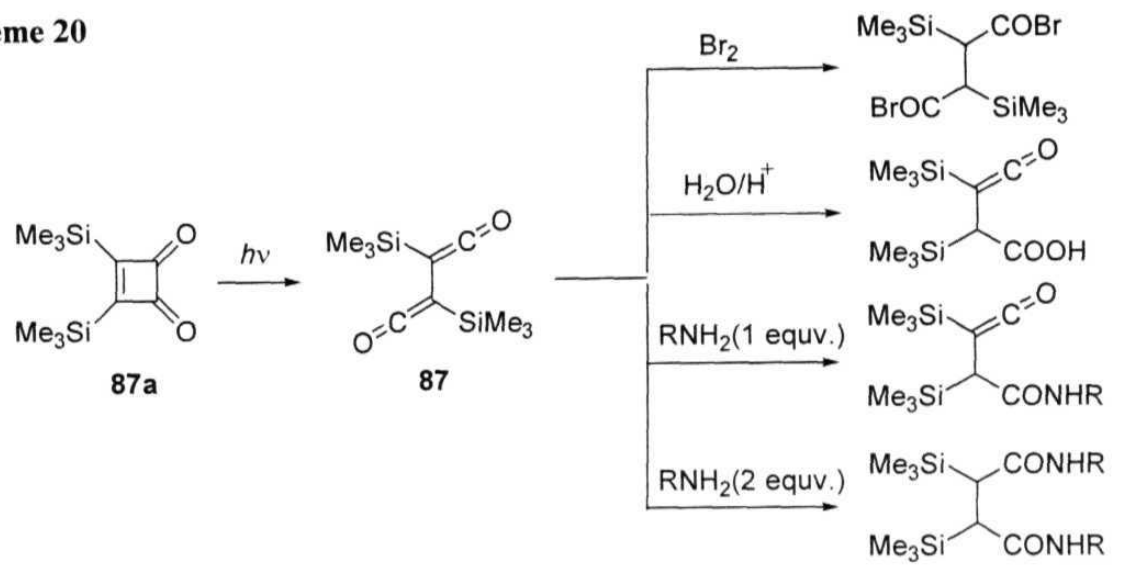
The photochemical ring opening of cyclobutene-1,2-diones (**9**) to 1,2-bisketenes (**86**) was discovered simultaneously by Mallory and Roberts[82] and by Blomquist and LaLancette[25d] in 1961 (eq 45). The 1,2-bisketenes were not directly observed but were inferred as reactive intermediates on the basis of the products formed. Since that time, this technique has been utilized to generate several 1,2-bisketenes, but usually, these species have only been observed at low temperatures, often in matrices because of their facile thermal ring closure to give back **9**.[83]



9 **86** --- Eq. 45

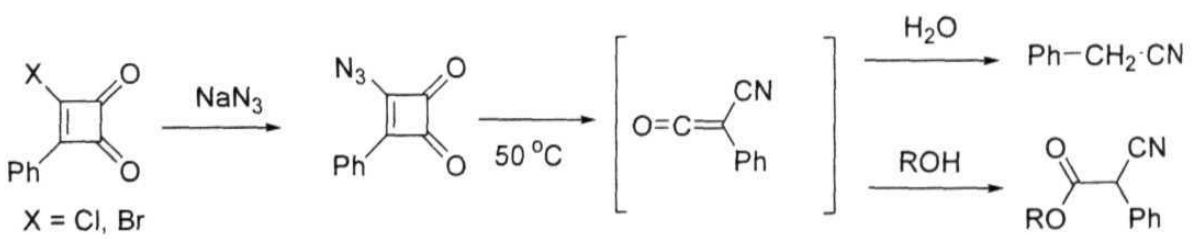
Recently, *Tidwell et al.*[84,85] found that the Me_3Si substituted 1,2-bisketenes **87** are thermodynamically stable compared to the cyclobutenediones **87a**. Hence, it can be isolated at room temperature. This opened the way for extensive studies[85] of the spectroscopic and chemical properties of 1,2-bisketenes (**Scheme 20**), including an X-ray crystallographic structure determination.[85f]

Scheme 20

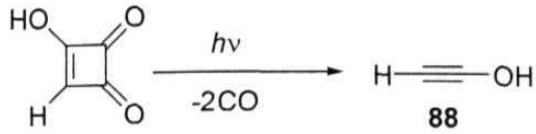


Halocyclobutenediones decomposes to cyanoketenes on sodium azide treatment with simultaneous evolution of N_2 and CO gas.[86] When the reaction is carried out in the presence of either water or alcohol the ring cleaved products such as 2-phenylacetonitrile and alkyl 2-cyano-2-phenylacetate are obtained, respectively (**Scheme 21**).

Scheme 21

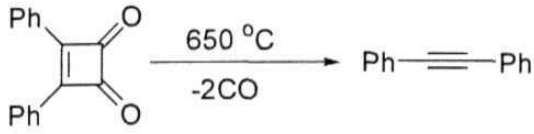


Ethynol **88**, a constituent of planetary atmosphere and interstellar clouds, was first synthesized by photolysis of semisquaric acid (eq. 46).[87] Similarly, pyrolysis of diphenylcyclobutenedione gives diphenylacetylene (eq. 47).[88]



88

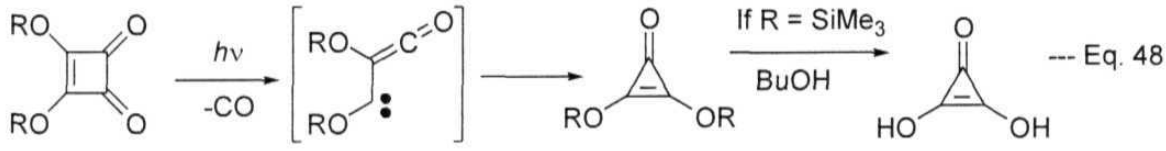
--- Eq. 46



--- Eq. 47

1.2.2 Synthesis of 3-membered Ring Compounds.

It has been reported that irradiation of squaric acid esters yield ring contraction products.[89] For example, deltic acid **89**, dihydoxycyclopropenone, was first synthesized by *West et al.*[90] by photolytic decarbonylation of bis(trimethylsilyloxy)cyclobutenedione **89a** (eq. 48).



89a = R = Et
89b = R = $SiMe_3$

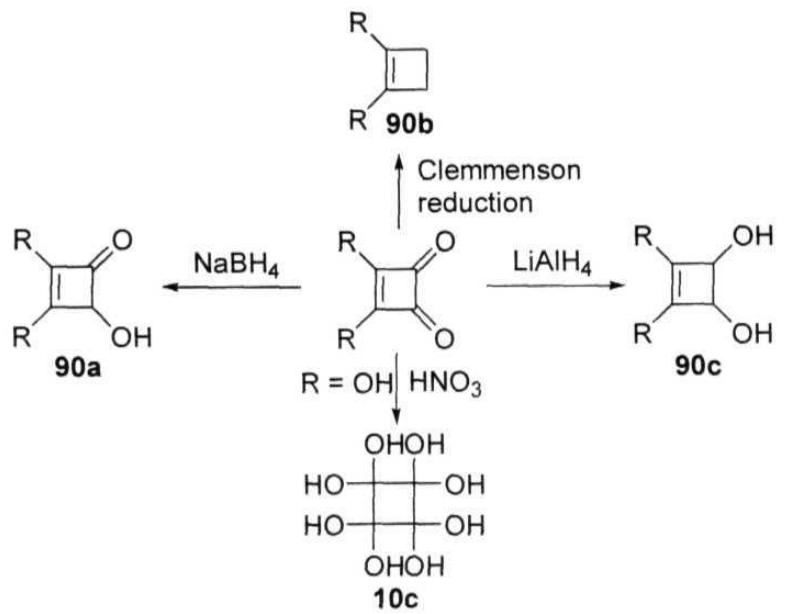
89

--- Eq. 48

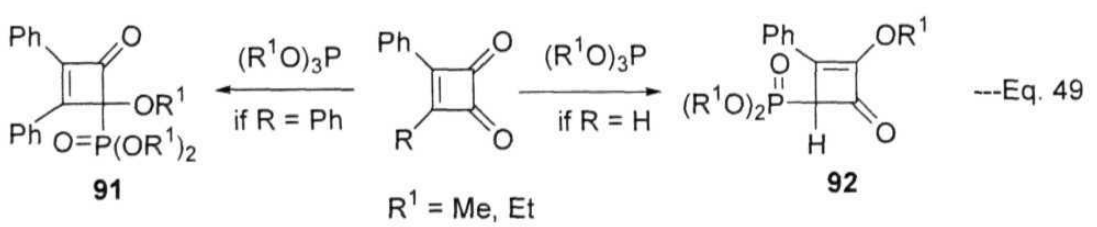
1.2.3 Synthesis of 4-membered Ring Compounds.

Cyclobutenediones are generally resistant to reducing agents and attempted catalytic hydrogenations were unsuccessful. However, under the drastic conditions of the Clemmensen reduction, cyclobutane is obtained.[1b] Whereas lithium aluminum hydride reduces both the carbonyls,[91] sodium borohydride reduces only one (**Scheme 22**).[55] Similarly, oxidation of squaric acid under mild conditions affords **10c**.[92]

Scheme 22



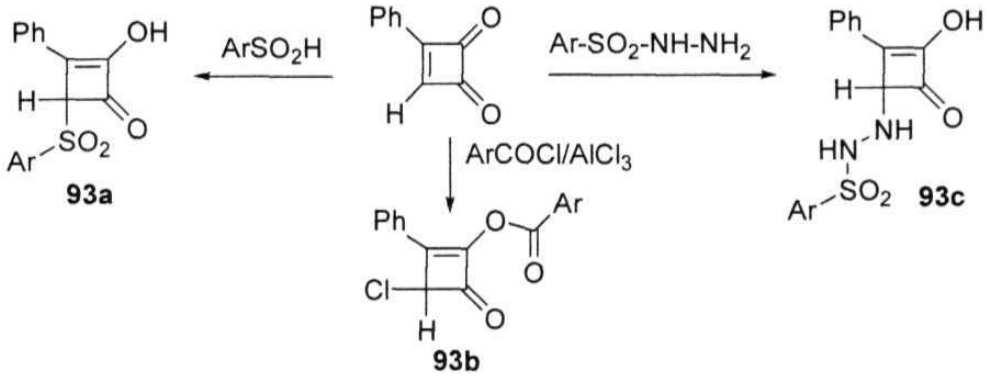
It has been reported that the cyclobutenediones do not condense with phosphite esters in a manner analogous to simple diketones, but form addition products.[93] For example, whereas reaction of diphenylcyclobutenedione with trialkylphosphite gives the 1,2 adduct **91,** phenylcyclobutenedione yields the 1,4 adduct **92** (eq. 49).[93b]



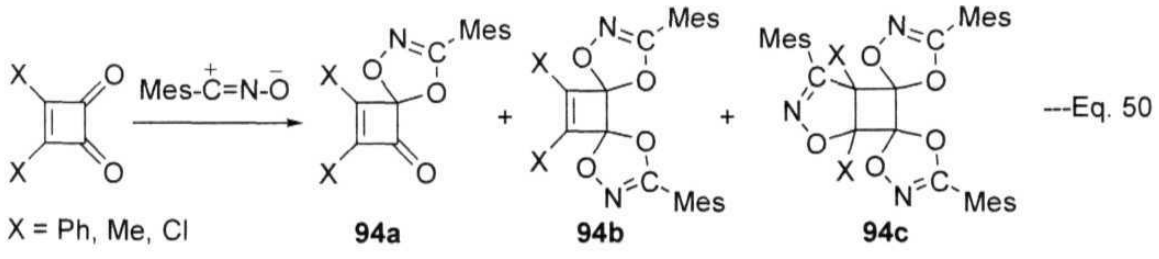
---Eq. 49

Acylation of phenylcyclobutenedione under Friedel Crafts condition provides 1,4 addition product **93**,[94] and the expected electrophilic substitution reaction on cyclobutenedione ring did not proceed. Similarly, 1,4 addition product **93c** was obtained with tosylhydrazines instead of anticipated hydrazones (**Scheme 23**).[95]

Scheme 23



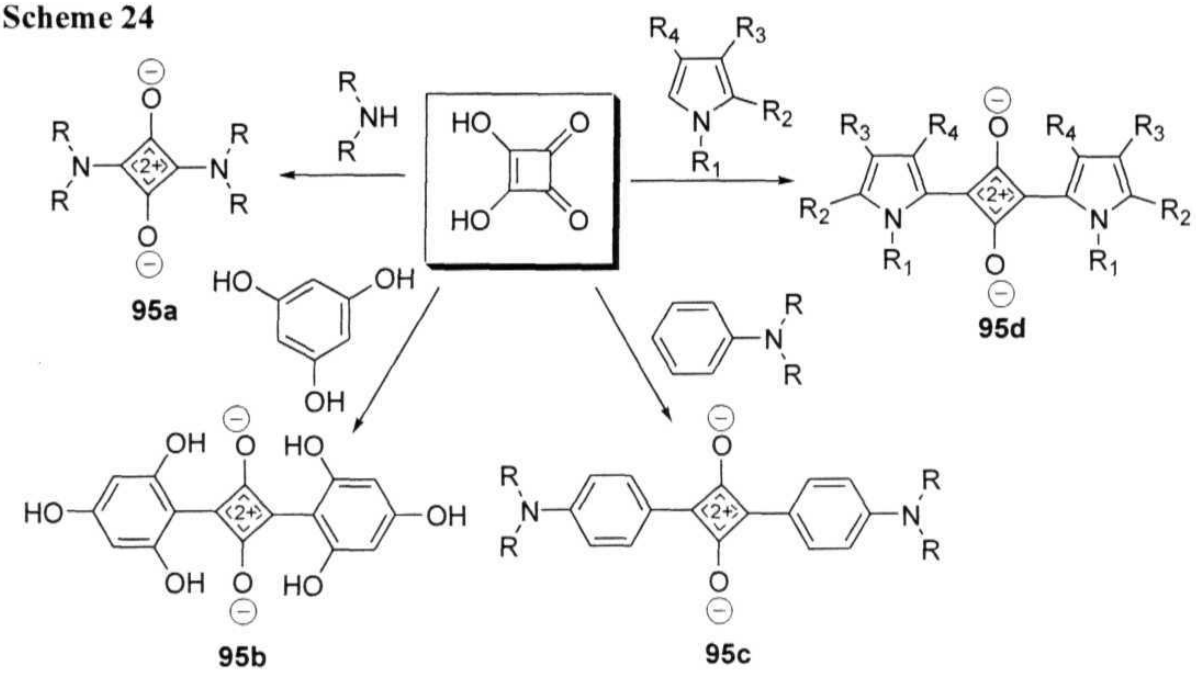
Cyclobutenediones have been reported to undergo 1,3 dipolar cycloadditions with mesitonirile oxide to give mono **94a**, bis **94b** and tri **94c** adducts (eq. 50).[96] It is evident from these reaction products that the 1,3-dipole attacks the carbonyl rather than the ethylene double bond, despite the usual low reactivity of C=O towards 1,3-dipoles.



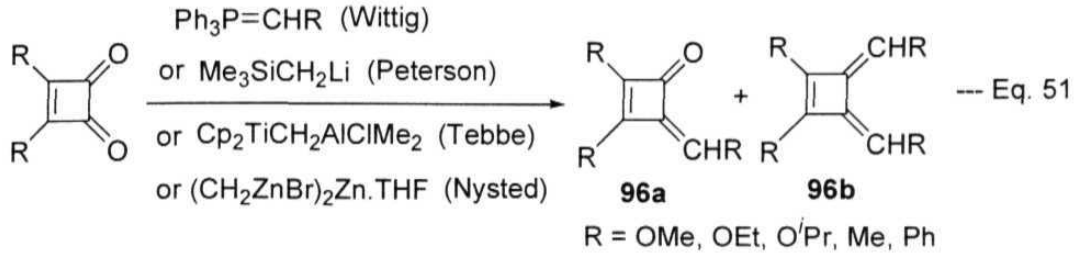
It has been reported that a variety of secondary amines readily react with squaric acid to give 1,3-amine derivatives, a new class of intramolecular salts **95a-c**.[97] Also, certain phenols, pyrroles and arylamines were employed in this reaction (**Scheme 24**). The condensation products of squaric and *N,N*-dialkylanilines are known as squarines **95c** and

they find applications in fluorescent dyes,[98] photoreceptors, [99] organic solar cells[100]and NLO materials.

Scheme 24

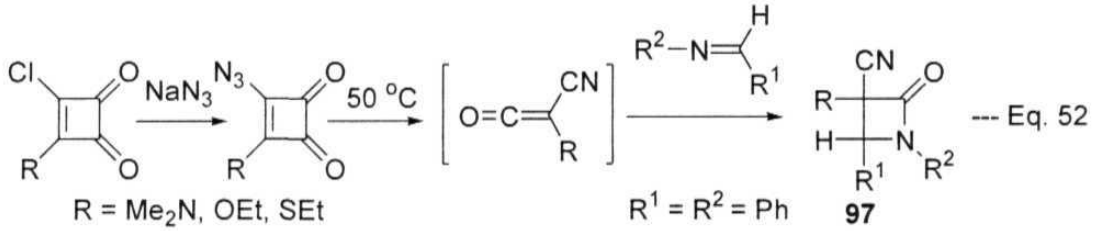


Also, it has been reported that methylenecyclobutenones can be prepared by the reaction of Wittig, Tebbe, Petasis, Peterson or Nysted reagents with cyclobutenediones (eq. 51).[101] Reaction of dione with one equivalent of Wittig reagent is highly selective giving only monoalkylidenation product, whereas with other olefination reagents bis(alkylidenation) product also formed in lower yields. The use of two equiv. of Cp_2TiMe gives bis(methyledene)cyclobutene exclusively.



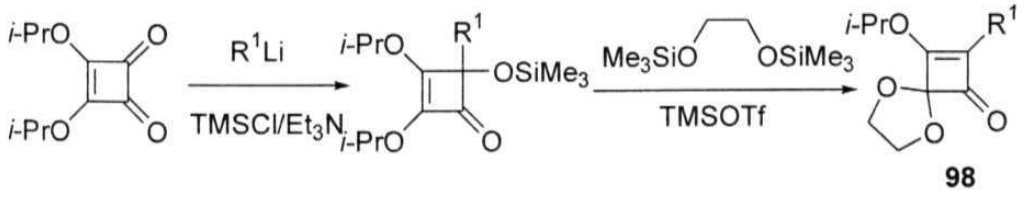
--- Eq. 51

The reaction of sodium azide with chlorosubstituted cyclobutenediones generates cyanoketenes which are trapped by various aldimines to give 3-cyano β-lactams **97** in good yield (eq. 52).[102]



--- Eq. 52

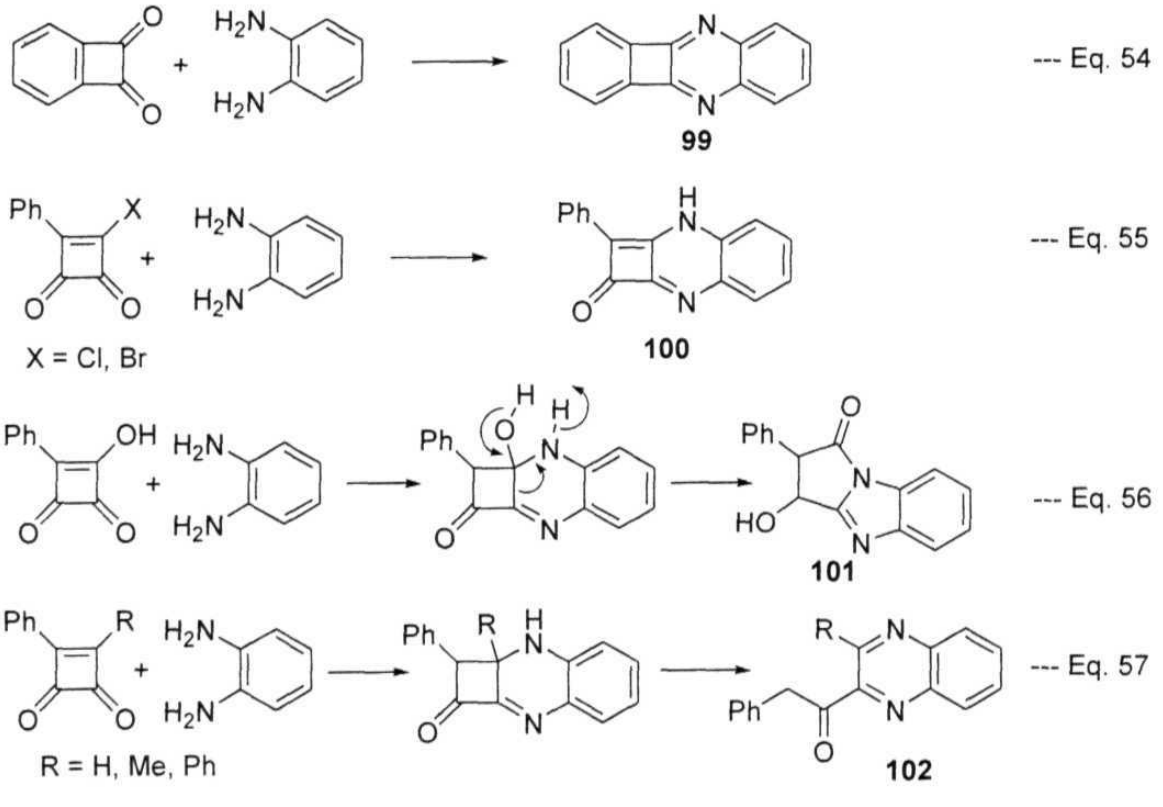
Regioselctive monoacetalisation of cylobutenediones could be readily achieved (eq. 53).[103] This sequence of reactions provides access to a wide range of isomeric cyclobutenedione monoacetals. Recently, monoehtylenedithioacetals **98** have been prepared.[104] These compounds were shown to be valuable precursors for the synthesis of multifunctional molecules.



--- Eq. 53

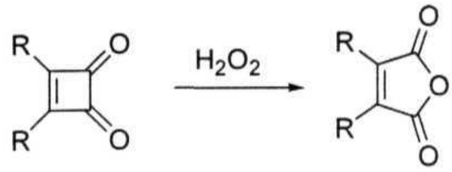
o-Phenylenediamine shows interesting reactivities with different cyclobutenediones, and substituents on dione have a large influence on the course of reaction.[105] For example,

benzocyclobutenedione[76] and halocyclobutenediones[1b,105a] give cyclobuta[b]quinoxalines **99** and **100**, a condensation product (eq. 54, 55).[105a-105c] Hydroxyphenylcyclobutene-dione[105b] **1d**, on the other hand, undergoes a novel ring expansion-oxidation reactions to give pyrrolobenzimidazole **101** (eq. 56). Whereas other disubstituted cyclobutenediones[105c] show entirely different reactivity and give the corresponding 2-phenylacetylquinoxalines **102**, a ring opened product (eq. 57).



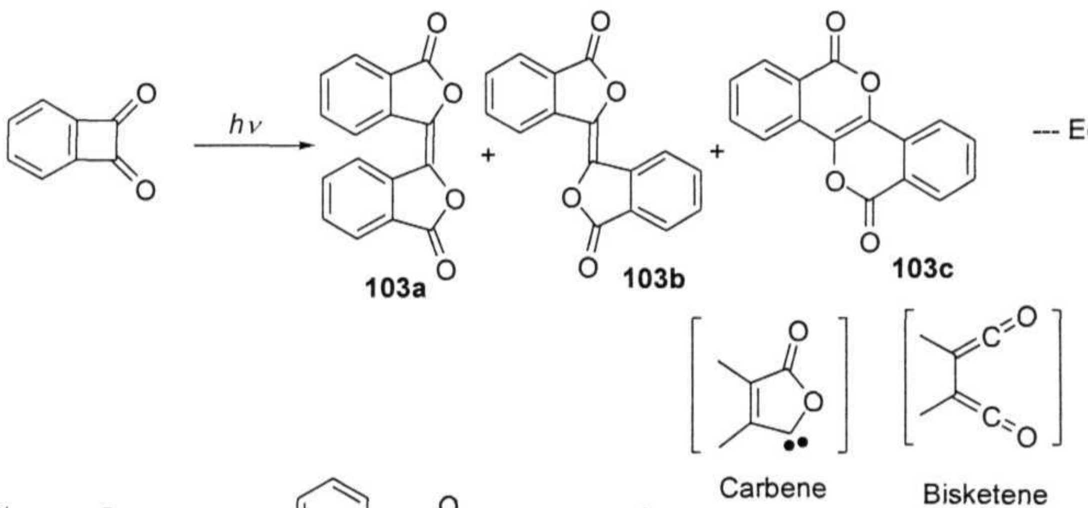
1.2.4 Synthesis of 5-membered Ring Compounds

It has been reported that cyclobutenediones undergo Bayer-Villiger type oxidaton with hydrogen peroxide to give maleic anhydride derivatives (eq. 58).[48a]

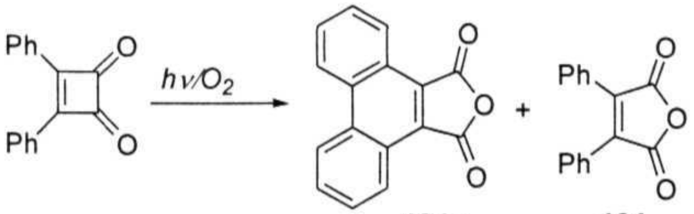


103 --- Eq. 58

Cyclobutenediones undergo facile ring expansion reactions to yield dimers or monomeric anhydrides under the influence of light (eqs. 59 and 60).[106] The formation of these five membered ring compounds is believed to occur either through the carbene or the bisketene intermediates.



103a 103b 103c --- Eq. 59

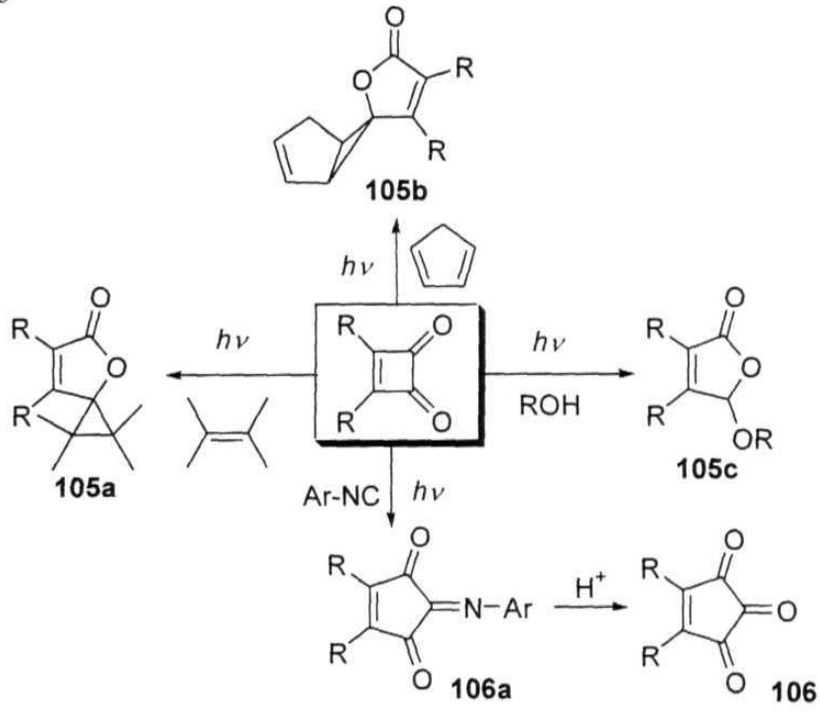


104a 104 --- Eq. 60

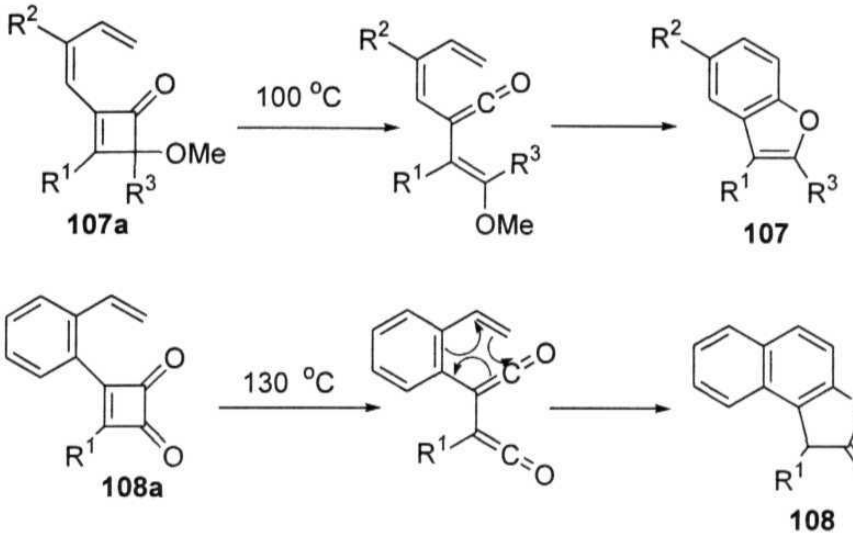
Photolysis of diones in the presence of some ketene trapping agents produce 1:1 adducts (**Scheme 25**). For example, olefins and dienes give 5-spirocyclopropyl $\Delta^{\alpha,\beta}$–

butenolides **105a** and **105b**.[107] While the irradiation of diphenylcyclobutenedione in the presence of isonitriles gives ring expanded product **106a**, which can be converted to cylopentenetrione **106** by hydrolysis.[108]

Scheme 25



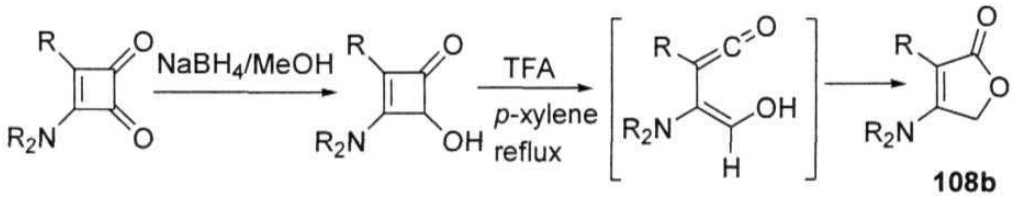
Thermolysis of 2-dienylcyclobutenones **107a** as well as 3-(2-ethynylphenyl)cyclobutenediones **108a** undergo novel intramolecular cyclisation of bisketenes to furnish annulated furans **107** and naphthofuranones **108** respectively (eqs. 61 and 62).[109]



107a 107 --- Eq. 61

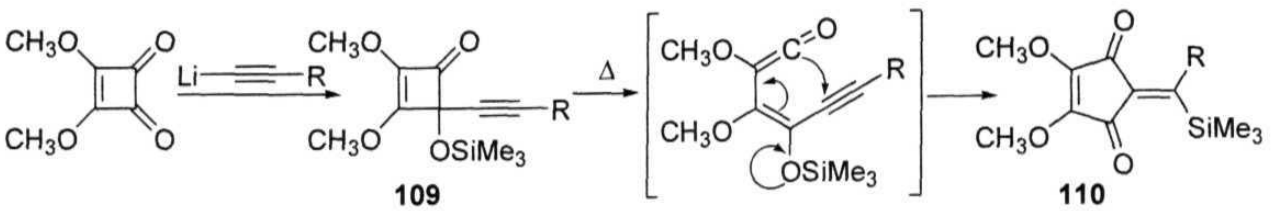
108a 108 --- Eq. 62

Similarly, 4-aminofuran-2(5H)-ones **108b** have been prepared by thermal ring expansion (eq. 63).[55]



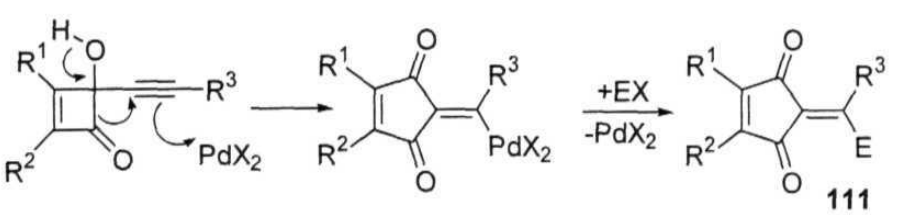
108b --- Eq. 63

Moore et al.[110,111] reported that thermolysis of 4-alkynyl-4-hydroxy or trimethylsilyloxy cyclobutenones **109** provides 2-alkylidene-4-cyclopentene-1,3-diones **110** (eq. 64). Presumably, these transformations proceed *via* electrocyclic ring opening of the cyclobutenone to an unsaturated vinylketene intermediate.

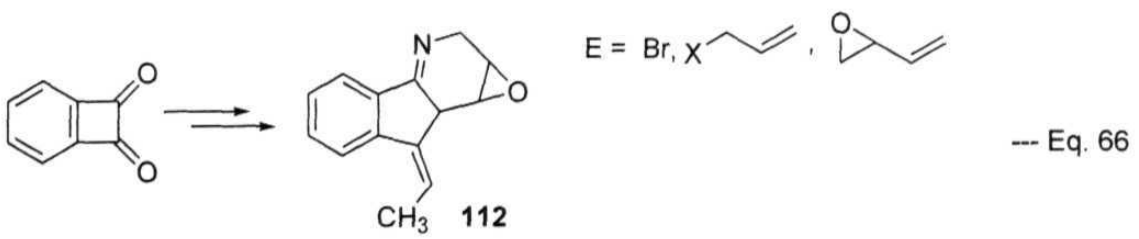


--- Eq. 64

Later, *Liebeskind et al.*[112] demonstrated that 4-alkynyl-4-hydroxycyclobutenones and their acetals would participate in an efficient tandem ring expansion-functionalisation sequences catalyzed by palladium(II) in the presence of suitable electrophiles such as H^+, NBS allyl bromide to provide 2-alkylidene-4-cyclopentene-1,3-diones **112** with high stereoselectivity at the exocyclic double bond (eq. 65).[36] Benzoabikoviromycin **113**, a potential antiviral agent has been synthesized following a similar strategy (eq. 66).[113]

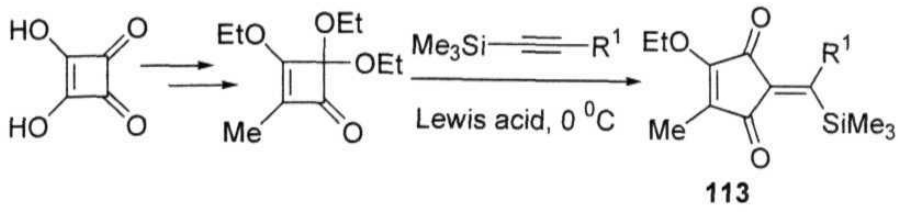


--- Eq. 65



--- Eq. 66

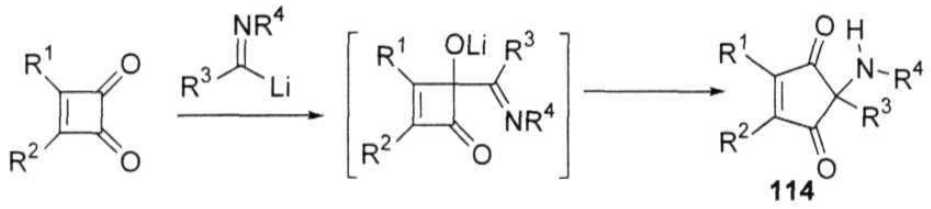
Also, cyclobutenedione monoacetals react with silylacetylenes in the presence of Lewis acid catalyst to form alkylidenecyclopentenediones **113** *via* cationic 1,2-silyl migration (eq. 67).[114]



113

--- Eq. 67

It was found that 2-(alkylamino)-4-cyclopentene-1,3-diones **109** could be prepared in good yields by the nucleophilic addition of imidoyl lithiates to cyclobutenediones (eq. 68).[115]

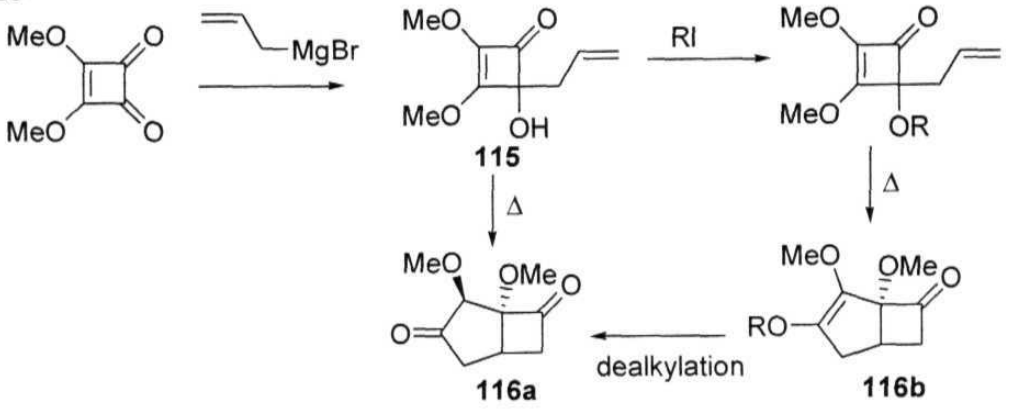


114

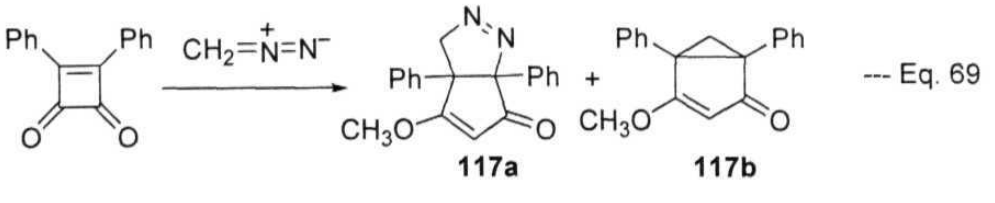
--- Eq. 68

It has been reported that 4-hydroxy-4-allyl-cyclobutenones **115**, prepared by the addition of allyl Grignard to dimethyl squarate, give functionalised bicyclic[3.2.0]heptane-3,7-diones **116a** or bicyclic[3.2.0]heptenones **116b** in good yields.[116] This transformation is envisaged to involve an electrocyclic ring opening of cyclobutenone and subsequent intramolecular [2+2] cycloaddition of the resulting vinylketene (**Scheme 26**).

Scheme 26



The action of excess diazomethane on diphenylcyclobutenedione leads to cyclopentapyrazole **117a** and bicyclo[3.1.0]hexanone **117b** in approximately 1:1 ratio (eq. 69).[117] The reaction is thought to proceed through 1,3-dipolar addition of diazomethane to the double bond of the cyclobutenedione followed by CH_2 insertion between carbonyl groups, and then enolization followed by methylation.

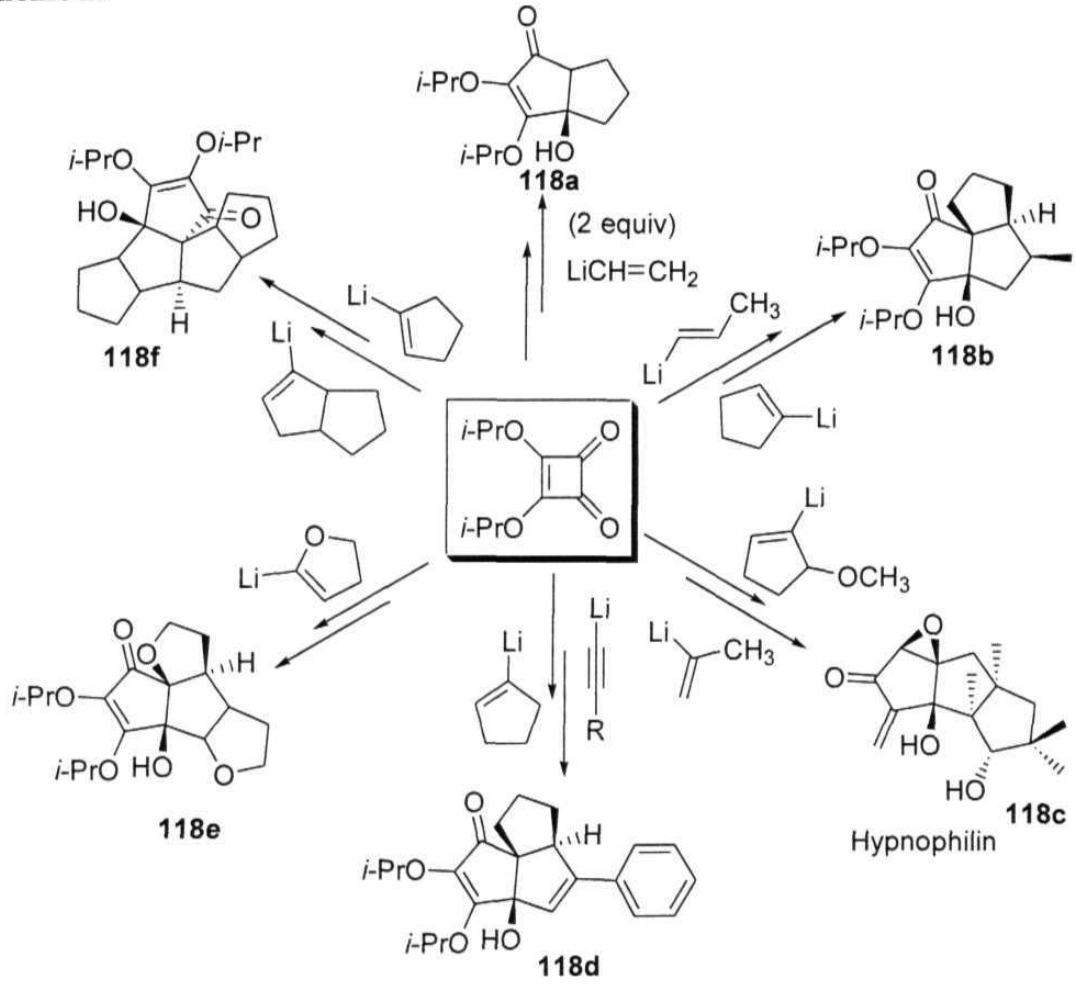


--- Eq. 69

Paquette et al.[118-127] discovered that 2-fold addition of alkenyl anions (same or different) to a squarate ester initiates a cascade of chemical events that ultimately leads to the formation of highly functionalized polyquinanes (**Scheme 27**). Various alkenyllithium and alkynyllithium reagents were employed to synthesize a wide range of quinanones

including heteroatom analog **118e**. Recently, this chemistry was applied to synthesize natural products like hypnophilin **118c**, a linearly fused triquinane.

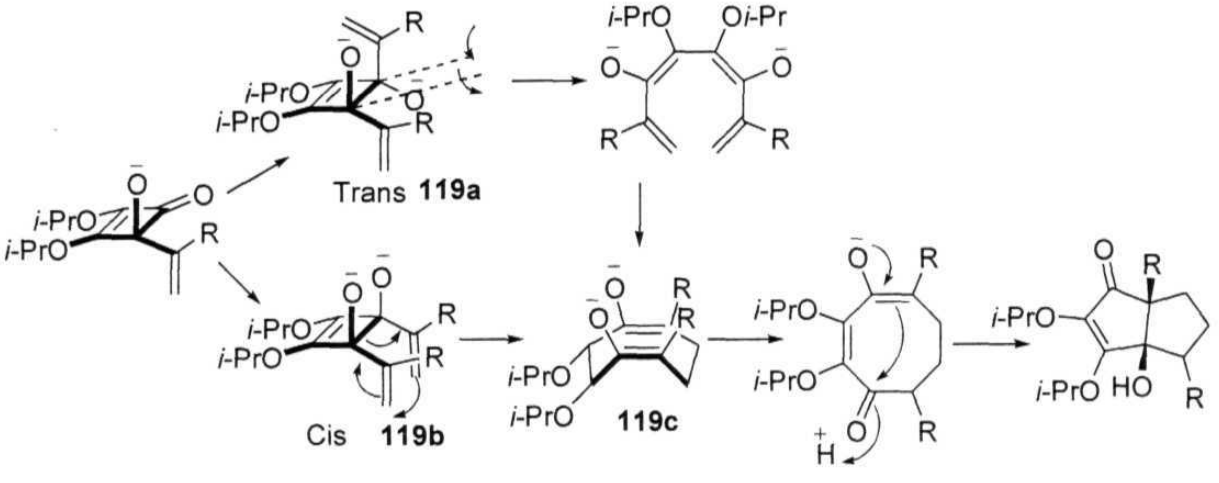
Scheme 27



Treatment of squarate ester with 2 equiv. of the same alkenyllithium reagent or 1 equiv. each of two different alkenyllithium reagents generates trans adducts, which undergoes charge-driven bond reorganization *via* an electrocyclic reaction. The stereochemical outcome of this reaction is not controlled by the diastereoselection

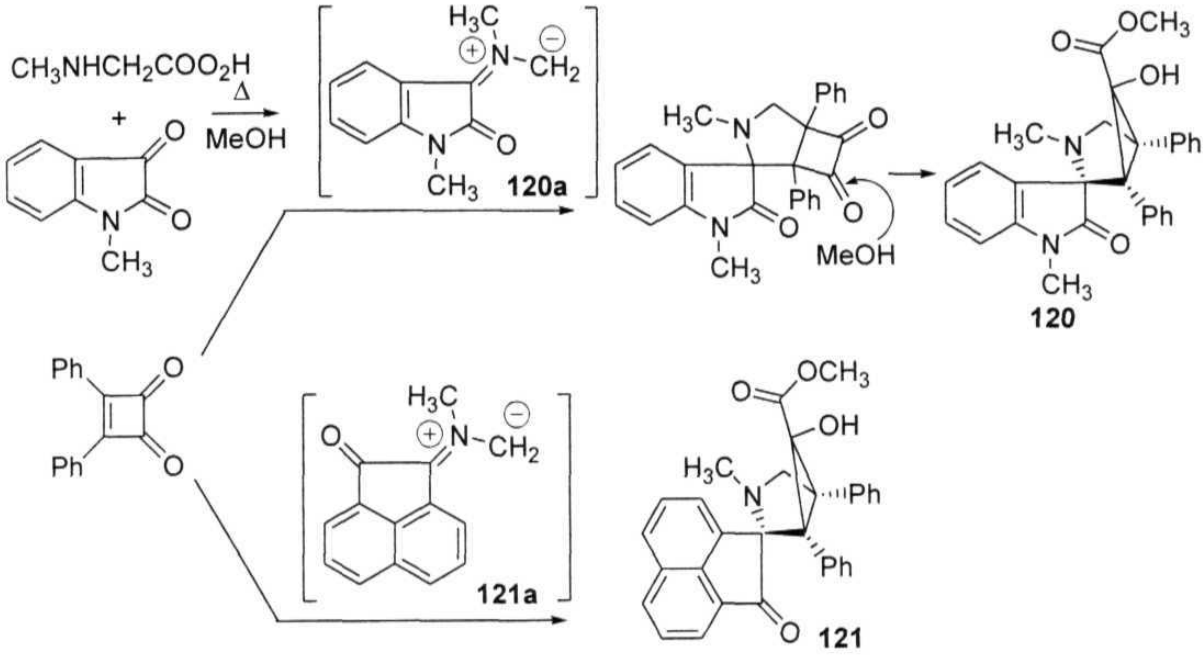
associated with the initial addition step because of helical equilibration at the tetraene stage. While generation of cis adduct triggers a sigmatropic rearrangement sequence dominated by a dianionic oxy-Cope rearrangement and transmission of stereochemical information of the first addition step occurs with high reliability (**Scheme 28**).[120,125]

Scheme 28



Recently, *Nair et al.*[128] observed the ring contraction of cyclobutenedione upon dipolar cycloaddition reactions. The reaction of 3,4-diphenylcyclobutene1,2-dione azomethine ylides **120** and **121**, generated from isatins or acetonaphthenequinone, yields novel spiro[oxindole-3,2'-pyrrolidine] derivatives (**Scheme 29**).

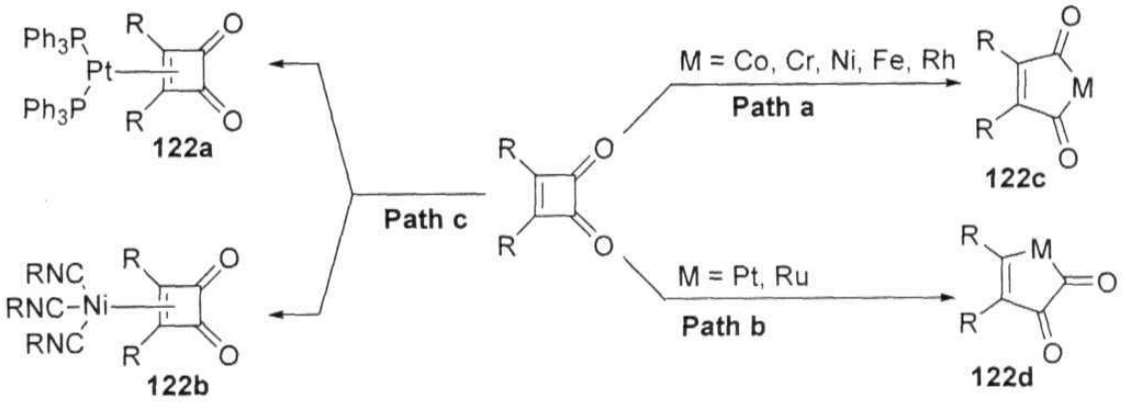
Scheme 29



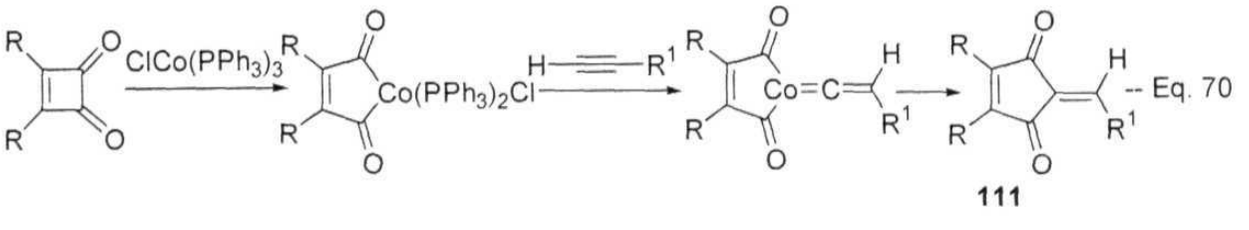
It has been reported that cyclobutenediones react with low-valent transition metal phosphine or carbonyl complexes to form stable metallocyclic complexes *via* C-C bond cleavage. The C-C single bond between a carbonyl and the α-carbon of cyclobutenedione is relatively weaker than other C-C single bonds. Moreover, carbonyl group kinetically facilitates the insertion of a transition metal into the α-C-C bond.[129] Activation of C-C bonds in cyclobutenediones by transition-metal complexes follows the two pathways illustrated in **Scheme 30**. Most transition-metal complexes, including those of rhodium, cobalt, iron, and nickel gave (maleoyl)metal complexes as a thermodynamic product resulting from insertion of the metal between two carbonyl groups in cyclobutenediones (**Path a**),[130] while treatment of cyclobutenediones with platinum or ruthenium[131]

complexes gave unsymmetrical cleavage of the four membered ring to give a kinetic product (**Path b**). Some of the platinum and nickel complexes also form stable olefin complexes (**Path c**).[132]

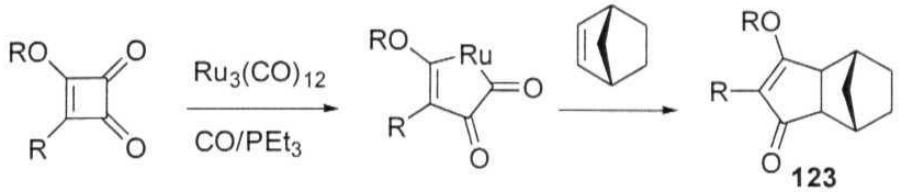
Scheme 30



Maleoyl metal complexes formed *via* **path a** can be selectively converted either to quinones or 2-alkylidene-4-cyclopentene-1,3-diones **111** using alkynes under appropriate reaction conditions (eq. 70).[133]



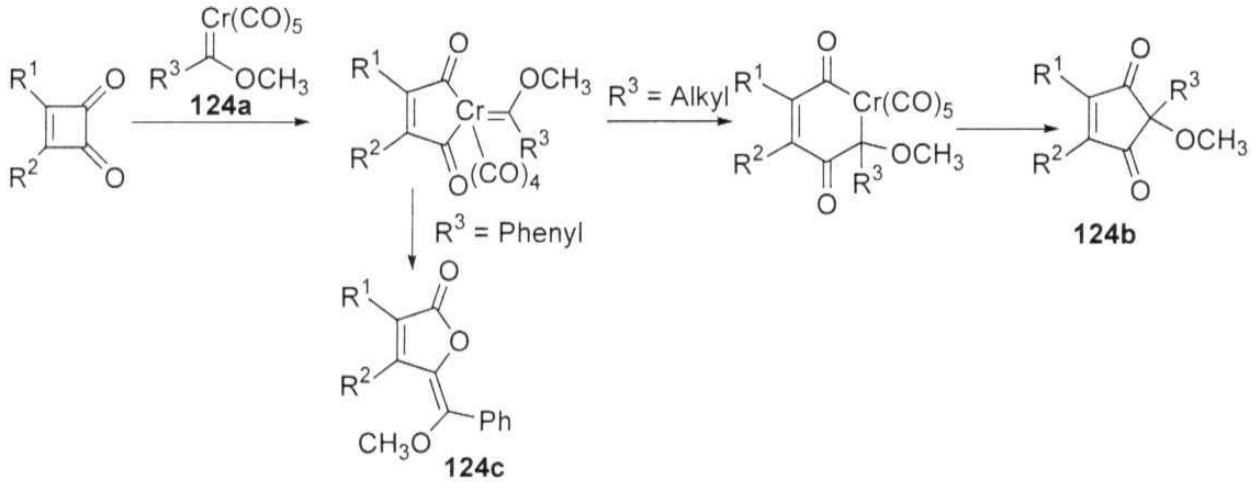
Very recently, $Ru_3(CO)_{12}$ catalysed unusual coupling of cyclobutenediones with alkenes was discovered for the preparation of cyclopentenone **123** with high stereoselectivity (*exo* 100%) (eq. 71).[134] The formation of cyclopentenones is believed to proceed *via* C-C bond cleavage (**Path b**).



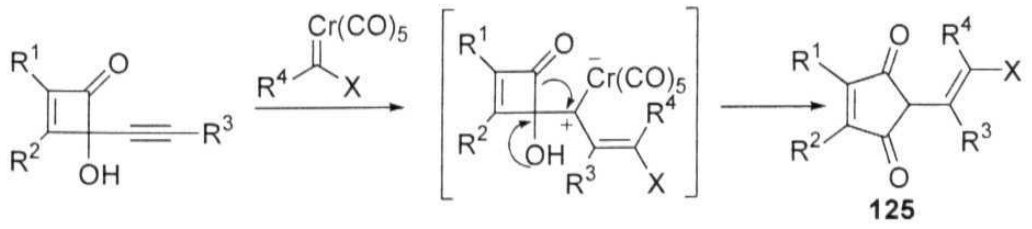
--- Eq. 71

A novel C-C bond insertion reaction of Fischer carbenes **124a** with cyclobutenediones to produce 2-alkoxy-4-cyclopentene-1,3-diones **124b** as well as **124c** has been discovered.[135] The proposed mechanism involves oxidative addition of the acyl-acyl C-C bond, followed by carbene insertion and reductive elimination (**Scheme 31**).

Scheme 31



Chromium carbene complexes are also shown to react with 1-alkynylcyclobutenols to generate 2-alkenyl-4-cyclopentene-1,3-diones **125** (eq. 72).[136]

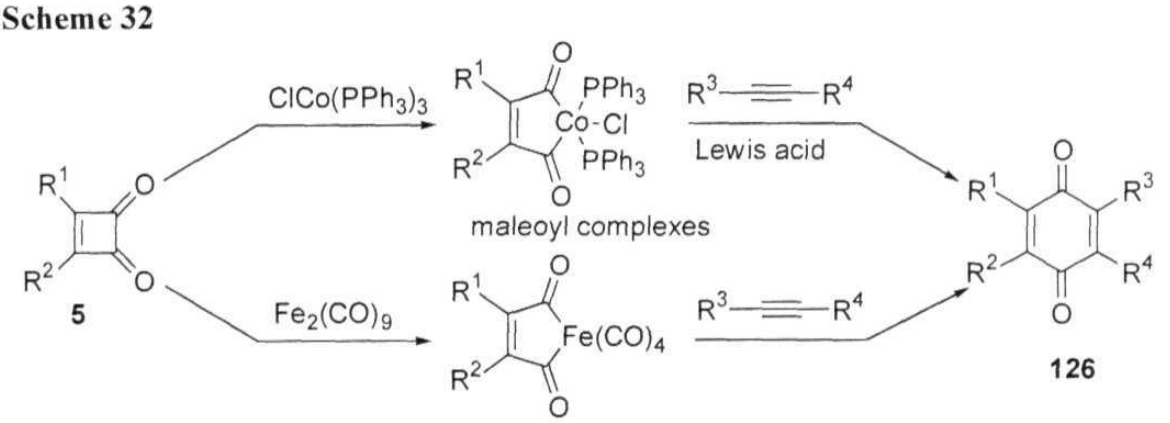


--- Eq. 72

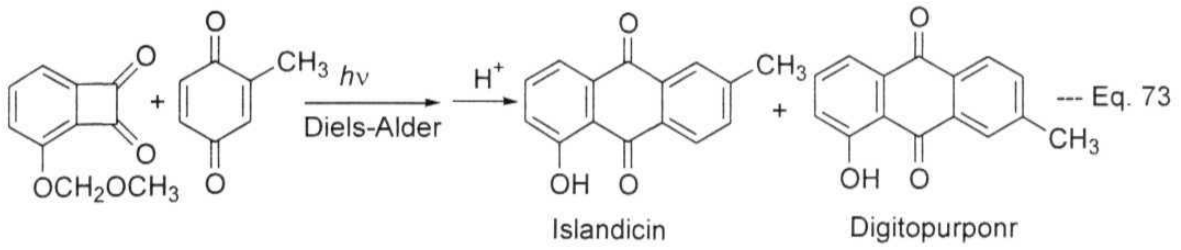
1.2.5 Synthesis of 6-membered Ring Compounds

Quinone moiety is an important functionality present in many different classes of biologically active molecules.[137] Efficient synthesis of various quinones starting from cyclobutenediones have been developed. Cyclobutenediones undergo oxidative addition of the acyl-acyl C-C bond with low valent metal reagents to form maleoyl complexes, which reacts with alkynes by an insertion-elimination sequence to produce quinones (**Scheme 32**). Cobalt maleoyl complexes are superior to iron complexes and they generate quinones with a variety of alkynes starting from electron rich to electron deficient and to sterically demanding alkynes.[138]

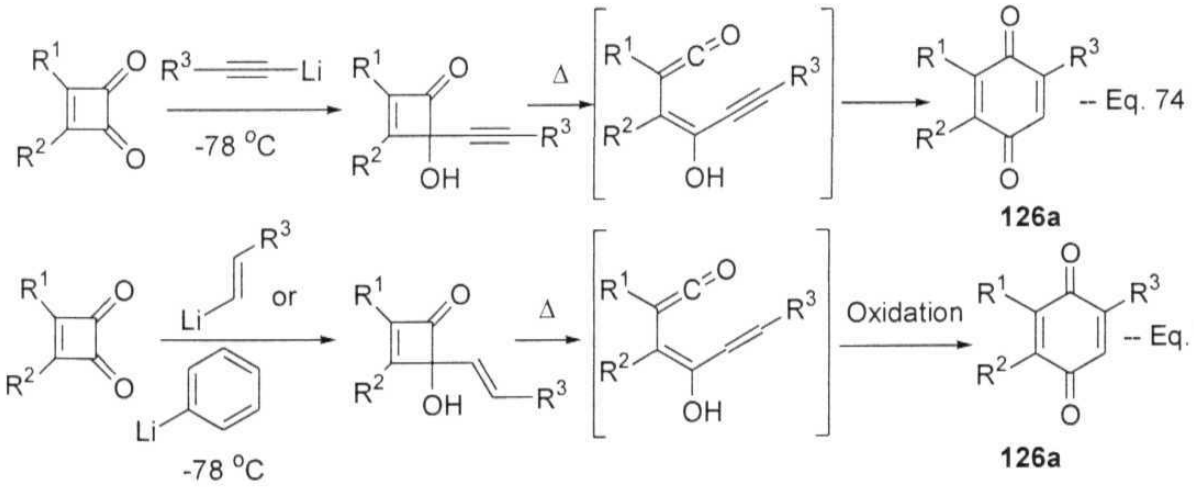
Scheme 32



Bisketenes formed in photolysis of cyclobutenediones undergo *in situ* Diels-Alder reactions with maleic anhydride, benzoquinone or naphthoquinone. The use of 2-methoxybenzoquinone and 3-alkoxybenzocyclobutenediones permits a straightforward total synthesis of the natural products, islandicin and digitopurpone (eq. 73).[139]

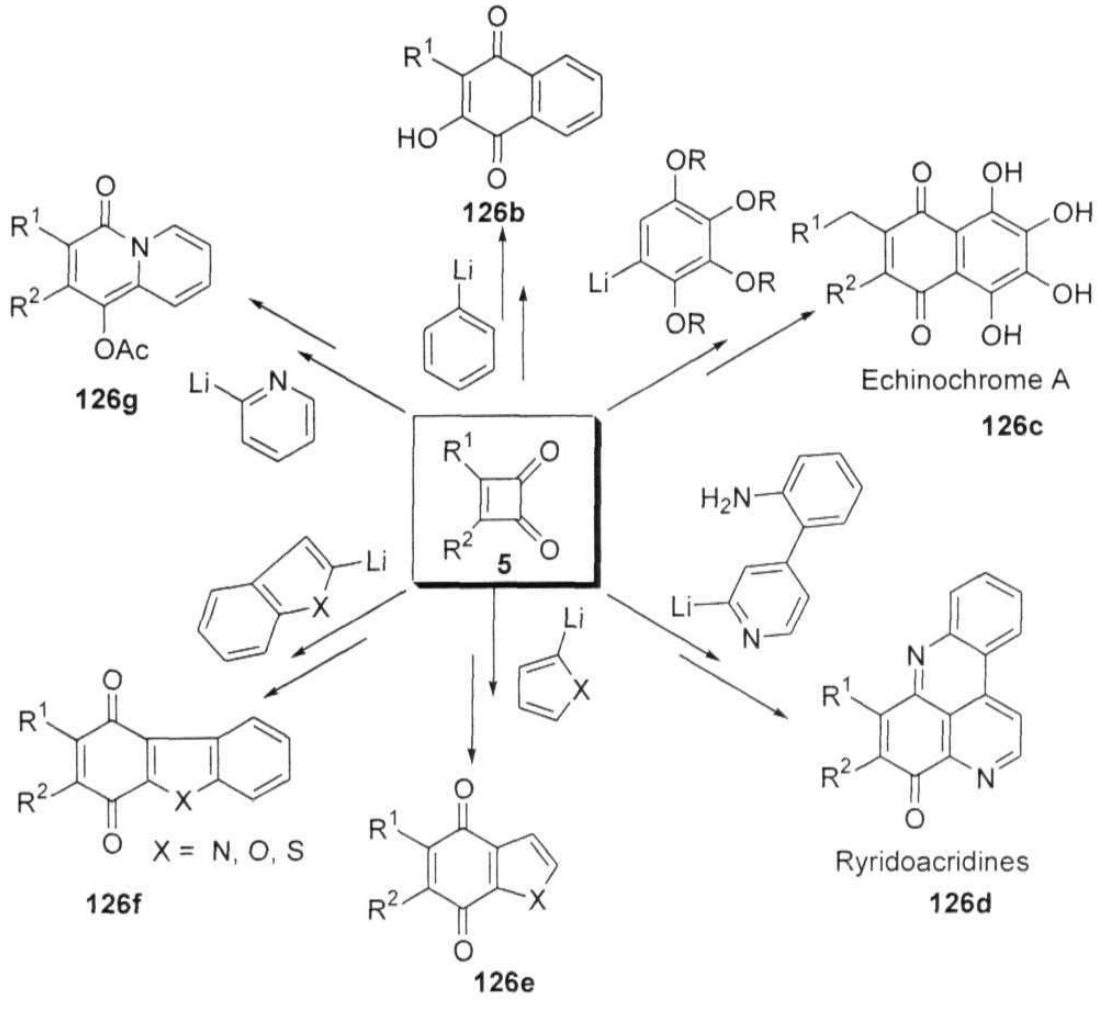


Powerful methodologies have been developed for the synthesis of quinones *via* electrocyclic ring opening of cyclobutenones which may be accessed by addition of lithium nucleophiles to cyclobutenediones. Thermolysis of 4-alkynyl cyclobutenones directly give substituted quinones *via* unsaturated ketenes (eq. 74) while 4-aryl or 4-alkenyl cyclobutenones give quinones after oxidation (eq. 75).



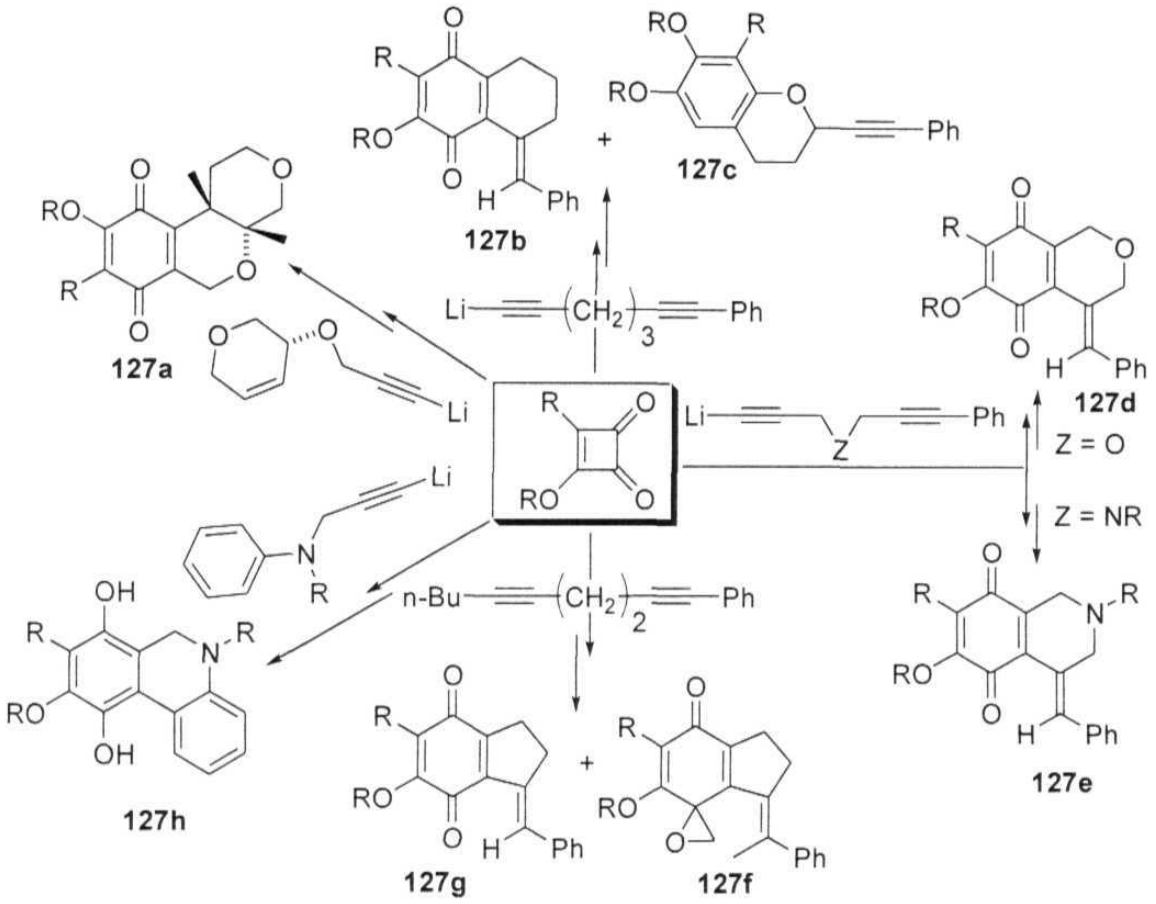
This chemistry has been extended to prepare a wide range of highly substituted quinones **126b-g** (**Scheme 33**).[140-143]

Scheme 33

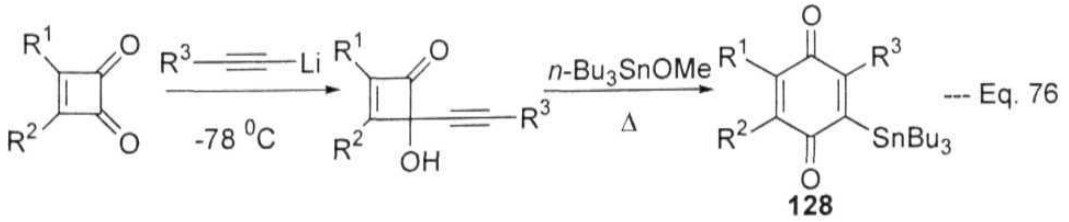


Also, it was observed that if the nucleophile is a diyne or enyne, further cyclization reactions results in formation of a wide range of highly functionalized molecules such as pyranoquinones **127a**, **127d**, piperidinoquinones **127e**, phenanthridinediols **127h**, annelated quinones, spiro epoxycyclohexadienones (**Scheme 34**).[144]

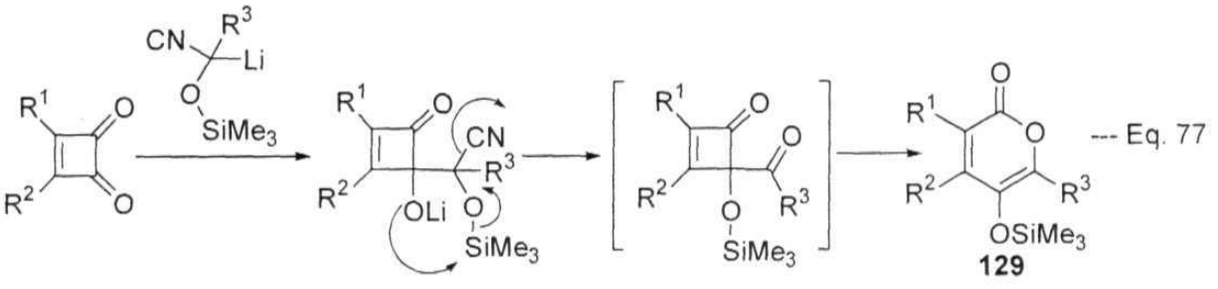
Scheme 34



Stannylquinone[145] **128**, a nucleophilic quinone and functionalised Stille cross coupling partner, has been synthesized by the thermolysis of 4-alkynyl-4-hydroxycyclobutenones in the presence of *n*-Bu_3SnOMe (eq. 76).[145a]

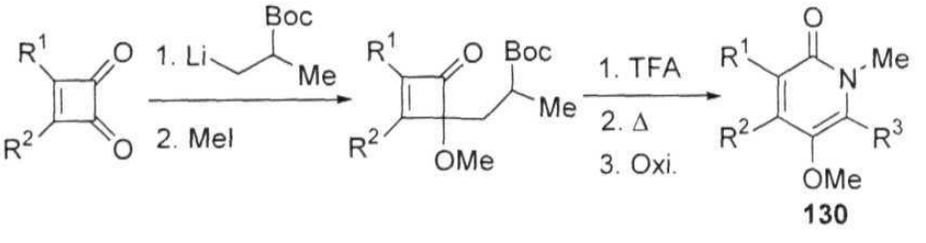


The above versatile chemistry has been extended to the synthesis of substituted α-pyrones.[146] The addition of a lithiated O-silylated cyanohydrin to a cyclobutenedione with subsequent intramolecular 1,4-silyl migration and displacement of cyanide would generate 4-acylcyclobutenone which undergo facile rearrangement to form substituted α-pyrones **129** (eq. 77).



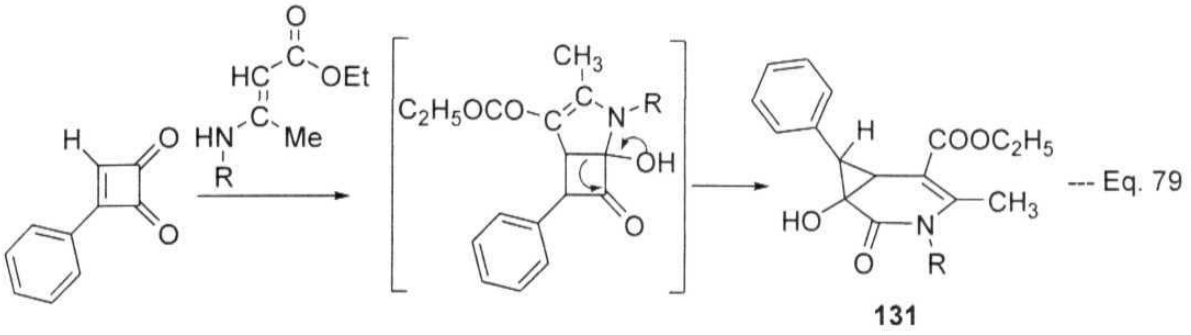
129 --- Eq. 77

Also, 2-pyridinones **130** were synthesized by the addition of N-protected α-amino carbanions to cyclobutenediones followed by deprotection and thermal ring expansion (eq. 78).[147]



130 --- Eq. 78

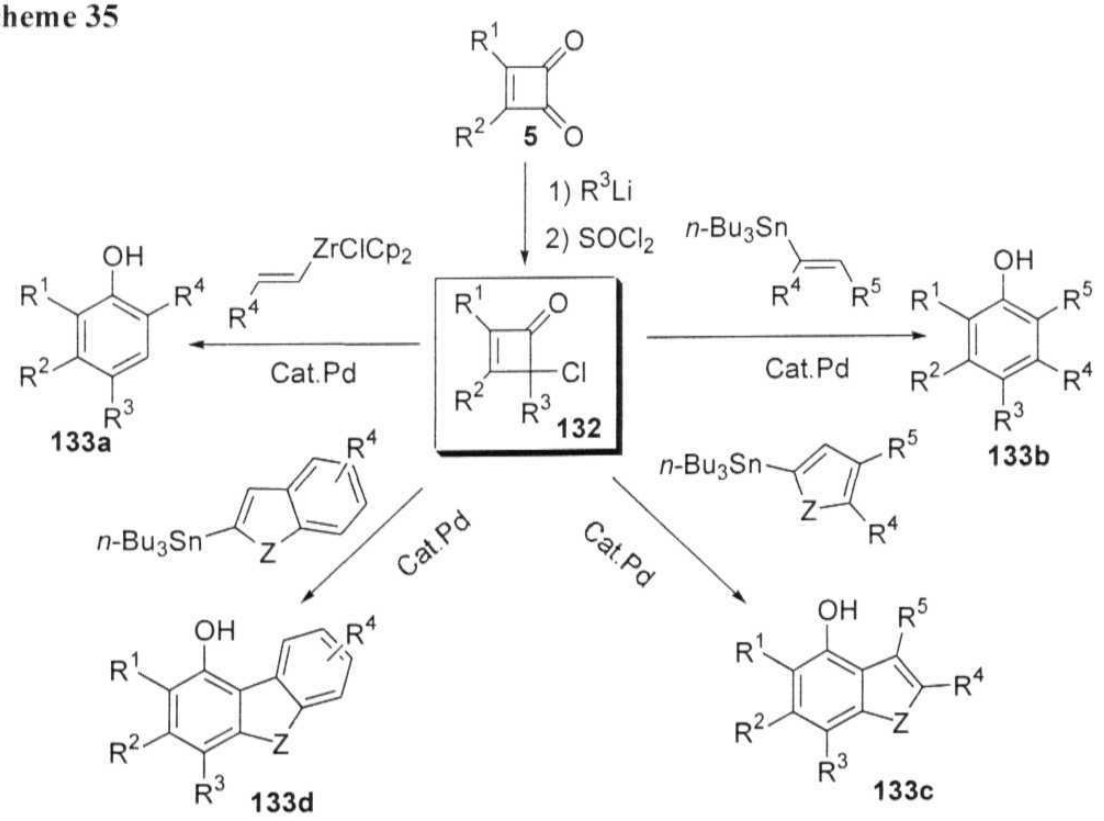
Simple stirring of the mixture of phenylcyclobutenedione and an enamine in benzene at room temperature leads to ring enlargement of dione to generate a bicyclic compound, 1-hydroxy-3-azabicyclo[4.1.0]hept-4-en-2-one **131** (eq. 79).[148]



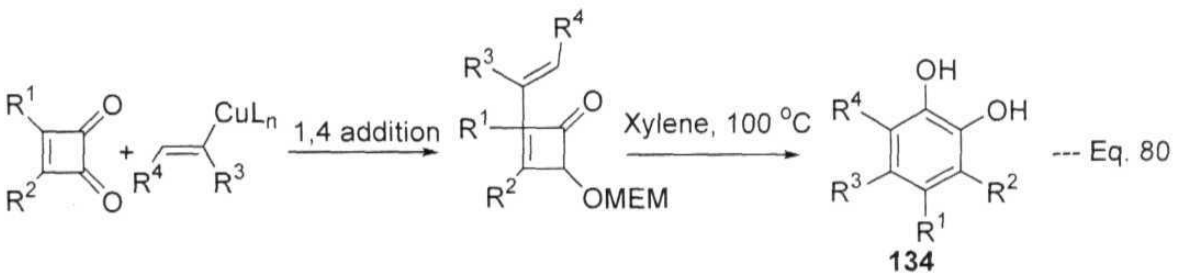
131 --- Eq. 79

Thermolysis of 4-vinyl or 4-aryl-2-cyclobutenones, prepared by the palladium catalysed cross coupling of organotin or organozirconium reagents with 4-chloro-2-cyclobutenones **132**, gives thermal-electrocyclic ring opening to provide highly substituted phenols **133a-d** (**Scheme 35**).[149]

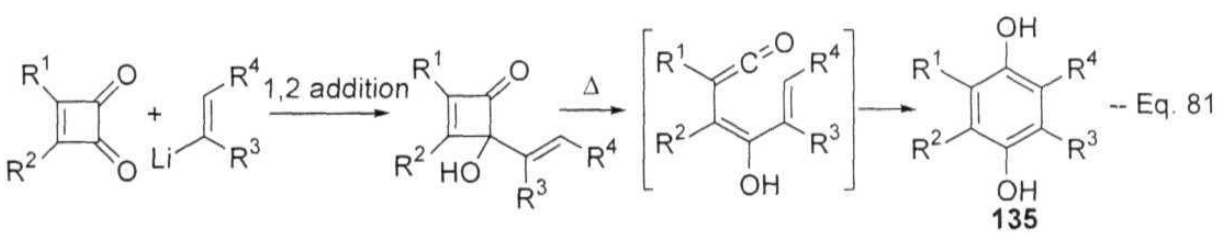
Scheme 35



A general method for the synthesis of substituted catecols **134** have been developed utilizing the 1,4-addition of vinyl, aryl and heteroarylcuprates to cyclobutenediones followed by thermal ring expansion (eq. 80).[150] Similarly, 1,4 hydroquinones **135** have been prepared using lithium reagents (eq. 81).

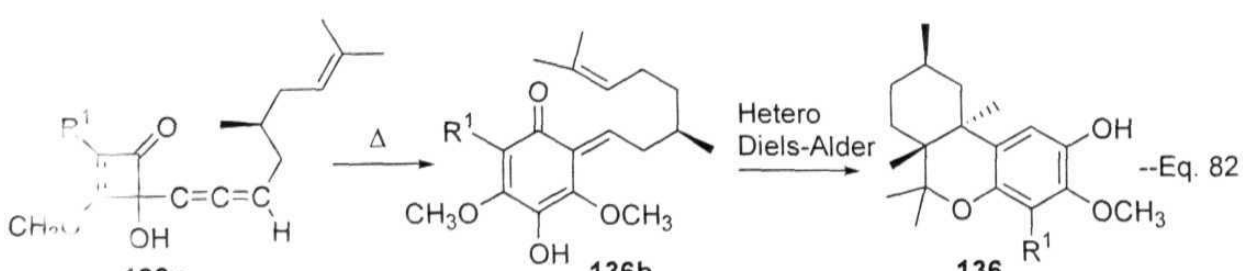


134



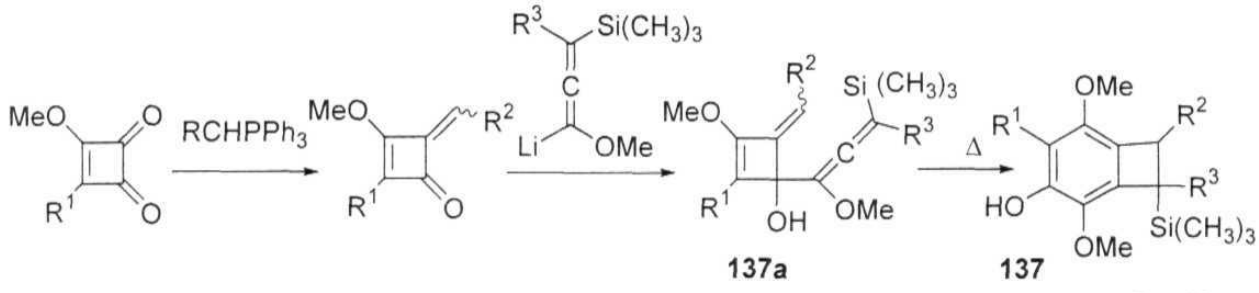
135

It has been reported that the thermolysis of 4-allenylcyclobutenones **136a** prepared using cyclobutenedione and appropriate lithium reagents, lead to highly substituted *o*-quinone methides **136b**, a synthetically useful class of reactive intermediates that are not readily available by a general route. These *o*-quinone methide intermediates were exploited in total synthesis, for example, hexahydrocannabinol **136** (HHC).[151]



136a **136b** **136**

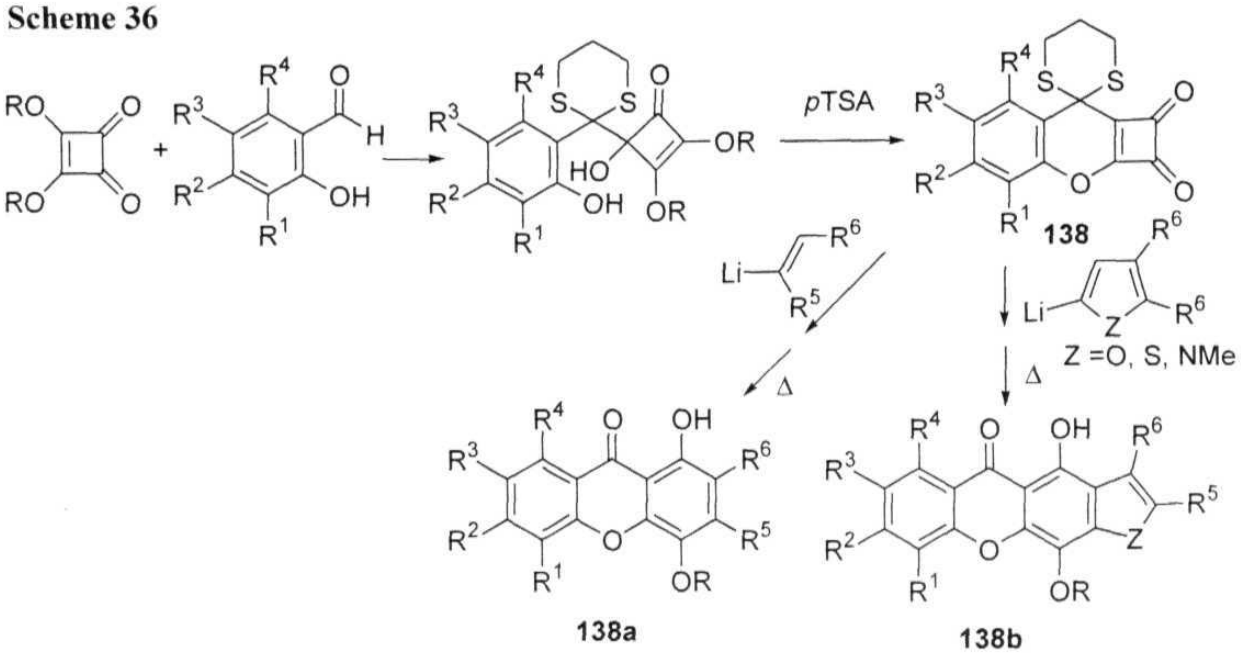
Also, some 3-alkylidene-4-allenylcyclobutenes **137a** were shown to undergo unusual thermal ring expansion to highly functonalized benzocyclobutenes **137**. The formation of benzocyclobutenes is envisaged to involve ring opening of the starting cyclobutene to the corresponding octa-1,2,4,6,7,-pentenes which lead to the quinodimethanes upon electrocyclic ring closure (eq. 83). [152]



---Eq. 83

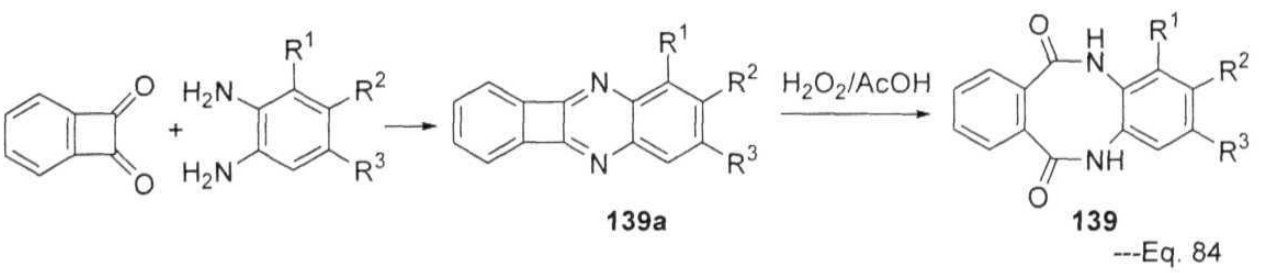
A novel approach to linearly-fused, highly functionalised xanthones **138a, 138b** was recently discovered based on the benzannulation of alkenyl, aromatic or heteroaromatic lithiates with dithiate protected benzopyrone-fused cyclobutenediones **138** (**Scheme 36**).[153a] This demonstrates the versatility of cyclobutenediones as scaffolds for the construction of a diverse range of molecular structures. Also, similar cyclobutenedione based chemistry was employed to synthesize angularly fused xanthone from *o*-anisoyl substituted cyclobutenediones.[153b]

Scheme 36

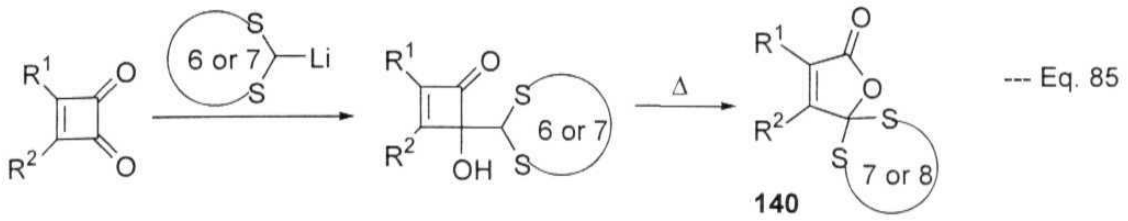


1.2.6 Synthesis of 7 and Large Ring Compounds

5,10-Diazabenzo[b]biphenylene **139a**, a condensation product of benzocyclobutene-1,2-dione and *o*-phenylenediamines, undergoes ring expansion-reaction upon hydrogen peroxide oxidation in acetic acid to generate dibenzodiazocine-5,12-dione **139** (eq. 84).[154]

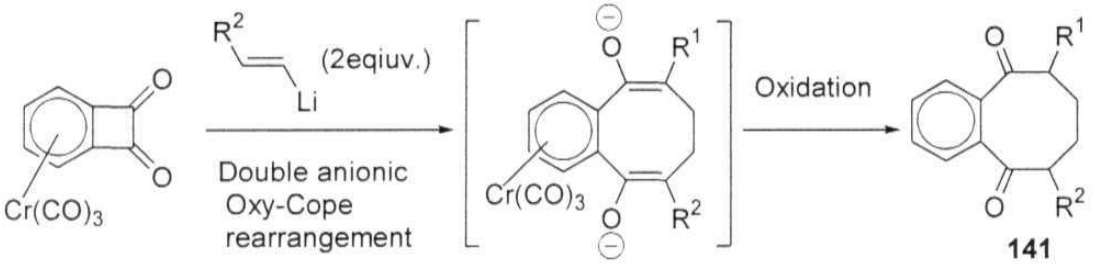


Recently, it was reported that the 4-alkyl-4-hydroxycylobutenones, in which the alkyl group bears sulphur atom at 2-position, undergoes an unusual thermal ring expansion to give spirobutenolide **140** (eq. 85).[155]



--- Eq. 85

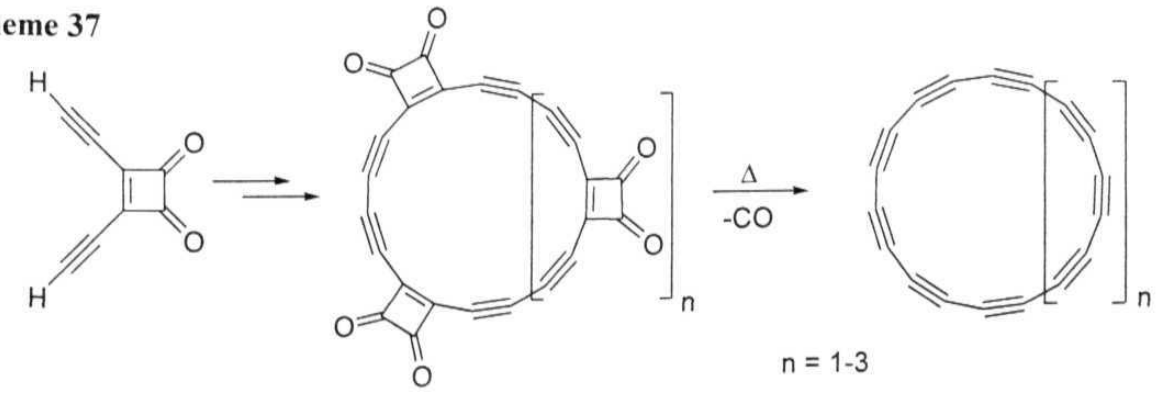
Benzocyclobutenedione coordinated to tricarbonylchromium moiety undergoes double anionic oxy-Cope rearrangement upon nucleophilic addition of vinyllithium reagents to form benzocyclooctan-1,4-diones **141** after oxidation of the metal carbonyl moiety (eq. 86).[156]



---Eq. 86

Recent review by *Diederich et al.*[88] gives an overview of the applications of cyclobutenediones in the synthesis of all carbon rods, rings and nets. Preparation of all carbon molecules rely on the use of 3-cyclobutene-1,2-dione, acetylene synthon, which readily loses its two carbonyl groups in pyrolytic or photolytic reactions (**Scheme 37**).

Scheme 37

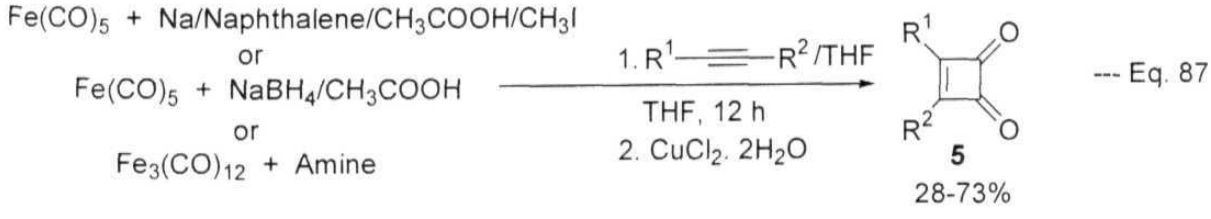


2. Results and Discussion

2.1 Reaction of Alkynes with the $Fe_3(CO)_{12}/Et_3N$ Reagent System

2.1.1 Preparation of Acyloxyferrole Complexes

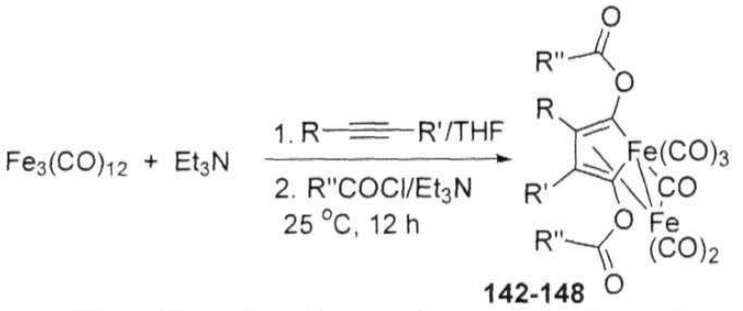
As outlined in the introductory section (**Chapter 1, Section 1.1.2**) several simple and convenient methods for the preparation of cyclobutenediones **5** have been developed in this laboratory based on the iron carbonyl chemistry (eq. 87). However, the nature of the intermediate species involved in these synthetically useful transformations is not clearly understood. Hence, we have undertaken research efforts so as to examine the nature of the species involved in these transformations since such studies would help in the optimization of the yields and also in further exploitation of these transformations for the synthesis of organic molecules with diverse functionality.



--- Eq. 87

Accordingly, we have chosen the reaction of alkynes with operationally simple $Fe_3(CO)_{12}/Et_3N$ reagent system to get information on the nature of the intermediate species. It was observed that the addition of Et_3N and RCOCl to the alkyne-iron carbonyl complex formed in the reaction of $Fe_3(CO)_{12}$, Et_3N and alkyne in THF, leads to the acylation of

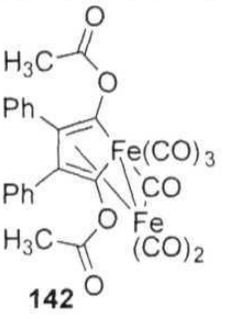
intermediate iron complexes (eq. 88).[157] These acyloxyferrole complexes are relatively stable under nitrogen but decompose upon long time exposure to air.



142-148 --- Eq. 88

The effect of various amines on the formation of the acyloxyferrole complex was examined (**Table 1**).

Table 1. Reaction of Diphenylacetylene with $Fe_3(CO)_{12}$/Amine in the Presence of RCOCl/Amine.

S. No.	Alkyne	Amine	Acid Chloride	Acyloxy Ferrole Complex[a]	Yield[b] %
1	Ph—≡—Ph	Et_3N	CH_3COCl	 **142**	76
2	Ph—≡—Ph	Bu_3N	CH_3COCl	**142**	35
3	Ph—≡—Ph	*n*-$BuNH_2$	CH_3COCl	**142**	20
4	Ph—≡—Ph	Pyridine	CH_3COCl	**142**	50
5	Ph—≡—Ph	DABCO	CH_3COCl	**142**	30
6	Ph—≡—Ph	Et_3N	*p*-$NO_2C_6H_4COCl$	**143**	68

[a]Product **142** was identified by the spectral data (IR, ^1H and ^{13}C NMR) and single crystal X-ray analysis.
[b]Yields are of the isolated products and based on the amount of alkynes used.

The reactions using DABCO, Bu_3N and pyridine gave the acyloxyferrole complex **142** in 30%, 35% and 50% yields respectively, in the reaction using diphenylacetylene.[157] The observed low yield (20%) of ferrole complex in the case of *n*-butyl amine could be due to further reaction of the *n*-$BuNH_2$ with the ferrole complex.[39]

The structural assignment of the hydroxyferrole complex, tricarbonyl-π-(1,1,1-tricarbonyl-3,4-diphenyl-2,5-diacetyloxyferracyclopentadiene)Iron, **142** was confirmed by single crystal X-ray analysis **(Fig 1)**. It contains a semi-bridged carbonyl group between Fe(1) and Fe(2) which is considered as a stabilizing factor.[158]

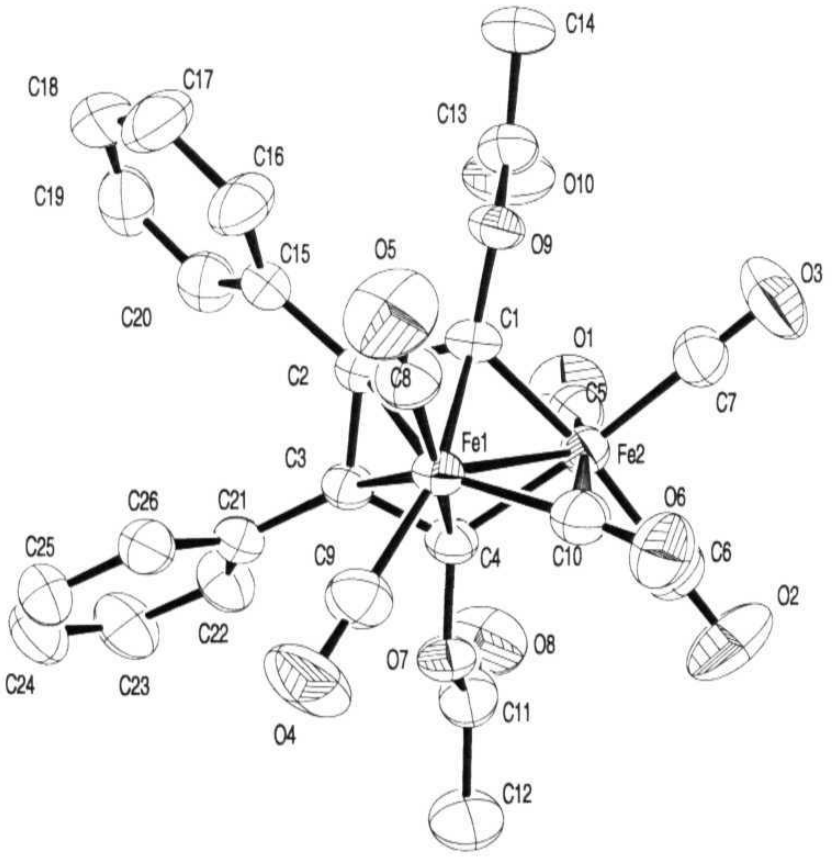


Fig 1. ORTEP Diagram of Acyloxyferrole Complex 142

Table 2. X-ray Data Collection and Structure Refinement for 142

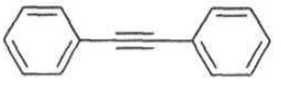
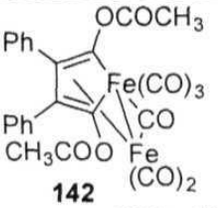
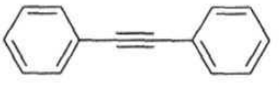
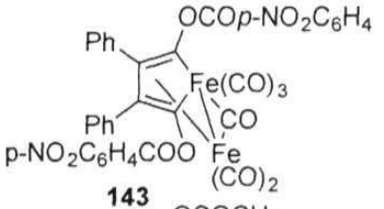
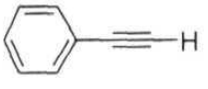
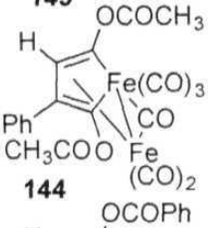
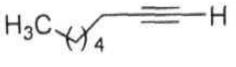
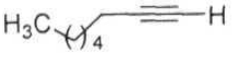
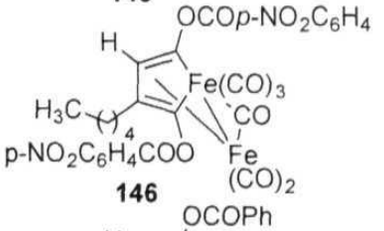
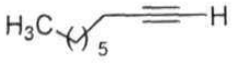
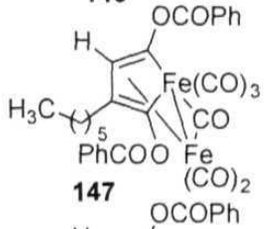
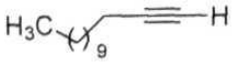
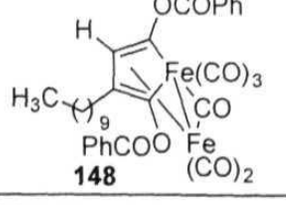
Empirical formula	$C_{26}H_{16}Fe_2O_{10}$
Fw	600.09
Temp., wavelength	293(2), 0.71073 Å
Cryst. syst., space group	monoclinic, $P_{-21}/n:b_2$ [IT-14]
Unit cell dimensions	a=17.129(4) Å, α=90°
	b=8.542(2) Å, β=113.17° (2)
	c=19.27(6) Å, γ =90°
Volume	2591.9(12) $Å^3$
Z, calcd. density	4, 1.538 mg/m^3
Abs. coeff.	1.175 mm^{-1}
F(000)	1216
Cryst. size	0.68×0.56×0.48 mm
θ range for data collection	1.35 to 27.47°
Limiting indices	$0\leq h\leq 22$, $0\leq k\leq 11$, $-25\leq l\leq 22$
Reflns. collected, unique	5927, 3602[R(int)=0]
Refinement method	full-matrix least-square on F^2
Data/restraints/params	3602/0/345
Goodness-of-fit on F^2	1.024
Final *R* indices[I> 2σ (I)]	R_1=0.0421, wR_2=0.0905
R indices (all data)	R_1=0.0938, wR_2=0.1076
Extinct. coeff.	0.0042(5)
Largest diff. peak and hole	0.644, -0.499 e. $Å^{-3}$

Previously, *Cotton*[158] interpreted that the stability of ferrole complexes with the bridged carbonyl is due to the relief of excess charge on Fe by back-donation to π^* of the bridged CO ligand. The X-ray structure determination of $Fe_2(CO)_6[C_4(CH_3)_2(OH)_2]$, reported by *Hock* and *Mills,*[159] confirmed the structure containing the semi-bridging carbonyl group.

As the present method affords good yields of ferrole complexes under ambient conditions, we have examined this transformation using various alkynes and acid chlorides. The results are summarized in **Table 3**.

The transformation of alkynes to acyloxy ferrole complexes can be explained by a tentative mechanism outlined in **Scheme 38**. Initial decomposition of the $Fe_3(CO)_{12}$ in the presence of R_3N would give coordinatively unsaturated reactive species. The UV spectrum recorded for these species shows the λ_{max} at 540 nm that corresponds to the absorptions previously reported for (amine)$Fe_3(CO)_{11}$ species.[160] These species may further split into other coordinatively unsaturated species before reaction with alkynes. The resulting species would then react with the alkyne followed by CO insertion to give the maleoyl iron complexes **149** which could undergo acylation in the presence of R"COCl.

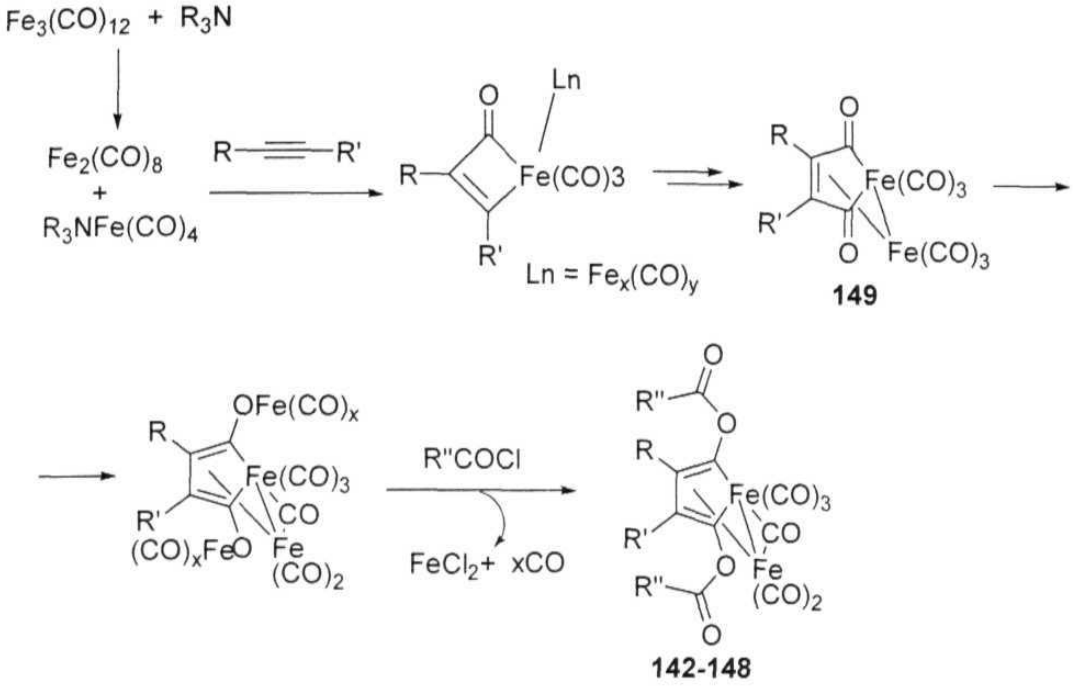
Table 3. Reaction of Alkynes with $Fe_3(CO)_{12}/Et_3N$ in the Presence of $RCOCl/Et_3N$.

S. No.	Alkyne	Acid Chloride	Acyloxy Ferrole Complex[a]	Yield[b] %
1		CH_3COCl	 **142**	76
2		$p\text{-}NO_2C_6H_4COCl$	 **143**	68
3		CH_3COCl	 **144**	72
4		PhCOCl	 **145**	70
5		$p\text{-}NO_2C_6H_4COCl$	 **146**	72
6		PhCOCl	 **147**	65
7		PhCOCl	 **148**	68

[a]Products were identified by the spectral data (IR, ^1H and ^{13}C NMR) and single crystal X-ray analysis for **142**.

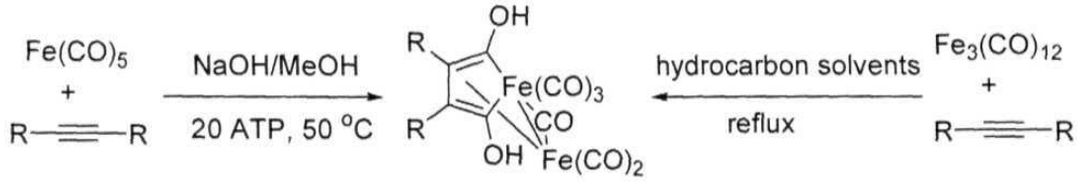
[b]Yields are of the isolated products and based on the amount of alkynes used.

Scheme 38



Analogous ferrole complexes were first synthesized by *Reppe* and *Vetter*[161] by the reaction of acetylene with an alkaline solution of iron pentacarbonyl at high pressure and temperature (**Scheme 39**). Later, *Wender et al.*[162] developed a slightly improved procedure for the synthesis of the hydroxyferrole complex. Also, similar complexes were prepared by refluxing a mixture of alkynes and $Fe_3(CO)_{12}$ in hydrocarbon solvents.[163] However, except for simple acetylene, the yields reported in the above methods are around 5% and never more than 18% even after three weeks of reaction.

Scheme 39

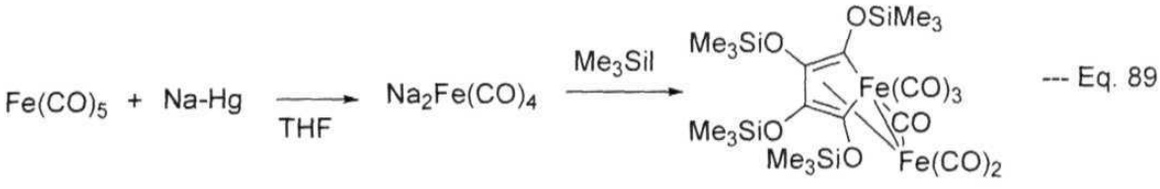


R = H, Me

150

5-18%

An unusual formation of trimethylsilyloxy ferrole complexes **151** was observed in the reaction of $Na_2Fe(CO)_4$ with Me_3SiI (eq. 89).[164,165]



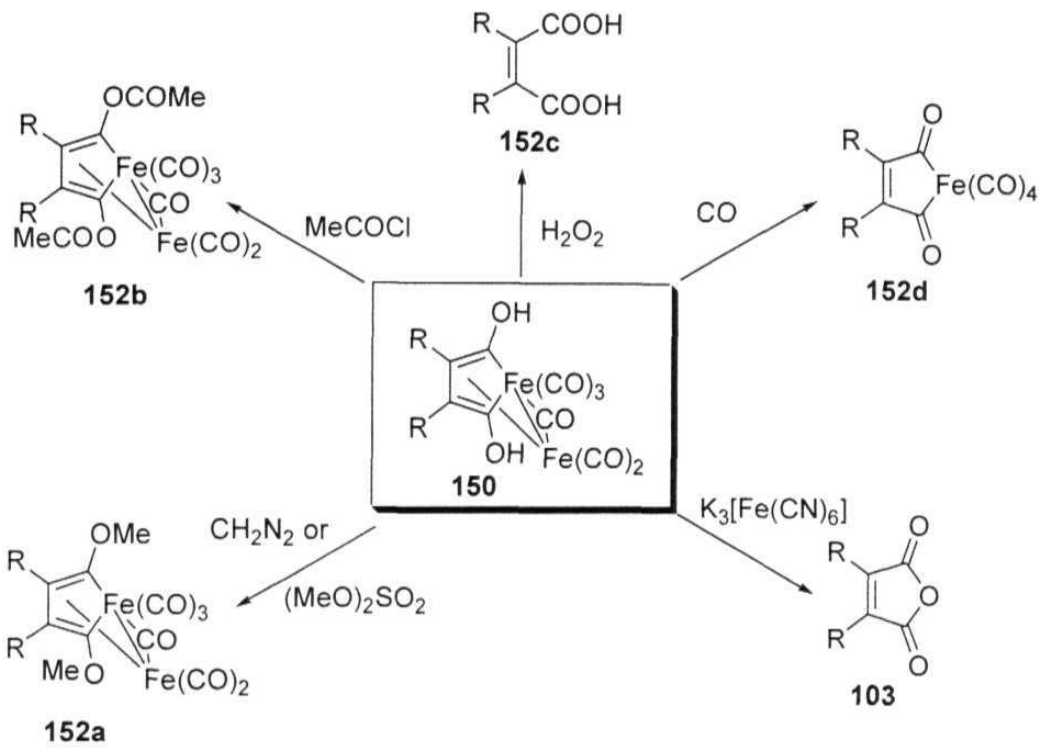
--- Eq. 89

151

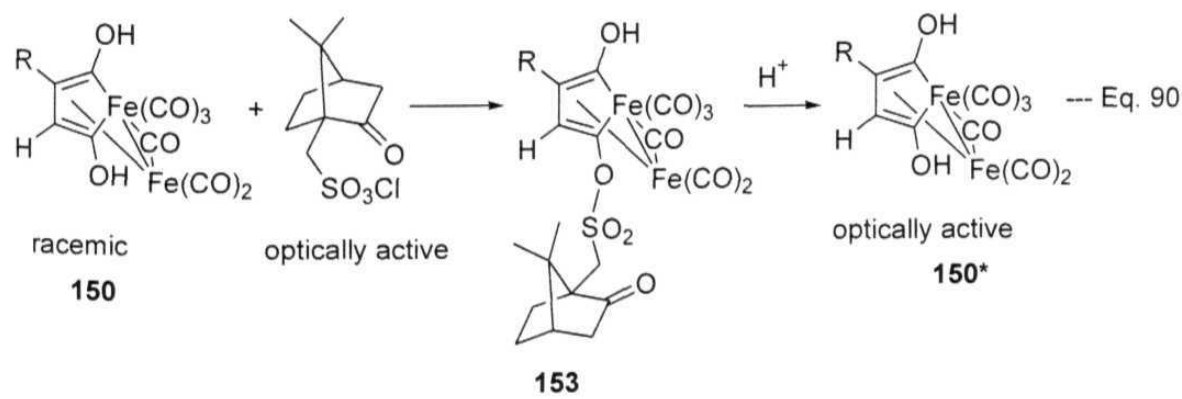
27%

The hydroxy ferrole complexes **150** are reported to undergo interesting organic transformations under various conditions (**Scheme 40**).[166] Some synthetically useful organic compounds such as maleic acids and maleoyl iron complexes were obtained from the ferrole complexes. Methyloxy as well as acyloxy derivatives were prepared by the reaction of hydroxy ferrole complex with appropriate reagents.[116]

Scheme 40

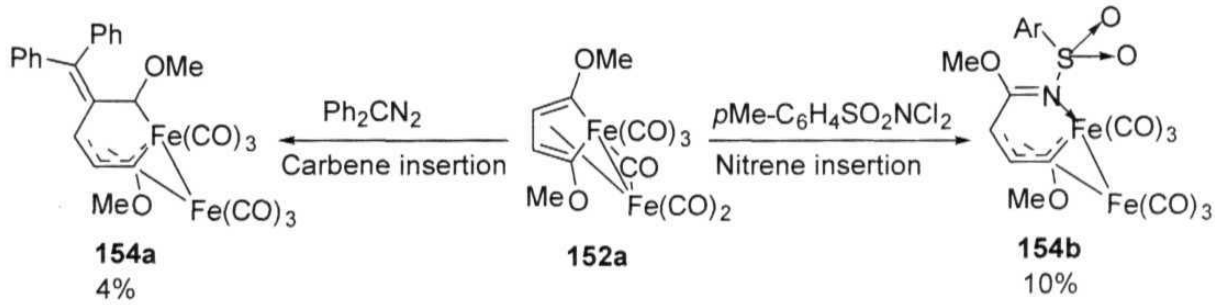


Also, hydroxy ferrole complexes were resolved to obtain enantiomers using optically active 10-camphorsulfonyl chloride (eq. 90).[34]



It has been reported that ferrole complex **152a** undergoes interesting reactions involving insertion of carbene and nitrene into the carbon-iron bond to generate complexes of the type **154a** and **154b** albeit in low yields (**Scheme 41**).[167]

Scheme 41



154a 4%

152a

154b 10%

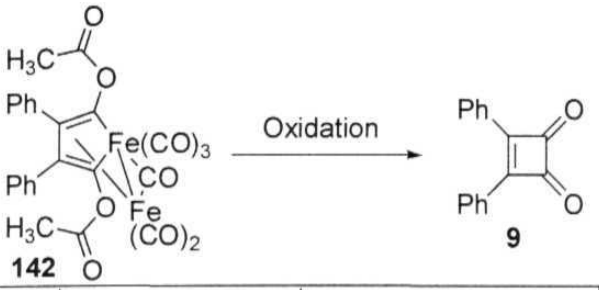
In spite of their rich chemistry, ferrole complexes are not well exploited in organic synthesis due to the lack of practically viable methods to prepare them in good amounts. Accordingly, synthesis of acyloxy ferrole derivatives through the method described here should help in further research work in this area.

2.1.2 Preparation of cyclobutenediones using acyloxyferrole complexes

We have examined the conversion of the acyloxyferrole complexes **142-148** to cyclobutenediones by oxidation under different conditions. Whereas the reaction of **142** with ceric ammonium nitrate or ferric chloride in alcoholic solvents gave unclean reaction, it remained unaffected using $CuCl_2$ in acetone solvent at 25 °C even after 24 h. Interestingly, the reaction of **142** with Br_2 in dichloromethane at -78 °C produced the corresponding cyclobutenedione in 80% yield. The use of I_2 or *N*-bromosuccinimide at 25 °C in the place of Br_2 for the oxidation of complex **142** gave the corresponding

cyclobutenedione in low yield (15%) besides a mixture of unidentified iron carbonyl complexes (**Table 4**).

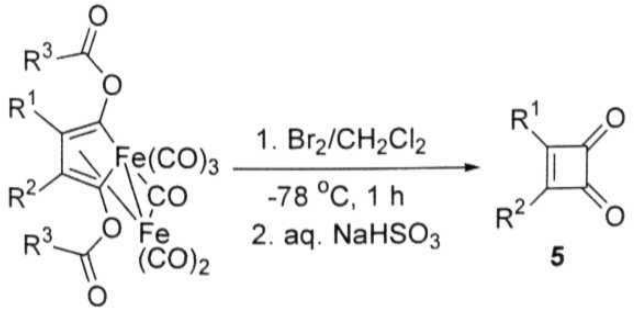
Table 4. Reaction of Acyloxyferrole Complexes with Oxidizing Agents



S. No.	Oxidising agent	Reaction conditions	Product[a]	Yield[b] %
1	Br_2	CH_2Cl_2/-78 °C/2 h	**9**	80
2	NBS	CH_2Cl_2/25 °C/3 h	**9**	15
3	I_2	CH_2Cl_2/25 °C/3 h	**9**	15

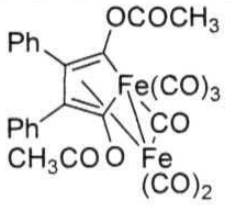
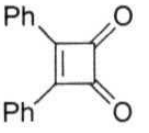
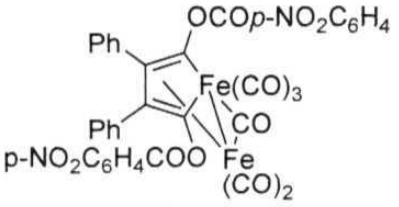
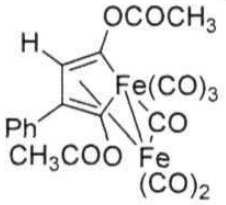
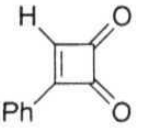
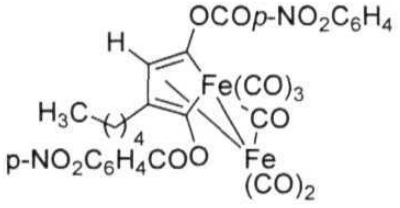
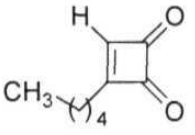
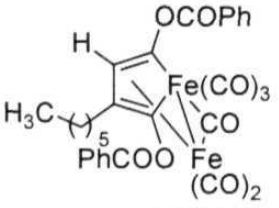
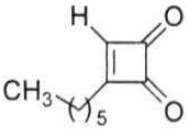
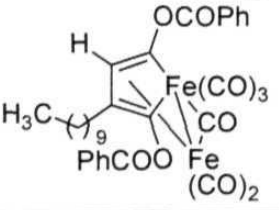
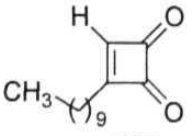
[a]Products were identified by the spectral data (IR, ^{1}H NMR, ^{13}C NMR and Mass) and comparison with the reported data.[168] [b]Yields are of the isolated cyclobutenedione and based on the amount of ferrole complexes used.

As bromine was found to be an efficient oxidant under mild conditions, we have examined the generality of this oxidation process. Several acyloxy ferrole complexes were converted to the corresponding cyclobutenediones in moderate to good yields (**Table 5**).[157] In the case of **145**, **147** and **148** (R^3=Ph) benzoic acid was isolated in ca. 60% yield.



--- Eq. 91

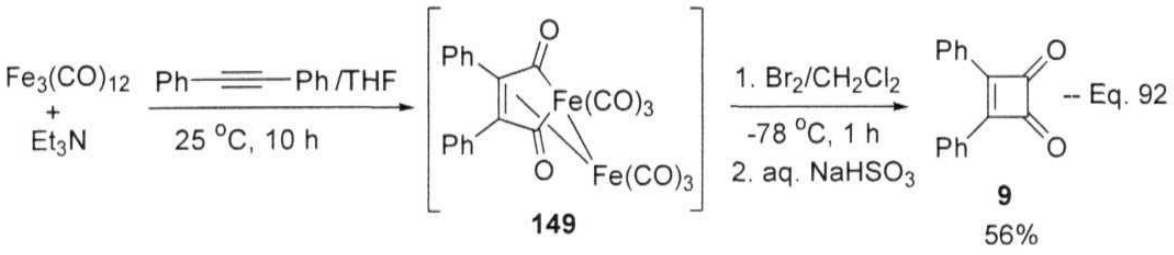
Table 5. Preparation of Cyclobutenediones Using Acyloxyferrole Complexes/Br_2.

S. No.	Acyloxy Ferrole Complex	Cyclobutenedione[a]	Yield[b] %
1		 **9**	90
2		**9**	81
3		 **28**	62
4		 **155**	60
5		 **156**	65
6		 **157**	63

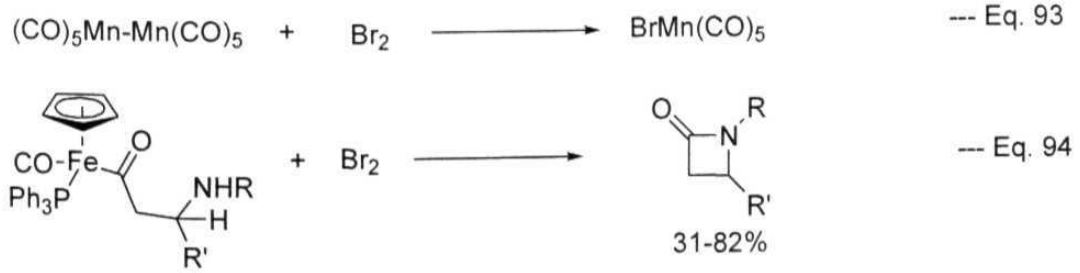
[a]Products were identified by the spectral data (IR, ^{1}H NMR, ^{13}C NMR and Mass) and comparison with the reported data.[168] [b]Yields are of the isolated products and based on the amount of acyloxyferrole complexes used.

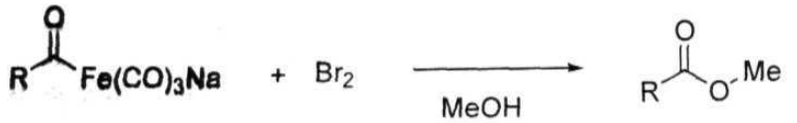
2.1.3 Use of Br_2 to Decomplex Alkyne-iron Carbonyl Complexes

In order to examine the applicability of bromine to decomplex the intermediate alkyne-iron carbonyl complexes, we have carried out the reaction of the maleoyl iron carbonyl complexes **149** prepared using $Fe_3(CO)_{12}/Et_3N$ reagent system and found that bromine could smoothly oxidize the intermediate species to the corresponding cyclobutenedione (eq. 92).[169]

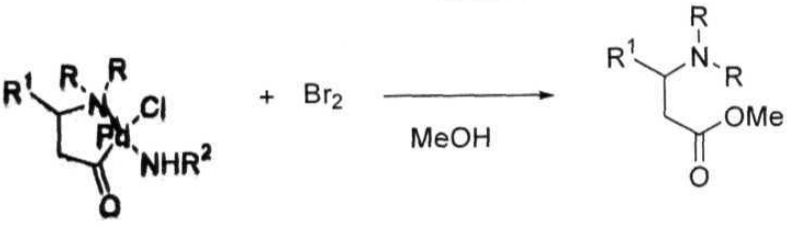


Bromine is known to oxidize various organometallic complexes through the cleavage of both M-C and M-M bonds. [170-173] Oxidative addition of bromine to dinuclear complexes is a classical example of M-M bond cleavage (eq. 93).[170] The Br_2 oxidation of some acyliron complexes generates the corresponding β-lactams (eq. 94)[171] and esters (eq. 95).[172] Similarly, oxidative cleavage of Pd-C bond in (β-aminoacyl)palladium complexes results in the rapid formation of esters (eq. 96).[173]



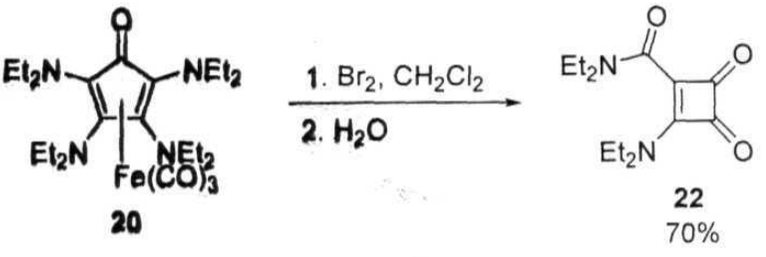


--- Eq. 95



--- Eq. 96

Oxidation of tetrakis(diethylamino)cyclopentadienone with bromine followed by **aqueous work up** affords a cyclobutenedione with an interesting functionality (eq. 97).[16a]

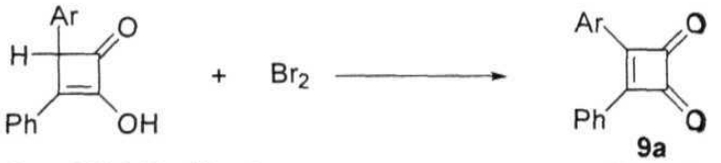


20

22
70%

--- Eq. 97

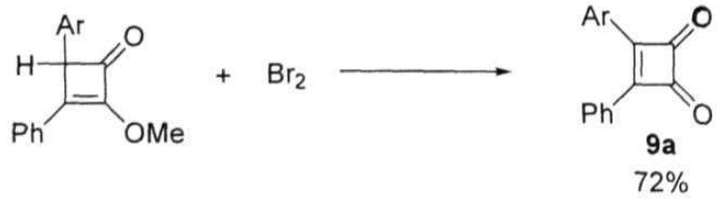
Also, bromine **has been used to oxidize** 4-aryl-2-hydroxy-3-phenyl-2-cyclobutene-1-ones as well as 4-aryl-2-methoxy-**3-phenyl-2-cyclobute**ne-1-ones to obtain the corresponding cyclobutenediones **9a** in good yie**lds (eqs. 98 and** 99).[174b]



Ar = SCH_2Ph, Fluryl

9a
20-80%

--- Eq. 98

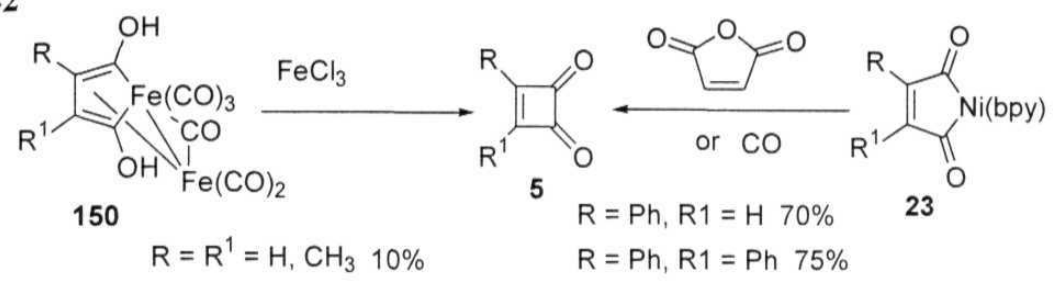


9a
72%

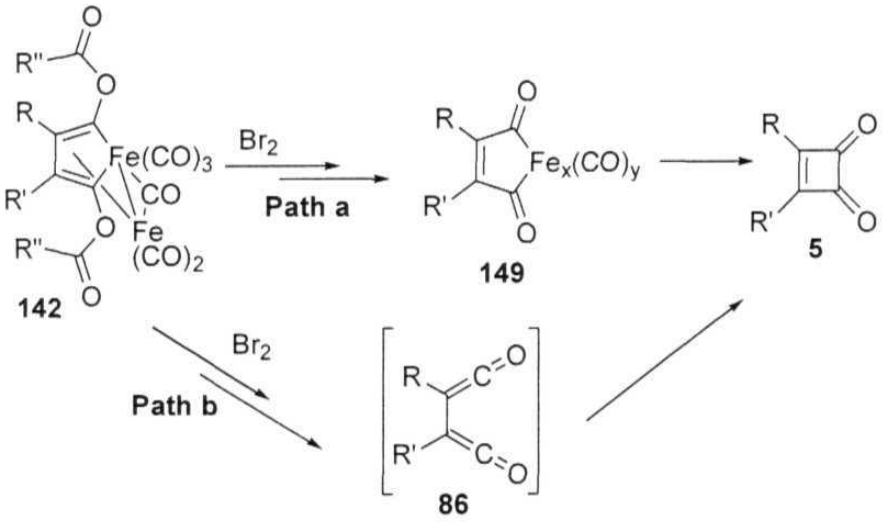
--- Eq. 99

The hydroxy ferrole complexes **150**[165] and the nickel complexes **23**[175] were reported to be readily decomplexed using $FeCl_3$ or maleic anhydride to obtain the corresponding cyclobutenediones (**Scheme 42**).

Scheme 42



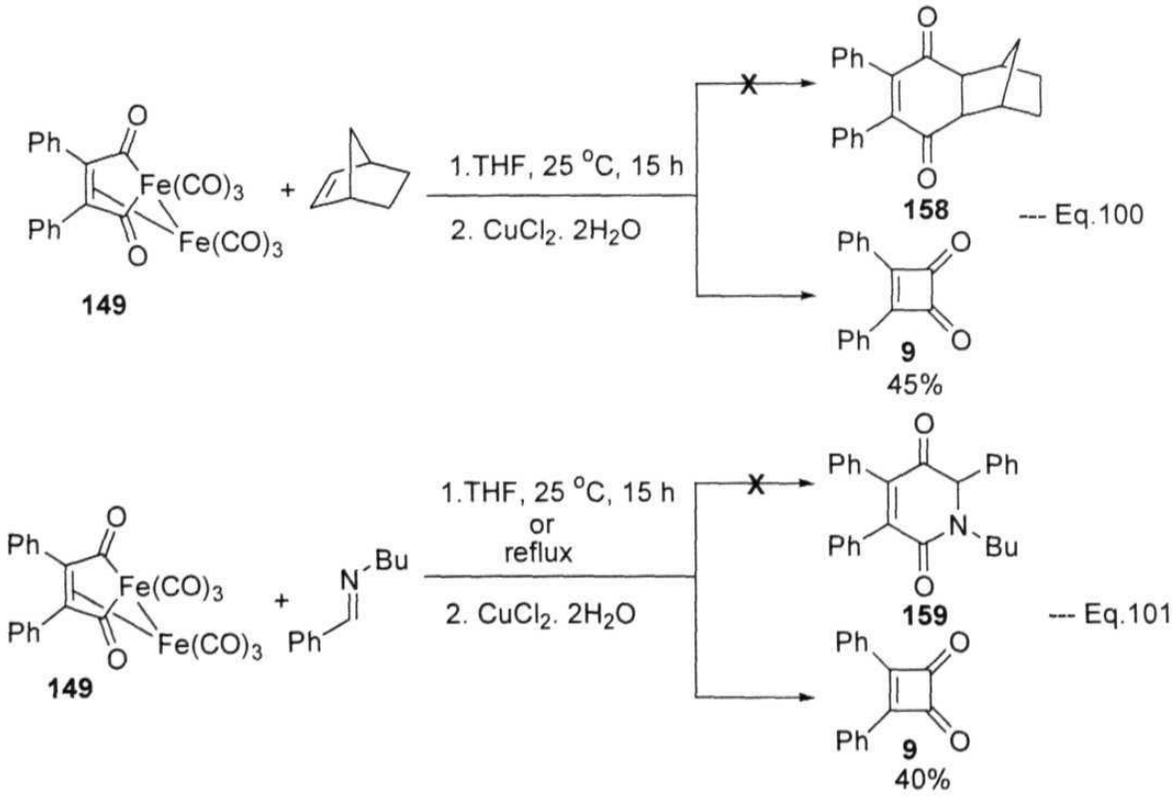
Scheme 43

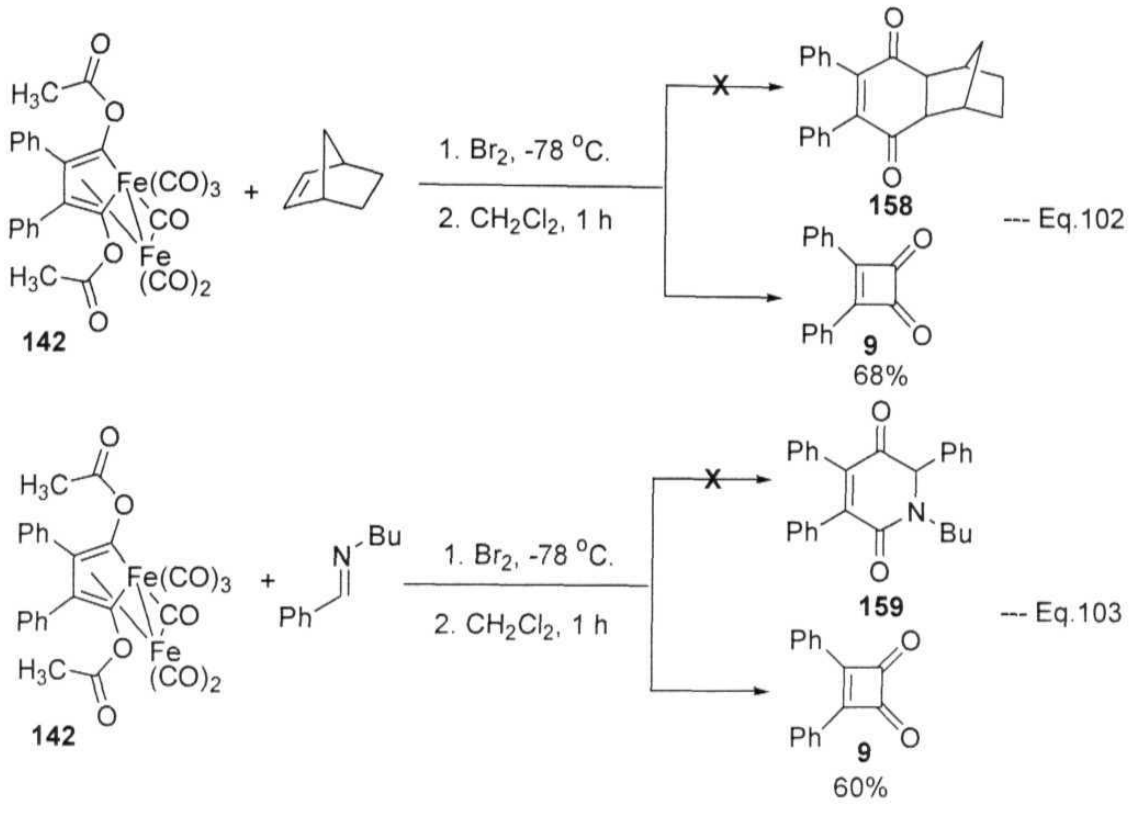


Accordingly, it is reasonable to assume that the decomplexation of the acyl complexes by bromine to the corresponding cyclobutenediones may go through intermediates similar to **149** (**Path a**, **Scheme 43**). Alternatively, formation of cyclobutenediones may also go through the initial oxidative cleavage of complex to give bisketene intermediates **86** that are known to give cyclobutenediones (**Path b**).[82,176] However, we do not have evidence in support of such intermediate species.

2.1.4 Reaction of Maleoyl and Acyloxyferrole Complexes with Olefins and Enamines

We have made efforts to utilise the anticipated maleoyl iron carbonyl complexes as well as acyloxyferrole complexes for synthetic applications. For example, alkyne-iron carbonyl complexes, prepared using $Fe_3(CO)_{12}/Et_3N$/alkyne, were treated with reactive olefins or enamines under various conditions. However, the expected addition products (**158**, **159**) were not obtained in these reactions (eqs. 100 and 101). Only, the corresponding cyclobutenedione was isolated (45% and 40%) along with mixtures of unidentified products. Similarly, bromine oxidation of acyloxyferrole complexes in the presence of either olefin or enamine gave only the corresponding cylobutenedione (eqs. 102 and 103).





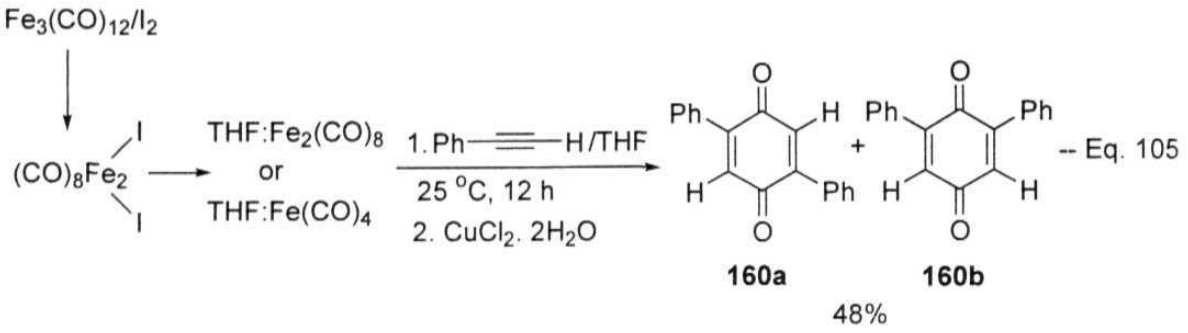
2.1.5 Reaction of Alkynes with $Fe_3(CO)_{12}/I_2$

Cotton et al.[177] reported that $Fe_3(CO)_{12}$ reacts with iodine under ambient conditions to generate the $Fe_2(CO)_8I_2$ complex (eq. 104). It was assumed that the $Fe_2(CO)_8I_2$ would undergo further dissociation to give coordinatively unsaturated reactive species (eq. 105). We have examined the preparation of such reactive species for synthetic applications.

$$Fe_3(CO)_{12} + I_2 \xrightarrow[THF,\ 25\ ^{\circ}C]{} Fe_2(CO)_8I_2 \qquad \text{--- Eq. 104}$$

Accordingly, we have carried out some preliminary experiments using the $Fe_3(CO)_{12}/I_2$ reagent system. We have observed that the reaction of phenylacetylene with

$Fe_3(CO)_{12}/I_2$ gave a mixture of benzoquinones after $CuCl_2$.$2H_2O$ oxidation (48%) (eq. 105).



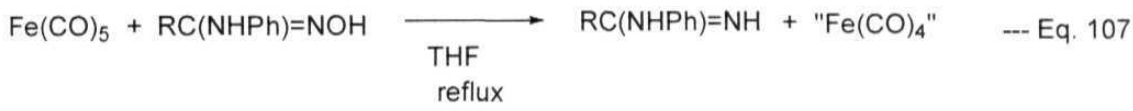
2.2 Reaction of Alkynes with the $Fe(CO)_5/R_3NO$ Reagent System

2.2.1 Reaction of Alkynes with $Fe(CO)_5$/Pyridine *N*-oxide

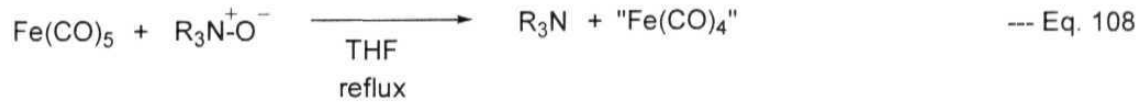
The $Fe_2(CO)_9$ is a quick source of "$Fe(CO)_4$" since simple stirring of $Fe_2(CO)_9$ with coordinating solvents at room temperature generates $Fe(CO)_4$.[178] However, the disadvantage is that the preparation of these di or tri nuclear species, ($Fe_2(CO)_9$[179a] or $Fe_3(CO)_{12}$,[179b] involves tedious processes starting from $Fe(CO)_5$. Hence, we became interested in the use of $Fe(CO)_5$, a less expensive and readily available metal carbonyl for the preparation of $Fe(CO)_4$. The direct synthesis of $Fe(CO)_4$ from $Fe(CO)_5$, either thermally or photochemically give lower yields along with side products (eq. 106).[180]

Previous methods developed in this laboratory for "$Fe(CO)_4$" generation involves the use of $Fe(CO)_5$/Na/Naphthalene and $Fe(CO)_5/NaBH_4/CH_3COOH$ reagent systems. In

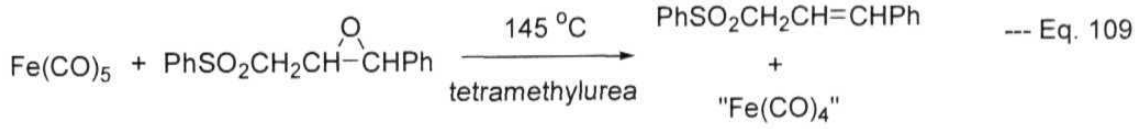
continuation of these studies, we have examined simpler methods of preparation of coordinatively unsaturated iron carbonyl species for the conversion of alkynes to the corresponding cyclobutenediones. It was reported that $Fe(CO)_5$ can act as a good reducing agent. For example, *N*-alkyl and *N*-arylbenzamide oximes undergo reduction with $Fe(CO)_5$ to give the corresponding amides (eq. 107).[181] Also, the reaction of amine oxides[182a] and some epoxides[182b] with $Fe(CO)_5$ gives the corresponding amines and olefins, respectively (eqs. 108 and 109). In all these transformations $Fe(CO)_5$ is believed to be converted to the "$Fe(CO)_4$" intermediate.



--- Eq. 107

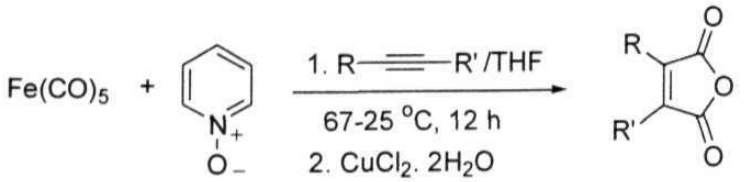


--- Eq. 108

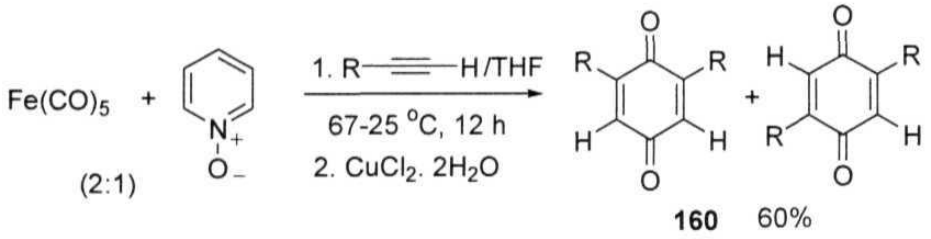


--- Eq. 109

Accordingly, it was of interest to examine the reactivity of "$Fe(CO)_4$" prepared in this way. We have carried out the reaction of alkynes with $Fe(CO)_5$ in the presence of pyridine *N*-oxide (1:1) at 70 °C and obtained the corresponding maleic anhydride derivatives after $CuCl_2.\ 2H_2O$ oxidation (eq. 110).[183] It was thought that the anhydride formation could be avoided using lesser amounts of amine oxide. Accordingly, in another run, $Fe(CO)_5$ and pyridine *N*-oxide were used in 2:1 ratio. In this case, a mixture of benzoquinones was obtained in 60% yield (eq. 111).[183]



--- Eq. 110



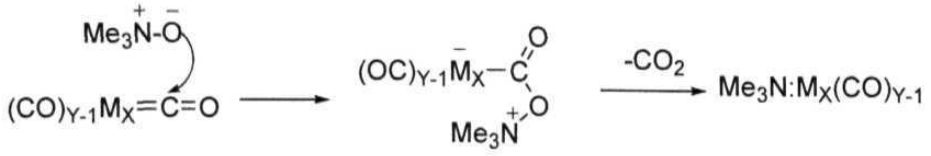
--- Eq. 111

Unfortunately, pyridine *N*-oxide decarbonylates $Fe(CO)_5$ only at higher temperatures. Accordingly, we have examined the use of Me_3NO, which is known to decarbonylate $Fe(CO)_5$ under mild conditions.

2.2.2 Reaction of Alkynes with the $Fe(CO)_5$/Trimethylamine *N*-oxide System

2.2.2.1 Synthesis of Cyclobutenediones Using Alkynes and $Fe(CO)_5/Me_3NO$

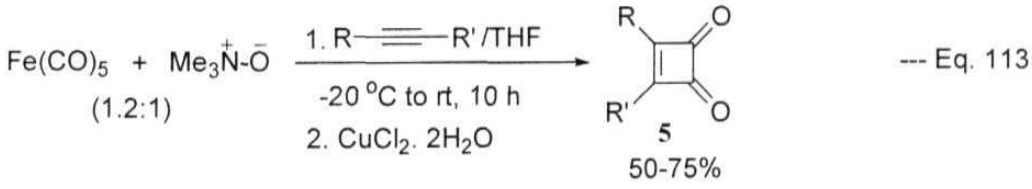
The use of trimethylamine *N*-oxide (Me_3NO), a mild and efficient oxidizing agent, to remove coordinated carbon monoxide was reported by *Shvo* and *Hazum*.[184,185] The CO is removed as carbon dioxide and the mechanism of oxidation involves the nucleophilic addition of amine oxide (eq. 112).



--- Eq. 112

Also, it has been reported that trimethylamine *N*-oxide induces the disengagement of organic ligands, usually a diene, from iron carbonyl complexes under mild conditions.[185] Further, the formation of $Fe(CO)_3$-diene complexes from $Fe(CO)_5$ and diene, was accomplished using Me_3NO.[184]

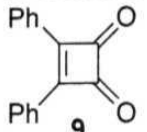
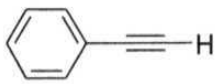
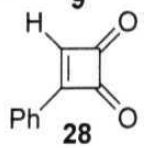
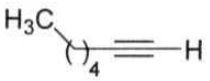
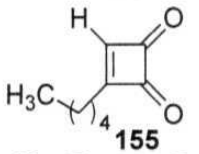
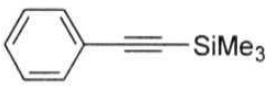
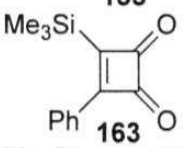
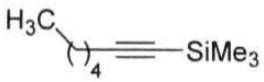
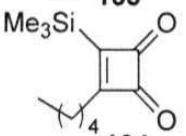
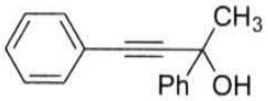
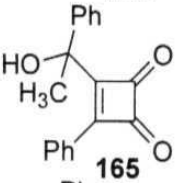
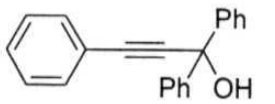
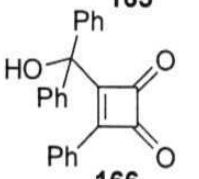
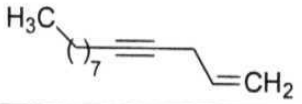
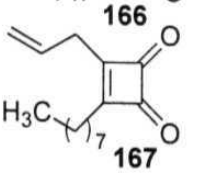
Accordingly, we have studied the reactivity of iron carbonyl, prepared in THF using Me_3NO and $Fe(CO)_5$ with alkynes. It was observed that the reaction of alkynes with 1:1.2 ratio of Me_3NO and $Fe(CO)_5$ gives the corresponding cyclobutenediones in moderate to good yields (50-75%) after $CuCl_2.2H_2O$ oxidation (eq. 113).[169]



--- Eq. 113

Several alkynes were converted to cyclobutenediones and the results are summarized in **Table 6**. Evidently, this reagent system can tolerate unmasked functional groups such as hydroxyl and silyl groups (**Entries 4, 5, 6, 7**). The formation of cyclobutenedione from enyne shows that this reagent system reacts with alkynes without affecting the olefin moiety (**Entry 8**). In the case of 1-heptyne, the corresponding cyclobutenedione was obtained in lower yield besides a mixture of the corresponding 2,5- and 2,6-dialkylbenzoquinones (30%, 60:40), (**Entry 3, Table 6**).

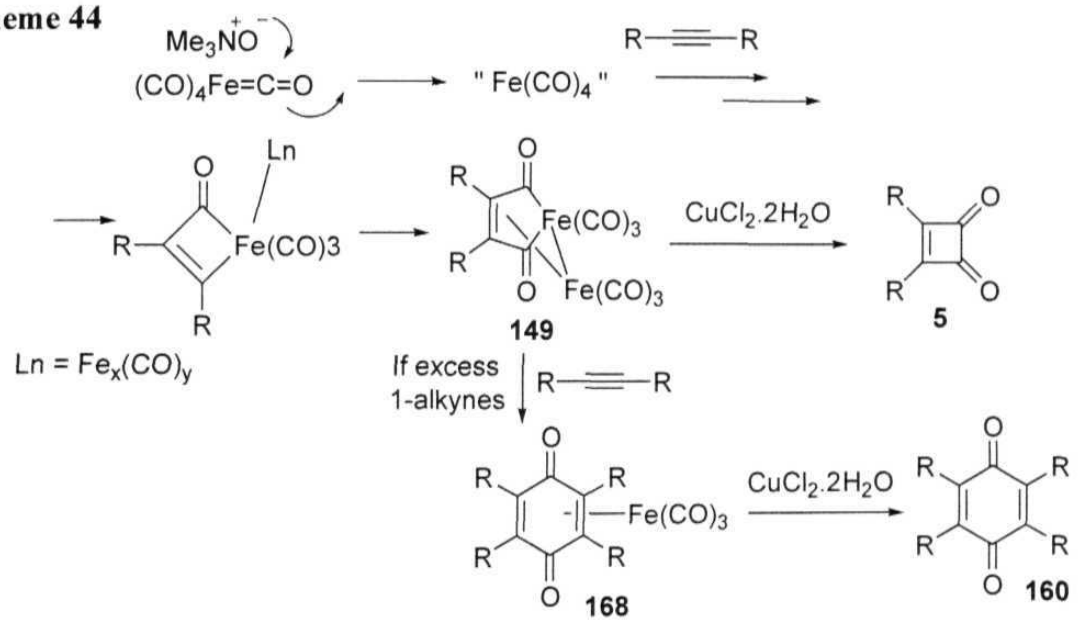
Table 6. Reaction of Alkynes with $Fe(CO)_5$ and Me_3NO Followed by $CuCl_2.2H_2O$ Oxidation

S. No.	Alkyne	Dione[a]	Yield %[b]
1		 **9**	73
2		 **28**	62
3		 **155**	50
4		 **163**	75
5		 **164**	68
6		 **165**	70
7		 **166**	65
8		 **167**	57

[a]Products were identified by the spectral data (IR, ^1H NMR, ^{13}C NMR, Mass and CHN analysis) and comparison with the reported data.[168] [b]Yields are of the isolated products and based on the amount of alkynes used.

Though, THF was found to be a suitable solvent, other coordinating solvents such as CH_3CN and CH_3COCH_3 also gave comparable results. However, the use of solvents like $CHCl_3$ and CH_2Cl_2 gave unidentified mixture of carbonyl products. Presumably, the coordinating solvents may form weak complexes with the $Fe(CO)_4$ species that help in this transformation.[185a,185b]

Scheme 44

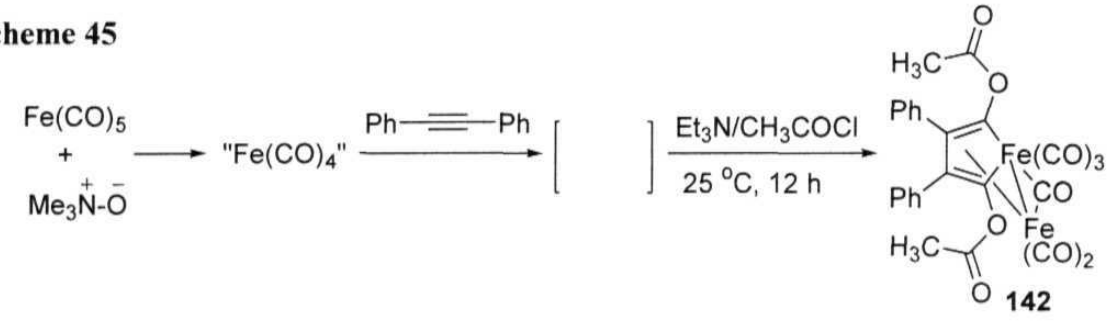


The formation of cyclobutenediones from alkynes can be tentatively explained by the mechanism depicted in **Scheme 44**. Addition of $Fe(CO)_5$ to a solution of Me_3NO in THF at –20 °C gives red colored solution with immediate evolution of CO_2 through the nucleophilic attack of amine oxide on the coordinated CO, leading to the formation of coordinatively unsaturated species $Fe(CO)_4$.[163] These species would further react with alkynes followed by CO insertion to give maleoyl complexes **149**, which could give cyclobutenediones after $CuCl_2.2H_2O$ oxidation.[168c,168d]

2.2.2.2 Acetyloxyferrole Complex from Alkynes, $Fe(CO)_5/Me_3NO$ and CH_3COCl/Et_3N

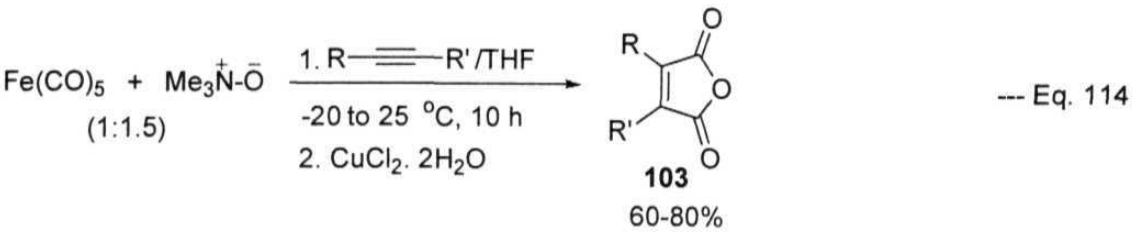
We have also made efforts to study the nature of the intermediate species involved in the above transformation. It was observed that the addition of Et_3N and CH_3COCl to the alkyne-iron carbonyl complexes, prepared using $Fe(CO)_5/Me_3NO$ and alkyne in THF, gives the acyloxyferrole complex (48%) (**Scheme 45**). This transformation may involve intermediates similar to that proposed in the reaction of $Fe_3(CO)_{12}/Et_3N/RCOCl$ system as discussed previously.

Scheme 45



2.2.2.3 Cyclic Anhydrides Using Alkynes and $Fe(CO)_5/Me_3NO$

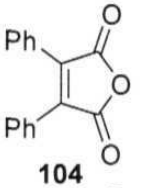
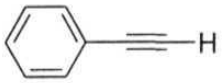
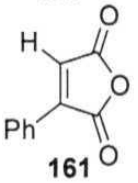
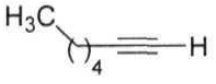
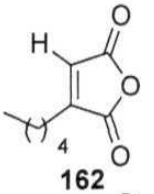
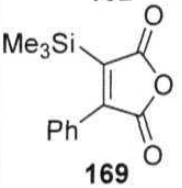
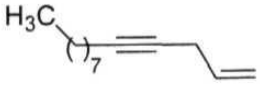
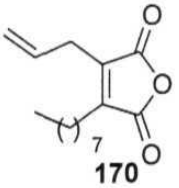
We have also observed that the use of $Fe(CO)_5/Me_3N$-O reagent system in 1:1.5 ratio in the reaction with alkynes leads to the corresponding cyclic anhydrides after $CuCl_2.2H_2O$ oxidation along with traces of cyclobutenediones (3-5%) (eq. 114).



--- Eq. 114

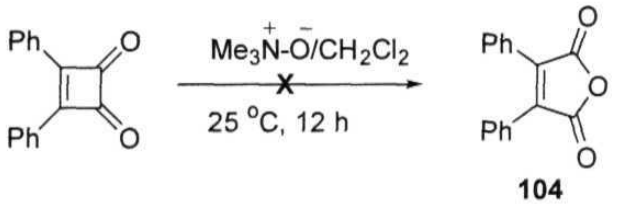
Several alkynes including a silyl substituted alkyne and an enyne (Entries 3 & 5) were converted to the corresponding cyclic anhydrides in moderate to good yields (60-80%), and the results are summarized in **Table 7**.

Table 7. Reaction of Alkynes with 1:1.5 Equiv. of $Fe(CO)_5$ and Me_3NO

S. No.	Alkyne	Anhydride[a]	Yield[b] %
1		 **104**	80
2		 **161**	72
3		 **162**	68
4		 **169**	71
5		 **170**	60

[a]Products were identified by the spectral data (IR, ^1H NMR, ^{13}C NMR, Mass and CHN analysis) and comparison with the reported data (Entries 1 and 2).[186] [b]Yields are of the isolated products and based on the amount of alkynes used.

In order to verify whether anhydrides are formed through the oxidation of cyclobutenediones, a solution of diphenylcyclobutenedione in dichloromethane was stirred with excess of trimethylamine *N*-oxide at room temperature for 12 h. In this case, the dione remained unaffected (eq. 115).

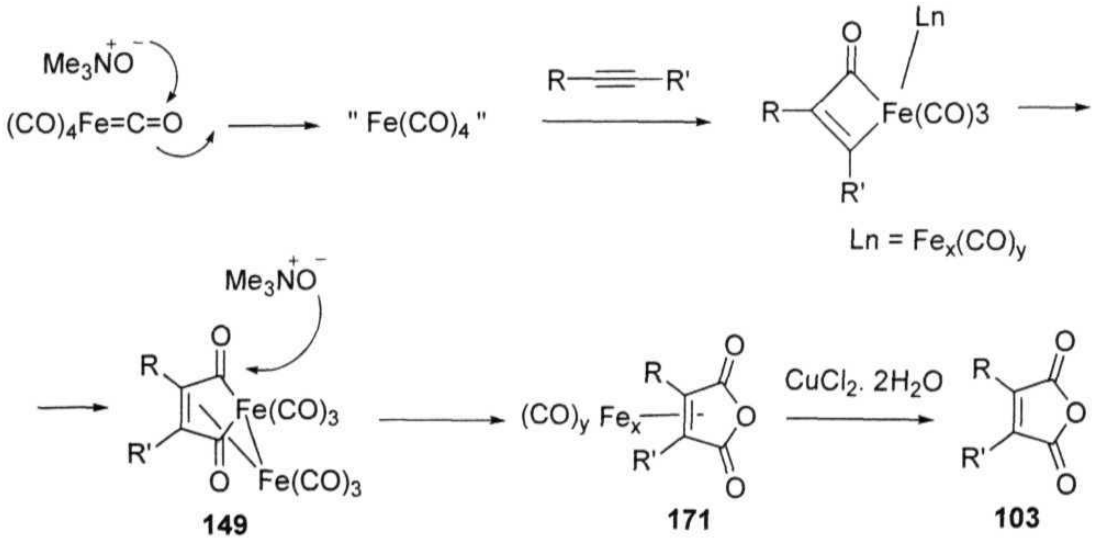


104

--- Eq. 115

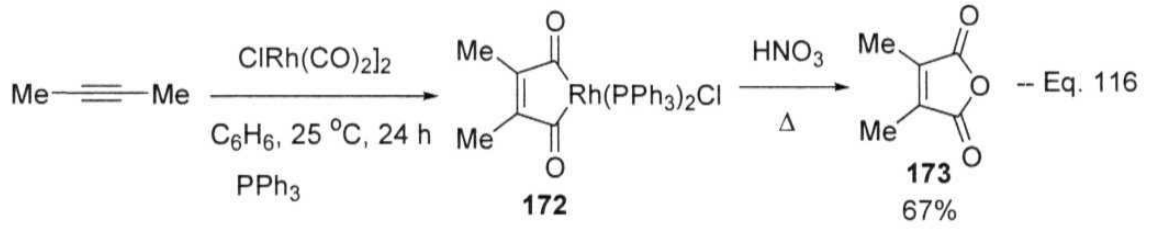
Presumably, the cyclic anhydrides are formed by the oxidation of iron carbonyl intermediates as outlined in **Scheme 46**. The maleoyl complexes **149** may undergo oxidative 'O' insertion in the presence of unreacted Me_3N-O, which upon further oxidation with $CuCl_2$. $2H_2O$ generates the corresponding maleic anhydride derivatives.

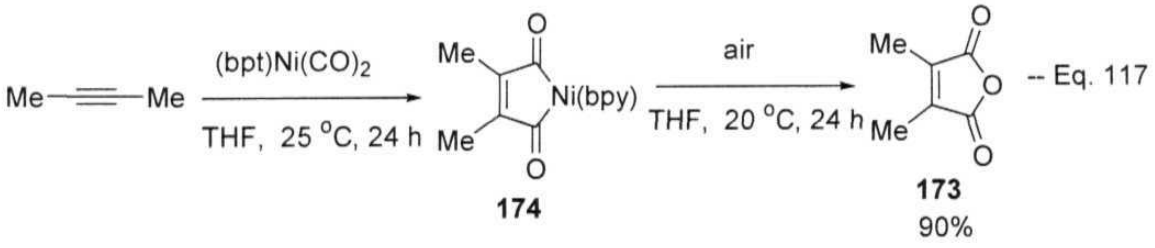
Scheme 46



149 **171** **103**

Previously, *Maitlis et al.* [187] observed that the rhodium maleoyl complexes (rhodacyclo-pentenedione) prepared using alkynes and rhodium carbonyl undergo oxidation by HNO_3 to give maleic anhydride derivatives (eq. 116). Later, *Hoberg et al.*[35,188] reported that analogous nickel complexes can be oxidized by air to give high yields of maleic anhydride (eq. 117). Accordingly, the steps outlined in **Scheme 46** for the formation of anhydrides by the oxidation of the maleoyl iron carbonyl complexes are not unreasonable.



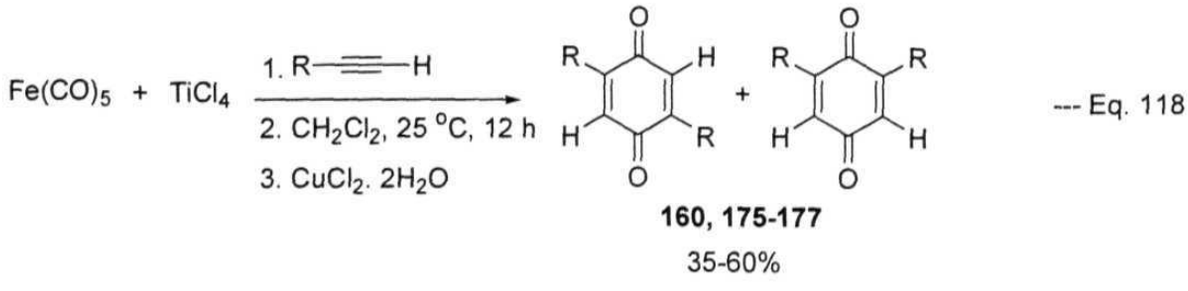


In conclusion, the present method of preparation of coordinatively unsaturated iron carbonyl species for the synthesis of cyclobutenediones has advantages over the hitherto known methods. The Me_3NO is a mild, efficient oxidizing agent and tolerant towards oxidation sensitive electron rich moieties. Since the trimethylamine *N*-oxide is transformed into the volatile trimethylamine, it does not interfere with the isolation of the products.

2.3 Reaction of Alkynes with the $Fe(CO)_5/TiCl_4$ Reagent System

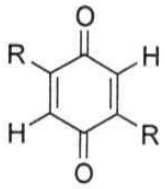
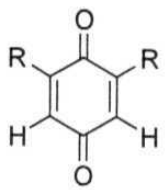
Previous reports reveal that some transition metal halides, CoX_2, NiX_2 and PdX_2 (X = Cl, Br), are effective catalysts for the substitution of CO on $Fe(CO)_5$ by isonitrile to yield a range of complexes of the type $Fe(CO)_{5-n}(NCR)_n$ (n = 1-5).[189-191] Also, it has been reported that addition of $TiCl_4$ to $(CO)_5W = C(OEt)C_4H_9$ brings about the slow evolution of one equivalent of carbon monoxide.[192] Accordingly, we have made efforts to develop $TiCl_4$ induced preparation of coordinatively unsaturated iron carbonyl species for examining their reactions with alkynes.

Thus, we have carried out the reaction of alkynes with $Fe(CO)_5$ in the presence of $TiCl_4$ (eq. 118). Addition of titanium tetrachloride to a light yellow solution of $Fe(CO)_5$ in DCM turns immediately to dark brown solution indicating the presence of polynuclear unsaturated ironcarbonyl species, which on reaction with alkynes at room temperature gave a mixture of benzoquinones after $CuCl_2.2H_2O$ oxidation.[169] Several 1-alkynes were converted to a mixture of 2,5- and 2,6-dialkylbenzoquinones (**Table 8**). Surprisingly, diphenylacetylene did not react under these conditions.



--- Eq. 118

Table 8. Reaction of Alkynes with the $Fe(CO)_5/TiCl_4$ Reagent System.

S. No.	Alkyne	Benzoquinones [a]		Yield[b] %
	R—≡—H	 **a**	 **b**	
1	$R = C_6H_5$	**160a**, 52%	**160b**, 48%	35
2	$R = C_5H_{11}$	**175a**, 60%	**175b**, 40%	60
3	$R = C_6H_{13}$	**176a**, 65%	**176b**, 35%	55
4	$R = C_8H_{17}$	**177a**, 70%	**177b**, 30%	53

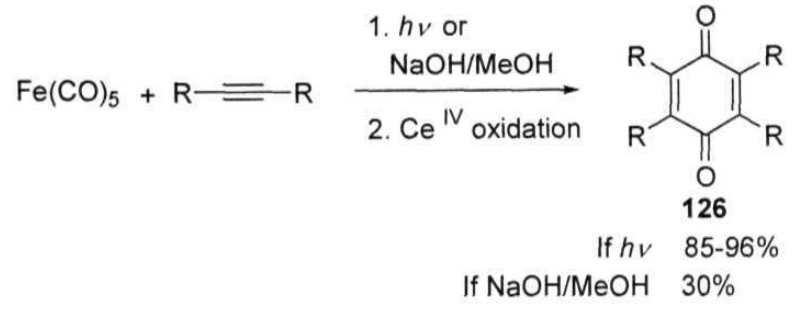
[a]Products were identified by the spectral data (IR, ^1H and ^{13}C NMR) and comparision with the reported data.[193]

[b]Yields are of the products isolated by column chromatography using hexane as eluent and based on the amount of 1-alkyne used.

[c]The percentage composition of isomers (a) and (b) were calculated from the ^1H NMR signal intensities of C=C<u>H</u> protons.

It has been reported that the reaction of $Fe(CO)_5$ with 1-alkynes under photolysis or in alkaline solution at high temperatures gives benzoquinones in moderate yields after oxidation (eq. 119).[193] The formation of benzoquinones was rationalized by considering the intermediacy of maleoyl complex **149**. Further, maleoyl complexes prepared from the

corresponding cyclobutenediones, were successfully converted to benzoquinones (eq. 120).[138]

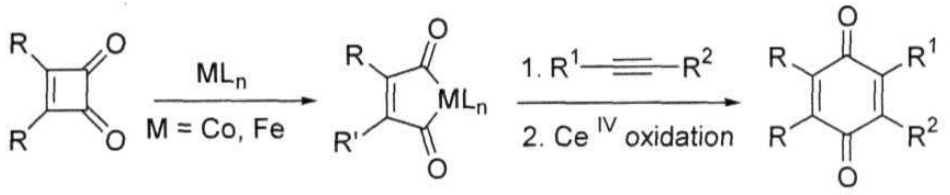


126

If $h\nu$ 85-96%

If NaOH/MeOH 30%

--- Eq. 119



126

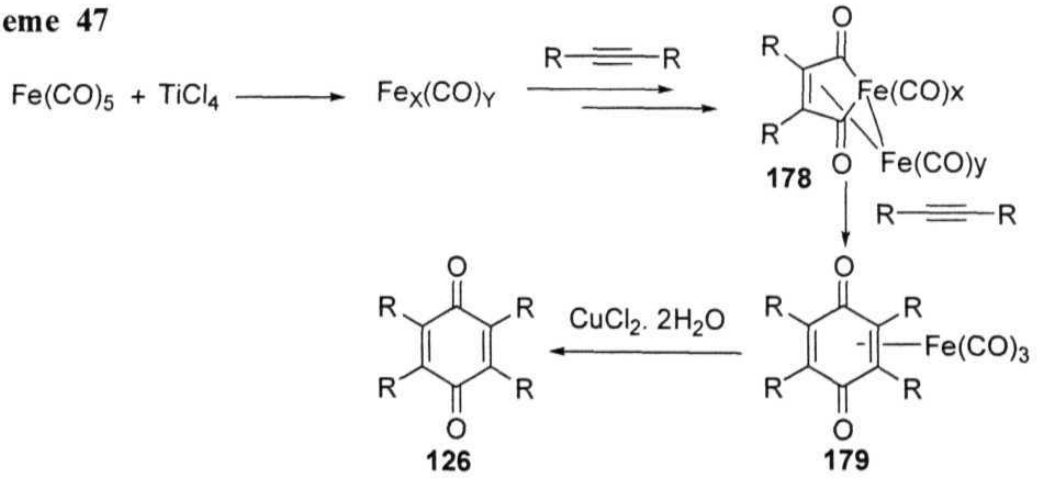
If M = Co 27-90%

If M = Fe 27-100%

--- Eq. 120

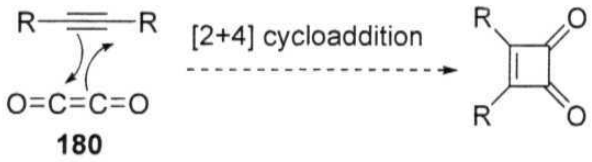
A similar type of species may be involved in the $TiCl_4$ promoted benzoquinone formation as shown in **Scheme 47**.

Scheme 47



2.4 Efforts Towards the Synthesis of Cyclobutenediones Using C_2O_2 Generated from CO and $TiCl_4$/Zn

The C_2O_2, ethyelenedione **180**, a dimer of CO is anticipated to be a potential double carbonylating agent. For instance, cycloaddition of alkynes with C_2O_2 would provide a direct method of synthesis of cyclobutenediones (eq. 121). There have been efforts in our laboratory and elsewhere to synthesize this long cherished elusive molecule.

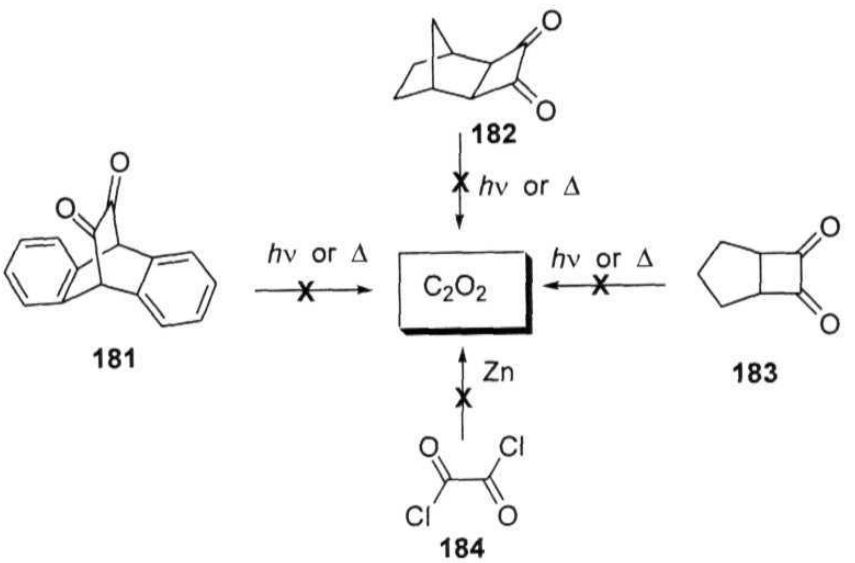


--- Eq. 121

It is not clear whether the repeated failures to prepare C_2O_2 are due to this molecule's inherent instability towards rapid dissociation to two molecules of CO or to the use of inappropriate synthetic methods. Theoretical studies predict that the C_2O_2 should exist as a triplet species in its ground state with linear structure.[194,195]

Attempts have been made to prepare C_2O_2 from organic substrates with CO-CO group (**Scheme 48**). So far this approach has not been successful for the preparation of C_2O_2.[196] However, *Strating* and coworkers reported the presence of a peak in the mass spectrum at m/e = 56, which corresponds to $C_2O_2^+$, when the compound **181** is subjected to either pyrolysis or photolysis.[197] A disadvantage of these methods is that the starting materials themselves require multiple step preparations and hence, even if the C_2O_2 is obtained as a reactive intermediate in these cases, it will not be useful for synthetic applications.

Scheme 48

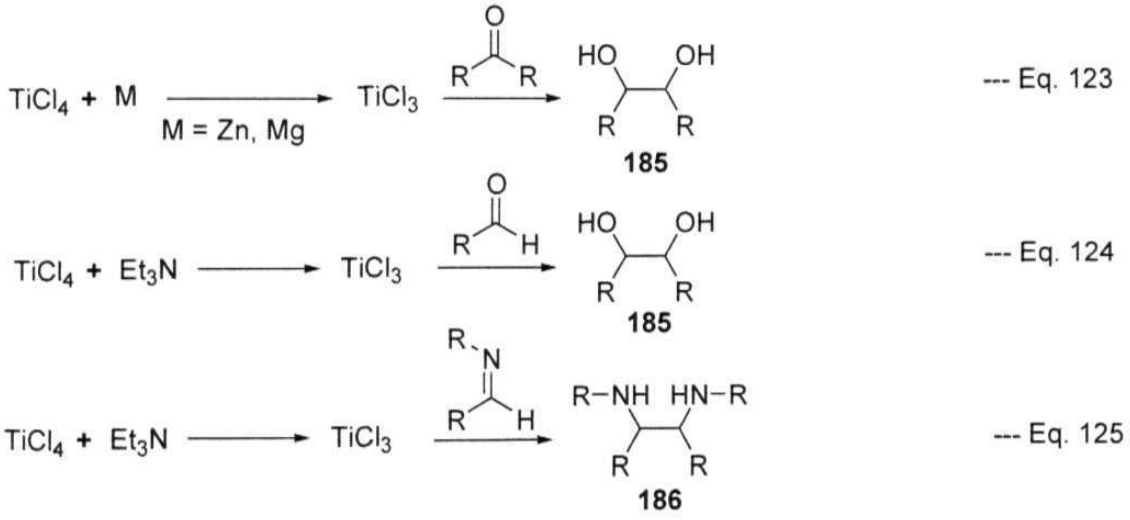


Another approach to get C_2O_2 is to dimerise CO. Since there is back donation of electrons from the oxygen of the CO to the carbene form of CO, it cannot dimerise to C_2O_2. However, the $CO^{\cdot-}$ species can be readily dimerised to give $C_2O_2^{-2}$. Accordingly, oxidation of $C_2O_2^{-2}$ with an appropriate reagent can be visualized to obtain C_2O_2 (eq. 122).

$$CO \xrightarrow[\text{Liq. } NH_3]{\text{Na or K}} 2\,CO^{\cdot-} \longrightarrow \bar{O}\text{-}C{\equiv}C\text{-}\bar{O} \xrightarrow{-2e} O{=}C{=}C{=}O \qquad \text{--- Eq. 122}$$

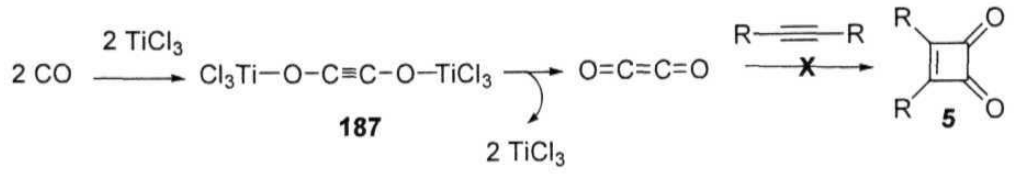
The $C_2O_2^{-2}$ has been prepared by reduction of CO with alkali metals in liquid ammonia (eq. 122).[198] Reduction of CO by potassium in liquid ammonia is not convenient as it gives the explosive adduct $K_2C_2O_2$. Moreover, the presence of traces of NH_3 could create complications in the reaction of $C_2O_2^{-2}$ with electrophiles. Further, the use of liquid NH_3 requires very low temperature, making this process synthetically not very attractive.

Therefore, we decided to examine the use of $TiCl_3$ as reducing agent to prepare C_2O_2 by reductive coupling of carbon monoxide. The low valent titanium species, $TiCl_3$, has exceptional reducing ability and hence widely applied in organic synthesis. The $TiCl_3$ has been generated from $TiCl_4$/metal or metal hydrides. [200] McMurry type coupling of carbonyl compounds is one of the well-exploited reactions of $TiCl_3$ chemistry (eq. 123).[200] Recently, it was observed in our laboratory that low valent titanium species generated from $TiCl_4/Et_3N$ can be used for reductive coupling of aldehydes and imines (eq. 124 and 125).[201]

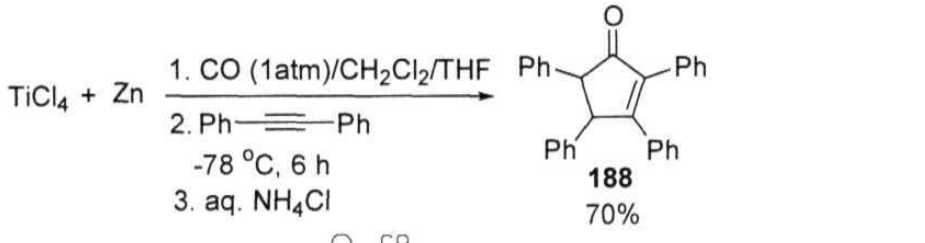


We expected a similar reaction of $TiCl_3$ with CO. In order to examine this possibility, we have carried out the reduction of CO with $TiCl_3$ generated *in situ* from $TiCl_4$ and Zn in the presence of alkyne at –78 °C (**Scheme 49**).

Scheme 49



Unfortunately, the expected cyclobutenedione was not formed. Instead, the corresponding cyclopentenone (R=Ph **188**) was obtained in good yield (eq. 126). Though the formation of a carbonylative cyclization product is not totally unexpected,[202] reduction of one of the double bonds is interesting.



--- Eq. 126

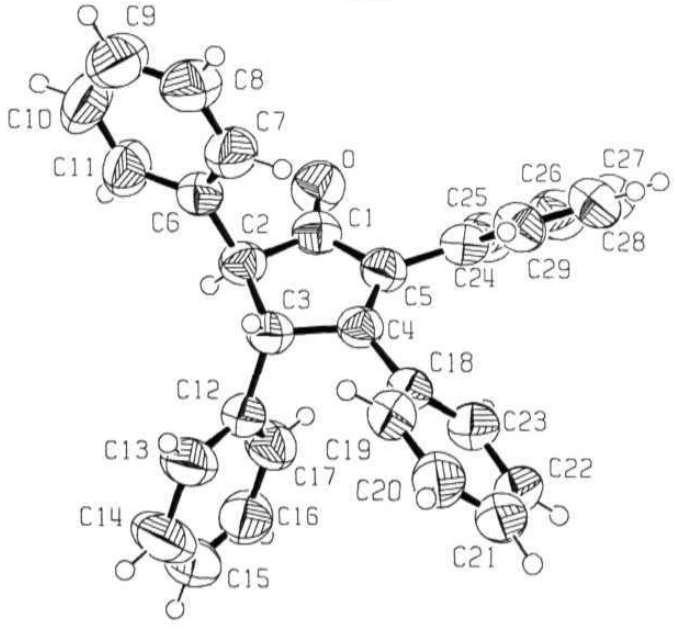
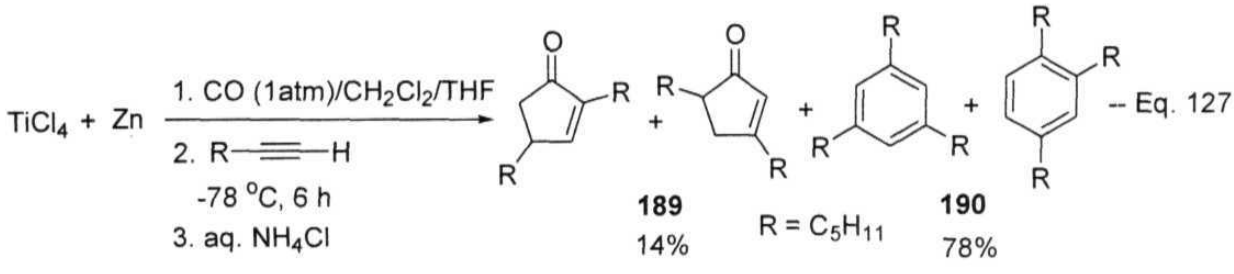


Fig 2. ORTEP Diagram of 2,3,4,5-Tetraphenyl-2-cyclopentenone 188

Table 9. X-ray Data Collection and Structure Refinement for 188

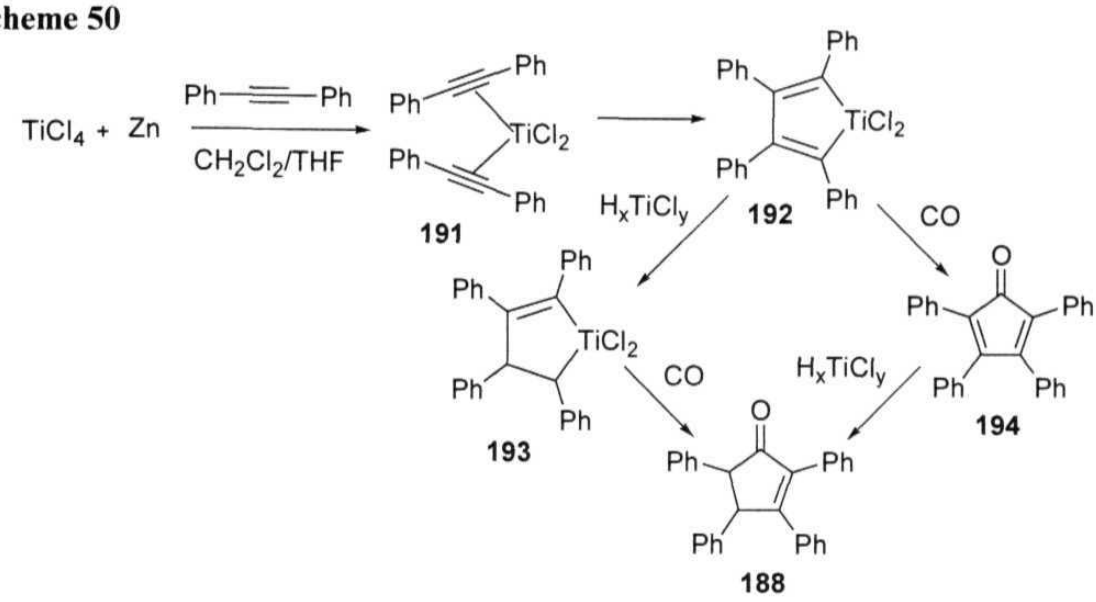
Empirical formula	$C_{29}H_{22}O$
Fw	386.47
Temp., wavelength	293(2), 0.71073 Å
Cryst. system	trigonal
Space group	R-3:h [IT-148]
Unit cell dimensions	a=23.9496(12) Å, α=90°
	b=23.9496(12) Å, β=113.17° (2)
	c=20.839(2) Å, γ =120°
Volume	10351.3(13) $Å^3$
Z, calcd. density	18, 1.116 mg/m^3
Abs. coeff.	0.066 mm^{-1}
F(000)	3672
Cryst. size	0.43×0.30×0.24 mm
θ range for data collection	1.70 to 28.29
Limiting indices	-23<=h<=31, -31<=k<=22, -27<=l<=27
Reflns. collected, unique	22194 / 5554 [R(int) = 0.0416]
Refinement method	full-matrix least-square on F^2
Data/restraints/params	5554 / 0 / 272
Goodness-of-fit on F^2	0.905
Final *R* indices[I> 2σ (I)]	R_1 = 0.0825, wR_2 = 0.2411
R indices (all data)	R_1 = 0.1479, wR_2 = 0.2819
Extinct. coeff.	0.00025(19)
Largest diff. peak and hole	0.305 and -0.202 e. $Å^{-3}$

As the present reaction seems to be convenient for the synthesis of cylopentenones, an important class of molecules, we have examined the generality of this transformation. It has been observed that the reaction of 1-heptyne under the same conditions gave the corresponding 1,3,5-and 1,2,4-trisubstituted benzenes as major products along with a mixture of cyclopentenones in lower yields (14%) (eq.127).



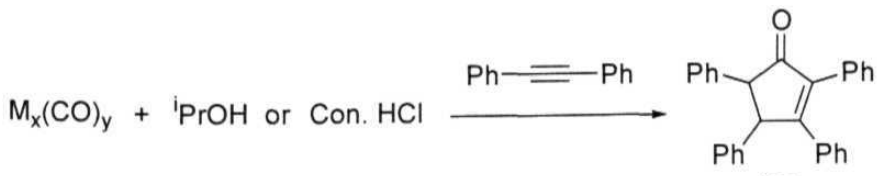
Presumably, the low valent titanium species (Ti^{+2} or Ti^{+3}) reacts with alkynes to form a dialkyne complex. Oxidative coupling of dialkyne complex gives the coordinatively unsaturated metallacyclopentadiene **192**. Previously, such complexes were prepared using a variety of organometallic reagents.[207] The complex **192** could undergo CO insertion either before or after the reduction of one of the double bonds. Presumably, the hydrido titanium species formed in the reaction of low valent titanium with THF may reduce the double bond.[204, 205] Finally, the reductive elimination of titanium complexes affords cyclopentenone (**Scheme 50**). In the absence of CO or with terminal alkynes where the acetylenic bond is less crowded, trimerization is the dominant reaction.

Scheme 50



We have anticipated that the reduction of $TiCl_4$ by Zn would give $TiCl_3$ which in turn would reduce CO to **187**. Presumably, in the presence of alkynes, the reduction follows a different course leading to the complexes of the type **191** and **192**.

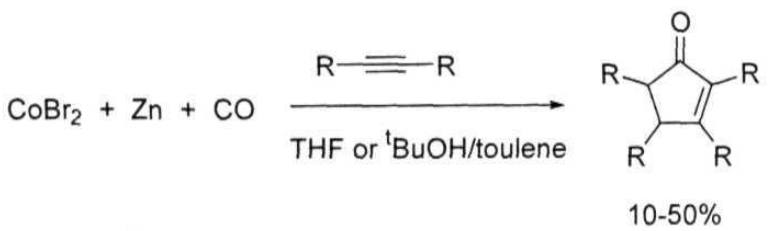
Previously, a similar transformation has been reported in the reaction of metal carbonyls with diphenylacetylene in the presence of either HCl or *i*-propanol (eq.128).[203] The H_2, generated from acid and metal carbonyl, is believed to be responsible for the reduction of one of the double bonds.



-- Eq. 128

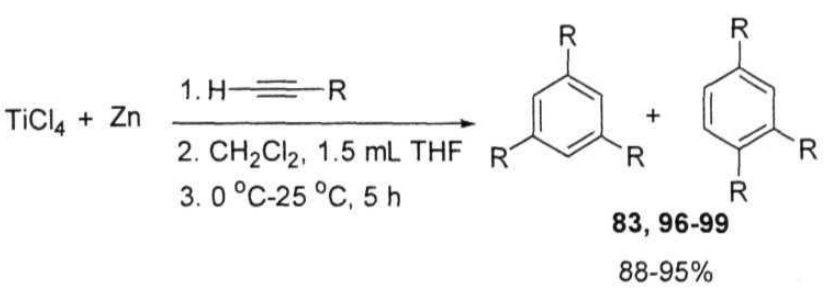
$M_x(CO)_y$ =		
	$Rh_4(CO)_{12}$	42%
	$Co_4(CO)_{12}$	41%
	$Ir_4(CO)_{12}$	9%
	$Ni(CO)_4$	37%

Also, it was observed in this laboratory that alkyne-cobalt complexes prepared using $CoBr_2$/Zn/alkyne under CO atmosphere give corresponding cyclopentenones in the presence of THF or ^{t}BuOH (eq. 129).[204, 205]



--- Eq. 129

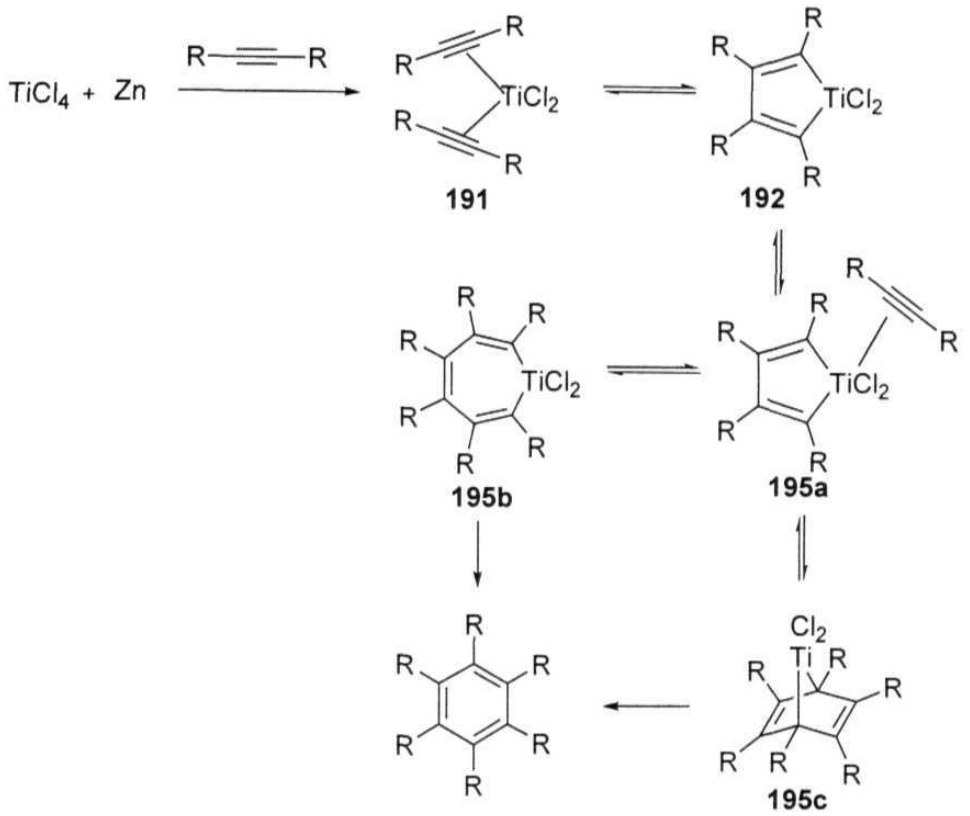
We have also examined the reaction of terminal alkynes with low valent titanium (LVT) at room temperature in the absence of carbon monoxide. In this case, the trimerised product has been obtained in good yields (eq. 130). Several 1-alkynes were transformed to the corresponding trisubstituted benzenes (**Table 10**).



-- Eq. 130

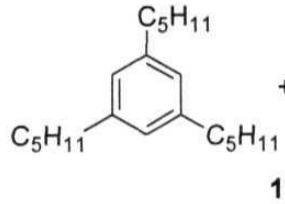
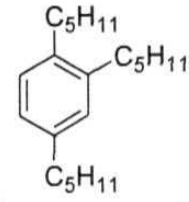
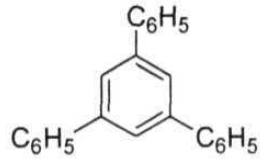
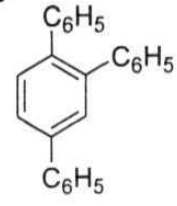
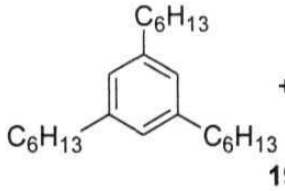
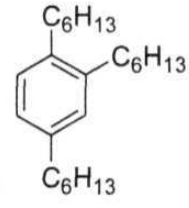
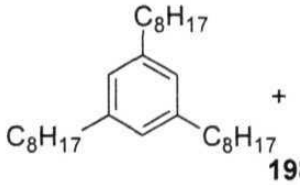
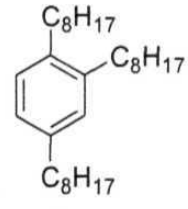
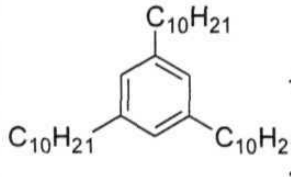
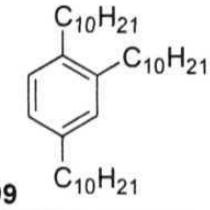
The formation of substituted benzenes can be explained following the mechanism reported previously for metal-catalyzed acetylene cyclotrimerizations as illustrated in **Scheme 51**.[207a-207c]

Scheme 51



Initially, two alkyne moieties could displace two ligands on the metal to a form dialkyne complex **191**. Oxidative coupling of dialkyne complex would give the coordinatively unsaturated metallacyclopentadiene **192**. Complexation of a third molecule of the alkyne followed by its insertion would lead to the formation of metallacycloheptatriene **195b** or Diels-Alder type product **195c**, which could undergo reductive elimination of the metal complex moiety to furnish the aromatic product.

Table 10. Reaction of Alkynes with the $TiCl_4$/Zn Reagent System

S. No.	Alkyne	Product[a] 1, 3, 5-substituted **A**	1, 2, 4-substituted **B**	Yield[b] %
1	C_5H_{11}—≡—H	 **190**		95
2	C_6H_5—≡—H	 **196**		88
3	C_6H_{13}—≡—H	 **197**		95
4	C_8H_{17}—≡—H	 **198**		92
5	$C_{10}H_{21}$—≡—H	 **199**		87

[a]Products were identified by the spectral data (IR, ^1H, ^{13}C NMR, NMR and Mass) and comparision with the reported data.[208]

[b]Yields are of the isolated products and based on the amount of alkyne used.

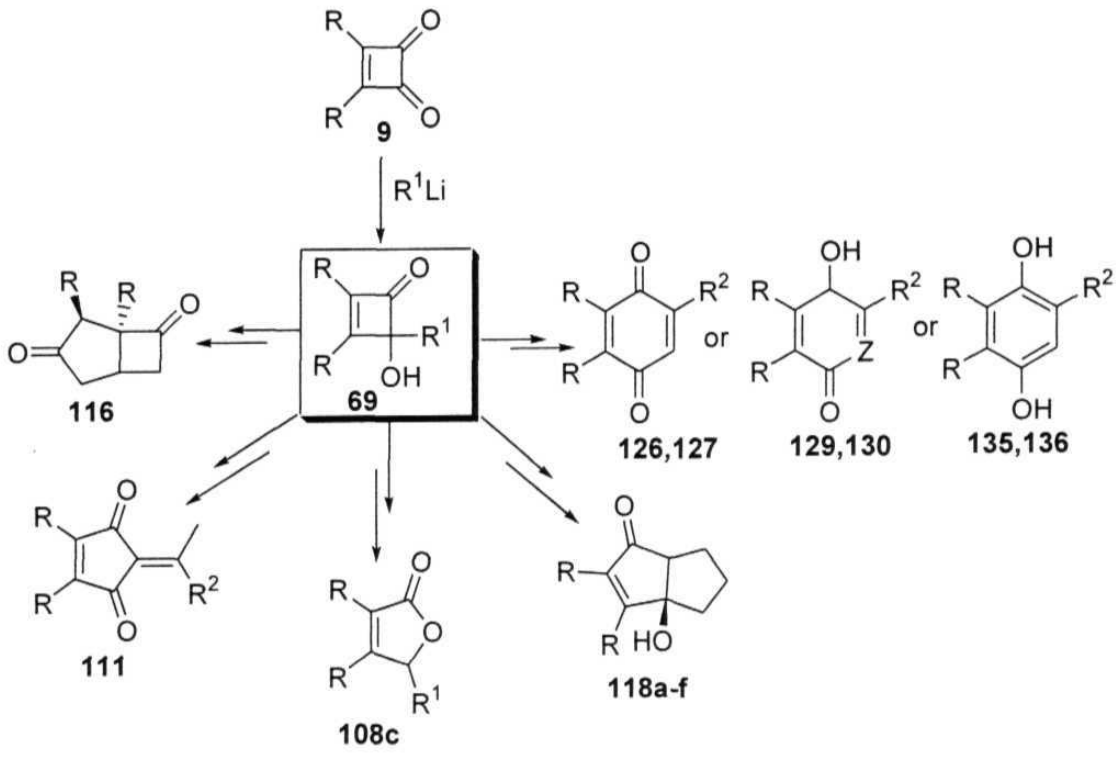
Various titanium[206] and other transition metal complexes[207] are known to promote acetylene cyclotrimerisation. Low chemo- and regio-selectivity of cyclotrimerisation lead to complex mixtures of products, which severely limits the synthetic utility of cyclotrimerisation in general and intermolecular cyclotrimerisation in particular. Recently, a few efficient catalysts were developed for selective cyclotrimerisation of acetylenes.[207b] However, new catalysts are still valuable to expand scope of the reaction.

2.5 Synthetic Applications of Cyclobutenediones

2.5.1 $TiCl_4$ Promoted Aldol Reaction of Ketones with Cyclobutenediones

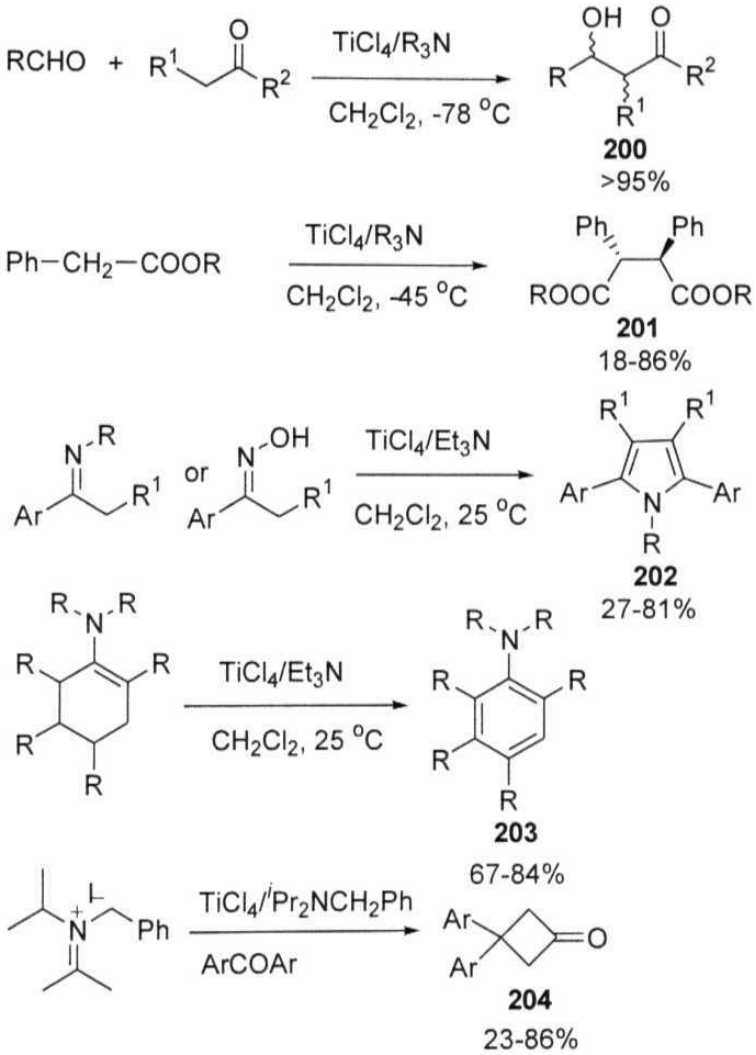
Extensive studies over last two decades, primarily by *Liebeskind, Moore* and *Paquette*, illustrated that the 4-subsituted-4-hydroxycyclobutenones **69**, are versatile C_4 synthons useful for the synthesis of highly functionalised carbocyclic compounds (**Scheme 52**).[14] The general strategy adopted for the synthesis of **69** involves addition of alkyllithium reagents to cyclobutenediones. We have made efforts to develop simple, convenient methods of preparation of 4-hydroxy-cyclobutenones using organotitanium reagents.

Scheme 52

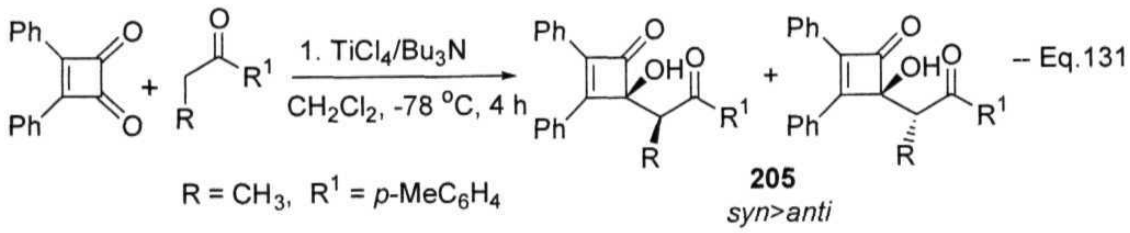


Recent reports illustrate the versatile reactivity pattern of the $TiCl_4/R_3N$ reagent system (**Chart 1**).[209-212] These reactions involve deprotonation of the organic substrates to yield the corresponding titanium species in a crucial step. We have decided to examine the reaction of the organotitanium species produced in this way with cyclobutenediones.

Chart 1



Accordingly, we have carried out the reaction of titanium enolates, generated *in situ* using ketones and $TiCl_4/Bu_3N$ at –78 °C, with cyclobutenediones, and found that the corresponding 4-hydroxy-4-alkyl-2-cyclobutenones are formed in good yields (eq. 131). The titanium enolates of acyclic ketones react with cyclobutenediones to give the corresponding 4-hydroxy-4-alkyl-2-cyclobutenones with *syn* selectivity, in accordance with the Lewis acid promoted aldol reactions.



The relative stereochemistry at the newly formed chiral centers of the alcohol **205** was confirmed by single crystal X-ray analysis (Fig.3). The OH (O2) and CH_3 (C25) are *syn* to each other.

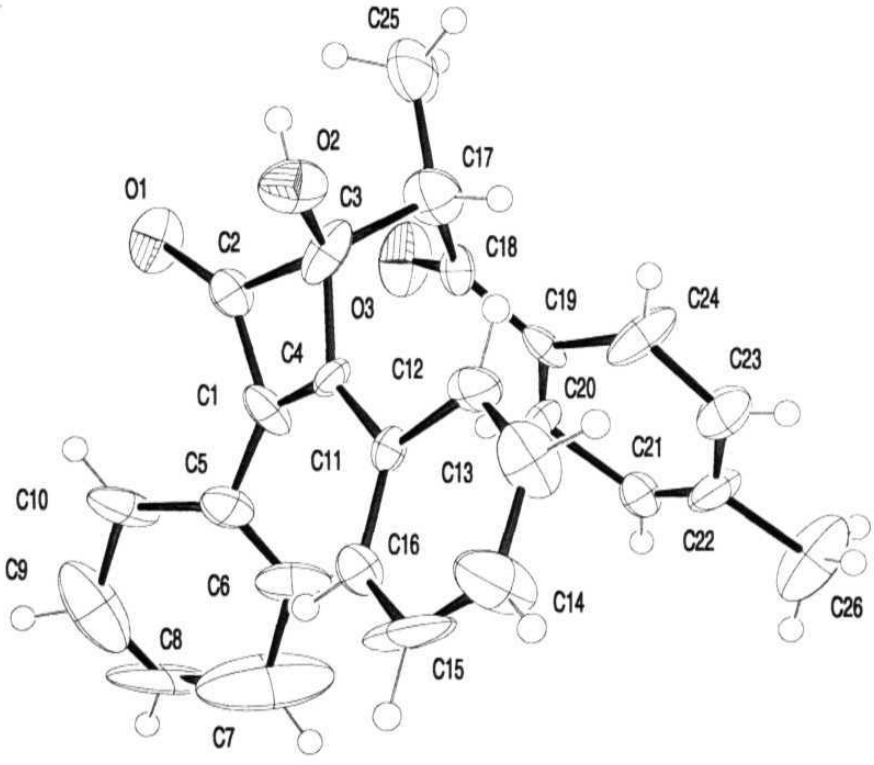


Fig. 3 ORTEP Diagram of Aldol Adduct 205

The stereochemical outcome of the major diastereomer obtained in the above aldol reaction (eq.131) may be rationalized by considering the cyclic six membered transition

state models (**Scheme 53**). It is well documented that acyclic ketones give *Z*-enolates under the kinetic conditions employed in these reactions.[211-212] Assuming that the Ar group of enolate occupies equatorial position, the geometry of *Z*-enolate would require the CH_3 group to be axial. In the transition state, **TS1**, phenyl substituted carbon of the cyclobutenedione is expected to be in equatorial position and the second carbonyl of the cyclobutenedione moiety would occupy the equatorial position and stabilized by further coordination with titanium. Whereas in the transition state, **TS2**, the phenyl substituted carbon would take an axial position leading to severe 1,3 diaxial repulsions and there will not be any CO-Ti coordination in this transition state. Hence, the **TS1** is expected to be preferred over the **TS2** leading to the formation of *syn* diastereomer as the major product.

Scheme 53. Six membered transition state model

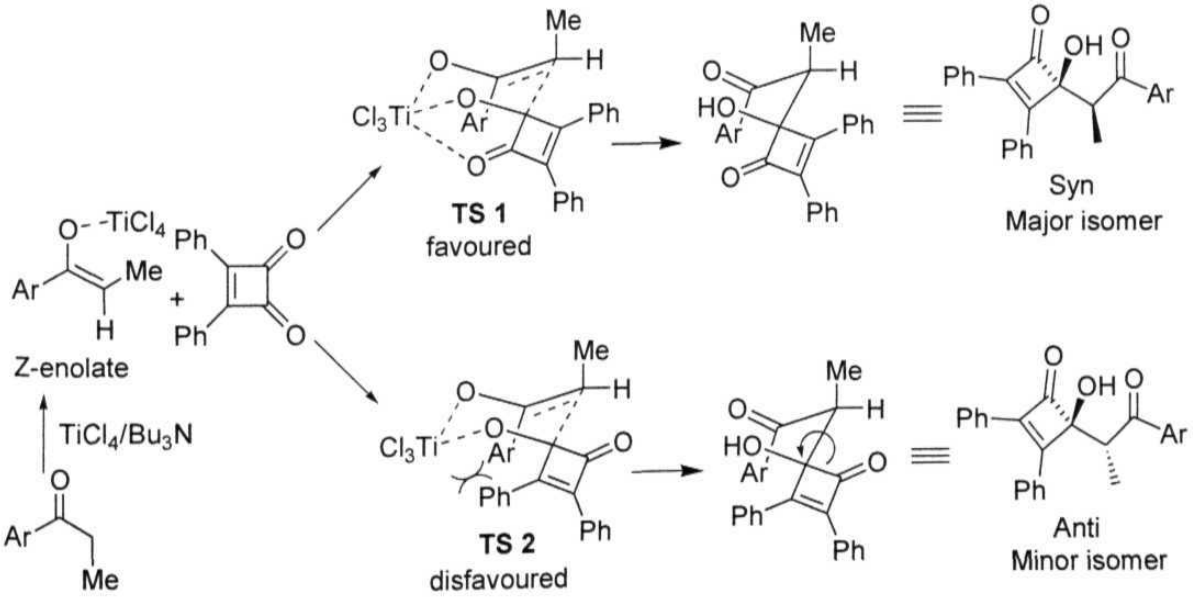
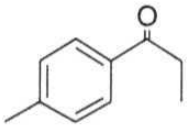
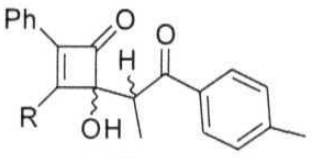
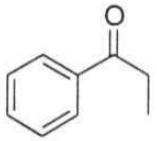
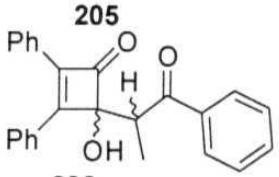
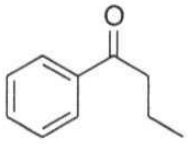
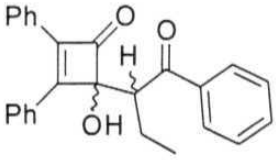
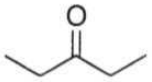
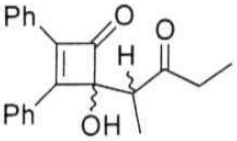
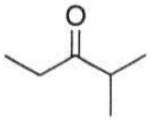
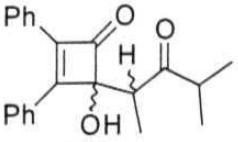


Table 11. X-ray Data Collection and Structure Refinement for 205

Empirical formula	$C_{26}H_{22}O_3$
Fw	382.44
Temp., wavelength	293(2), 0.71073 Å
Cryst. syst., space group	monoclinic, P21/c:b1 [IT no:14]
Unit cell dimensions	a=17.5948(10) Å, α=90°
	b=11.5693(7) Å, β=103.8260° (10)
	c=20.8120(12) Å, γ =90°
Volume	4113.7(4) $Å^3$
Z, calcd. density	8, 1.235 mg/m^3
Abs. coeff.	0.080 mm^{-1}
F(000)	1616
Cryst. size	0.38 X 0.42 X 0.28 mm
θ range for data collection	2.02 to 28.26 °
Limiting indices	-23<=h<=23, -15<=k<=15, -27<=l<=27
Reflns. collected, unique	47261 / 9861 [R(int) = 0.0685]
Refinement method	full-matrix least-square on F^2
Data/restraints/params	9861/0/529
Goodness-of-fit on F^2	0.968
Final *R* indices[I> 2σ (I)]	R_1 = 0.0492, wR_2 = 0.1298
R indices (all data)	R_1 = 0.0967, wR_2 = 0.1477
Largest diff. peak and hole	0.191 and -0.197 e. $Å^{-3}$

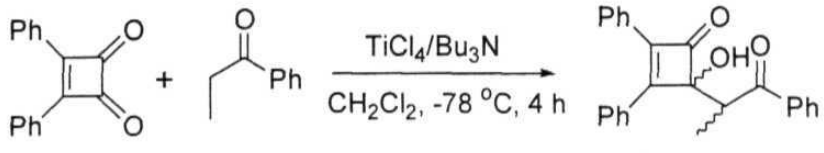
It was found that the Bu_3N successfully promotes aldol reaction between various acyclic ketones and cyclobutenediones (**Table 12**). The relative configuration of the major diastereomers of aldol adducts **206-209** were assigned as "*syn*" by comparision of the spectral data with that obtained for compound **205**.

Table 12. $TiCl_4/Bu_3N$ Promoted Reaction of Acyclic Ketones with Cyclobutenediones

S. No.	Ketone	Aldol adduct[a]	Yield[b]	syn:anti[c]
1		 **205**	89	88:12
2		 **206**	94	90:10
3		 **207**	82	85:15
4		 **208**	86	85:15
5		 **209**	83	68:32

[a]Products were identified by IR, ^1H NMR, ^{13}C NMR, Mass Spectral data and CHN analysis.
[b]Yields are of the isolated products and based on the amount of cyclobutenedione used.
[c]*syn:anti* ratios were determined by the ratios of ^{13}C NMR intensities of the tertiary alcoholic carbon. Stereochemistry of **205** was assigned as *syn* by X-ray structure analysis.

We have examined the use of other amine bases like Et_3N, *i*-Pr_2NEt and TMEDA for the aldol reaction of propiophenone with diphenylcyclobutenedione. Whereas the use of *i*-Pr_2NEt in this transformation gave the products in 48% yield, Et_3N and TMEDA gave much lower yields (10%) (eq. 132). The higher yields realized in the case of Bu_3N may be due to the fact that it forms a loose and reversible complex with $TiCl_4$ and hence would smoothly generate enolates.[212a] On the other hand, the Et_3N and TMEDA would form stable complex with $TiCl_4$ and hence the enolate formation would not be efficient.[212b]



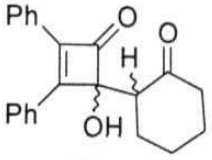
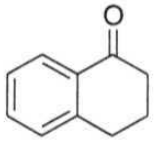
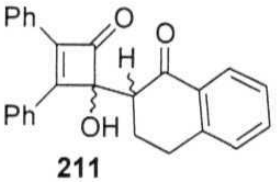
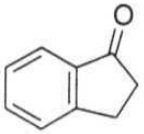
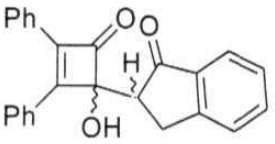
--- Eq. 132

206
syn>anti

R_3N	yield
Et_3N	10%
i-Pr_2NEt	48%
TMEDA	10%
Bu_3N	94%

We have also examined this transformation by using some representative cyclic ketones (**Table 13**).

Table 13. $TiCl_4/Bu_3N$ Promoted Reaction of Cyclic Ketones with Cyclobutenediones

S. No.	Ketone	Aldol adduct[a]	Yield[b] %	Diastereomeric ratio[c]
1		 **210**	85	82:18
2		 **211**	93	92:8
3		 **212**	85	69:31

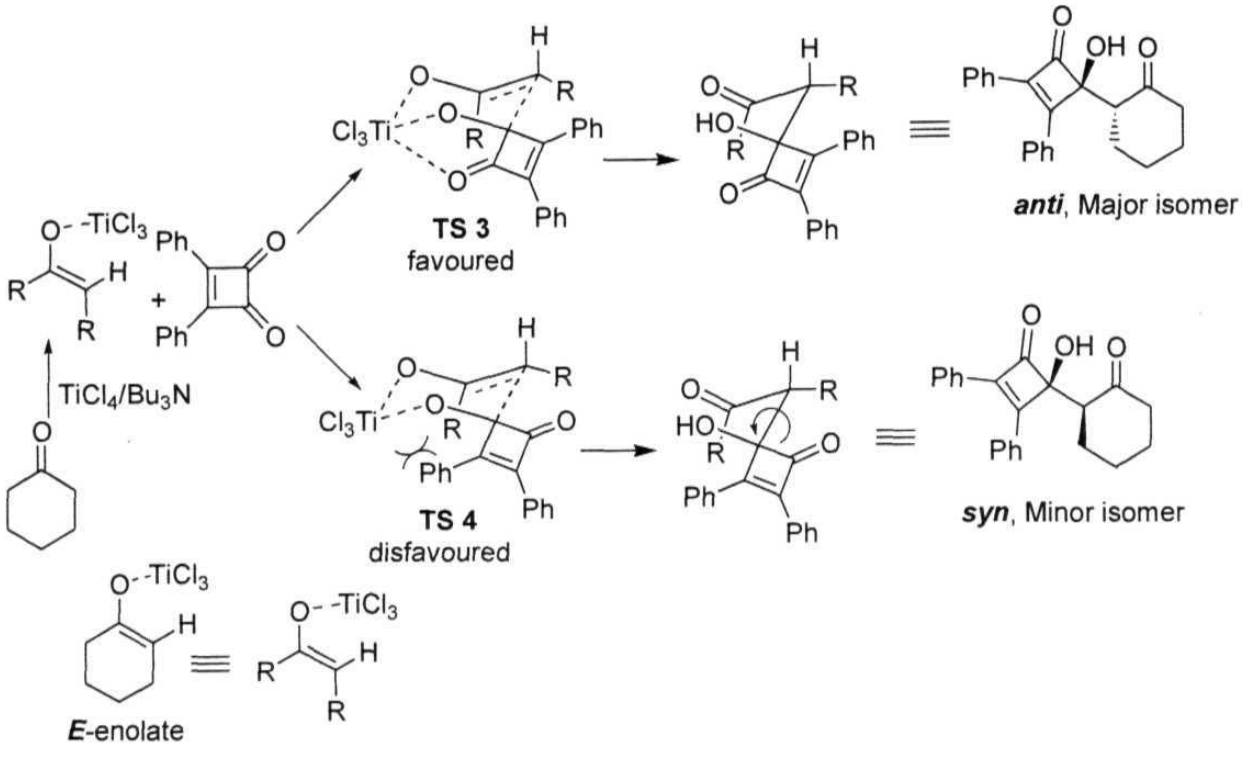
[a]Products were identified by IR, ^{1}H NMR, ^{13}C NMR, Mass Spectral data and CHN analysis.

[b]Yields are of the isolated products and based on the amount of cyclobutenedione used.

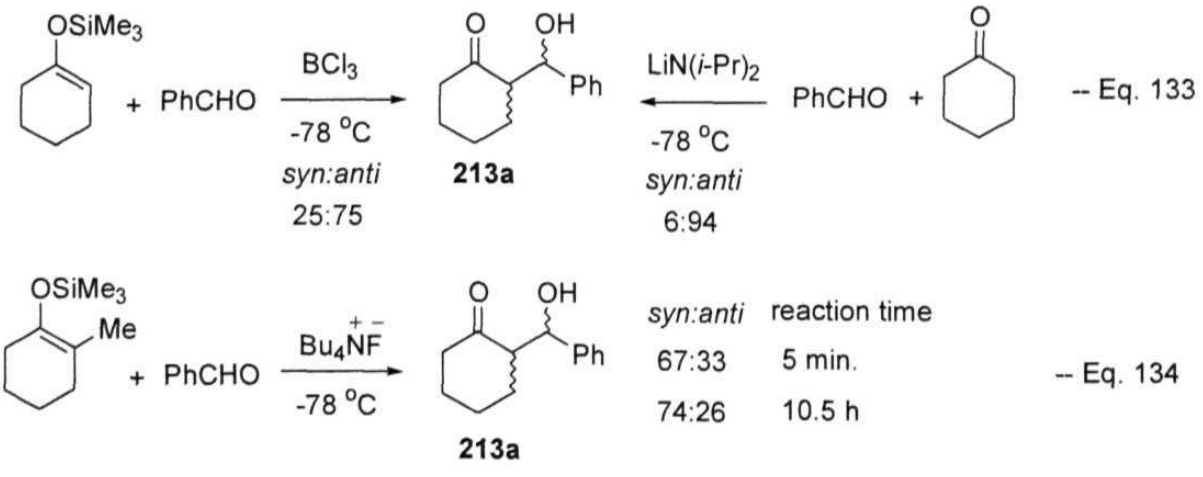
[c]Diastereomeric ratios were determined by the ratios of ^{13}C NMR intensities of the tertiary alcoholic carbon.

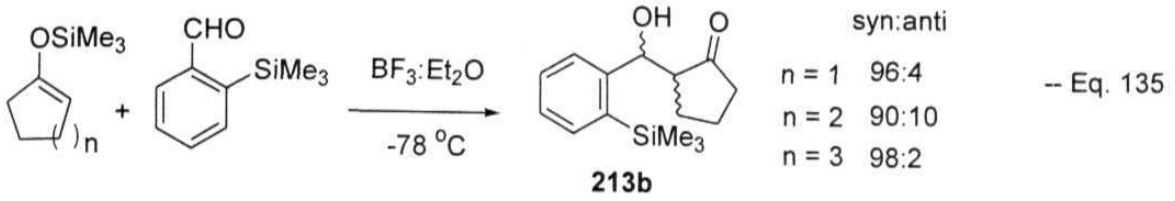
The major diastereomer in these reactions would be most probably the "*anti*" isomer because the *E*-enolates would be formed from cyclic ketones (**TS3**, **Scheme 54**). Both the substituents of the *E*-enolate would be expected to adopt equatorial position and the phenyl substituted carbon of the cyclobutenedione would also occupy the equatorial position in the favoured transition state **TS3**.

Scheme 54. Six membered transition state model



Generally, cyclic ketones give *anti* aldols *via E*-enolates (eq. 133).[213] However, in some cases *syn* aldol adducts were obtained as major products even with cyclic ketones (eqs. 134 and 135).[214]



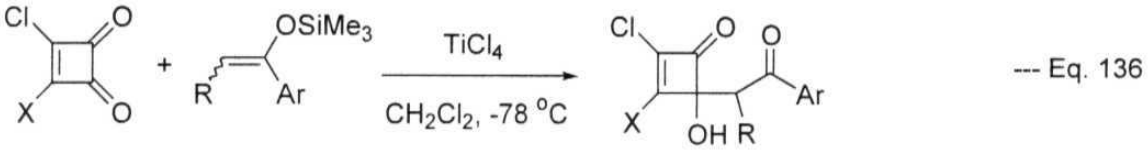


213b

-- Eq. 135

Hence, the stereochemistry of the products **210-212** needs to be further confirmed by single crystal X-ray analysis.

Previously, analogous 4-hydroxycyclobutenones have been synthesized by titanium mediated addition of silylenol ethers to chlorocyclobutenediones (eq. 136).[215a-c] However, the distereomeric ratio and the relative stereochemistry of the products were not disclosed.



X = Cl, OMe
R = H, Me

214
8-86%

--- Eq. 136

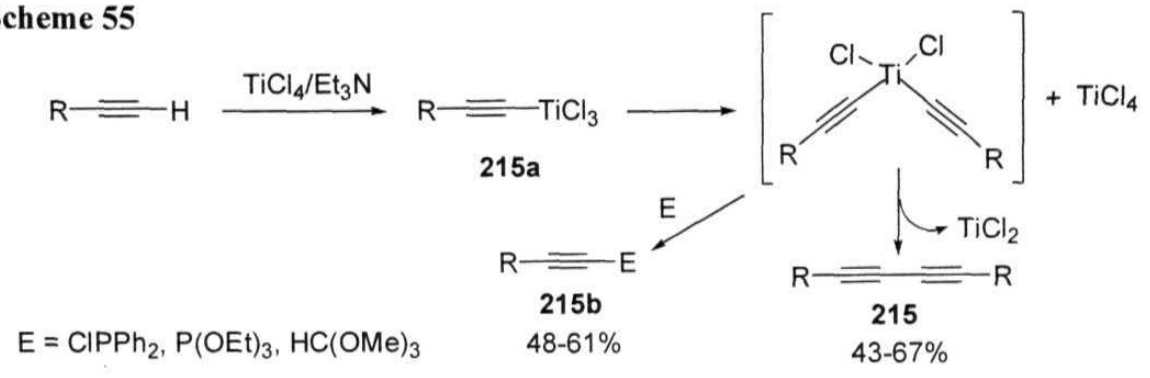
The present method has advantage since this facilitates the direct addition of ketones to cyclobutenediones.

2.5.2 Reaction of Alkynyltitanium Reagents with Cylobutenedione 9

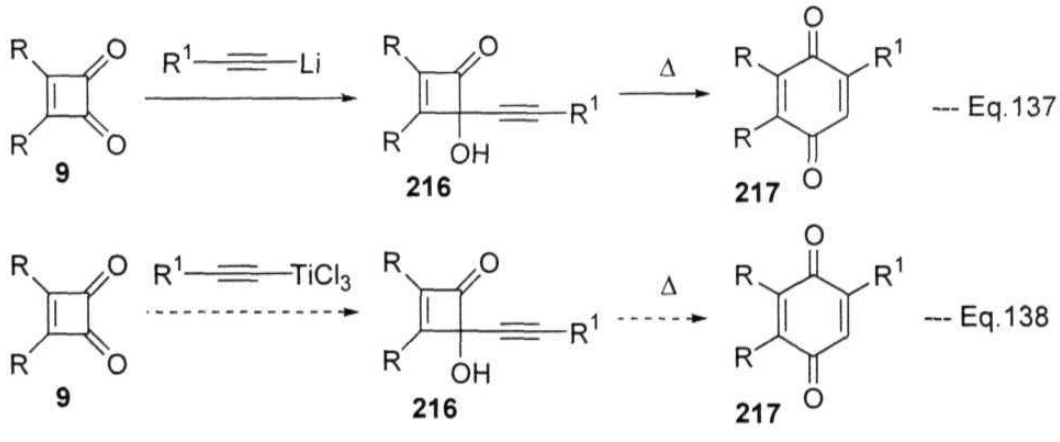
Recently, $TiCl_4/Et_3N$ reagent system was used for the direct metalation of organic compounds.[216] For example, the preparation of alkynyltitanium reagents **215a** has been achieved using 1-alkynes and the $TiCl_4/Et_3N$ reagent system without using other organometallic reagents such as RLi or RMgX.[216] These alkynyltitanium species readily undergo dimerization to give symmetrical 1,3-diynes **215** at room temperature in the

absence of electrophiles. Whereas the corresponding addition products are obtained in the presence of electrophiles (**Scheme 55**).

Scheme 55

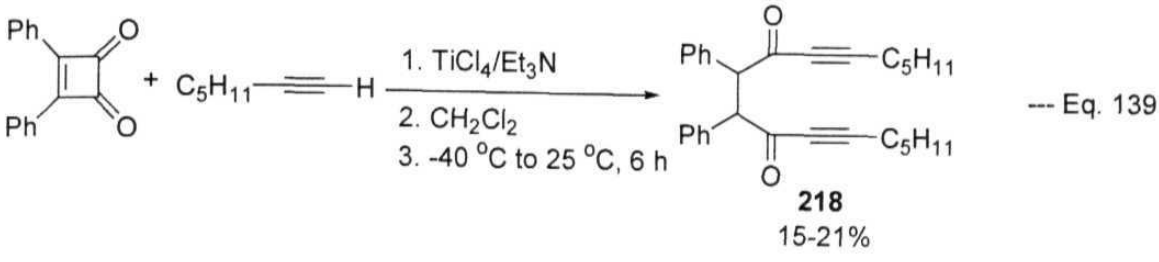


Previously, formation of quinones from cyclobutendiones was reported in the reaction of lithium reagents followed by rearrangement (eq. 137).[140-143] We have decided to examine this transformation using $TiCl_4/Et_3N$/1-alkyne reagent system (eq. 138).



Accordingly, we have carried out the reaction of alkynyltitanium reagents **215a**, prepared using 1-alkyne and the $TiCl_4/Et_3N$ reagent system, with diphenylcyclobutenedione at room temperature. We have obtained the corresponding diyne as major isolable product

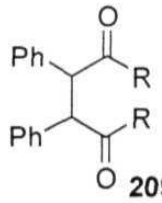
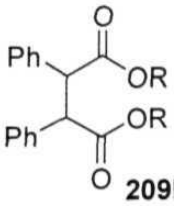
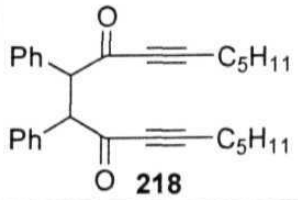
along with a mixture of unidentified products. However, when the reaction was performed at –40 °C, a *dl:meso* mixture of 1,8-dialkyl-4,5-diphenyl-1,7-octadiyne-3,6-diones **218** was isolated along with unreacted cyclobutenedione (eq 139).



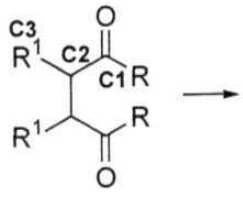
--- Eq. 139

Previously, a few of this class of compounds have been reported[217] but the relative stereochemistry in these compounds was not assigned. We have identified the major diastereomer formed in the above reaction (eq. 139) as the *dl* isomer by comparison with the ^{1}H NMR data reported for the related molecules (**Table 14**).[218,219]

Table 14

 **209a**	R = Me	*dl* 4.41 (s, 2H) *meso* 4.63 (s, 2H)
	R = Ph	*dl* 5.4 0 (s, 2H) *meso* 5.78 (s, 2H)
 **209b**	R = Me	*dl* 4.25 (s, 2H) *meso* 4.40 (s, 2H)
	R = Allyl	*dl* 4.33 (s, 2H) *meso* 4.47 (s, 2H)
 **218**		*dl* 4.57 (s, 2H) *meso* 4.77 (s, 2H)

Graham et al. proposed the following generalization to identify *dl/meso* isomers of 3,4-disubstituted-1,4-diones based on ^{13}C NMR chemical shifts.[220] In *meso* derivatives, (**Fig.4**) the carbonyl groups are gauche to methyl (R^1), but in the *dl* isomer carbonyl groups are gauche to each other. The alkyl group would exert greater shielding than does the carbonyl group. Hence, the carbonyl carbon (C1) would be more shielded in the *meso* isomer and would appear at upfield. Whereas the C3 of R^1 would be more shielded in the *dl* isomer since the two R^1 groups are gauche to each other (**Fig. 5**). A similar pattern of chemical shift differences were observed for *dl:meso* isomers of compound **218** (**Table 15**) (**Spectra 38 and 39**). Accordingly, the relative stereochemistry of the major isomer of compounds **218-222** may be assigned as *dl*.



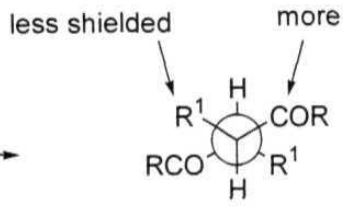


Fig. 4 *meso*

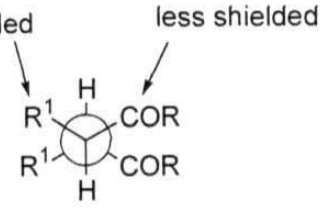
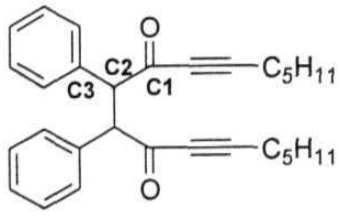


Fig. 5 *dl*

Table 15

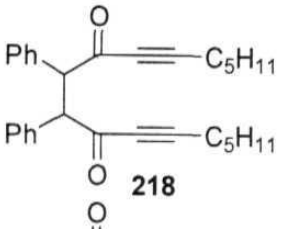
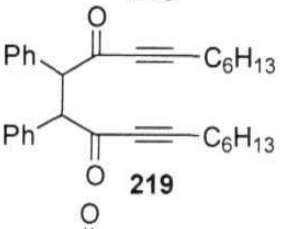
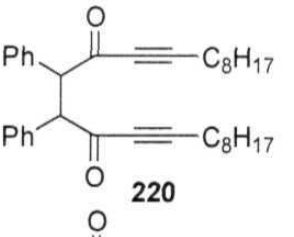
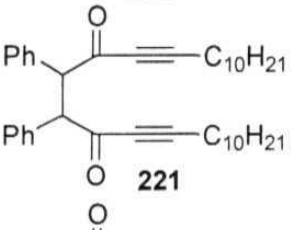
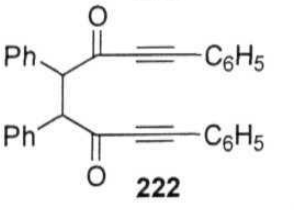


218

^{13}C NMR data of **218**	
meso	**dl**
C1 184.3	**C1** 185.6
C2 62.1	**C2** 62.7
C3 135.2	**C3** 134.7

Several 1-alkynes were employed in this reaction (**Table 16**). However, the yields are poor in these cases and the reactions are not clean under these conditions.

Table 16. Reaction of Cyclobutenedione with Alkyne/ $TiCl_4/Et_3N$

S. No.	Alkyne	Product[a]	Yield[b] %	*dl:meso*[c]
1	H—≡—C_5H_{11}	 **218**	20	65:35
2	H—≡—C_6H_{13}	 **219**	21	70:30
3	H—≡—C_8H_{17}	 **220**	15	75:25
4	H—≡—$C_{10}H_{21}$	 **221**	17	75:25
5	H—≡—C_6H_5	 **222**	15	0:100

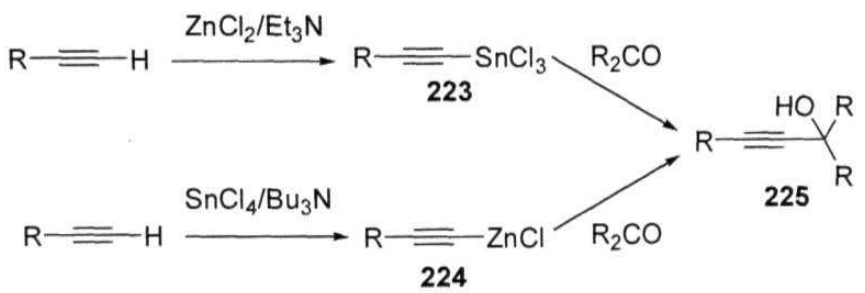
[a]The products were identified using spectral data (IR, ^{1}H NMR, ^{13}C NMR, Mass and CHN analysis) and comparison with the reported data for **222**.[217]

[b]Yields are of the isolated products and based on the amount of cyclobutenedione used.

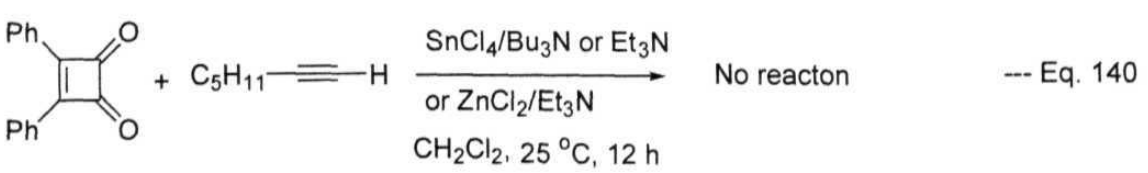
[c]*dl:meso* ratios were determined by ^{1}H NMR intensities of the Ph-CH-CO signals.

Previously, *Yamaguchi et al.*[221] reported the preparation of alkynyltin species using $SnCl_4/Bu_3N$ and alkynes (**Scheme 56**). Similarly, alkynylzinc species were prepared by the reaction of alkynes with $ZnCl_2/Et_3N$.[222] Also, these alkynylmetal reagents have been utilized for the synthesis of various propargyl alcohols **225**.

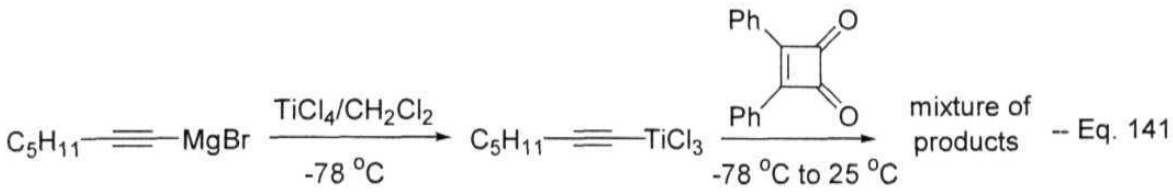
Scheme 56



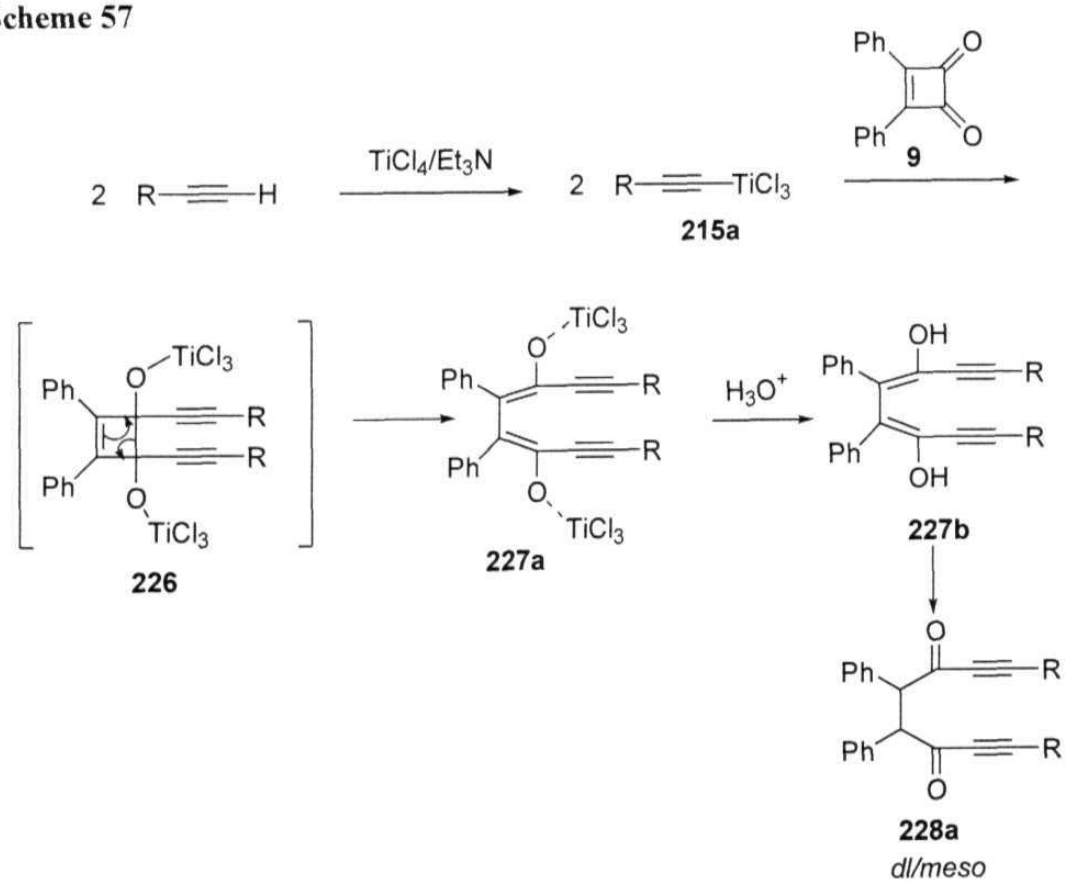
We have examined the use of these reagent systems with a view to improve the yields of **218-222** since alkynyltin and zinc reagents would not undergo oxidative coupling to 1,3-diynes, which is major side reaction in the case of $TiCl_4/Et_3N$/alkyne reagent systems. Accordingly, we have carried out the reaction of 1-heptyne with diphenylcyclobutenedione in the presence of $SnCl_4/Bu_3N$ or $ZnCl_2/Et_3N$, but the reaction did not proceed in these runs (eq. 140).



We have also examined the reactivity of alkynyltitanium species prepared *via* transmetalation by the addition of $TiCl_4$ to alkynyl Grignad reagent at low temperature.[223] The reaction of these titanium reagents with cyclobutenedione gave a complex mixture of products (eq. 141) and the products of the type **218-222** could not be obtained.

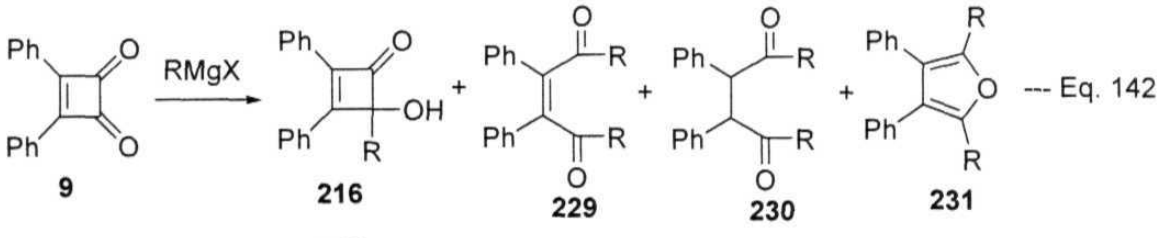


Scheme 57

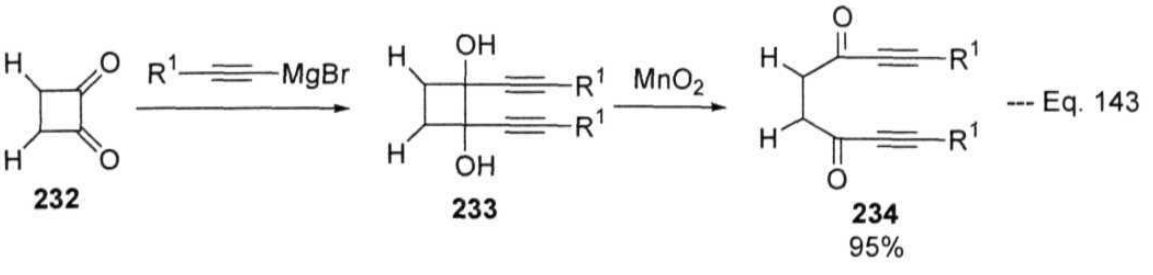


The formation of 1,4,5,8-tetrasubstituted-1,7-octadiyne-3,6-diones **218-222** (eq.140) can be rationalized by considering a sequence of intermediates as depicted in **Scheme 57**. Nucleophilic addition of two equivalents of alkynyltitanium species to cyclobutenedione may lead to the intermediate **226**. This could undergo electrocyclic ring opening to give the dienol after hydrolysis, which would then tautomerize to the products **218-222**.

Previously, similar compounds were isolated along with several other addition products in the reaction of Grignard reagents with diphenylcyclobutenedione (eq. 142).[217a] Also, addition of alkynyl magnesium compounds to cyclobutanedione **232** yields similar products after MnO_2 oxidation (eq. 143).[217b]



R = ≡—Ph 54%
≡—Si(CH3)3 25%
≡—C(CH3)3 54%

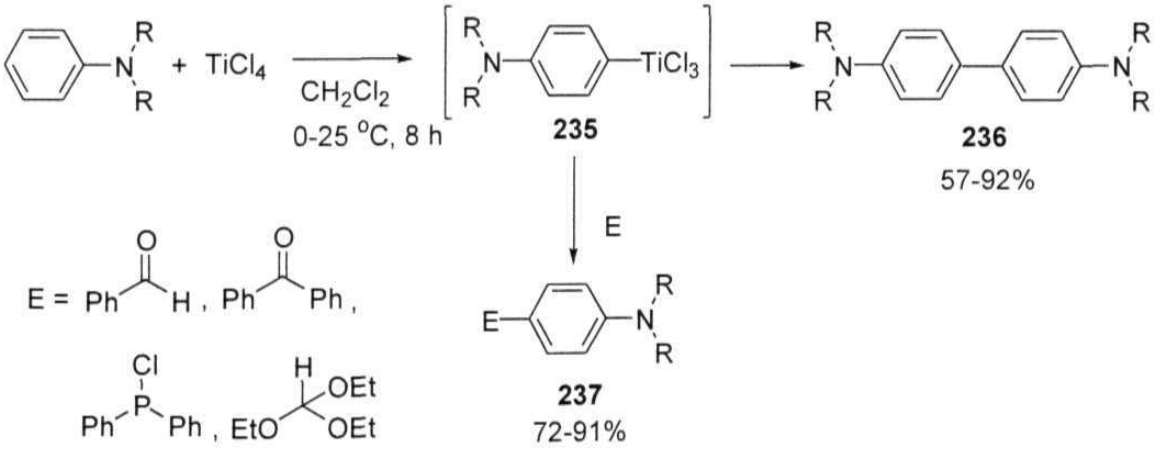


Unfortunately, the yields are poor in the present method (**Table 16**). Further optimization of reaction conditions to improve the yields is desirable.

2.5.3 Reaction of Aryltitanium Reagents with Cylobutenedione 9

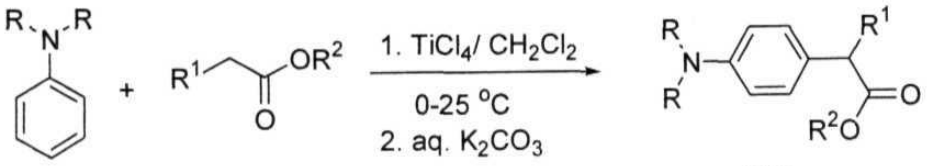
Previously, aryltitanium **235** species were prepared in this laboratory by the reaction of *N,N*-dialkylarylamines with $TiCl_4$ under ambient conditions, without using any other organometallic reagents (**Scheme 58**).[224] These species undergo oxidative coupling to produce *N,N,N',N'*-tetraalkylbenzidines **236** in good yields in the absence of electrophiles.[224] However, the intermediate can be trapped using electrophiles.[224]

Scheme 58



The reaction of the aryltitanium species gave α-arylation using enolizable esters as electrophiles. For example, the reaction of aryltitanium with enolizable esters like

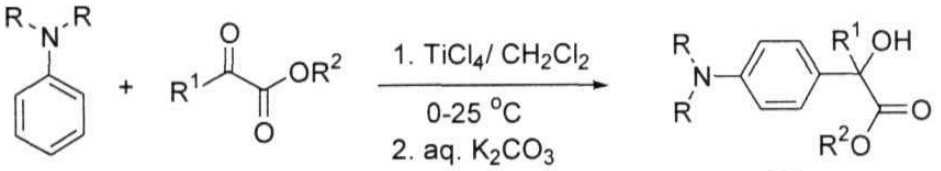
arylacetic acid esters produced the corresponding α-arylated products in good yields (eq. 144).[225]



238
65-90%

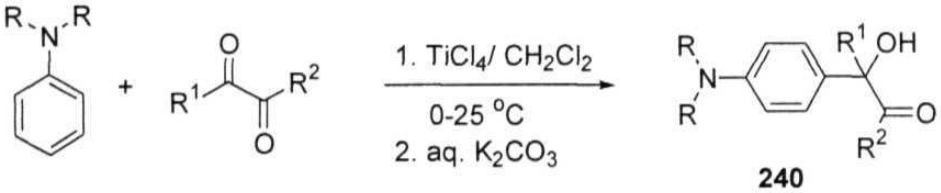
-- Eq. 144

However, Grignard type reactions were realized using non-enolisable α-ketoesters and α-diketones (eqs. 145 and 146).



239
67-91%

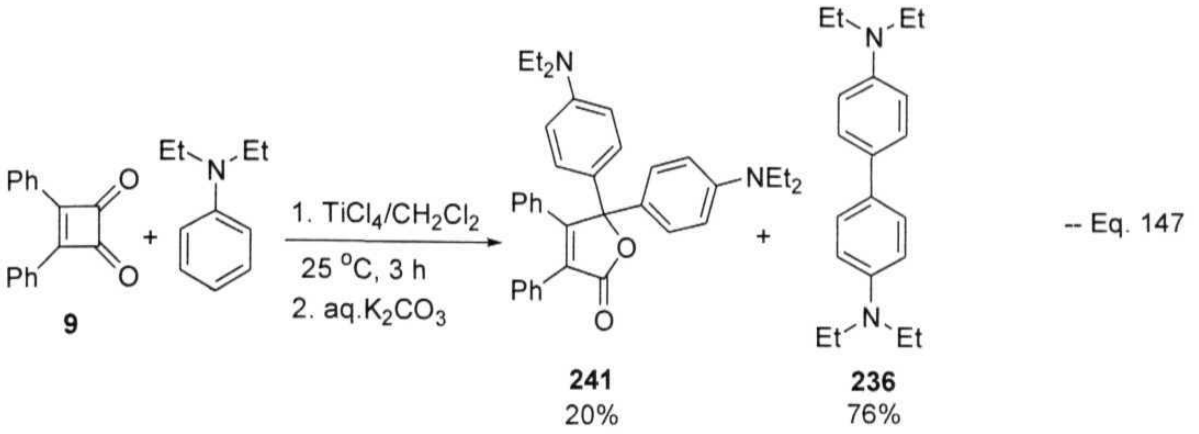
-- Eq. 145



240
70-85%

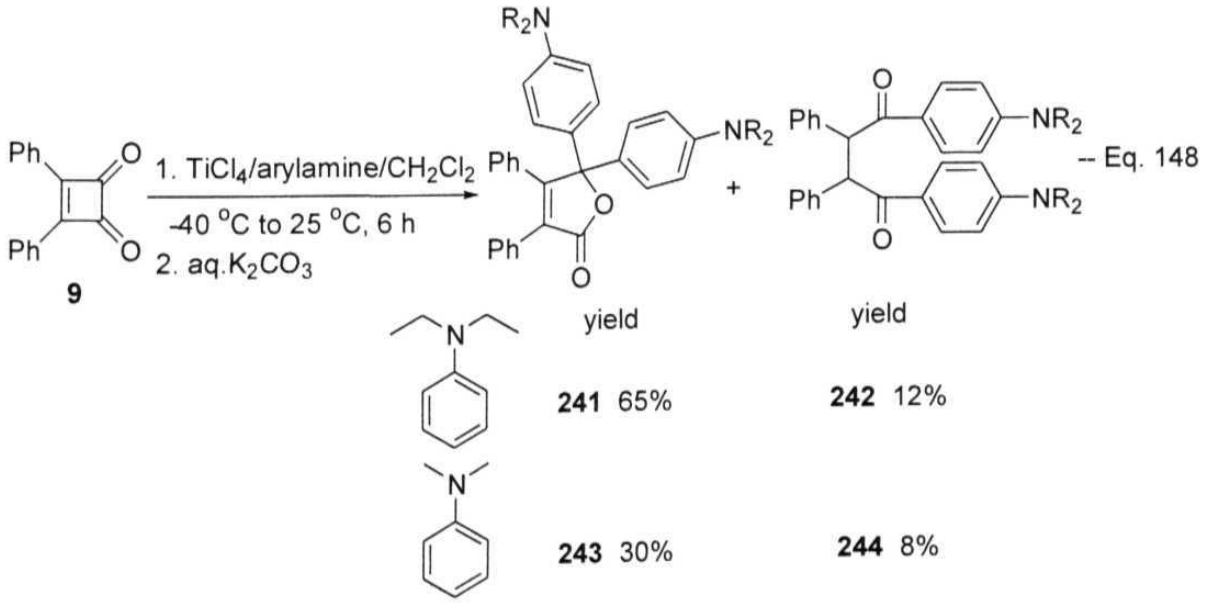
-- Eq. 146

We have examined the reactivity of aryltitanium reagents prepared in this way using cyclobutenedione **9**. It was observed that the reaction of aryltitanium species, prepared using 1:2 ratio of $TiCl_4$ and *N,N*-dialkylarylamines, with 3,4-diphenyl-3-cyclobutene-1,2-dione **9** at room temperature is not clean. A small amount (20%) of butenolide **241** along with benzidine (76%) and other highly coloured compounds were obtained (eq. 147).



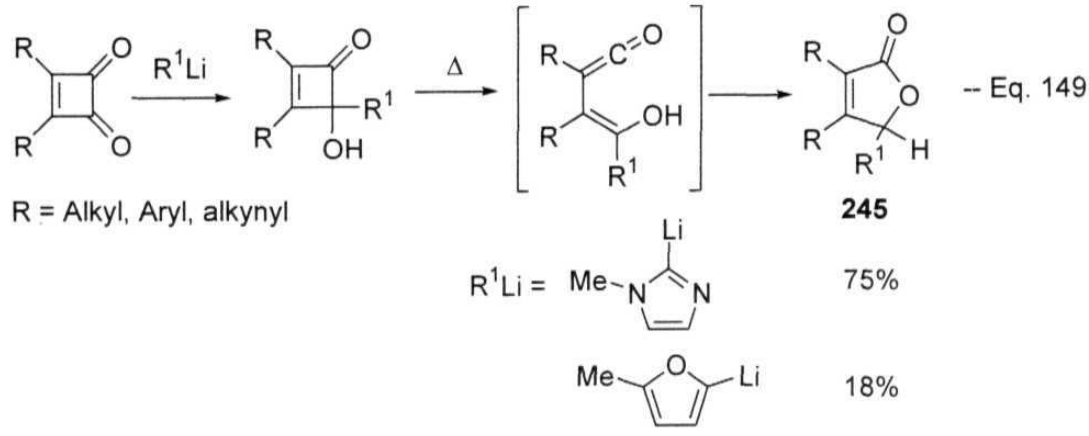
-- Eq. 147

However, the formation of benzidine could be avoided by carrying out the reaction at lower temperatures. In a run using *N,N*-diethylaniline, butenolide **241** was obtained in as high as 65% yield along with 1,4-diketone **242**, a ring opened product (eq. 148). Only one diastereomer of **242** was obtained out of the possible *dl* and *meso* isomers. Whereas the *N,N*-dimethylaniline gave lower yields of the corresponding butenolide **243**. In this case, a small amount of *N*-demethylated products (26%) was also obtained.[224]



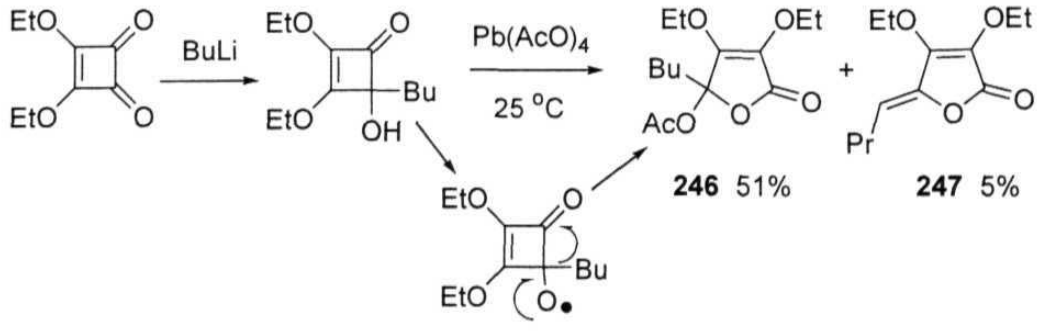
-- Eq. 148

Previously, some butenolides were prepared from cyclobutenediones *via* 4-hydroxycyclobutenones by thermolysis (eq. 149).[140e,h] The formation of butenolides was rationalized by the attack of hydroxyl group on the transient vinyl ketene intermediate.



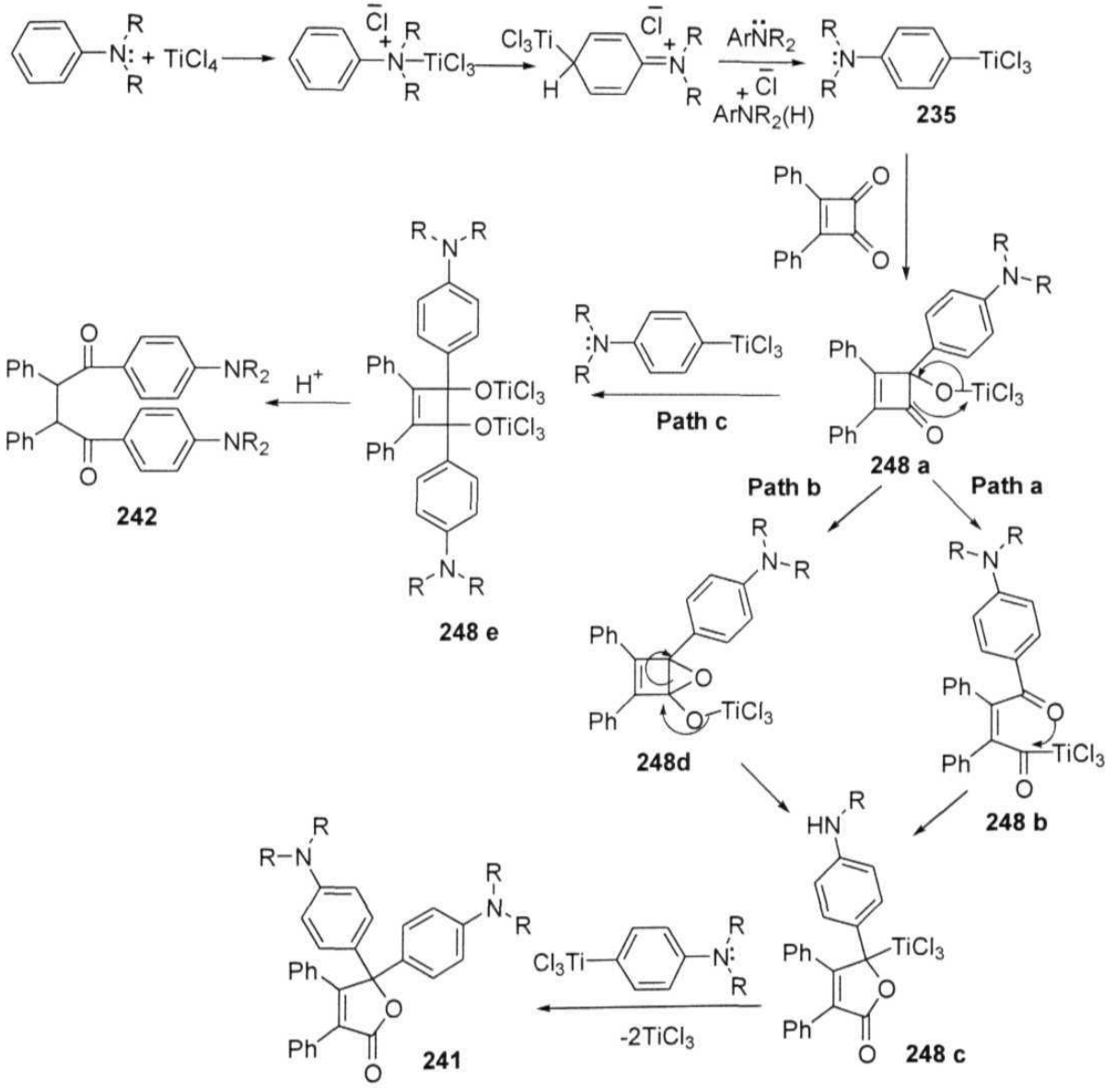
Eguchi et al.[214c] reported a radical mediated rearrangement of 4-hydroxycyclobutenones to the butenolides **246** and **247** at room temperature, in which ring opening is triggered by an oxy-radical generated by lead(IV) acetate (**Scheme 59**).

Scheme 59



The formation of butenolides using arylamines and $TiCl_4$ can be explained by considering a tentative mechanism as outlined in **Scheme 60**.

Scheme 60



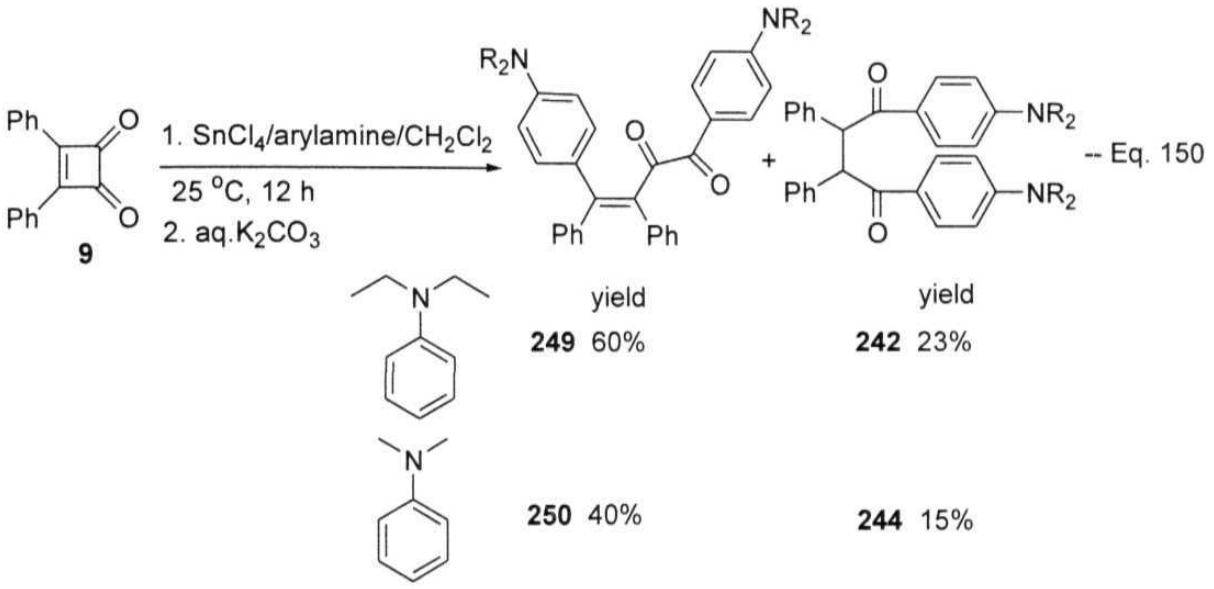
Addition of one equivalent of aryltitanium reagent to the cyclobutenedione **9** would give **248a**, which could undergo β-scission to produce the acyltitanium intermediate **248b**.

Cyclization of **248b** to **248c** could then take place through the addition of the acyltitanium to carbonyl oxygen. The resulting intermediate could react with another equivalent of aryltitanium species to give the final product **(Path a)**.[215d] Alternatively, the intermediate **248a** could give the 5-oxabicyclo[2.1.0]pent-2-enyloxytitanium intermediate **248d (Path b)**, which could then undergo ring opening to afford **248c** *via* the process demonstrated in the Dowd's ring-expansion reaction.[226] However, recent calculations revealed that the radical process similar to the sequence **248a→248b→248c** is also energetically favourable.[227]

The formation of 1,4-diketone **242** can be rationalized by the reaction of two equivalents of aryltitanium reagents with the cyclobutenedione **9** to give **248e**. This intermediate upon electrocyclic ring opening could afford the final product **242 (Path c)**. Comparison of the ^{1}H NMR data indicate that the single diastereomer formed in these reactions could most probably be the thermodynamically more stable *meso* isomer.[218-220]

2.5.4 Reaction of cyclobutenedione with the arylamine/$SnCl_4$ reagent system

We have also examined the reactivity of arylamines with cyclobutenediones in the presence of other Lewis acids like $SnCl_4$. It was observed that the addition of 1:2 ratio of $SnCl_4$ and *N,N*-diethylaniline to the 3,4-diphenyl-3-cyclobutene-1,2-dione **9** at room temperature gives a novel ring cleaved product **249** (60%) along with the expected 1,4-diketone **242** (23%) (eq. 150).



The compound **249** was identified as the *Z* isomer by single crystal X-ray analysis

Fig. 6.

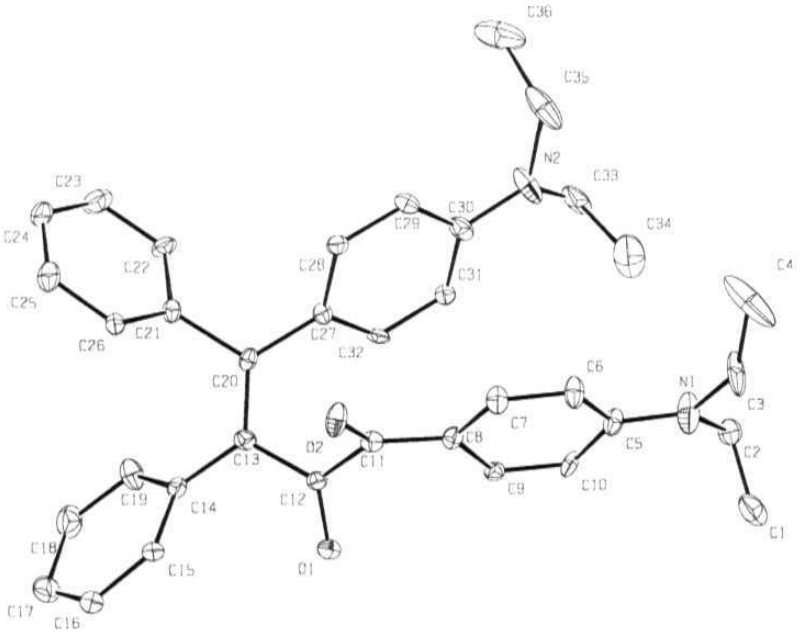
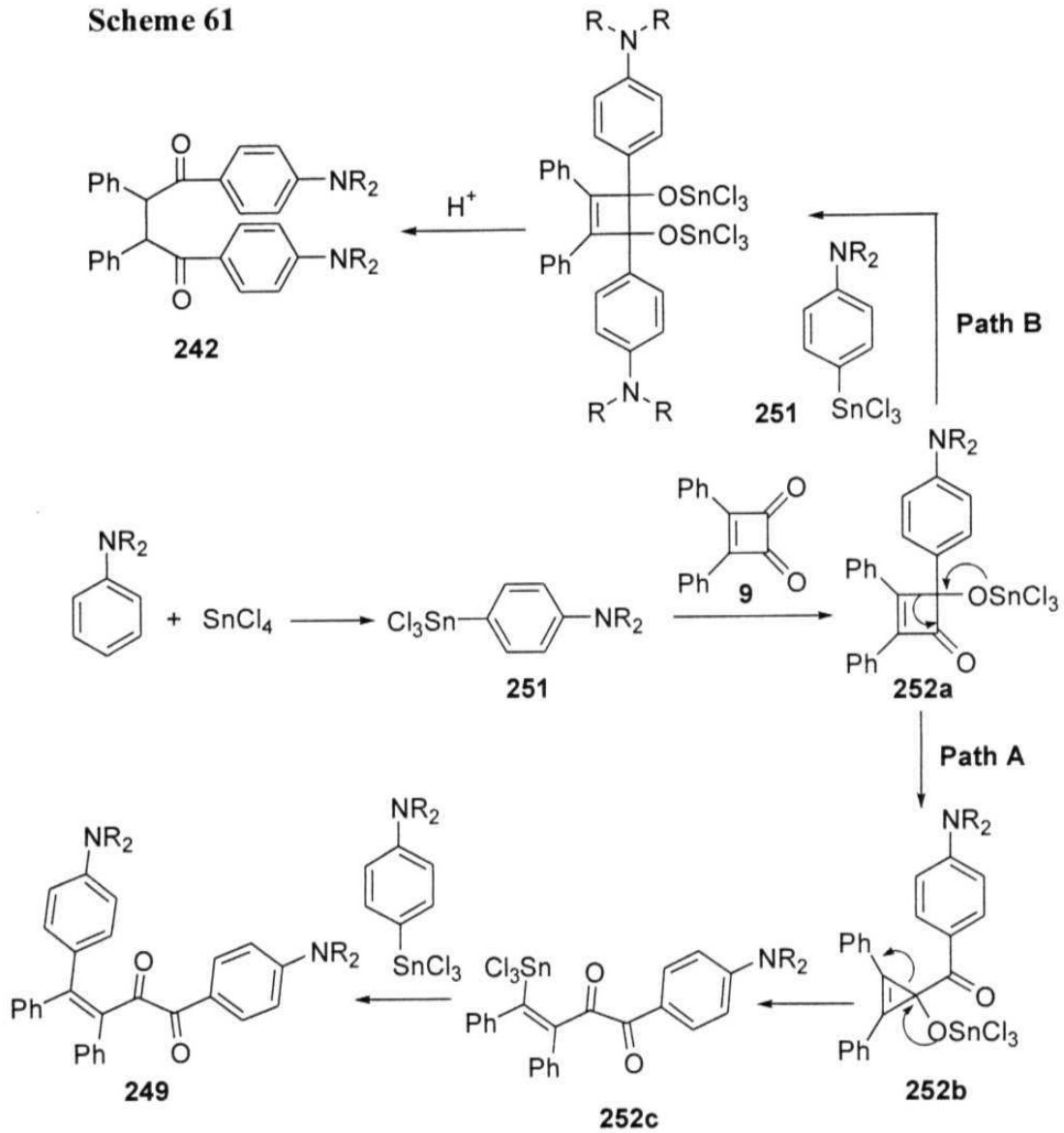


Fig. 6 ORTEP Diagram of Compound 249

Scheme 61



The plausible route to the formation of **249** and **250** may involve an anionic mechanism as depicted in **Scheme 61**. Addition of one equivalent of aryltin species to the cyclobutenedione **9** may lead to benzilic acid type rearrangement to generate cyclopropenol derivative **252b**. Ring opening would then give **252c**, which could undergo coupling with another aryltin species to afford the final product **249**. The compound **242**

(**Scheme 61**) could form through reaction with 2 equiv. of aryltin species similar to reactions realized in the case of aryltitanium species (**Scheme 60**).

Table 17. Crystal Data and Structure Refinement for the Compound 249

Empirical formula	$C_{36}H_{38}N_2O_2$
Formula weight	530.68
Temp., wavelength	293(2) K, 0.71073 Å
Cryst sys. space group	monoclinic, Pn:b2 [IT no.7]
Unit cell dimensions	a=9.5855(18) Å, α=90
	b=30.343(5) Å, β=102.80(3)
	c=10.715(7) Å, γ=90
Volume	3039(2) $Å^3$
Z, calculated density	2,1.160 mg/m^3
Absorption coefficient	0.071 mm^{-1}
F(000)	1136
Crystal size	0.64 X 0.52 X 0.68 mm
θ range for data collection	1.34 to 27.48°.
Limiting indices	0<=h<=12,0<=k<=39,-13<=l<=13
Reflections collected/unique	6992/6992[R(int)=0.0000]
Refinement method	full-matrixleast-squaresonF^2
Data/restraints/parameters	6992/5/722
Goodness-of-fiton F^2	1.049
Final *R* indices [I>2sigma(I)]	R_1=0.0635, wR_2=0.1360
R indices (alldata)	R_1=0.1766, wR_2=0.1896
Extinction coefficient	0.0015(7)
Largest diff.peak and hole	0.199 and -0.182e. $Å^{-3}$

2.6 Conclusions

The nature of intermediate alkyne-iron carbonyl complexes involved in the reaction of alkynes with $Fe_3(CO)_{12}$/Amine reagent system was identified through acylation. This transformation is also a simple and convenient method for the synthesis of acyloxyferrole complexes in good yields. Also, the acyloxyferrole complexes prepared in this way were successfully converted to the corresponding cyclobutenediones.

A variety of cyclobutenediones were synthesized from alkynes using the $Fe(CO)_5/Me_3NO$ reagent system in 1.2:1 ratio under ambient conditions. The present method has advantage over the hitherto reported methods since this method avoids the use of $Fe_3(CO)_{12}$ or $Fe_2(CO)_9$ which are in turn prepared from $Fe(CO)_5$. As the Me_3NO is a mild, efficient oxidizing agent and is tolerant towards oxidation of sensitive electron rich moieties, this synthetic protocol should be widely applicable. The use of $Fe(CO)_5/Me_3NO$ in 1:1.5 ratio led to the formation of cyclic anhydride derivatives.

Efforts were undertaken to prepare coordinatively unsaturated iron carbonyl species using the $Fe_3(CO)_{12}/I_2$ and $Fe(CO)_5/TiCl_4$ reagent systems for applications in organic synthesis. Reaction of such species with 1-alkynes affords a mixture of 2,5- and 2,6-disubstituted benzoquinones after $CuCl_2.2H_2O$ oxidation.

Reactions of $TiCl_4$/Zn/CO reagent system with alkynes were studied. Whereas diphenylacetylene gives the corresponding cyclopentenone in this reaction, 1-alkynes gave a mixture of 1,3,5- and 1,2,4-trisubstituted benzenes as major products.

A diastereoselective aldol reaction of various acyclic and cyclic ketones with diphenylcyclobutenedione was accomplished using the $TiCl_4/Bu_3N$ reagent system at to obtain the corresponding 4-hydroxy-4-sustituted-2-cyclobutenones.

Studies were carried out to examine the reactivity of organotitanium reagents prepared *in situ* with cyclobutenediones. Reaction of alkynyltitanium reagents with diphenylcyclobutenedione gave the corresponding 1,8-disubstituted-4,5-diphenyl-1,7-octadiyne-3,6-dione.

Diphenylclobutenedione was shown to undergo interesting reactions with aryltitanium species to provide butenolides and 1,4 diketones. Whereas, the aryltin species were observed to give a novel ring opened product, 1,4-bis(4-diethylaminophenyl)-3,4-diphenyl-3-butene-1,2-dione.

3. Experimental section

3.1 General information:

^{1}H NMR (200 MHz), ^{13}C NMR (50 MHz), and ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) spectra were recorded on Bruker-AC-200 and Bruker-Avance-400, respectively in $CDCl_3$ and TMS was used as reference (δ = 0 *ppm*). IR (KBr) spectra were recorded on JASCO FT-IR spectrophotometer model 5300 and all the neat IR spectra were recorded on SHIMADZU FT-IR spectrophotometer model 8300 with polystyrene as reference. Mass spectral analyses were carried out on VG 7070H mass spectrometer using EI technique at 70 eV. Elemental analysis was performed on a Perkin-Elmer elemental analyzer model-240C and Thermo Finnigan analyzer series Flash EA 1112. The UV spectrum was recorded with a JASCO model 7800 spectrophotometer. Melting points reported in this thesis are uncorrected and were determined using a Buchi-510 capillary point apparatus. Analytical thin layer chromatographic tests were carried out on glass plates (3 x 10 cm) coated with 250 mμ acme's silica gel-G or GF_{254} containing 13% calcium sulphate as binder. The spots were visualized by short exposure to iodine vapor or UV light.

All glassware was pre-dried at 140 °C in an air oven for 4h, assembled hot and cooled under a steam of dry nitrogen. Unless, otherwise mentioned, all the operations and transformations of reagents were carried out using standard syringe, septum technique recommended for handling air sensitive organometallic compounds. Reagents prepared *in*

situ in solvents were transformed using a double-ended stainless steel (Aldrich) needle under a stream of nitrogen whenever required.

In all the experiments, a round bottom flask of appropriate size with a side arm, a side septum, a magnetic stirring bar, a condenser and a connecting tube attached to a mercury bubbler were used. The outlet of the mercury bubbler was connected to a long tube to the atmosphere. All dry solvents and reagents (liquids) used were distilled from appropriate drying agents just before use. As a routine practice, all organic extracts were concentrated on Buchi-EL-rotary evaporator. All yields reported are isolated yields of material judged homogenous by TLC, IR and NMR spectroscopy.

Iron pentacarbonyl supplied by Fluka, Switzerland and Aldrich, USA was used. $NaBH_4$ supplied by Aldrich, USA was used. THF was distilled over sodium benzophenone ketyl system. Et_3N, *N,N*-diethylaniline and *N,N*-dimethylaniline, supplied by Spectrochem Ltd., India, were distilled and stored over KOH. DCM was distilled over calcium hydride and stored over molecular sieves. Alkynes, except 1-heptyne, used in the reactions were prepared following a reported procedure.[229] 1-Heptyne was supplied by Fluka, Switzerland. $Fe_3(CO)_{12}$ was prepared following a reported procedure starting from $Fe(CO)_5$.[230]

The X-ray diffraction measurements for compounds **142** and **249** were carried out on an automated Enraf-Nonious MACH 3 diffractometer using graphite monochromator, Mo-Kα (λ = 0.71073 Å) radiation. Intensity data was collected by the ω–scan mode. The X-ray diffraction measurements for compounds **188** and **205** were carried out at 293 K on

Bruker SMART APEX CCD area detector system and the data was corrected for absorption effects using the multiscan technique (SADABS). The data was reduced using the XTAL program. No absorption correction was applied. The refinement for structures was made by full matrix least squares on F^2 (SHELX 97).

3.2 Preparation of $Fe_3(CO)_{12}$

A reported procedure involving MnO_2 oxidation of $NaHFe(CO)_4$ was followed.[226] The $Fe(CO)_5$ (30 g, 0.015 mol) and methanol (85 mL) were placed in a three necked 1lit. flask fitted with a stirrer, nitrogen inlet and a refluxing condenser. The reaction mixture was treated with a solution of NaOH (22.5 g) in H_2O (45 mL). The mixture was stirred for 30 min. and then treated with saturated NH_4Cl solution (70 mL) to obtain $NaHFe(CO)_4$ in solution.

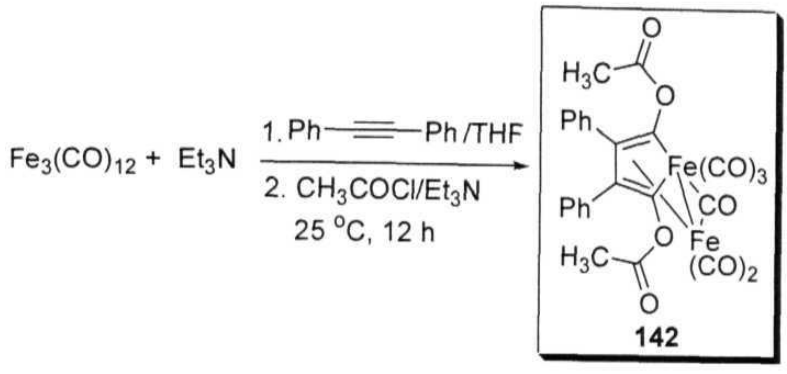
Meanwhile the MnO_2 was prepared by cautiously adding $KMnO_4$ (32.3 g) in water (150 mL) with of 95% ethanol (50 mL) under stirring in a large beaker covered with a watch glass. Stirring was continued further to get a brown precipitate of MnO_2. The suspension of MnO_2 thus obtained was added to the $HFe(CO)_4^-/NH_4Cl$ solution. The reaction mixture was stirred for 2-3 h. The excess MnO_2 was then decomposed by gradual addition of a solution of $FeSO_4$. $7H_2O$ (20 g) dissolved in dil. H_2SO_4 (about 2N, 125 mL). The mixture was then treated with 1:1 H_2SO_4:H_2O (150 mL). The black precipitate of $Fe_3(CO)_{12}$ was then filtered and washed successively with hot dil. H_2SO_4 (~2N, 200 mL),

95% ethanol (100 mL) and pentane (75 mL) and dried under reduced pressure. Yield 18 g (70%).

3.3 General Procedure for the Preparation of Acyloxyferrole Complexes

A mixture of $Fe_3(CO)_{12}$ (2.01 g, 4 mmol) and Et_3N (1.01 g, 10 mmol) in THF (40 mL) was stirred for 5 min. under dry nitrogen. Diphenylacetylene (0.53 g, 3 mmol) was added and stirred for 30 min. Then Et_3N (1.01 g, 10 mmol) and CH_3COCl (1.17 g, 15 mmol) were added and the contents were further stirred for 12 h. Ether (100 mL) was added and the reaction mixture was washed successively with H_2O (40 mL), brine (2X50 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to column chromatography (silica gel, hexane-EtOAc). Ethyl acetate (1%) in hexane eluted the ferrole complex **142**. These complexes are relatively stable but long time standing or exposure to atmosphere leads to decomposition. The product **142** was identified by single crystal X-ray analysis.

Crystals suitable for single crystal X-ray analysis were grown as follows: Complex **142** (100 mg) was dissolved in minimum amount of hot methanol (~ 4 mL) and allowed to cool down to room temperature under N_2 atmosphere.



Yield : 76% (1.369 g)

mp : 152-155 °C (dec.)

IR (KBr) : 2083, 2042, 2005, 1956, 1749 cm^{-1}

^{1}H NMR : (200 MHz) δ = 1.9 (s, 6 H), 7.18-7.25 (m, 10 H) *ppm*

(Spectrum No. 1)

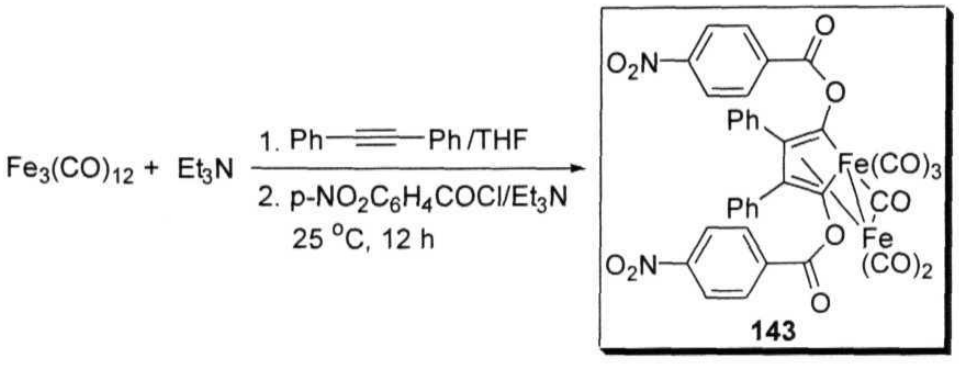
^{13}C NMR : (50 MHz) δ = 211.8, 207.7, 205.3, 185.5, 168.4, 130.7, 130.5, 128.5, 127.9, 125.6, 20.6 *ppm* **(Spectrum No. 2)**

Analysis : for $C_{26}H_{16}Fe_2O_{10}$

Calculated: C, 52.04%; H, 2.69; Fe, 18.61%; O, 26.66%

Found: C, 52.11%; H, 2.68%

The above procedure was followed for the conversion of other alkynes to the corresponding acyloxyferrole complexes.



Yield : 68% (1.662 g)

mp : 158-160 °C (dec.)

IR (KBr) : 2081, 2044, 2027, 1988, 1726 cm^{-1}

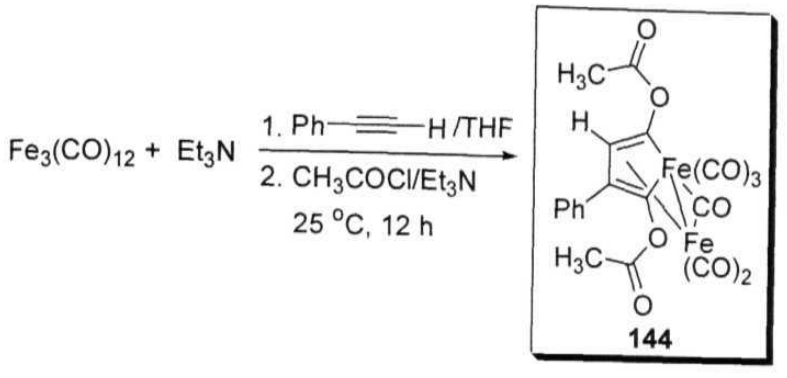
^{1}H NMR : (200 MHz) δ= 9.95 (d, J = 8.6Hz, 4H), 9.65 (d, J = 8.6Hz, 4H), 8.8-9.0 (m, 10H) *ppm*

^{13}C NMR : (50 MHz) δ= 211.3, 208.4, 204.9, 184.7, 162.7, 150.8, 134.2, 131.5, 130.6, 130, 128.9, 128.1, 125.9, 123.7 *ppm*

Analysis : for $C_{36}H_{18}N_2Fe_2O_{14}$

Calculated: C, 53.11%; H, 2.23%; N, 3.44%; Fe, 13.72%; O, 27.51%

Found: C, 53.25%; H, 2.26%; N, 3.52%



Yield : 72% (1.132 g)

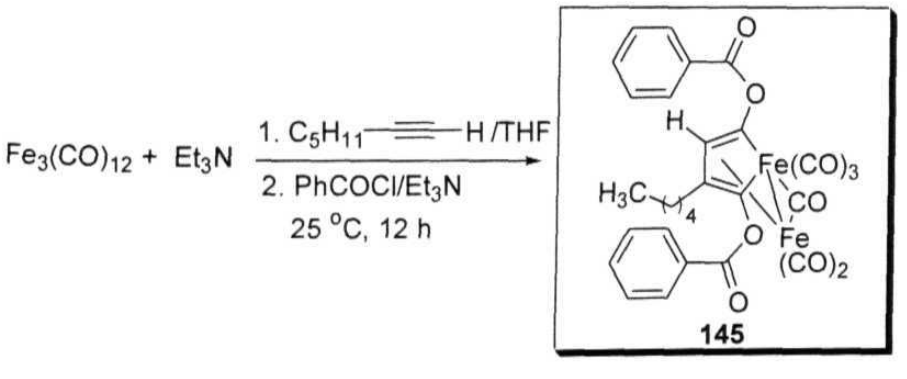
mp : 150-152 °C (dec.)

IR (neat) : 2083, 2007, 1953, 1759 cm^{-1}

^{1}H NMR : (200 MHz) δ= 7.3 (m, 5H), 6.1 (s, 1H), 2.1 (s, 3H), 2.0 (s, 3H) *ppm*

(Spectrum No. 3)

^{13}C NMR : (50 MHz) δ= 210.6, 208.2, 206.1, 190.7, 188.1, 168.1, 168, 131.2, 129.3, 129.0, 128.6, 118.7, 99.7, 21.0, 20.8 *ppm* **(Spectrum No. 4)**

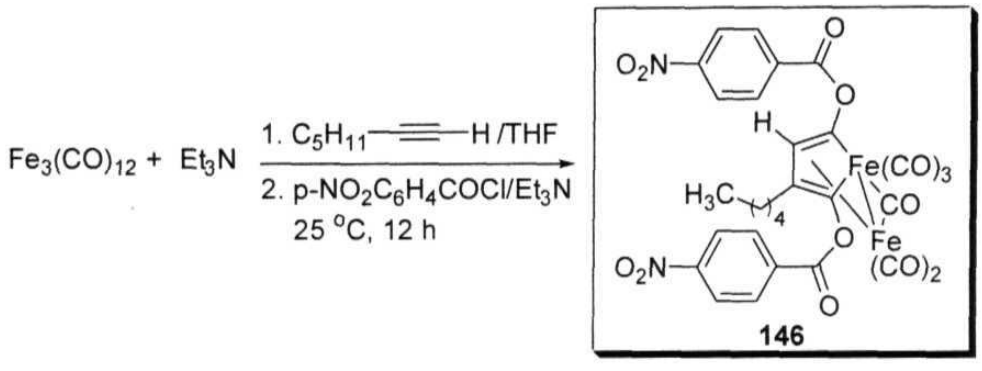


Yield : 70% (1.348 g)

IR (neat) : 2081, 2040, 2000, 1957, 1732 cm^{-1}

^{1}H NMR : (200 MHz) δ= 7.5-8.0 (m, 10H), 6.1 (s, 1H), 0.7-2.5 (m, 11H) *ppm*

^{13}C NMR : (50 MHz) δ= 211.3, 208.4, 205.6, 191.5, 186.5, 164.1, 133.6, 129.8, 129.1, 128.6, 122.0, 99.4, 31.6, 29.2, 27.1, 22.2, 13.7 *ppm*



Yield : 72% (1.582 g)

mp : 122-125 °C (dec.)

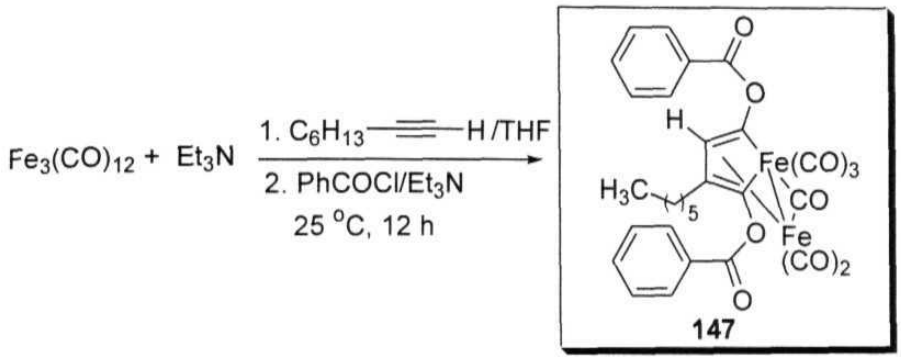
IR (neat) : 2091, 2040, 1994,1965, 1730 cm^{-1}

^{1}H NMR : (200 MHz) δ= 8.1-8.5 (m, 8H), 6.15 (s, 1H), 0.8-2.8 (m, 11H) *ppm*

(Spectrum No. 5)

^{13}C NMR : (50 MHz) δ= 210.6, 207.8, 205.5, 190.6, 185.4, 162.4, 151.0, 134.2, 130.9, 123.8, 121.8, 99.2, 31.5, 29.1, 27.1, 22.1, 13.7 *ppm*

(Spectrum No. 6)



Yield : 65% (1.279 g)

IR (neat) : 2081, 2040, 2003, 1957, 1732 cm^{-1}

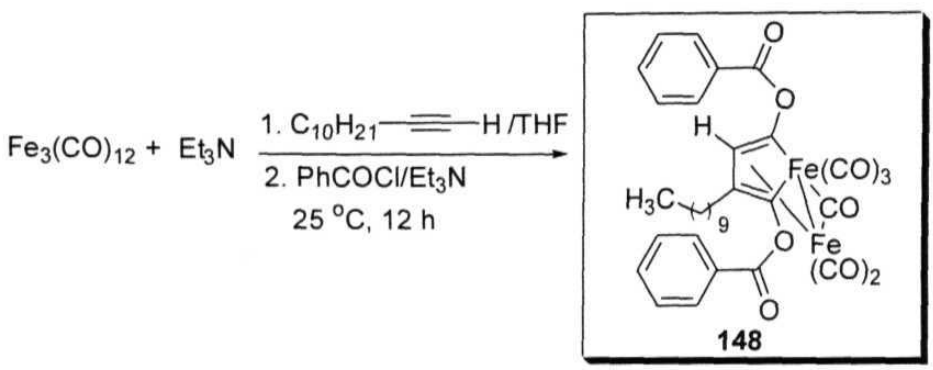
^{1}H NMR : δ= 8.1-8.4 (m, 4H), 7.4-7.7 (m, 6H), 6.1 (s, 1H), 0.8-2.5 (m, 13H) *ppm*

^{13}C NMR : (50 MHz) δ= 211.4, 208.5, 205.7, 191.7, 186.5, 164.2, 134.4, 133.7, 130.5, 129.9, 129.8, 129.1, 128.8, 128.7, 122.0, 99.5, 31.3, 29.6, 29.1, 27.2, 22.4, 13.8 *ppm*

Analysis : for $C_{30}H_{24}Fe_2O_{10}$

Calculated: C, 54.91%; H, 3.69%; Fe, 17.03%; O, 24.38%

Found C, 54.85%; H, 3.62%



Yield : 68% (1.453 g)

IR (neat) : 2081, 2040, 2005, 1957, 1732 cm^{-1}

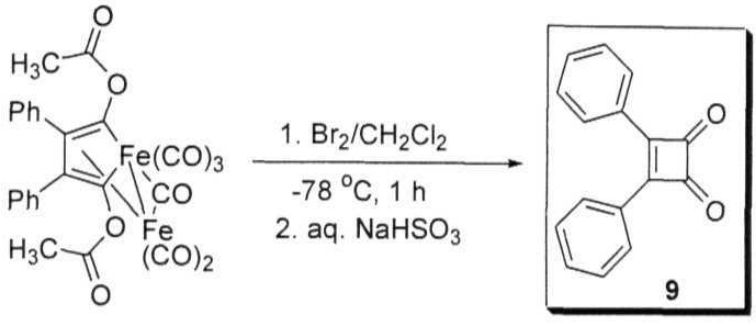
^{1}H NMR : (200 MHz) δ= 8.0-8.2 (m, 4H), 7.4-7.7 (m, 6H), 6.1 (s, 1H), 0.8-2.2 (m, 21H) *ppm*

^{13}C NMR: (50 MHz) δ= 211.3, 208.4, 205.6, 191.6, 186.5, 164.1, 133.6, 129.8, 129.1, 128.6, 122.0, 99.4, 31.8, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 27.2, 22.6, 14 *ppm*

3.4 General Procedure for the Preparation of Cyclobutenedione from Acyloxyferrole Complexes

To a solution of ferrole complex **142** (0.6 g, 1 mmol) in CH_2Cl_2 (10 mL) was added Br_2 (0.48 g, 3 mmol) in 2 mL CH_2Cl_2 at –78 °C under nitrogen atmosphere, and the reaction mixture was stirred at the same temperature for 1 h. The contents were brought to 25 °C and the excess bromine was destroyed using aqueous $NaHSO_3$. The organic layer was extracted with DCM (100 mL) and the combined organic mixture was washed with H_2O

(40 mL), brine (2 X 50 mL), dried over Na_2SO_4 and concentrated. The residue was subjected to column chromatography (silica gel, hexane-EtOAc). Ethyl acetate (1.5%) in hexane eluted the 3,4-diphenyl-3-cyclobutene-1,2-dione **9**.



Yield : 90% (0.212 g)

mp : 95-96 °C (Lit.[24,168] mp 97 °C)

IR (KBr) : 1780 cm^{-1}

^{1}H NMR : (200 MHz) δ = 7.45-7.68 (m, 6 H), 8.14 (m, 4 H) *ppm*

(Spectrum No. 7)

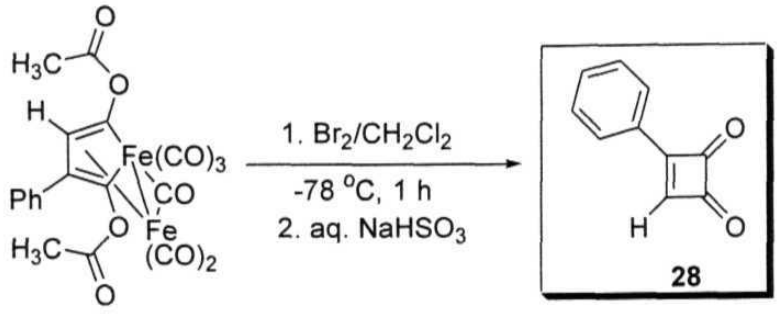
^{13}C NMR : (50 MHz) δ = 196.1, 187.4, 134.6, 131.2, 129.7, 128.7 *ppm*

(Spectrum No. 8)

MS (EI) : *m/z* 235 (M^+, 12%), 179 [(M+1)-(Ph_2C_2+1), 100%]

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the reported data.[24,168]

The above procedure was followed for the conversion of other acyloxyferrole complexes to the corresponding cyclobutenediones.



Yield : 62% (0.099 g)

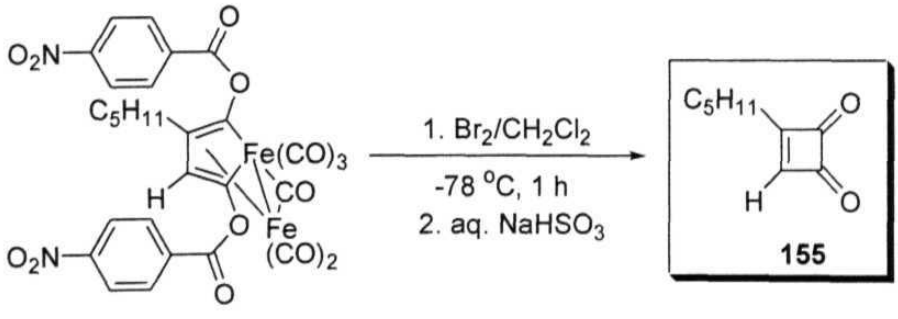
mp : 152-153 °C (Lit.[24,168] mp 152-153 °C)

IR (KBr) : 1768 cm^{-1};

^{1}H NMR : (200 MHz) δ= 9.5 (s, 1H), 7.3-8.0 (m, 5H) *ppm*

^{13}C NMR : (50 MHz) δ= 197.7, 196.0, 195.5, 178.3, 134.6, 129.5, 129.4, 128.6 *ppm*

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the reported data.[24,168]



Yield : 60% (0.091 g)

IR (neat) : 1778 cm^{-1}

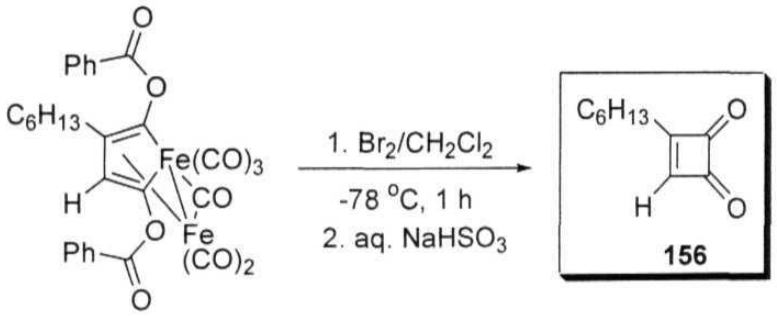
^{1}H NMR : (200 MHz) δ= 9.20 (s, 1H), 2.81 (t, J = 7.3 Hz, 2H), 1.70-1.83(m, 2H), 1.27-1.40 (m, 4H), 0.82 (t, J = 7.3 Hz, 3H) *ppm*

(Spectrum No. 9)

^{13}C NMR : (50 MHz) δ= 208.3, 199.9, 196.6, 184.8, 31.2, 27.1, 25.6, 22.1, 13.7 *ppm* **(Spectrum No. 10)**

MS (EI) : *m/z* 152 (M^+, 13%), 81[M^+-C_5H_{11}, 20%]

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the reported data.[168]



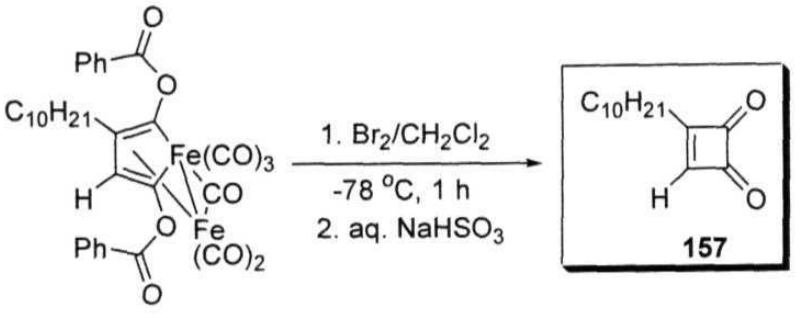
Yield : 65% (0.108 g)

IR (neat) : 1786 cm^{-1}

^{1}H NMR : (200 MHz) δ= 9.1 (s, 1H), 2.81 (t, J = 7.2 Hz, 2H), 2.7-1.2 (m, 8H), 0.89 (t, J = 7.3 Hz, 3H) *ppm*

^{13}C NMR : (50 MHz) δ= 208.3, 199.9, 196.7, 184.9, 31.8, 29.6, 28.9, 26.8, 25.9, 13.9 *ppm*

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the reported data.[168]



Yield : 63% (0.139 g)

IR (neat) : 1774 cm^{-1}

^{1}H NMR : (200 MHz) δ= 9.21(s, 1H), 2.75 (t, J = 7.4Hz, 2H), 2.42-1.23 (m, 16H), 0.81 (t, J = 7.2 Hz, 3H) *ppm*

^{13}C NMR: (50 MHz) δ= 203.4, 199.4, 199.1, 198.7, 31.9, 31.8, 29.6, 29.5, 29.2, 29.1, 26.3, 25.9, 22.6, 13.9 *ppm*

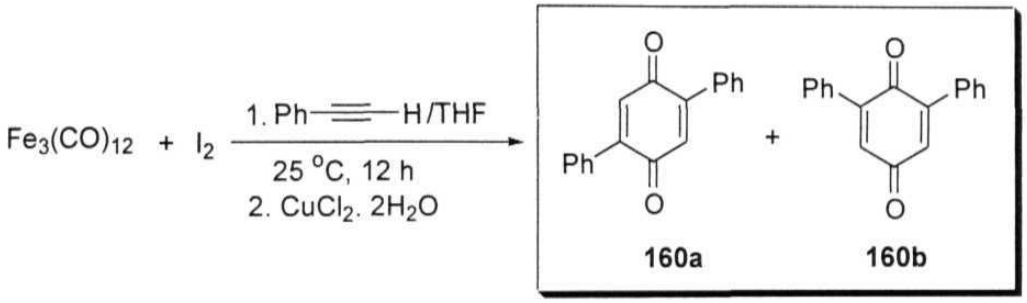
MS (EI) : *m/z* 222 (M^+, 25%), 81[M^+-$C_{10}H_{21}$, 60%]

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the reported data.[168]

3.5 Reaction of Alkynes with the $Fe_3(CO)_{12}/I_2$ Reagent System

$Fe_3(CO)_{12}$ (1.51 g, 3 mmol) was taken in THF (40 mL) and I_2 (1.01, 4 mmol) was added dropwise stirred for 5 min. under dry nitrogen at 25 °C. Phenylacetylene (0.204 g, 2 mmol) was added and the contents were furthter stirred for 12 h at the same temperature Then metal carbonyl complexes were oxidised by transferring reaction mixture into a

conical flask containing $CuCl_2.2H_2O$ (3.4 g, 20 mmol) in acetone (10 mL) and stirred for 30 min. Saturated NaCl solution was added and the resulting solution was extracted with ether (100 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography (silica gel, hexane-EtOAc). Ethyl acetate (1%) in hexane eluted the benzoquinones.



Yield : 48% (0.25 g)

IR (KBr) : 1649 cm^{-1}

^{1}H NMR : (200 MHz) δ = 7.45 (m, 20 H for **160a** and **160b**), 6.88 (s, 2 H for **160b**), 6.84 (s, 2 H for **160a**) *ppm*

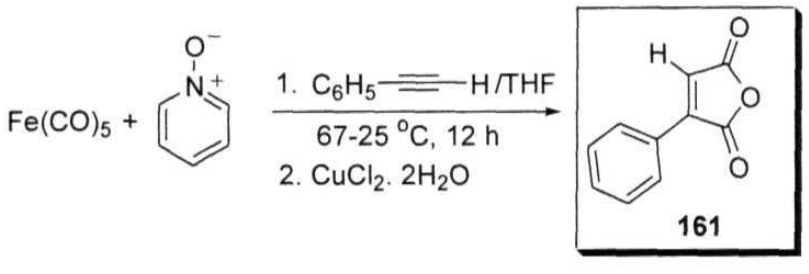
^{13}C NMR : (50 MHz) δ = 187.5, 146.5, 133.2, 132.6, 130.0, 129.4, 128.4 *ppm*

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the reported data.[193]

3.6 Reaction of 1-Alkynes with Pyridine *N*-oxide/$Fe(CO)_5$

A mixture of $Fe(CO)_5$ (1.96 g, 10 mmol) and pyridine *N*-oxide (0.95 g, 10 mmol) in THF (50 mL) was stirred at 67 °C until the colour changed from light yellow to dark brown (ca. 1 h). Phenylacetylene (0.20 g, 2 mmol) was added and the refluxing was

continued for further 12 h. The metal carbonyl complexes were oxidised by pouring the reaction mixture to a conical flask containing $CuCl_2.2H_2O$ (3.4 g, 20 mmol) in acetone (10 mL). The contents were stirred for 30 min. Saturated NaCl solution was added and the resulting solution was extracted with ether (100 mL), dried over anhydrous $MgSO_4$ and concentrated. The residue was subjected to column chromatography (silica gel, hexane-EtOAc). Ethyl acetate (1%) in hexane eluted the cyclic anhydride **161**.



Yield : 59% (0.2 g)

mp : 119-120 °C (Lit.[186a] mp 120-121 °C)

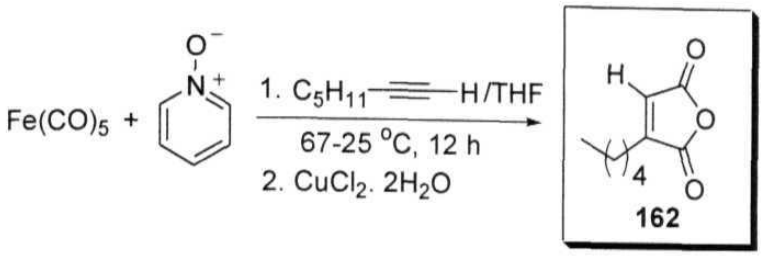
IR (neat) : 3117, 1839, 1765 cm^{-1}

^{1}H NMR : (200 MHz) δ= 7.3-7.9 (m, 5H), 7.0 (s, 1H) *ppm*

^{13}C NMR : (50 MHz) δ= 164.5, 163.6, 146.6, 146.5, 133.7, 129.3, 129, 126.4 *ppm*

MS (EI) : *m/z* 174 (M^+, 10%)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the reported data.[186]



Yield : 64% (0.22 g)

IR (neat) : 3111, 1842, 1772 cm^{-1}

^{1}H NMR : (200 MHz) δ= 6.5 (s, 1H), 2.5 (t, J = 7.1 Hz, 2H), 0.8-1.9 (m, 9H) *ppm*

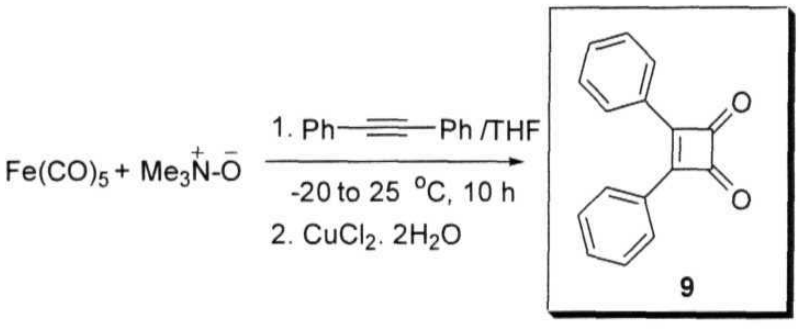
^{13}C NMR : (50 MHz) δ= 165.8, 164.0, 153.8, 128.4, 31.1, 26.5, 25.8, 22.1, 13.7 *ppm*

MS (EI) : *m/z* 168 (M^+, 12%)

3.7 General Procedure for the Preparation of Cyclobutenedione Using Alkynes and $Me_3NO/Fe(CO)_5$

To a solution of anhydrous Me_3NO (0.9 g, 12 mmol) in THF (30 mL) was dropwise added $Fe(CO)_5$ (2.94 g, 15 mmol) in THF (40 mL) over a period of 30 minutes at -20 °C under dry nitrogen. The reaction starts with immediate evolution of CO_2 and the colour of the reactoin mixture changes from yellow to dark brown. The reaction mixture was stirred for another 1 h and the contents were slowly brought to room temperature.

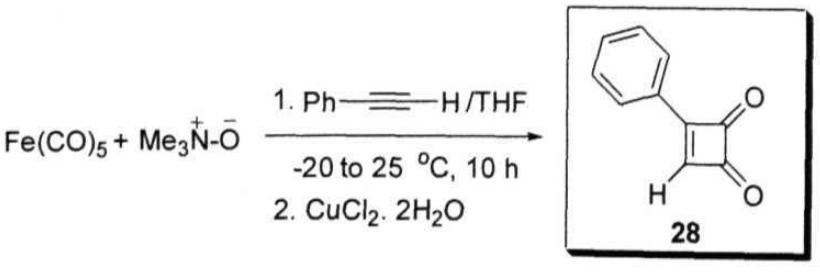
Diphenylacetylene (0.44 g, 2.5 mmol) was added and the contents were furthur stirred for 10 h at 25 °C. The metal carbonyl complexes were oxidised using $CuCl_2.2H_2O$ (4.2 g, 25 mmol) in acetone (15 mL). Saturated NaCl solution (50 mL) was added and the contents were extracted with ether (2x75 mL) dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to column chromatography (silica gel, hexane-EtOAc). Ethyl acetate (1.5%) in hexane eluted the cyclobutenedione **9**.



Yield : 73% (0.43 g)

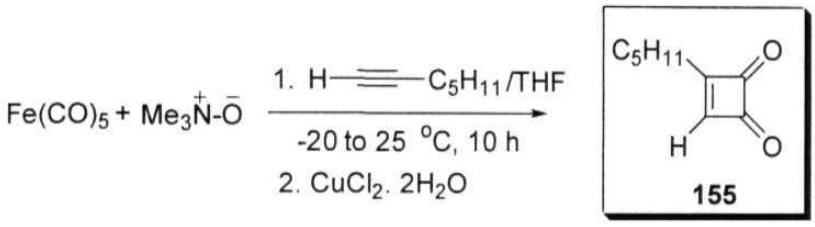
The IR, ^1H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound obtained in Br_2 oxidation of the corresponding acyloxyferroles.

The above procedure was followed for the conversion of other alkynes to the corresponding cyclobutenediones.



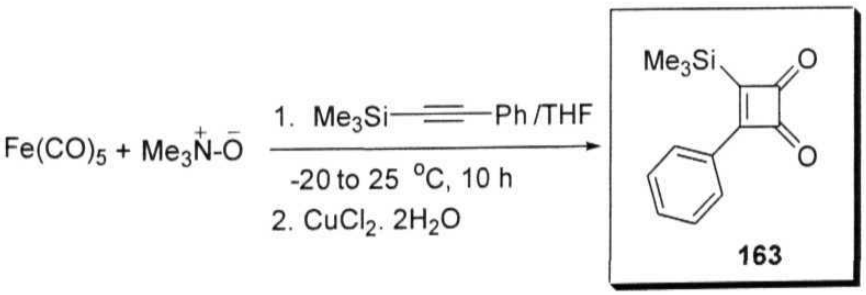
Yield : 62% (0.24 g)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound obtained in Br_2 oxidation of acyloxyferroles.



Yield : Yield: 50% (0.19g)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound obtained in Br_2 oxidation of the corresponding acyloxyferroles.



Yield : 75% (0.43 g)

mp : 101-102 °C (Lit.[168d] mp 102.8-103.2 °C)

IR (neat) : 1774, 1766 cm^{-1}

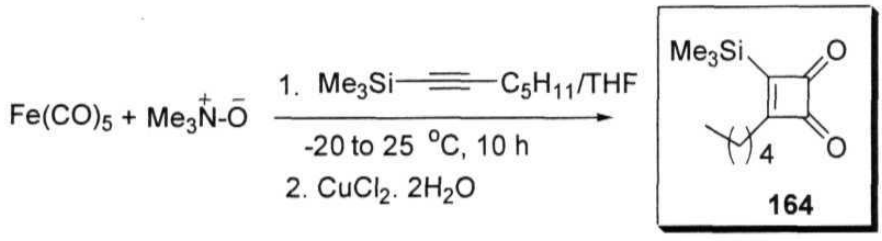
^{1}H NMR : (400 MHz) δ= 7.8-7.2 (m, 5H), 0.45 (s, 9H) *ppm*

(Spectrum No. 11)

^{13}C NMR : (50 MHz) δ= 202.6, 200.3, 199.3, 197.8, 133.5, 129.4, 129.3,129.2, -1.8 *ppm* **(Spectrum No. 12)**

MS (EI) : *m/z* 230 (M^+, 8%) **(Spectrum No. 15)**

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the reported data.[168d]



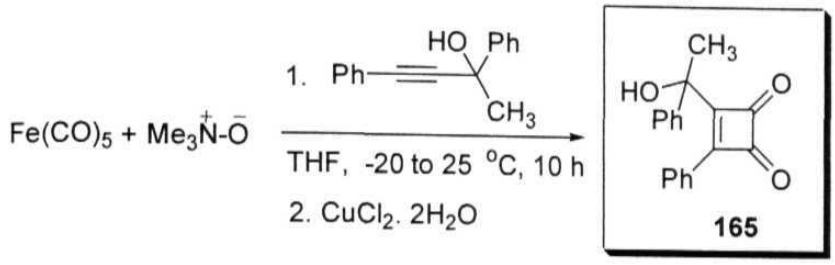
Yield : 68 % (0.38 g)

IR (neat) : 1778, 1766 cm^{-1}

^{1}H NMR : (200 MHz) δ = 2.87 (t, *J* = 7.3, 2H), 1.17-1.67 (m, 6H), 0.92 (t, *J* = 6.9 Hz, 3H), 0.35 (s, 9H) *ppm*

^{13}C NMR : (50 MHz) δ = 211.3, 207.7, 201.5, 200.1, 31.7, 29.1, 26.9, 22.2, 13.7, -2.1 *ppm*

MS (EI) : *m/z* 224 (M^+, 10%), 154[(M^+-$CH_2(CH_2)_3CH_3$), 100%], 73[$(SiMe_3)^+$, 60%]



Yield : 70% (0.49 g)

IR (neat) : 3479, 1789, 1770 cm^{-1}

^{1}H NMR : (400 MHz) δ= 8.2-7.2 (m, 10H), 2.9 (s, 1H), 2.1 (s, 3H) *ppm*

(Spectrum No. 13)

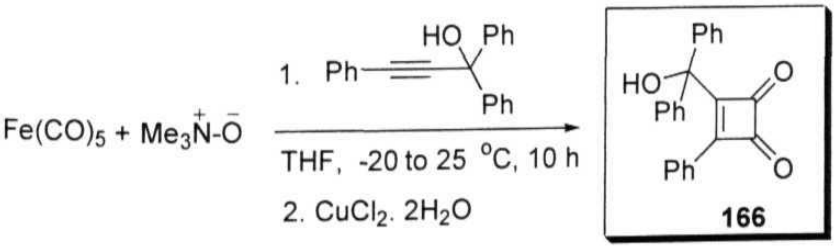
^{13}C NMR : (50 MHz) δ= 197.8, 196.5, 195.8, 189.2, 142.6, 133.6, 131.2, 128.9, 128.8, 128.4, 127.6, 124.9, 74.9, 28.2 *ppm* **(Spectrum No. 14)**

MS (EI) : *m/z* 278 (M^+, 15%)

Analysis : for $C_{18}H_{14}O_3$

Calculated: C, 77.68%; H, 5.07%; O, 17.25%

Found: C, 77.69%; H, 4.95%



Yield : 65% (0.55 g)

IR (neat) : 3483, 1784, 1768 cm^{-1}

^{1}H NMR : (400 MHz) δ= 8.4-7.3 (m, 15H), 3.2 (s, 1H) *ppm*

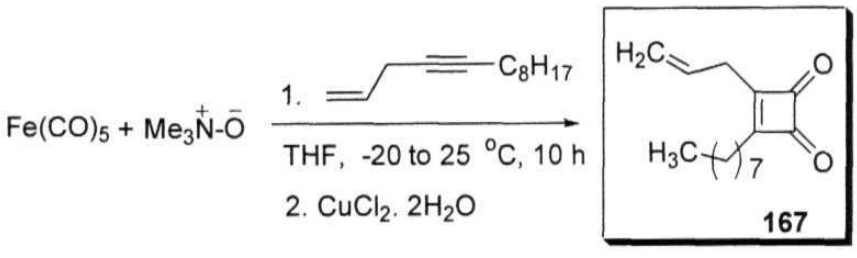
^{13}C NMR : (50 MHz) δ= 198.4, 197.5, 195.2, 189.8, 141.4, 133.5, 131, 128.9, 128.8, 128.7, 128.4, 80.5 *ppm*

MS (EI) : *m/z* 340 (M^+, 8%) **(Spectrum No. 16)**

Analysis : for $C_{23}H_{16}O_3$

Calculated: C, 81.16%; H, 4.74%; O, 14.1%

Found: C, 81.22%; H, 4.73%



Yield : 57% (0.33 g)

IR (neat) : 3033, 1776, 1768, 1631, cm^{-1}

^{1}H NMR : (400 MHz) δ= 7.3-7.1 (m, 1H), 6.4 (dd, J = 10.7, 1.5 Hz, 2H), 2.6 (t, J = 7.5 Hz, 2H); 1.9 (dd, J = 5.5, 1.5 Hz, 2H); 1.6 (m, 2H), 1.2 (m, 10H), 0.8 (t, J = 7.0 Hz, 3 H) *ppm* **(Spectrum No. 17)**

^{13}C NMR : (50 MHz) δ= 198.2, 197.8, 195.6, 190.4, 146.5, 119.4, 31.7, 29.6, 29.1, 29, 26.5, 26.2, 22.5, 20, 14 *ppm* **(Spectrum No. 18)**

MS (EI) : *m/z* 234 (M^+, 12%) **(Spectrum No. 19)**

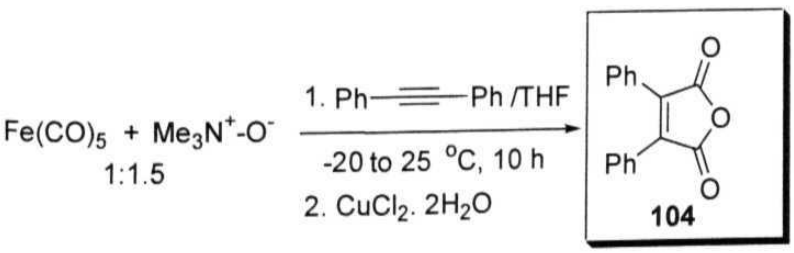
Analysis : for $C_{15}H_{22}O_2$

Calculated: C, 76.88%; H, 9.46%; O, 13.65%

Found: C, 77.06%; H, 9.47%

3.8 General Procedure for the Preparation of Cyclic Anhydrides Using Alkynes and $Fe(CO)_5$/excess Me_3NO

To a solution of Me_3NO (1.1 g, 15 mmol) in THF (30 mL) was dropwise added $Fe(CO)_5$ (1.96 g, 10 mmol) in THF (40 mL) over a period of 30 min. at -20 °C under dry nitrogen. Diphenylacetylene (0.44 g, 2.5 mmol) was added and the contents were slowly brought to room temperature. Stirring was furthur continued for 10 h at room temperature. The metal carbonyl complexes were oxidised using $CuCl_2.2H_2O$ (4.2 g, 25 mmol) in acetone (15 mL). After usual workup, the residue was subjected to column chromatography (silica gel, hexane-EtOAc). Ethyl acetate (1%) in hexane eluted the cyclic anhydride **104**.



Yield : 80% (0.5 g)

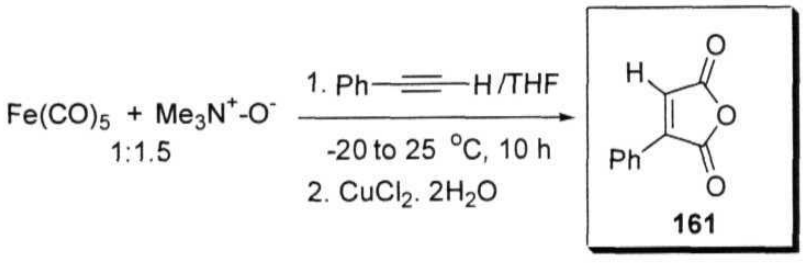
mp : 156-158 °C (Lit.[186b] mp 156 °C)

IR (neat) : 1822, 1757, 1637 cm^{-1}

^{1}H NMR : (200 MHz) δ= 8.1-7.2 (m, 10H) *ppm*

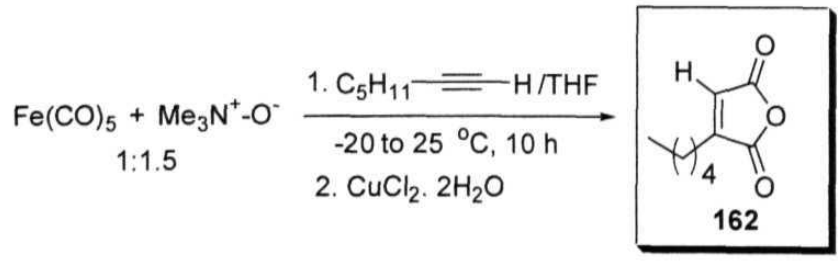
^{13}C NMR : (50 MHz) δ=164.8, 138.2, 131.1, 129.7, 128.9, 127.2 *ppm*

The above procedure was followed for the conversion of other alkynes to the correspon-ding maleic anhydride derivatives.



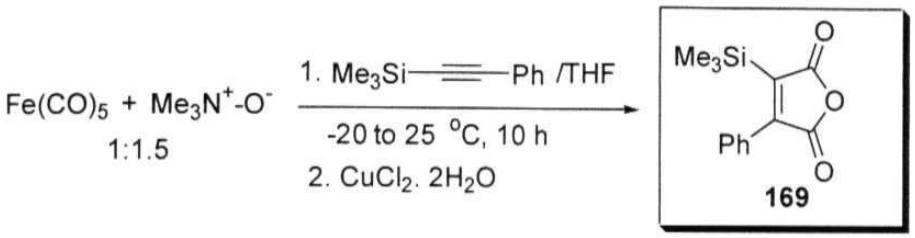
Yield : 72% (0.313 g)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound obtained in a reaction of alkyne with $Fe(CO)_5$/pyridine *N*-oxide.



Yield : 68% (0.29 g)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound obtained in a reaction of alkyne with $Fe(CO)_5$/pyridine *N*-oxide.



Yield : 75% (0.46 g)

mp : 99-101 °C

IR (KBr) : $\tilde{\nu}$ = 1832, 1770 cm^{-1}

^{1}H NMR : (400 MHz) δ= 7.59-7.45 (m, 5H), 0.25 (s, 9H) *ppm*

(Spectrum No. 21)

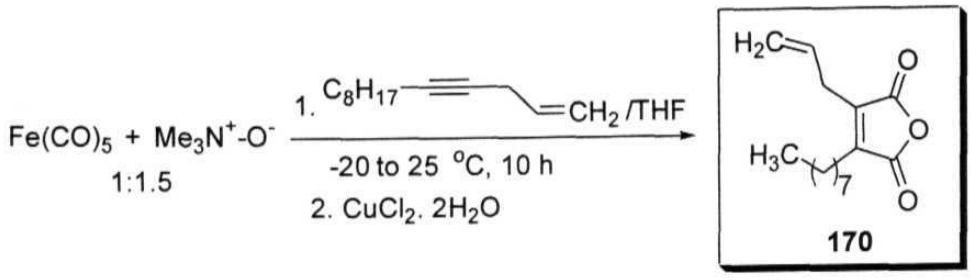
^{13}C NMR : (100 MHz) δ= 168.3, 166.6, 156.8, 145.4, 132, 130.5, 129.8, 129.3, -0.1 *ppm* **(Spectrum No. 22)**

MS (EI) : *m/z* 246 (M^+, 10%)

Analysis : for $C_{13}H_{14}O_3Si$

Calculated: C, 63.39%; H, 5.73%; O, 19.48%; Si, 11.4%

Found: C, 63.43%; H, 5.79%



Yield : 70% (0.37 g)

IR (neat) : 1840, 1769 cm^{-1}

^{1}H NMR : (200 MHz) δ= 5.8 (m, 1H), 5.2 (dd, J =7.5, 1.5 Hz , 2H), 3.1 (d, J =6.3 Hz , 2H), 2.4 (t, J = 7.0 Hz , 2H), 1.4 (m, 2H) 1.1 (m, 10H), 0.7 (t, J = 6.2 Hz, 3H) *ppm* **(Spectrum No. 23)**

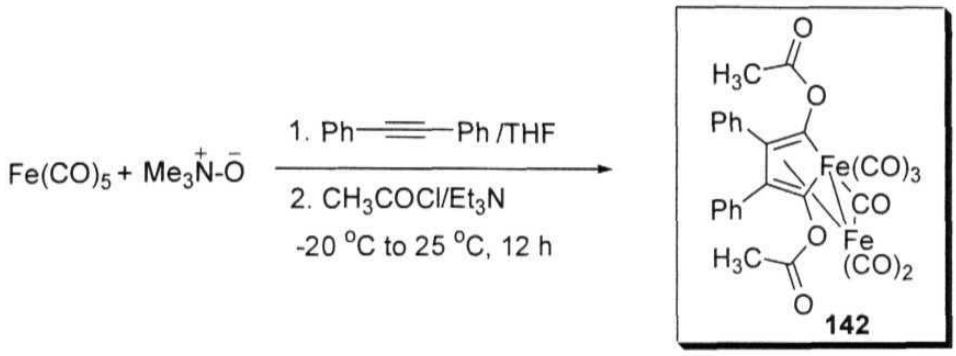
^{13}C NMR : (50 MHz) δ=165.6, 165.4, 145.2, 141.3, 131.1, 118.2, 31.6, 29.4, 29.1, 28.9, 28.2, 27.6, 24.2, 22.5, 13.8 *ppm* **(Spectrum No. 24)**

MS (EI) : *m/z* 250 (M^+, 8%) **(Spectrum No. 20)**

3.9 Preparation of Acyloxyferrole Complex Using Alkyne, $Fe(CO)_4$/ Me_3NO and CH_3COCl/Et_3N

To the "$Fe(CO)_4$" species generated in THF using anhydrous Me_3NO (0.9 g, 12 mmol) and $Fe(CO)_5$ (2.92 g, 15 mmol) at -25 °C was added diphenylacetylene (0.44 g, 2.5 mmol) and stirred for 2 h 25 °C. Then, Et_3N (1.01 g, 10 mmol) and CH_3COCl (1,17 g, 15 mmol) were added and the contents were further stirred for 12 h. Ether (100 mL) was added and the reaction mixture was washed successively with H_2O (40 mL), brine (2 X 50

mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to column chromatography (silica gel, hexane-EtOAc). Ethyl acetate (1%) in hexane eluted the ferrole complex.



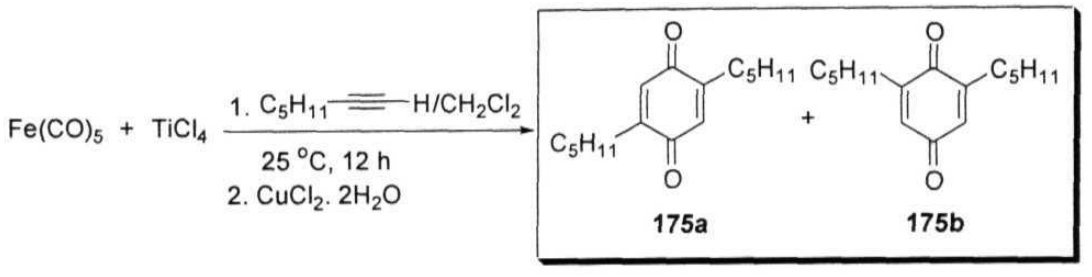
Yield : 48% (0.72 g)

The IR, ^1H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound obtained in a reaction of alkyne with $Fe_3(CO)_{12}$/RCOCl/Et_3N.

3.10 General Procedure for the Preparation of Benzoquinones Using Alkynes and $Fe(CO)_5/TiCl_4$

To a solution of $Fe(CO)_5$ (1.95 g, 10 mmol) in CH_2Cl_2 (40 mL) was added $TiCl_4$ (2.2 mL of 1:1 solution of $TiCl_4/CH_2Cl_2$,10 mmol) at 0 °C and stirred for 10 min. under dry nitrogen. 1-Heptyne (0.289 g, 3 mmol) was added and the contents were brought to 25 °C and stirred for 12 h at 25 °C. The metal carbonyl complexes were oxidised using $CuCl_2.2H_2O$ (4.2 g, 25 mmol) in acetone (15 mL). Saturated NaCl solution was added and the contents were extracted with ether (2x75 mL), dried over anhydrous Na_2SO_4 and

concentrated under reduced pressure. The residue was subjected to column chromatography (silica gel, hexane-EtOAc). Ethyl acetate (1%) in hexane eluted a mixture of 2,5- and 2,6 disubstituted benzoquinones.

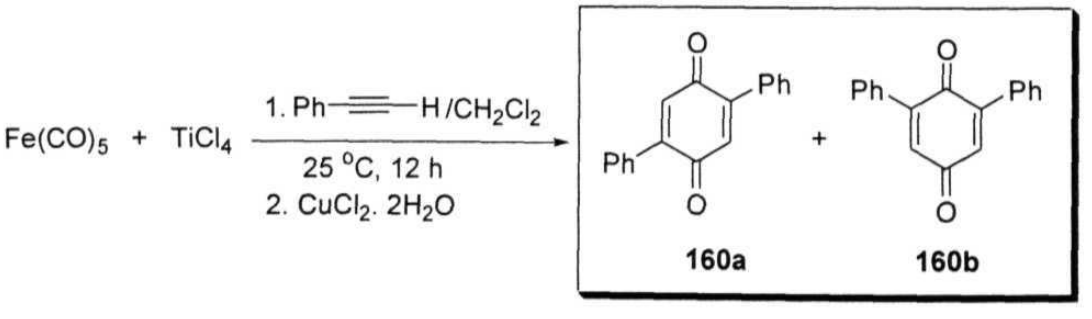


Yield : 60% (0.45 g)

IR (neat) : 1657 cm^{-1}

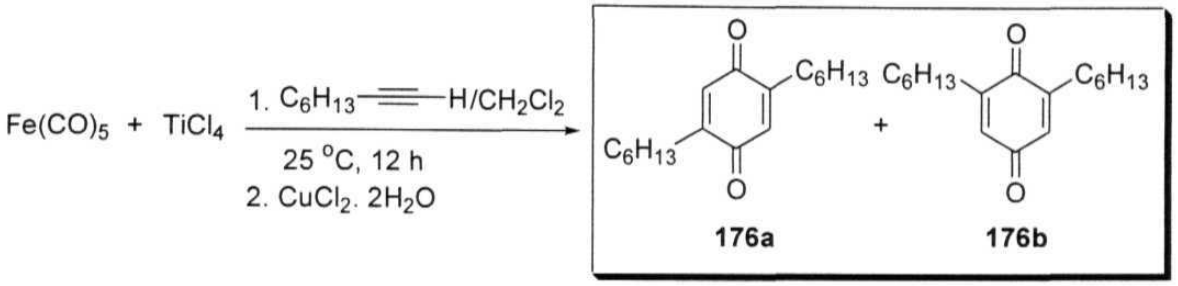
^{1}H NMR : (200 MHz) δ= 6.52 (s, 2 H for **175b**), 6.50 (s, 2 H for **175a**), 1.16-2.46 (m, 32 H for **175a** and **175b**), 0.89 (t, J=6.8 Hz, 12 H) *ppm* **(Spectrum No. 25)**

^{13}C NMR : (50 MHz) δ= 187.9, 187.6, 149.7, 149.2, 132.5, 132, 31.4, 29, 28.5, 27.5, 22.3, 13.8 *ppm* **(Spectrum No. 26)**



Yield : 35% (0.27 g)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound obtained in the reaction of alkynes with $Fe_3(CO)_{12}/I_2$.

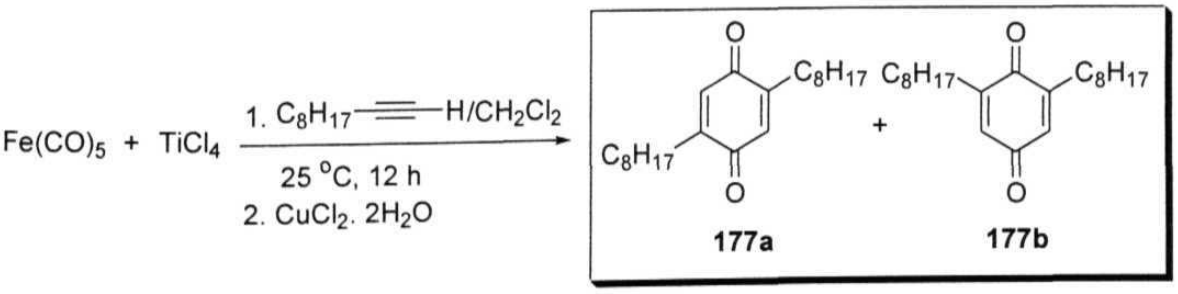


Yield : 55% (0.46 g)

IR (neat) : 1657 cm^{-1}

^{1}H NMR : (200 MHz) δ= 6.52 (s, 2H for **176b**), 6.50 (s, 2 H for **176a**), 1.16-2.46 (m, 40 H for **176a** and **176b**), 0.89 (t, J=6.8 Hz, 12 H for **176a** and **176b**) *ppm*

^{13}C NMR : (50 MHz) δ= 187.6, 187.3, 149.5, 149.1, 132.4, 131.9, 31.1, 29.0, 28.6, 27.3, 22.1, 13.6 *ppm*



Yield : 53% (0.53 g)

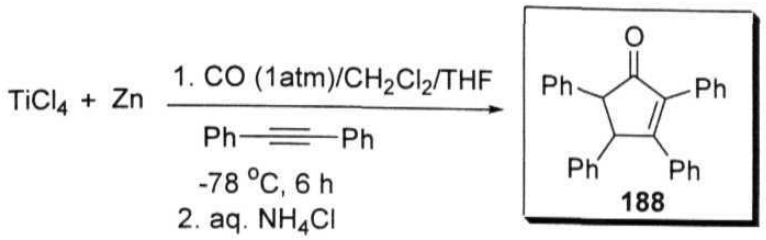
IR (neat) : 1655 cm^{-1}

^{1}H NMR : (200 MHz) δ = 6.51 (s, 2H for **177b**), 6.48 (s, 2 H for **177a**), 2.44 (m, 8 H for **177a** and **177b**), 1.18-1.70 (m, 48 H for **177a** and **177b**), 0.90 (t, J=6.7 Hz, 12 H for **177a** and **177b**) *ppm*

^{13}C NMR : (50 MHz) δ = 187.8, 187.3, 149.5, 149.1, 132.4, 131.6, 31.7, 29.7, 29.2, 29.0, 28.6, 27.8, 22.5, 13.9 *ppm*

3.11 Reaction of Alkynes with CO in the Presence of $TiCl_4$/Zn

To a solution of $TiCl_4$ (3.3 mL of 1:1 solution of $TiCl_4/CH_2Cl_2$, 15 mmol) and Zn (1.95 g, 30 mmol) in DCM (50 mL) was added THF (1.5 mL) and stirred for 1 h at 25 °C under nitrogen atmosphere. Then, the contents were cooled to –78 °C while continuously bubbling CO gas. Diphenylacetylene (0.44 g, 2.5 mmol) was added and stirred for 5 h at –78 °C. Then, the contents were brought to room temperature and stirred for 1 h. The reaction mixture was quenched with NH_4Cl solution. Dichloromethane (100 mL) was added and the organic layer was washed successively with H_2O (40 mL), brine (2 X 50 mL), dried over Na_2SO_4 and concentrated. The residue was subjected to column chromatography (silica gel, hexane-EtOAc). The cyclopentenone **188** was eluted with ethyl acetate (1.5%) in hexane.



Yield : 70%, (0.68 g)

mp : 160-161 °C (Lit.[9a] mp 161-162 °C)

IR (neat) : 1840, 1769 cm^{-1}

^{1}H NMR : (200 MHz) δ = 7.1-7.5 (m, 20H), 4.6 (dd, *J* = Hz , 1H), 3.8 (dd, *J* = Hz , 1H) *ppm* **(Spectrum No. 27)**

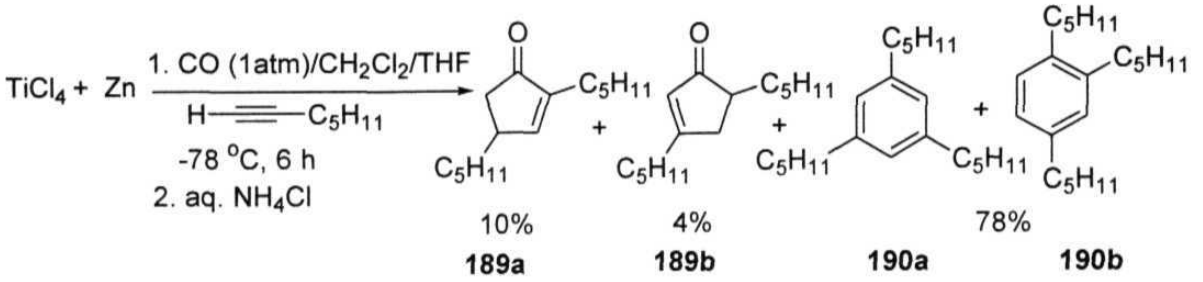
^{13}C NMR : (50 MHz) δ = 205.8, 168.9, 141.5, 140.1, 139.3, 134.7, 131.8, 129.8, 129.4, 129.0, 128.4, 128.3, 128.1, 127.8, 127.6, 127.2, 127.0, 63.1, 57.7 *ppm* **(Spectrum No. 28)**

Analysis : for $C_{29}H_{22}O$

Calculated: C, 90.12%; H, 5.74%; O, 4.14%

Found: C, 90.07%; H, 5.72%

The above procedure was followed for 1-heptyne, but the reaction scale was doubled [$TiCl_4$ and Zn (30 mmol:60 mmol), heptyne (5 mmol)]



Cyclopentenone 189a

Yield : 10% (0.11 g)

IR (neat) : 2928, 2858, 1707, 1631 cm^{-1}

^{1}H NMR : (200 MHz) δ= 7.1 (bs, 1H), 2.6-0.8 (m, 25H) *ppm*

^{13}C NMR : (50 MHz) δ= 211.5, 155.4, 145.7, 45.4, 33.4, 31.7, 31.5, 27.3, 26.8, 24.7, 22.4, 13.8 *ppm*

Cyclopentenone 189b

Yield : 4% (0.044 g)

IR (neat) : 2928, 2860, 1701, 1618 cm^{-1}

^{1}H NMR : (200 MHz) δ= 5.9 (bs, 1H), 2.8-0.8 (m, 25H) *ppm*

^{13}C NMR : (50 MHz) δ= 212.1, 181.5, 128.7, 46.2, 38.3, 33.4, 31.7, 31.4, 26.8, 26.7, 22.4, 22.3, 13.9 *ppm*

Tripentyl benzenes 190a and **190b**

Yield : 78% (1.12 g)

IR (neat) : 3005, 1602 cm^{-1}

^{1}H NMR : (200 MHz) δ= 7.23-7.01 (m, 2H for **190b**), 6.92 (s, 4H for **190a** and

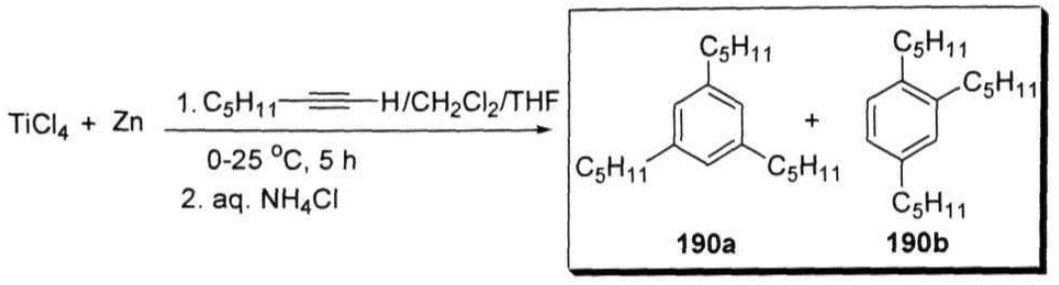
190b), 2.65 (m, 12H), 1.71 (m, 12H), 1.46 (m, 24H), 1.0 (m, 18H) *ppm*

^{13}C NMR : (50 MHz) δ= 142.8, 126.1 (for **190a**) 140.4, 140.3, 137.8, 129.5, 129.2, 126.0 (for **190b**) 36.3, 36.0, 33.1, 32.7, 32.4, 32.0, 31.6, 31.4, 22.9, 14 *ppm*

MS (EI) : *m/z* 288 (M^+, 83%)

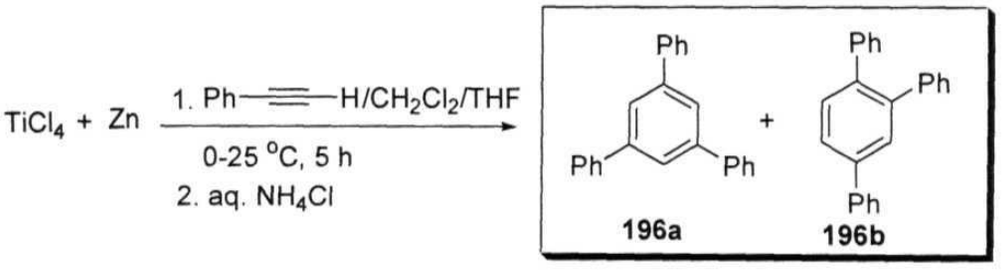
3.12 General Procedure for the Preparation of Trisubstituted Benzenes Using Alkynes and $TiCl_4$/Zn

To a solution of $TiCl_4$ (2.2 mL of 1:1 solution of $TiCl_4/CH_2Cl_2$, 10 mmol) and Zn (1.3 g, 20 mmol) in DCM (50 mL) was added THF (1.5 mL) and stirred for 30 min. at 25 °C under nitrogen atmosphere. Alkyne (2.5 mmol) was added and the contents were stirred for 5 h. Then, the reaction mixture was quenched with NH_4Cl solution. Dichloromethane (100 mL) was added and the organic layer was washed successively with H_2O (40 mL), brine (2X50 mL), dried over Na_2SO_4 and concentrated. The residue was subjected to column chromatography (silica gel, hexane). 1,3,5-and 1,2,4-Trisubstituted benzenes were eluted with hexane.



Yield : 95% (0.68 g)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of a compound obtained in a reaction of 1-heptyne with $TiCl_4$/Zn and CO reagent system.



Yield : 88% (0.67 g)

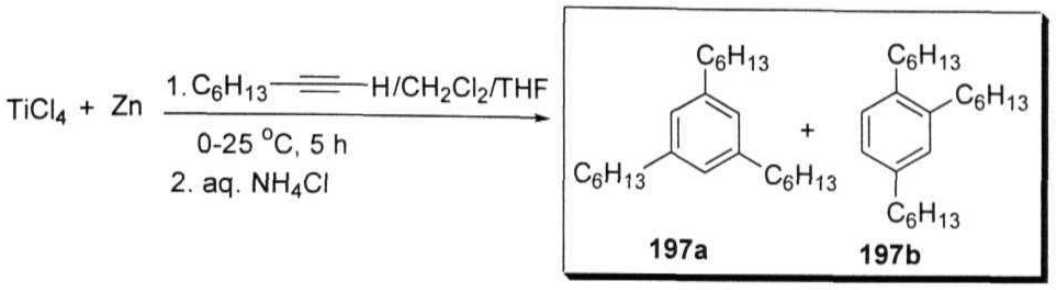
mp : 148-150 °C

IR (KBr) : 3045, 3015, 1593, 1494 cm^{-1}

^{1}H NMR : (200 MHz) δ= 8.12-8.01 (m, 2H for **196b**), 7.8 (s, 4H for **196a** and **196b**), 7.75-7.3 (m, 30H) *ppm*

^{13}C NMR : (50 MHz) δ= 142.4, 141.2, 139.7, 139, 5 139 2, 137.8, 129.7, 129 4, 128.9, 127.5, 127.4, 125.5 *ppm*

MS (EI) : *m/z* 306 (M^+, 100%)

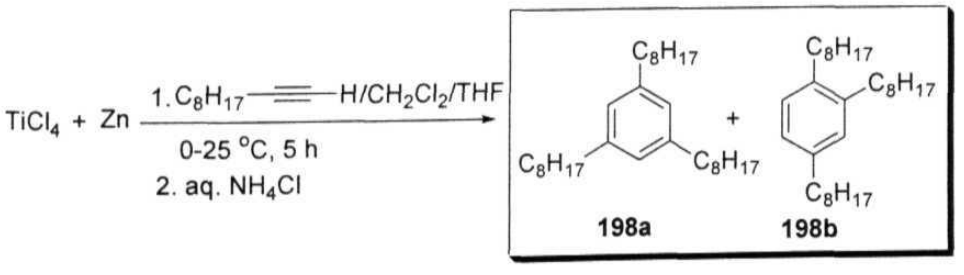


Yield : 95% (0.78 g)

IR (neat) : 3005, 1602 cm^{-1}

^{1}H NMR : (200 MHz) δ= 7.23-7.0 (m, 2H for **197b**), 6.91 (s, 4H for **197a** and **197b**), 2.63 (m, 12H), 1.69 (m, 12H), 1.46 (m, 36H), 0.9 (m, 18H) *ppm*

^{13}C NMR : (50 MHz) δ= 142.8, 126.2 (for **197a**), 140.4, 140.3, 137.8, 129.5, 129.2, 126.1 (for **197b**), 36.3, 36.0, 33.8, 33.1, 32.6, 32.3, 31.9, 31.4, 30.7, 23.2, 14.3

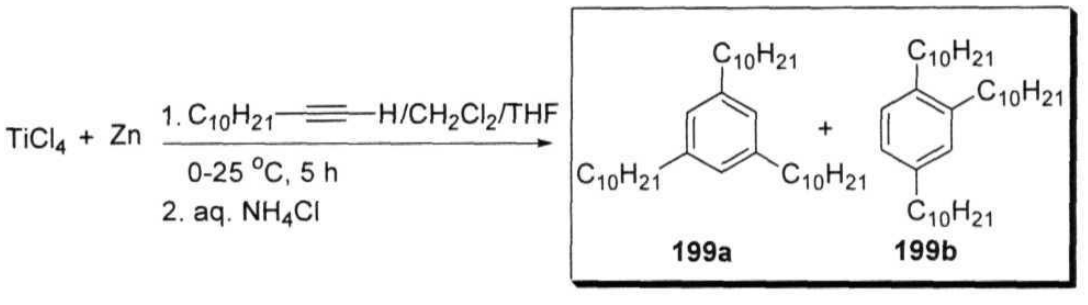


Yield : 92% (0.95 g)

IR (neat) : 3004, 1602 cm^{-1}

^{1}H NMR : (200 MHz) δ= 7.12-6.9 (m, 2H for **198b**), 6.83 (s, 4H for **198a** and **198b**), 2.57 (m, 12H), 1.59 (m, 12H), 1.31 (m, 60H), 0.91(m, 18H) *ppm* **(Spectrum No. 29)**

^{13}C NMR : (50 MHz) δ= 142.7, 125.9 (for **198a**), 140.3, 140.1, 137.7, 129.3, 129.0, 125.8 (for **198b**), 36.3, 36.1, 35.7, 32.8, 32.4, 32.0, 31.6, 315, 29.9, 29.6, 29.4, 22.7, 14.1 *ppm* **(Spectrum No. 30)**



Yield : 87% (1.08 g)

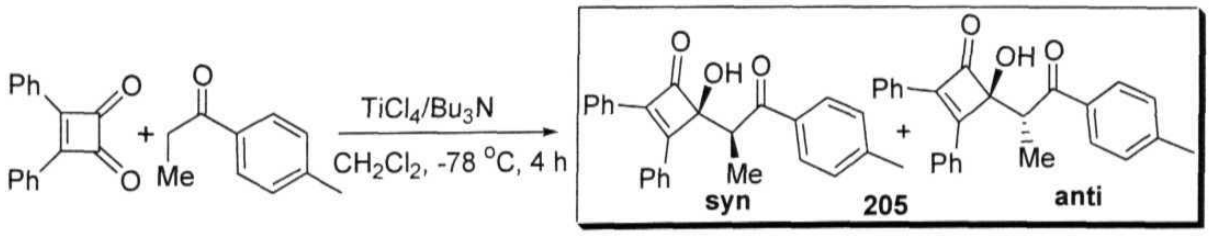
IR (neat) : 3004, 1602 cm^{-1}

^{1}H NMR : (200 MHz) δ= 7.12-6.9 (m, 2H for **199b**), 6.83 (s, 4H for **199a** and **199b**), 2.5 (m, 12H), 1.6 (m, 12H), 1.3 (m, 84H), 0.9 (m, 18H) *ppm*

^{13}C NMR : (50 MHz) δ= 142.7, 125.9 (for **199a**), 140.3, 140.1, 137.7, 129.3, 129.0, 125.8 (for **199b**), 36.1,36.2, 35.7, 33.0, 32.9, 32.5, 32.0, 31.7, 31.5, 29.9, 29.8, 29.6, 9.5,28.8, 28.7, 22.8, 14.1 *ppm*

3.13 $TiCl_4/Bu_3N$ Promoted Aldol Reaction of Ketones with Cyclobutenediones

$TiCl_4$ (0.13 mL of 1:1 solution of $TiCl_4/CH_2Cl_2$, 1.2 mmol) was added drop-wise to a solution of 4-methylpropiophenone (0.162 g, 1.1 mmol) in CH_2Cl_2 5 mL at –78 °C under N_2 atmosphere (the contents become yellow slurry). After 5 min. of stirring, Bu_3N (0.28 g, 1.5 mmol) was added-drop wise and the resulting deep red solution is stirred at –78 °C under N_2 for 1.5 h. After the drop-wise addition of 3,4-diphenylcyclobutenedione (0.234 g, 1 mmol) in CH_2Cl_2 (2 mL), stirring was continued at the same temperature for 3 h. The reaction was quenched by addition of 2 mL water at low temperature and the solvent was removed under reduced pressure. The crude mixture was washed with dilute HCl and aqueous layer was extracted with ether. The product **205** was isolated using column chromatography (silica gel, hexane/ethylacetate 94:6).



Yield : 89% (0.34 g)

syn:anti 88:12

mp : 95-97 °C

IR (neat) : 3386, 1755, 1674, 1630 cm^{-1}

^{1}H NMR : (200 MHz) δ = (syn) 7.89-7.67 (m, 6H), 7.43-7.18 (m, 8H), 5.18 (s, 1H), 4.17 (q, J = 6.9 Hz, 1H), 2.38 (s, 3H), 1.36 (d, J = 6.9 Hz, 3H), (anti) 3.82 (q, J = 6.5 Hz, 1H), 2.31 (s, 3H), 1.42 (d, J = 6.5 Hz, 3H) *ppm* **(For syn:anti Spectrum no. 31, For syn Spectrum no. 33)**

^{13}C NMR : (50 MHz) δ = (syn) 203.2, 192.7, 168.5, 146, 144.5, 133, 131, 130.7, 130.6, 129.8, 129.7, 128.6, 128.5, 127.7, 127.6, 126.8, 95.8, 43.6, 21.6, 14.6, (anti) 203.5, 189.6, 169.6, 145.9, 144.3, 132.8, 96.2, 42.9, 14.8 *ppm* **(For syn:anti Spectrum no. 32, For syn Spectrum no. 34)**

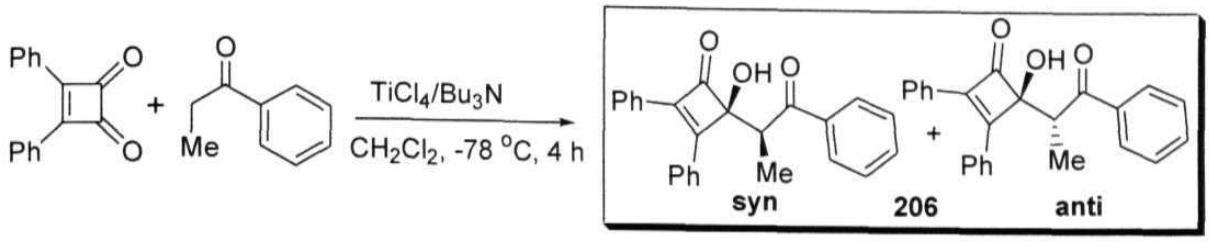
MS (EI) : *m/z* 382 (M^+ 17%), 119 [$(MeC_6H_4CO)^+$ 100%]

Analysis : for $C_{26}H_{22}O_3$

Calculated: C, 81.65%; H, 5.8%; O, 12.55%

Found: C, 81.61%; H, 5.8%

The above procedure was followed for the addition of other ketones to diphenylcyclobutenedione.



Yield : 94% (0.35 g)

syn:anti 90:10

mp : 102-104 °C

IR (neat) : 3417, 1753, 1679, 1622 cm^{-1}

^{1}H NMR : (200 MHz) δ = (syn) 7.92-7.45 (m, 15 H), 5.12 (s, 1H), 4.25 (q, J = 7.5 Hz, 1H), 1.44 (d, J = 7.5 Hz, 3H), (anti) 4.23 (q, J = 7.5 Hz, 1H), 1.54 (d, J = 7.5 Hz, 3H) *ppm*

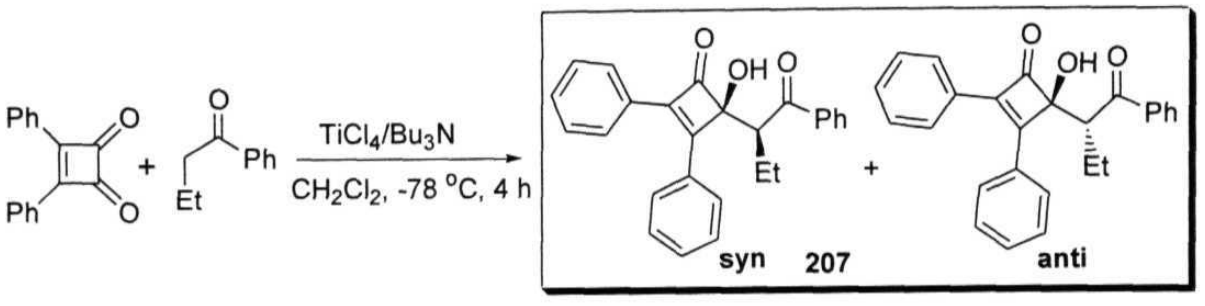
^{13}C NMR : (50 MHz) δ = (syn) 203.5, 192.9, 168.5, 146.3, 136, 133.5, 131.7, 131.4, 131.1, 129.8, 129.6, 128.7, 128.4, 128.2, 127.9, 127.8, 95.7, 44, 14.6, (anti) 203.7, 191.3, 170.2, 146.2, 136.1, 96,1, 14.7 *ppm*

MS (EI) : *m/z* 368 (M^+ 14%), 105 [$(PhCO)^+$ 100%]

Analysis : for $C_{25}H_{20}O_3$

Calculated: C, 81.5%; H, 5.47%; O, 13.03%

Found: C, 81.5 %; H, 5.46 %



Yield : 82% (0.31 g)

syn:anti : 85:15

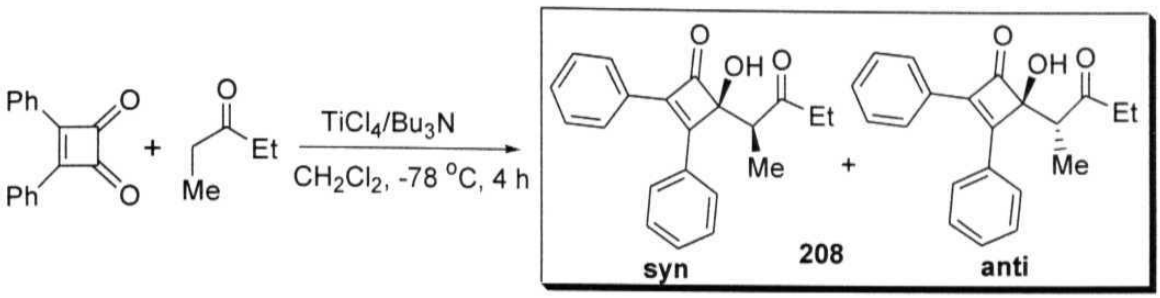
mp : 90-92 °C

IR (neat) : 3433, 1747, 1681, 1624 cm^{-1}

^{1}H NMR : (200 MHz) δ = (syn) 7.78-7.19 (m, 15 H), 5.65 (s, 1H), 4.16 (q, J = 7.2 Hz, 1H), 2.16-199 (sextet, J = 7.1 Hz, 2H), 0.89 (t, J = 7.1 Hz, 3H), (anti) 4.15 (q, J = 7.2 Hz, 1H), 2.1-189 (sextet, J = 7.1 Hz, 2H), 0.91 (t, J = 7.1 Hz, 3H) *ppm*

^{13}C NMR : (50 MHz) δ = (syn) 203.6, 192.9, 168.5, 146.2, 137.9, 131.6, 130.9, 130.4, 129.9, 129.8, 129.6, 128.9, 128.4, 127.9, 127.4, 126.9, 95.7, 51.4, 23, 12.5, (anti) 204.6, 191.3, 171.1, 146, 137.7, 131.2, 96.2, 51.1, 23.3, 12.4. *ppm*

MS (EI) : *m/z* 382 (M^+ 12%), 105 [$(PhCO)^+$ 100%]



Yield : 86% (0.27 g)

syn:anti : 85:15

mp : 68-70 °C

IR (neat) : 3433, 1755, 1712, 1620 cm^{-1}

^{1}H NMR : (400 MHz) δ = (syn) 7.8-7.68 (m, 4 H), 7.46-7.34 (m, 6 H), 4.92 (s, 1H), 3.24 (q, J = 6.8 Hz, 1H), 2.48 (q, J = 7.1 Hz, 2H), 1.22 (d, J = 6.8 Hz, 3H), 0.96 (t, J = 7.1 Hz, 3H), (anti) 3.22 (q, J = 6.8 Hz, 1H), 2.4 (q, J = 7.1 Hz, 2H), 1.24 (d, J = 6.8 Hz, 3H), 0.94 (t, J = 7.1 Hz, 3H) *ppm*

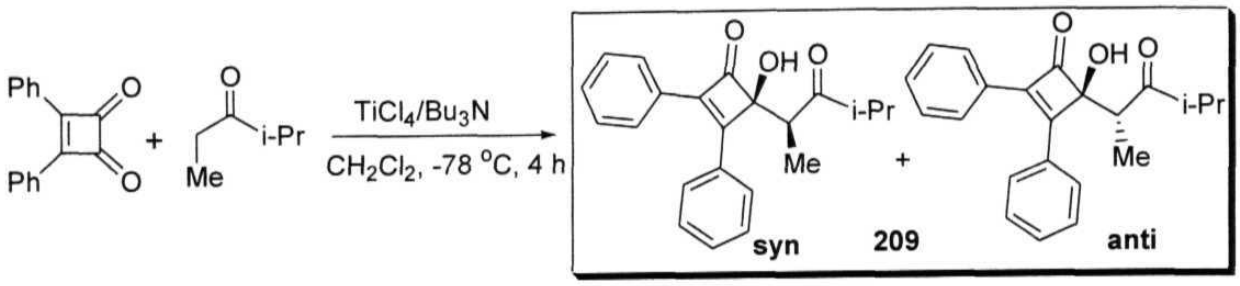
^{13}C NMR : (50 MHz) δ = (syn) 214.9, 192.9, 169, 146.3, 131.6, 129.7, 129.2, 129, 128.8, 128.7, 128, 127.8, 95.4, 48.5, 36.1, 13.3, 7.4, (anti) 215, 192.3, 169.1, 131.2, 129.3, 128.7, 96.2, 48.8, 35, 13.5 *ppm*

MS (EI) : *m/z* 320 (M^+ 15%), 178 [$(Ph_2C_2)^+$ 100%]

Analysis : for $C_{21}H_{20}O_3$

Calculated: C, 78.73%; H, 6.29%; O, 14.98%

Found: C, 78.81%; H, 6.24%



Yield : 83%, (0.28 g)

syn:anti : 68:32

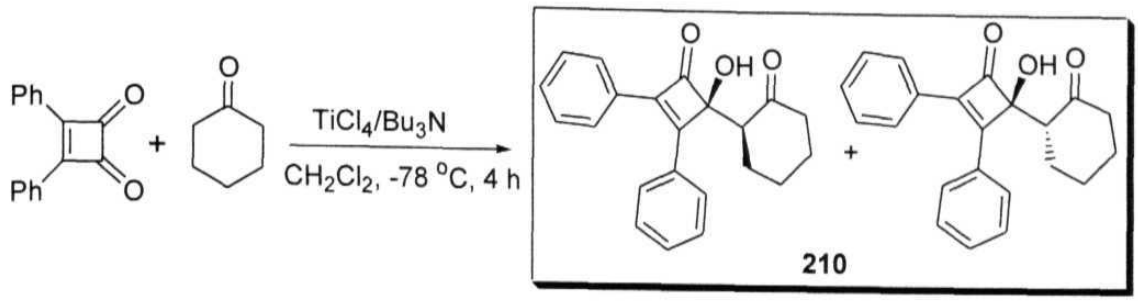
mp : 60-65 °C

IR (neat) : 3425, 1755, 1708, 1620 cm^{-1}

^{1}H NMR : (200 MHz) δ = (syn) 7.89-7.67 (m, 4 H), 7.43-7.32 (m, 6 H), 5.1 (s, 1H), 3.39 (q, J = 7.6 Hz, 1H), 2.65(quintet, J = 6.9 Hz, 1H), 1.2 (d, J = 7.6 Hz, 3H), 1.0 (d, J = 6.9 Hz, 6H), (anti) 3.37 (q, J = 7.2 Hz, 1H), 2.65 (quintet, J = 6.8 Hz, 1H), 1.3 (d, J = 7.2 Hz, 3H), 0.8 (d, J = 6.8 Hz, 6H) *ppm*

^{13}C NMR : (50 MHz) δ = (syn) 217.7, 193, 168.5, 146.3, 131.6, 129.7, 129.6, 129, 128.8, 128.4, 128, 127.8, 95.4, 47.1, 41.1, 17.8, 13.8, (anti) 218.6, 191.3, 170.1, 146, 131.3, 96.4, 40.5, 18, 14 *ppm*

MS (EI) : *m/z* 334 (M^+ 8 %), 178 [$(Ph_2C_2)^+$ 100 %]



Yield : 85% (0.28 g)

dr : 82:18

mp : 55-57 °C

IR (neat) : 3409, 2935, 1755, 1708, 1635 cm^{-1}

^{1}H NMR : (200 MHz) δ = (major) 7..37-7.21 (m, 10H), 5.49 (s, 1H), 4.56 (t, J = 8.6 Hz, 1H), 2.38 (t, J = 8.9 Hz, 2H), 1.89-1.64 (m, 6H). (minor) 4.53 (t, J = 8.6 Hz, 1H) *ppm*

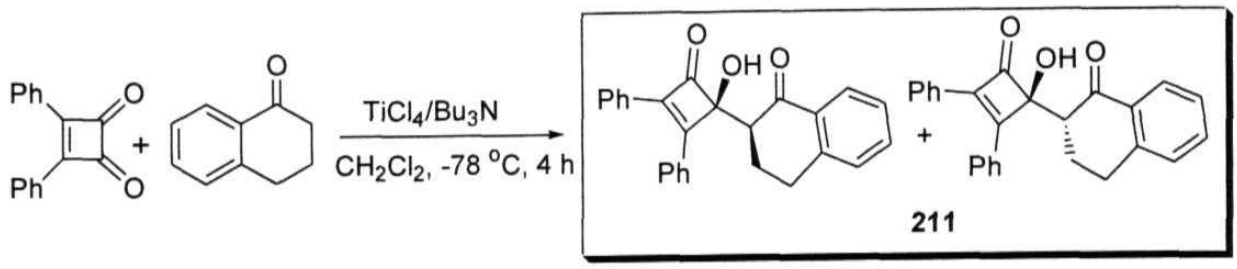
^{13}C NMR : (50 MHz) δ = (major) 213.5, 191.4, 166.3, 146.8, 131.7, 130.7, 129.6, 129.1, 128.7, 128.3, 128.1, 127.9, 95.8, 51.4, 42, 29.3, 25.8, 24.1, (minor) 214.2, 191.6, 170.1, 147, 96.5, 51.9, 42.5, 30.2, 26.9, 24.5 *ppm*

MS (EI) : *m/z* 332 (M^+ 16%), 178 [$(Ph_2C_2)^+$ 100%]

Analysis : for $C_{22}H_{20}O_3$

Calculated: C, 79.5 %; H, 6.06 %; O, 14.44 %

Found: C, 80.01 %; H, 6.03 %



Yield : 93% (0.36 g)

dr : 92:8

mp : 164-165 °C

IR (KBr) : 3382, 1755, 1662, 1620 cm^{-1}

^{1}H NMR : (200 MHz) δ = (major) 8.12 (d, J = 7.8 Hz, 1H), 7.99 (m, 2 H), 7.74 (m, 2 H), 7.5-7.14 (m, 9 H), 6.59 (s, 1H), 3.27-3.18 (dd, J = 8.8 Hz, J = 4.9 Hz 1H), 2.84 (t, J = 4.8 Hz, 2H), 1.95 (m, 2H), (minor) 3.3-3.27 (dd, J = 8.8 Hz, J = 4.9 Hz 1H), 2.7 4 (t, J = 4.8 Hz, 2H), 1.8 5 (m, 2H) *ppm*

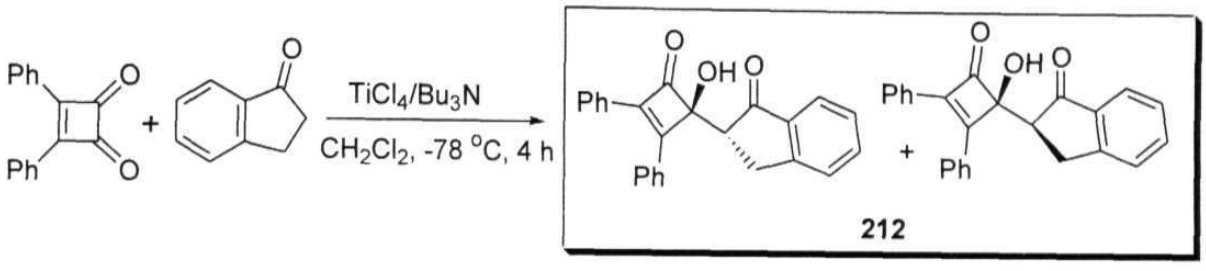
^{13}C NMR : (50 MHz) δ = (major) 200.8, 191.8, 166.4, 147.1, 144.2, 134.5, 131.9, 130.8, 130.6, 130.3, 129.8, 129.5, 129.3, 128.8, 128.6, 128.3, 127.9, 127, 97.4, 48.3, 28.6, 26, (minor) 201.2, 190.3, 167.2, 147, 144.1, 134.4, 97.6, 48.0, 28.6, 26. *ppm* **(Spectrum no. 35)**

MS (EI) : *m/z* 380 (M^+ 22%), 105 [$(PhCO)^+$ 100%]

Analysis : for $C_{26}H_{20}O_3$

Calculated: C, 82.09%; H, 5.30%; O, 12.62%

Found: C, 81.81%; H, 5.33%



Yield : 85% (0.31 g)

dr : 31:69

mp : 142-144 °C

IR (KBr) : 3398, 1747, 1712, 1630 cm^{-1}

^{1}H NMR (400 MHz) δ = (major) 7.99 (d, J = 5.9 Hz, 1H), 7.76 (m, 2 H), 7.59-7.35 (m, 11 H), 6.15 (s, 1H), 3.43 (dd, J = 4.8 Hz, J = 3.9 Hz 1H), 3.13 (d, J = 4.8 Hz, 1H), 2.91(d, J = 3.9 Hz, 1H) (minor) 3.5 (dd, J = 4.8 Hz, J = 3.9 Hz 1H), 3.15 (d, J = 4.8 Hz, 1H), 2.8(d, J = 3.9 Hz, 1H) *ppm*

^{13}C NMR : (50 MHz) δ = (major) 208, 191.6, 167.5 , 153.5, 147.1, 136.2, 135.7, 131.8, 130.8, 129.9, 129.4, 128.8, 128.2, 127.9, 127.6, 126.5, 124.5,

123.8, 96.7, 48.3, 29.5 (minor) 207.3, 191.1, 170.9, 153.9, 147, 136, 135.4, 131.1, 130.7, 129.8, 129.2, 128.7, 96.1, 48.7, 29.8 *ppm* **(Spectrum no. 36)**

MS (EI) : *m/z* 366 (M^+ 26%), 178 [$(Ph_2C_2)^+$ 100%] **(Spectrum no. 37)**

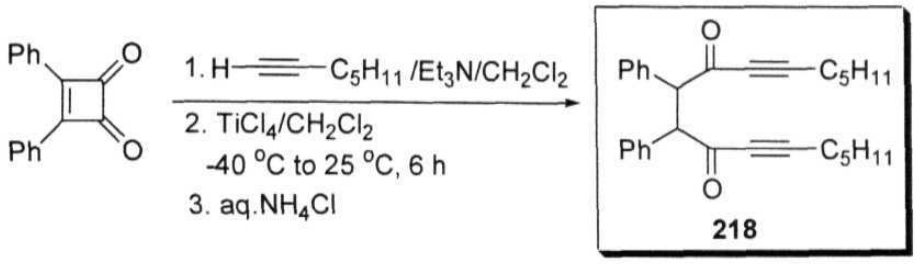
Analysis : for $C_{25}H_{18}O_3$

Calculated: C, 81.95%; H, 4.95%; O, 13.1%

Found: C, 81.83%; H, 4.97%

3.14 Reaction of Cyclobutenedione with Alkynyltitanium Reagents

To a mixture of 3,4-diphenyl-3-cyclobutene-1,2-dione (0.234 g, 1 mmol), triethylamine (0.35 g, 3.5 mmol) and 1-heptyne (0.29 g, 3 mmol) in CH_2Cl_2 (20 mL), $TiCl_4$ (0.66 mL of 1:1 solution of $TiCl_4/CH_2Cl_2$, 3 mmol) in CH_2Cl_2 5 mL was added dropwise at -40 °C under N_2 atmosphere. The contents were stirred for 6 h at the same temperature. The reaction mixture was brought to room temperature and quenched with 5 mL of saturated NH_4Cl solution and extracted with CH_2Cl_2 (2X50 mL). The combined organic extract was washed with brine solution and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was chromatographed on a silica gel column. The product was eluted using hexane/ethylacetate 99:1.



Yield : 20% (0.085 g)

dl:meso : 65:35

mp : 76-78 °C

IR (neat) : 3030, 2933, 2210, 1668 cm^{-1}

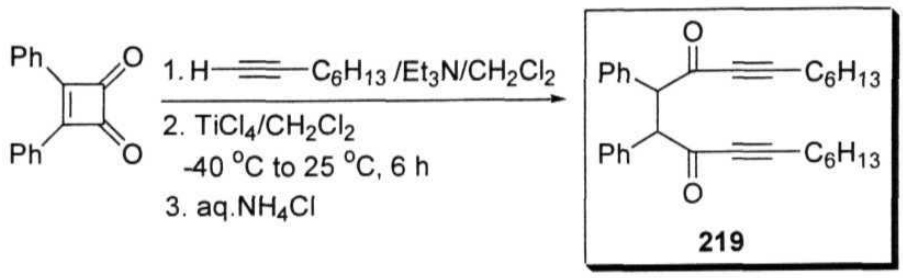
^{1}H NMR : (200 MHz) δ = (*dl*) 7.45-6.97 (m, 10H), 4.57 (s, 2H), 2.21 (t, *J* = 6.8, 2H), 1.46-1.21 (m, 6H), 0.85 (t, *J* = 7.1, 3H), (*meso*) 4.77 (s, 2H) *ppm* **(Spectrum no. 38)**

^{13}C NMR : (50 MHz) *δ* = (*dl*) 185.6, 134.7, 128.8, 128.5, 127.4, 96.5, 80.8, 62.7, 30.8, 27.2, 22, 18.9, 13.7, (*meso*) 184.3, 135.2, 96.7, 62.1, 30.7 *ppm* **(Spectrum no. 39)**

Analysis : for $C_{30}H_{34}O_2$

Calculated: C, 84.47%; H, 8.03%; O, 7.50%

Found: C, 84.61%; H, 8.05%



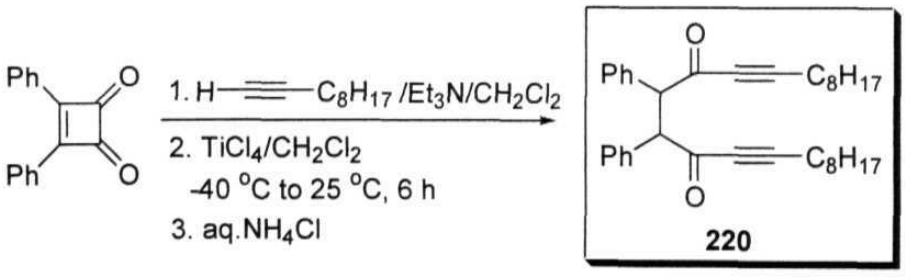
Yield : 21% (0.095 g)

dl:meso : 70:30

IR (neat) : 3030, 2929, 2212, 1669 cm^{-1}

^{1}H NMR : (200 MHz) δ = (*dl*) 7.38-6.99 (m, 10H), 4.57 (s, 2H), 2.72 (t, J = 7.1, 2H), 1.46-1.21 (m, 8H), 0.85 (t, J = 7.3, 3H), (*meso*) 4.77 (s, 2H) *ppm*

^{13}C NMR : (50 MHz) δ = (*dl*) 185.7, 134.7, 128.6, 128.5, 127.4, 96.6, 80.8, 62.7, 31.1, 27.4, 21.9, 18.9, 13.8, (*meso*) 184.4, 135.2, 96.7, 80.8 *ppm*



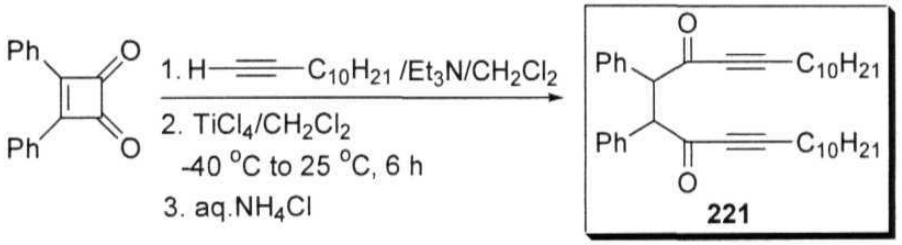
Yield : 15% (0.077 g)

dl:meso : 85:15

IR (neat) : 3030, 2925, 2212, 1674 cm^{-1}

^{1}H NMR : (200 MHz) δ = (*dl*) 7.28-6.99 (m, 10H), 4.58 (s, 2H), 2.29 (t, J = 7.5, 2H), 1.49-1.24 (m, 12H), 0.9 (t, J = 7.4, 3H), (*meso*) 4.8 (s, 2H) *ppm*

^{13}C NMR : (50 MHz) δ = (*dl*) 185.9, 134.6, 129.2, 128.5, 127.5, 96.8, 80.7, 62.7, 31.8, 29, 28.9, 28.7, 27.5, 22.6, 19, 14, (*meso*) 184.8, 134.4, 96.9, 80.7, 62.2 *ppm*



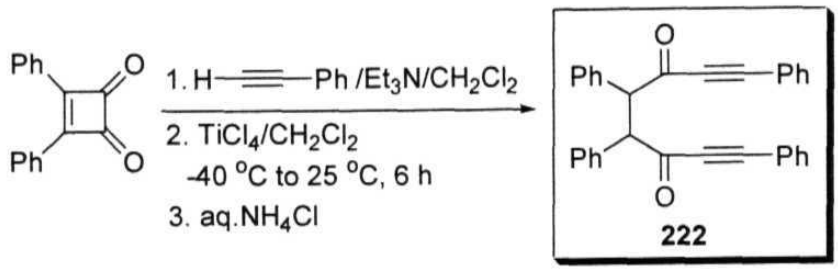
Yield : 17% (0.097 g)

dl:meso : 75:25

IR (neat) : 3030, 2925, 2214, 1672 cm^{-1}

^{1}H NMR : (200 MHz) δ = (*dl*) 8.01-7.0 (m, 10H), 4.58 (s, 2H), 2.27 (t, J = 7.5, 2H), 1.48-1.27 (m, 16H), 0.89 (t, J = 7.3, 3H), (*meso*) 4.8 (s, 2H) *ppm*

^{13}C NMR : (50 MHz) δ = (*dl*) 185.8, 134.6, 129.2, 128.8, 127.9, 96.9, 80.7, 62.6, 31.9, 29.5, 29.4, 29.3, 29, 28.8, 27.5, 22.7, 19, 14, (*meso*) 184.6, 135.1, 96.8, 62 *ppm*



Yield : 15% (0.066 g)

mp : 210-213 °C (Lit [219] 215 °C)

IR (neat) : 3032, 180, 1660 cm^{-1}

^{1}H NMR : (200 MHz) δ = (*meso*) 7.48-7.15 (m, 20H), 4.81 (s, 2H) *ppm*

(Spectrum no. 40)

^{13}C NMR : (50 MHz) δ = 185.6, 134.5, 133, 130.7, 130.3, 129.3, 128.7, 127.7, 120, 93.1, 87.9, 62.7. *ppm* **(Spectrum no. 41)**

Analysis : for $C_{32}H_{22}O_2$

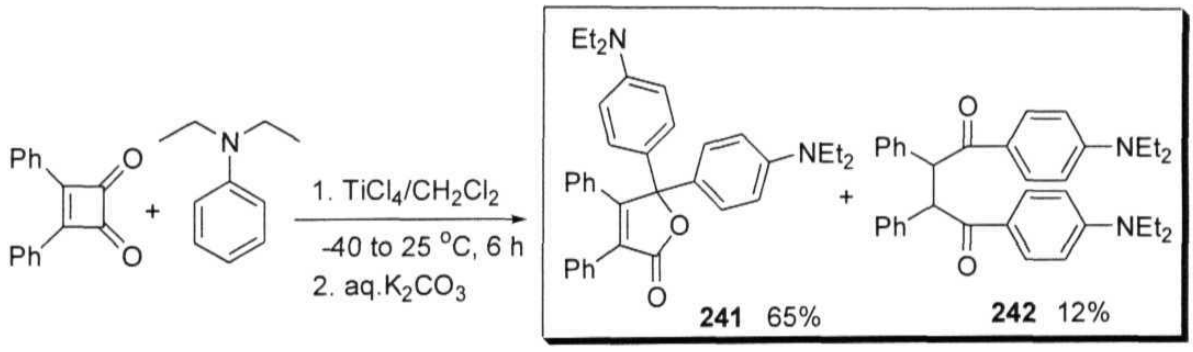
Calculated: C, 87.65%; H, 5.06%; O, 7.3 %

Found: C, 87.68%; H, 5.06%

3.15 Reaction of Cyclobutenedione with $TiCl_4$/ *N,N*-dialkylaniline Reagent System

To a mixture of 3,4-diphenyl-3-cyclobutene-1,2-dione (0.234 g, 1 mmol) and *N,N*-diethylaniline (0.37 g, 2.5 mmol) in CH_2Cl_2 (20 mL), $TiCl_4$ (0.13 mL of 1:1 solution of

$TiCl_4/CH_2Cl_2$, 1.2 mmol) in CH_2Cl_2 5 mL was added dropwise at –78 °C under N_2 atmosphere. The contents were stirred for 6 h at the same temperature. Then, the reaction mixture was brought to room temperature and quenched with 5 mL of saturated K_2CO_3 solution and extracted with CH_2Cl_2 (2X50 mL). The combined organic extract was washed with brine solution and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was chromatographed on a silica gel column. The products **241** and **242** were eluted using hexane/ethylacetate 97:3



Compound 241

Yield : 65% (0.34 g)

mp : 81-83 °C

IR (KBr) : 3050, 2975, 1747 cm^{-1}

^{1}H NMR : (400 MHz) δ = 7.81-7.24 (m, 14H),6.7 (d, J = 7.6, 2H), 6.6 (d, J = 8.6, 2H), 3.43 (q, J = 7.0, 4H), 3.36 (q, J = 7.0, 4H), 1.25-1.17 (q, J = 7.0, 12H) *ppm* **(Spectrum no. 42)**

^{13}C NMR : (50 MHz) δ = 191.5, 162.3, 148.3, 146.9, 141.1, 133.9, 130, 129.9, 129.3, 128.7, 128.6, 128.3, 128.2, 127, 126.8, 116.4, 111.7, 111.2, 44.4, 44.3, 12.7 *ppm* **(Spectrum no. 43)**

Analysis : for $C_{36}H_{38}N_2O_2$

Calculated: C, 81.48 %; H, 7.22%; N, 5.28%; O, 6.03 %

Found: C, 81.43 %; H, 7.29%; N, 5.14%

Compound 242

Yield : 12% (0.06 g)

mp : 107-108 °C

IR (KBr) : 3032, 2972, 1683 cm^{-1}

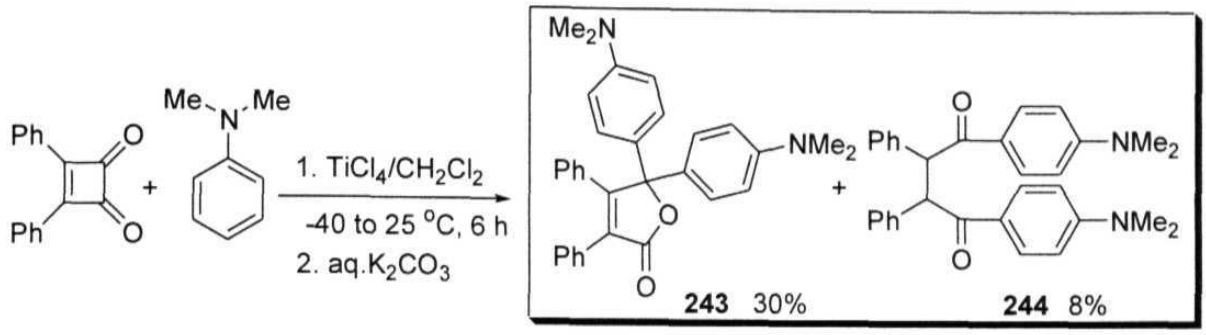
^{1}H NMR : (400 MHz) δ = 8.02-7.28 (m, 14H), 6.67 (d, J = 9.2, 4H), 4.31 (s, 2H), 3.46 (q, J = 7.2, 8H), 1.28-1.14 (q, J = 7.2, 12H) *ppm* **(Spectrum no. 44)**

^{13}C NMR : (50 MHz) δ = 218.2, 148.1, 134.8,, 133.1, 129.9, 129, 128.6, 128, 110.1, 45.5, 44.5, 12.5 *ppm* **(Spectrum no. 45)**

Analysis : for $C_{36}H_{40}N_2O_2$

Calculated: C, 81.17%; H, 7.57%; N, 5.26%; O, 6.01%

Found: C, 81.09%; H, 7.6%; N, 5.32%



Compound 243

Yield : 30% (0.14 g)

mp : 126-129 °C

IR (KBr) : 3030, 2982, 1748 cm^{-1}

^{1}H NMR : (400 MHz) δ = 7.99-7.26 (m, 14H), 6.79 (d, J = 9.2, 2H), 6.68 (d, J = 8.7, 2H), 2.97 (s, 6H) 2.88 (s, 6H) *ppm*

^{13}C NMR : (50 MHz) 191.6, 162.3, 148.3, 147, 141.3, 133.9, 130.2, 129.2, 128.8, 128.7, 128.6, 128.3, 127.9, 127.2, 127, 116.7, 112.6, 112.4, 40.1, 40.2 *ppm*

Compound 244

Yield : 8% (0.037 g)

mp : 150-153 °C

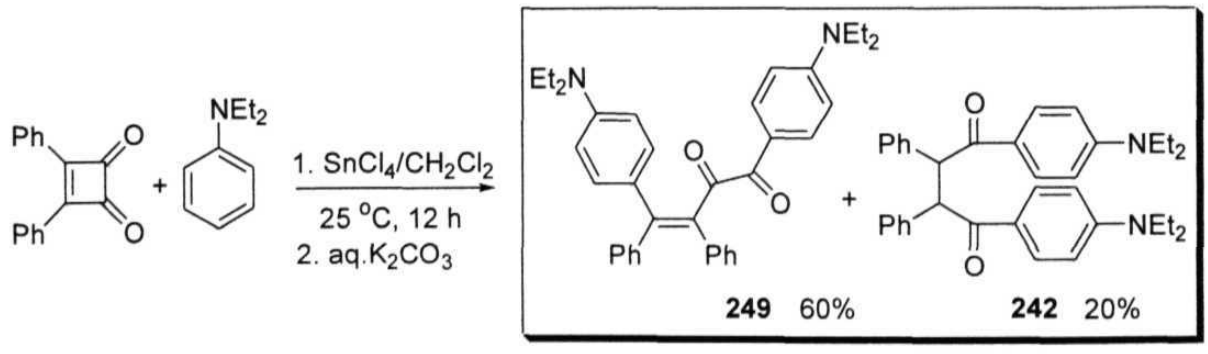
IR (KBr) : 3032, 2983, 1690 cm^{-1}

^{1}H NMR : (400 MHz) δ = 8.0-7.26 (m, 14H), 6.78 (d, J = 8.9, 4H), 4.31 (s, 2H), 3.05 (s, 12H) *ppm*

^{13}C NMR : (50 MHz) δ = 218.2, 148.6, 134.8,, 133.1, 130, 129.3, 128.6, 127.8, 112.1, 46, 40.7 *ppm*

3.16 Reaction of Cyclobutenedione with $SnCl_4$/*N,N*-dialkylaniline Reagent System

A mixture of 3,4-diphenyl-3-cyclobutene-1,2-dione (1 mmol) $SnCl_4$ (1. 2 mmol) in CH_2Cl_2 (20 mL) was stirred for 10 min. and *N,N*-diethylaniline (2.5 mmol), added at 25 °C under N_2 atmosphere. The contents were stirred for 12h. at the same temperature. The reaction was quenched with 5 mL of saturated K_2CO_3 solution and extracted with CH_2Cl_2 (2X50 mL). The combined organic extract was washed with brine solution and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was chromatographed on a silica gel column. The compound **242** was eluted using hexane/ethylacetate 97:3 while the compound **249** was eluted using hexane/ethylacetate 95:5



Compound 249

Yield : 60% (0.32 g)

mp : 138-140 °C

IR (KBr) : 3042, 2972, 1625 cm^{-1}

^{1}H NMR : δ = 7.72 (d, J = 9.2, 2H), 7.28-6.97 (m, 10H), 6.96 (d, J = 8.8, 2H), 6.47(d, J = 9.2, 2H), 6.26 (d, J = 8.8, 2H), 3.4 (q, J = 6.8, 4H), 3.2 (q, J = 7.2, 2H), 3.15 (q, J = 7.2, 2H), 1.16 (t, J = 6.8, 6H), 1.1 (t, J = 7.2, 3H) 0.99 (t, J = 7.2, 3H) *ppm* **(Spectrum no. 46)**

^{13}C NMR : (50 MHz) δ = 198.4, 190, 155, 151.2, 148.6, 141.3, 140.3, 140, 137, 133.5, 133.4, 132.5, 131.9, 131.8, 131.7, 131.6, 131.3, 128.6, 128.2, 127.9, 127.8, 127.5, 126.8, 121, 110.8, 110.1, 109.6, 109.3, 44.4, 44.1 *ppm* **(Spectrum no. 47)**

Analysis : for $C_{36}H_{38}N_2O_2$

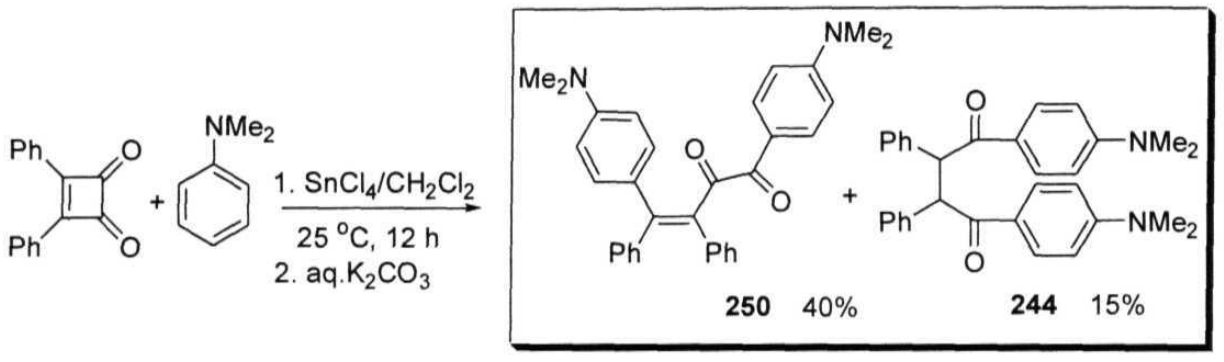
Calculated: C, 81.48 %; H, 7.22%; N, 5.28%; O, 6.03 %

Found: C, 81.43 %; H, 7.24%; N, 5.22%

Compound 242

Yield : 20% (0.126 g)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the sample obtained using $TiCl_4$/ *N,N*-diethylaniline.



Compound 250

Yield : 40% (0.19 g)

mp : 170-171°C

IR (KBr) : 3057, 2916, 1655 cm^{-1}

^{1}H NMR : (400 MHz) δ = 7.89 (d, J = 9.1, 2H), 7.28-6.84 (m, 10H), 6.65 (d, J = 8.9, 2H), 6.42 (d, J = 9.1, 2H), 6.26 (d, J = 8.9, 2H), 2.93 (s, 3H), 2.85 (s, 3H) *ppm*

^{13}C NMR : (50 MHz) δ = 198.6, 190.1, 154.6, 151.3, 148.6, 141.3, 140.3, 139.8, 137,33.5, 133.4, 132.5, 131.9, 131.8, 131.7, 131.6, 131.3, 128.6, 128.2, 127.9, 127.8, 127.5, 126.8, 121, 112.7, 112.3, 111.8, 111.5, 40.6, 40.4 *ppm*

Analysis : for $C_{32}H_{32}N_2O_2$

Calculated: C, 80.64%; H, 6.77%; N, 5.88%; O, 6.71%

Found: C, 80.53%; H, 6.74%; N, 5.82%

Compound 244

Yield : 15% (0.07 g)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the sample obtained using $TiCl_4$/ *N,N*-dimethylaniline.

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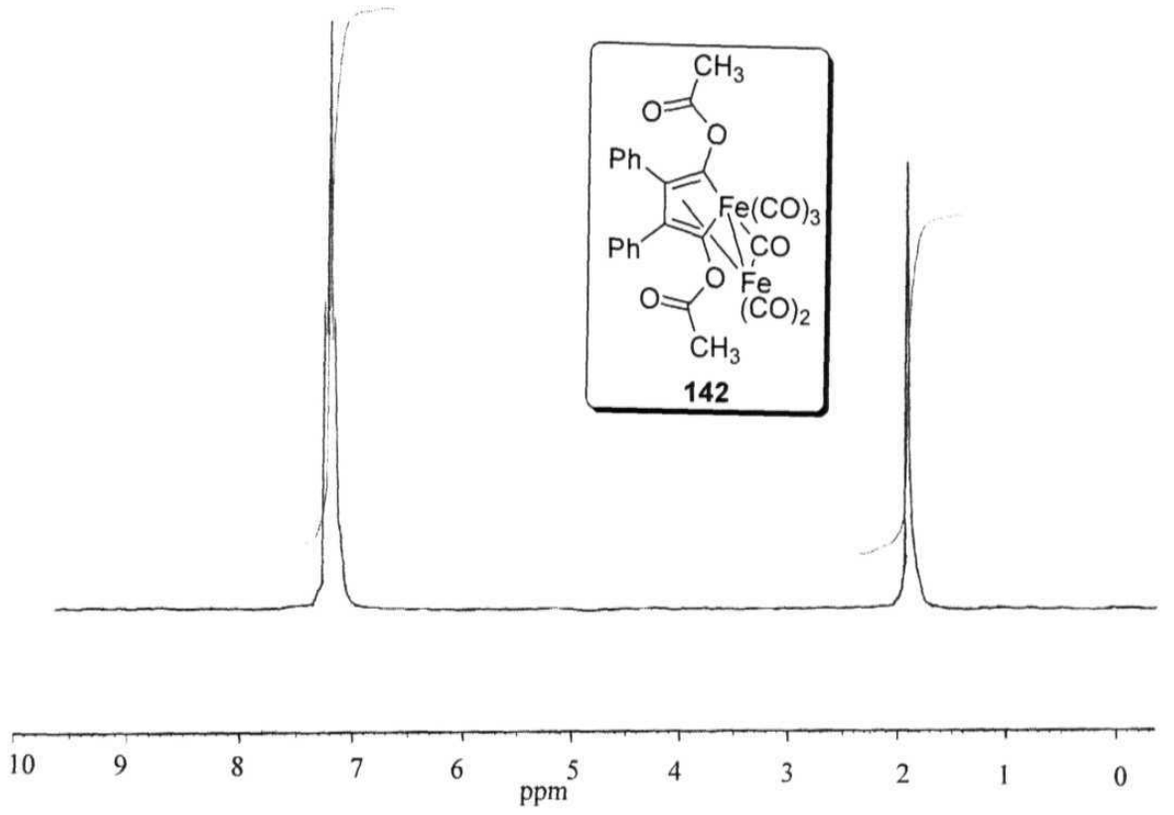
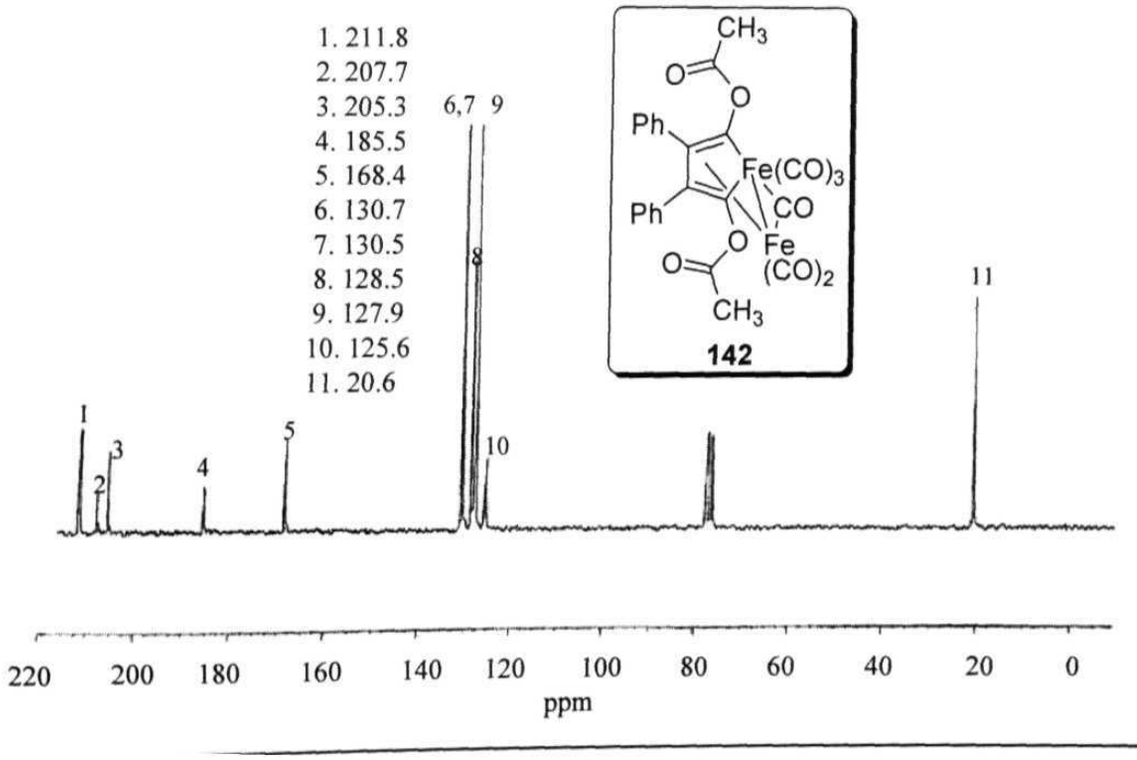
Appendix I

Representative Spectra

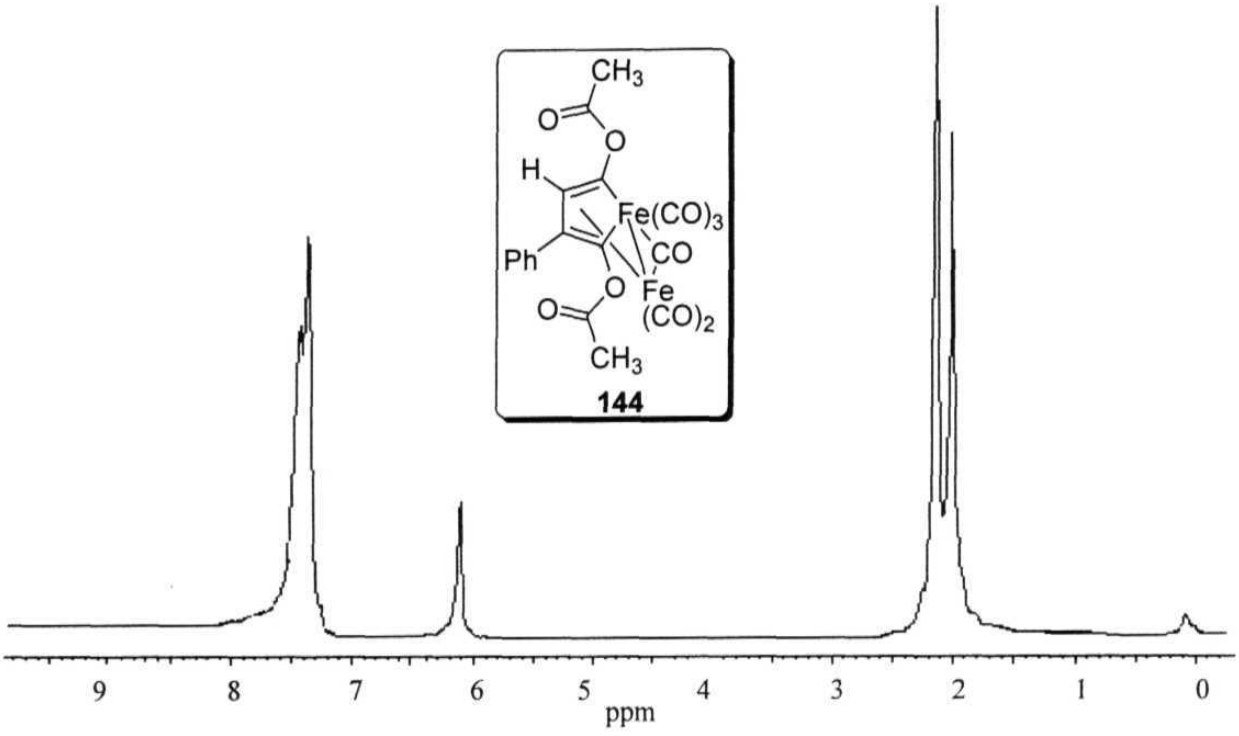
Spectrum No. 1 (Chapter 3, Section 3.3) ^{1}H NMR Spectrum (200 MHz, $CDCl_3$)



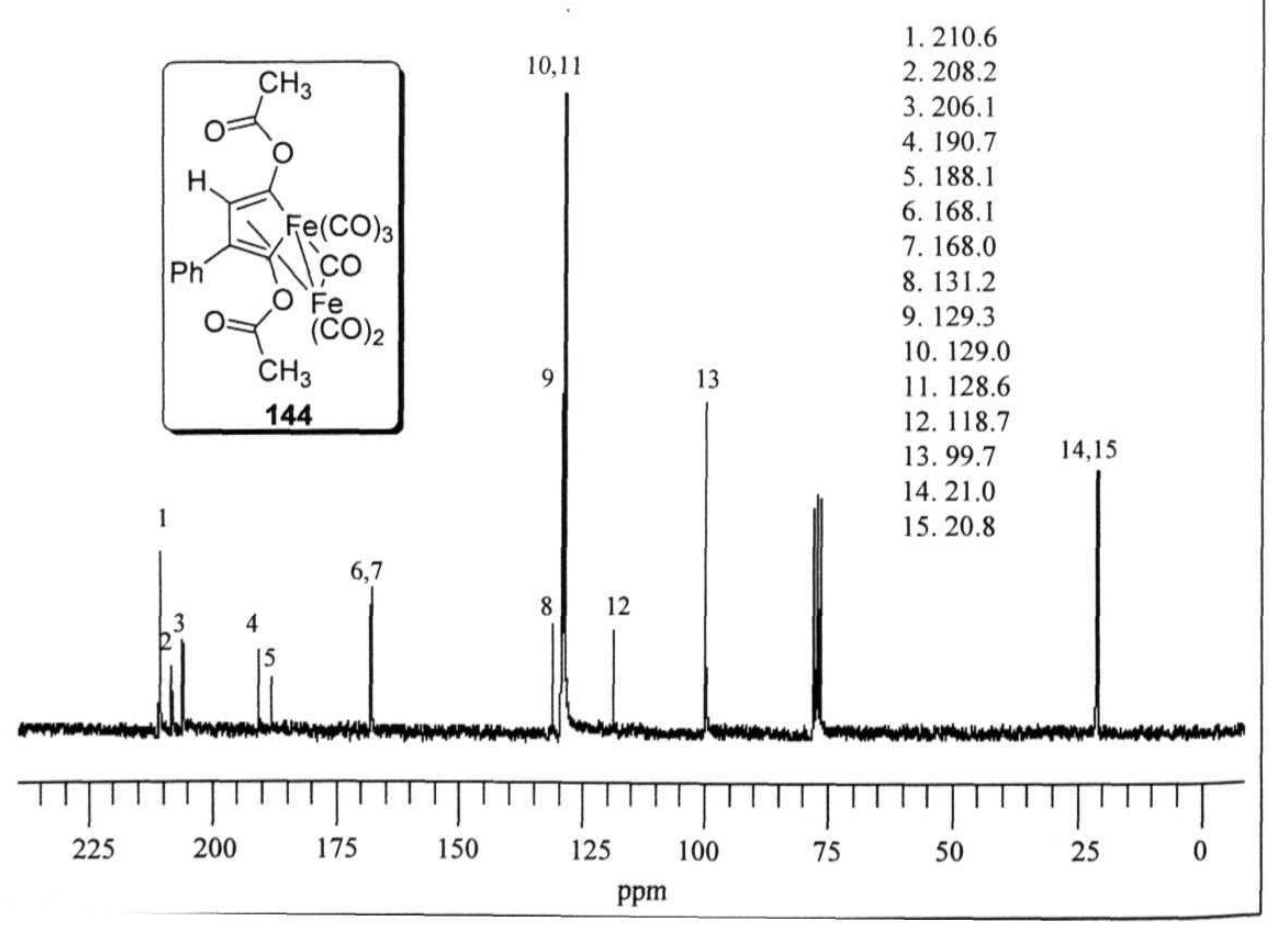
Spectrum No. 2 (Chapter 3, Section 3.3) ^{13}C NMR Spectrum (50 MHz, $CDCl_3$)



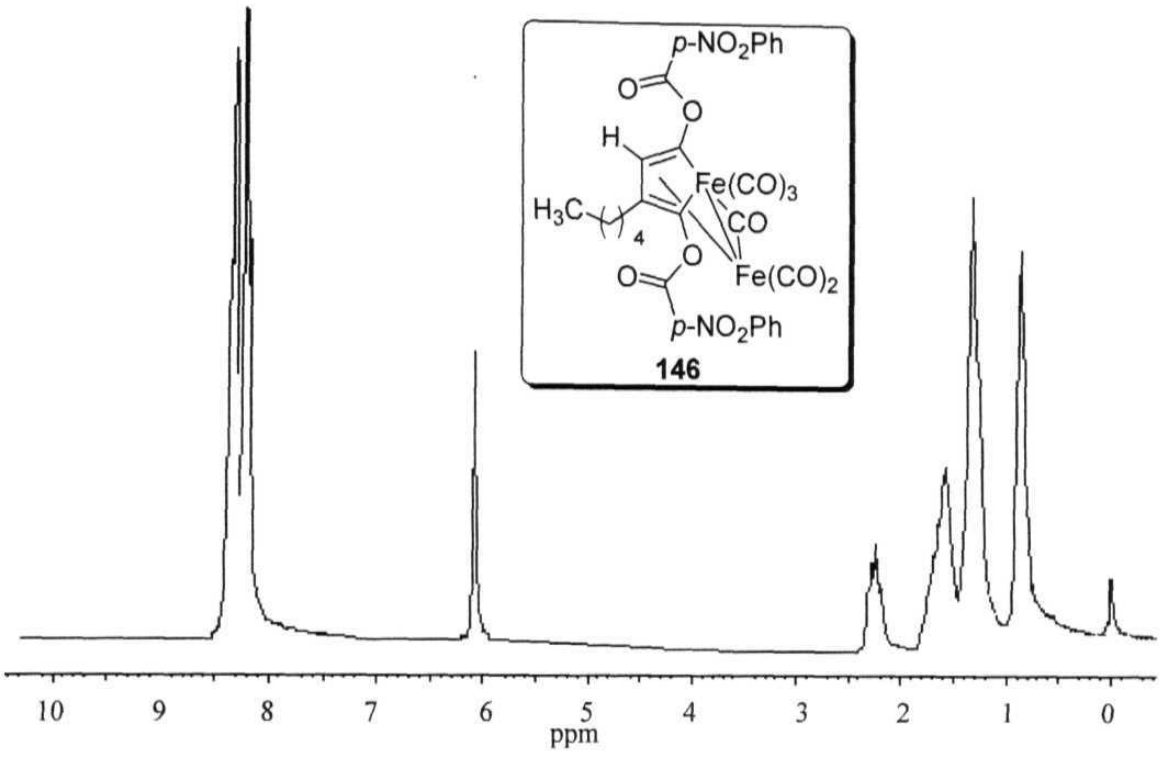
Spectrum No. 3 (Chapter 3, Section 3.3) ^{1} H NMR Spectrum (200 MHz, $CDCl_3$)



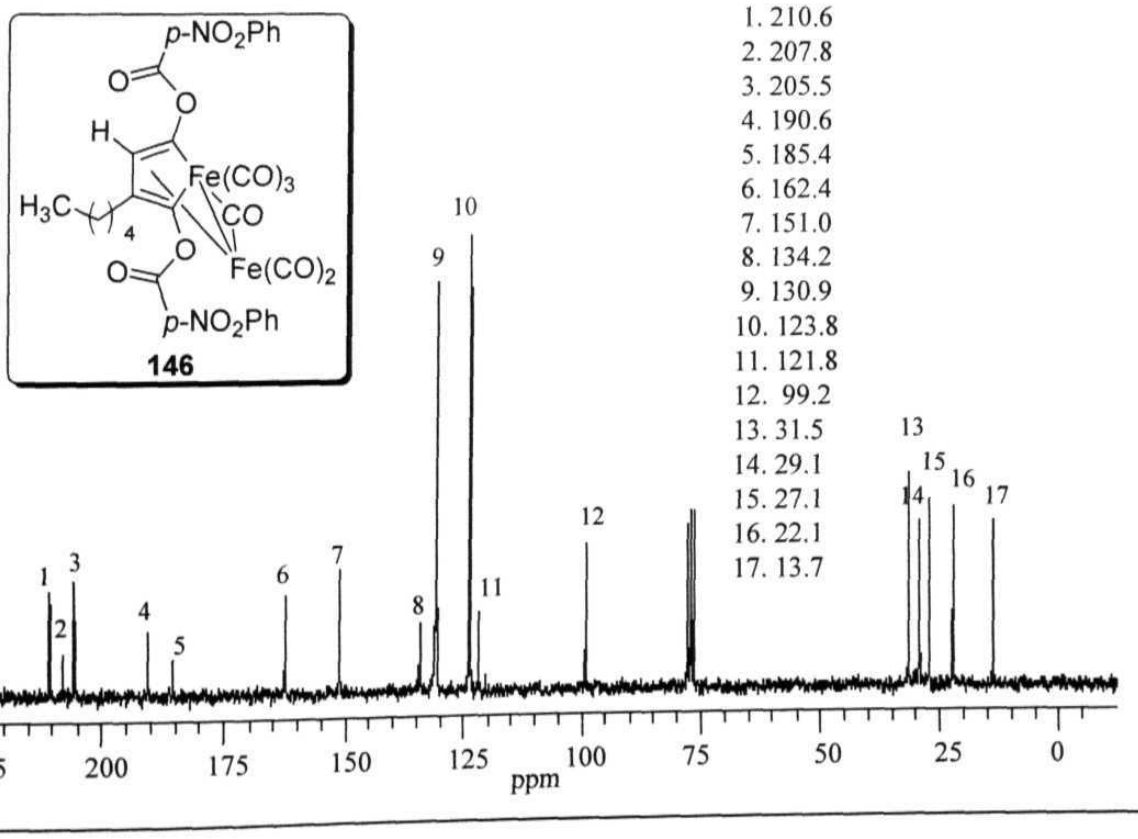
Spectrum No. 4 (Chapter 3, Section 3.3) ^{13} C NMR Spectrum (50 MHz, $CDCl_3$)



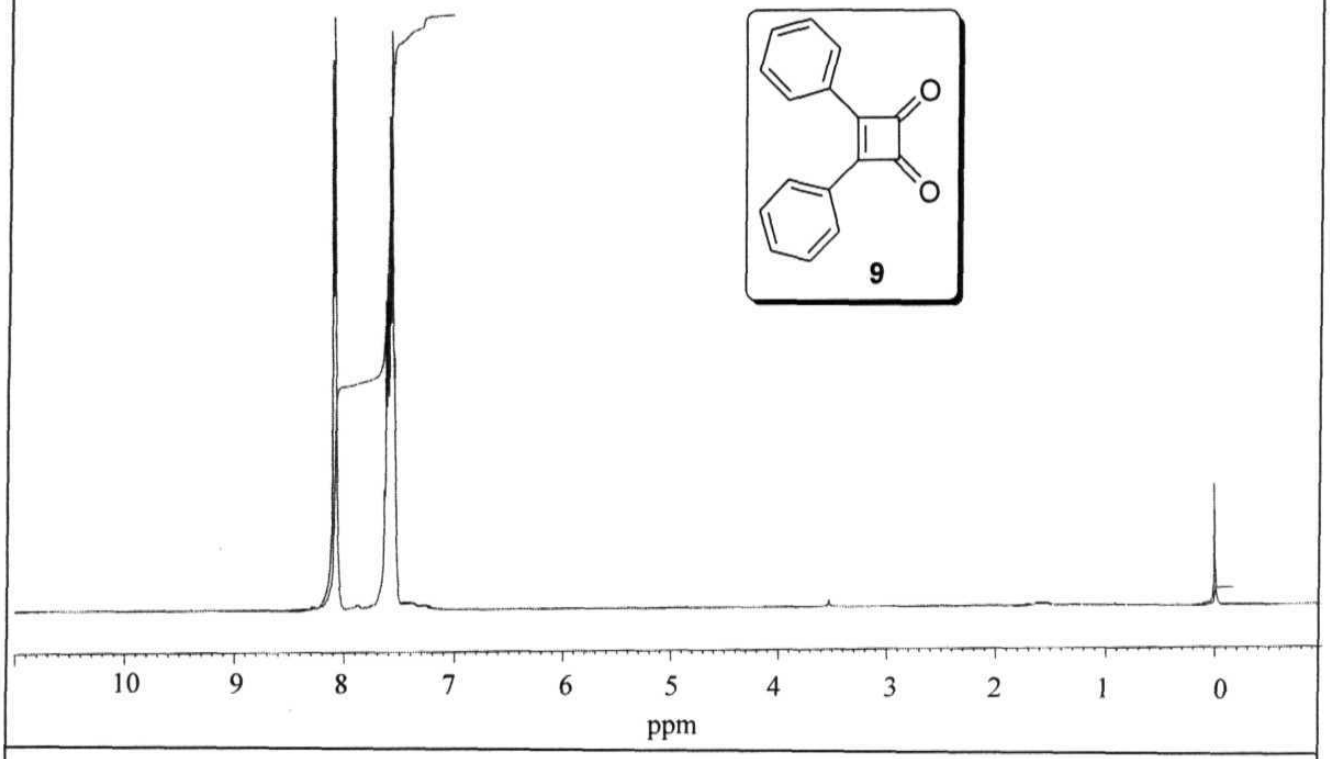
Spectrum No. 5 (Chapter 3, Section 3.3) ^{1}H NMR Spectrum (200 MHz, $CDCl_3$)



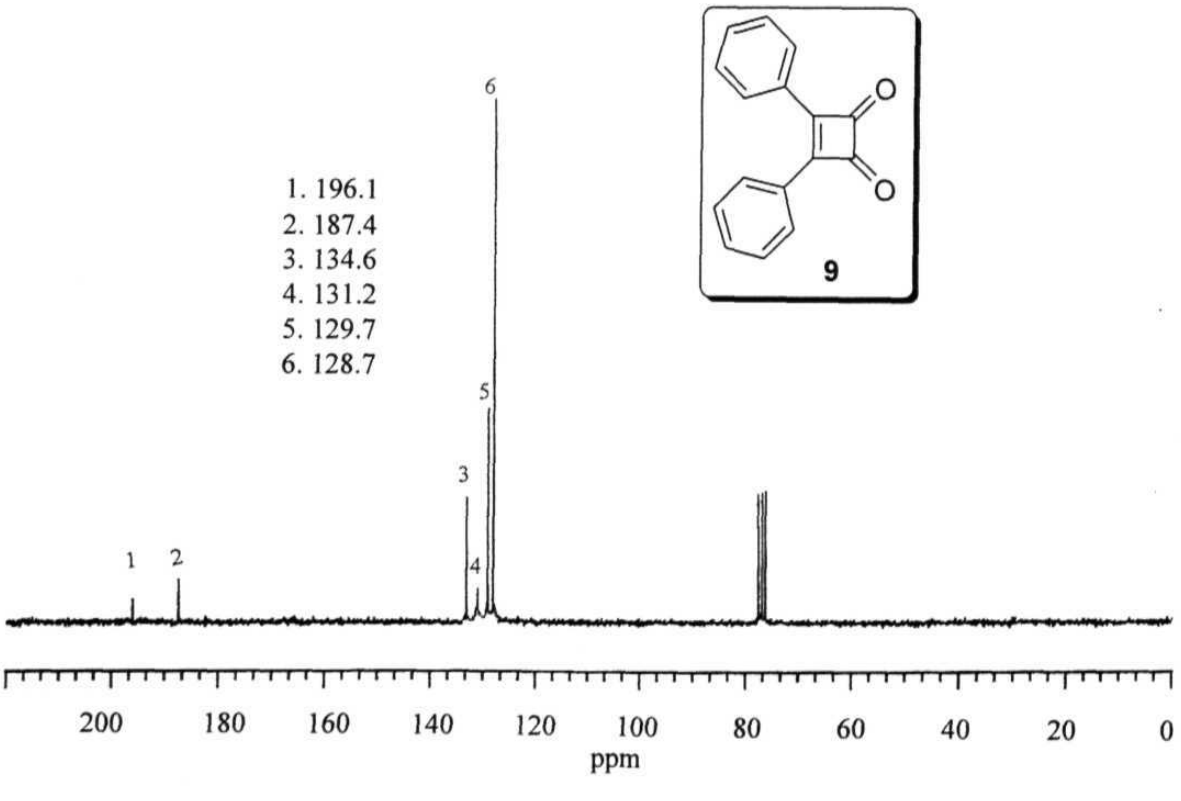
Spectrum No. 6 (Chapter 3, Section 3.3) ^{13}C NMR Spectrum (50 MHz, $CDCl_3$)



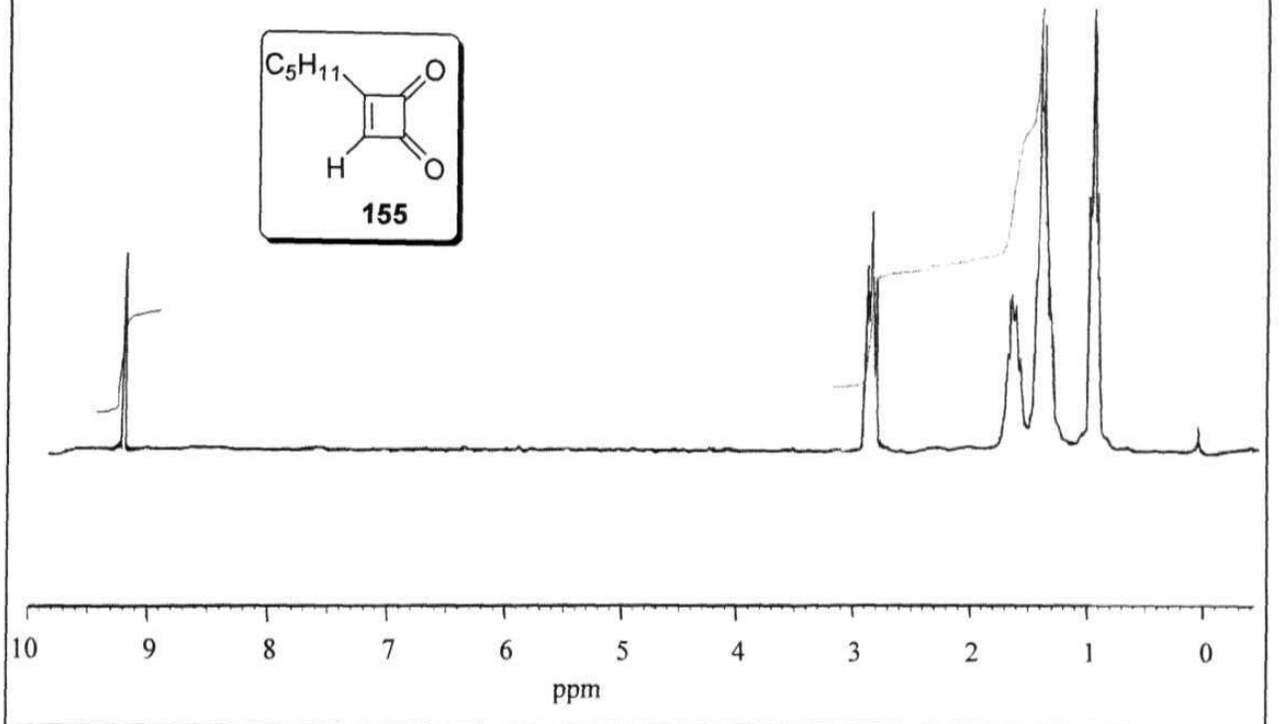
Spectrum No. 7 (Chapter 3, Section 3.4) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



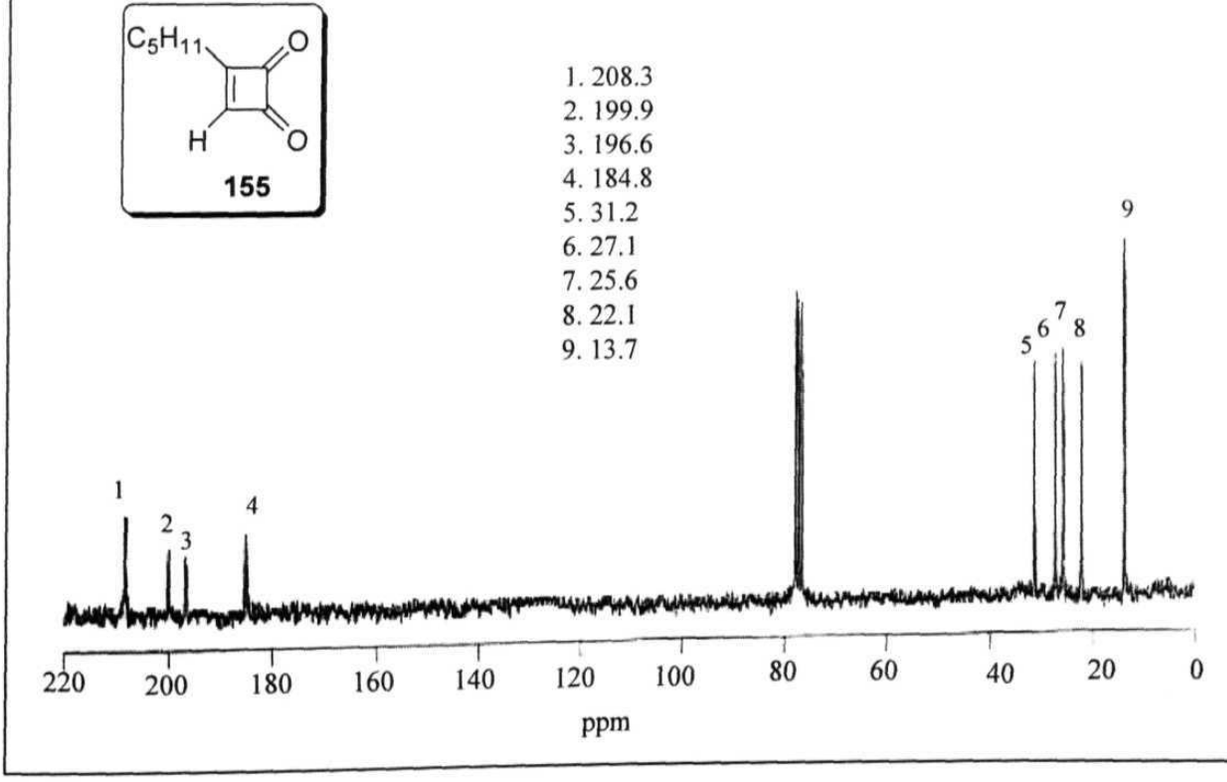
Spectrum No. 8 (Chapter 3, Section 3.4) ^{13}C NMR Spectrum (50 MHz, $CDCl_3$)



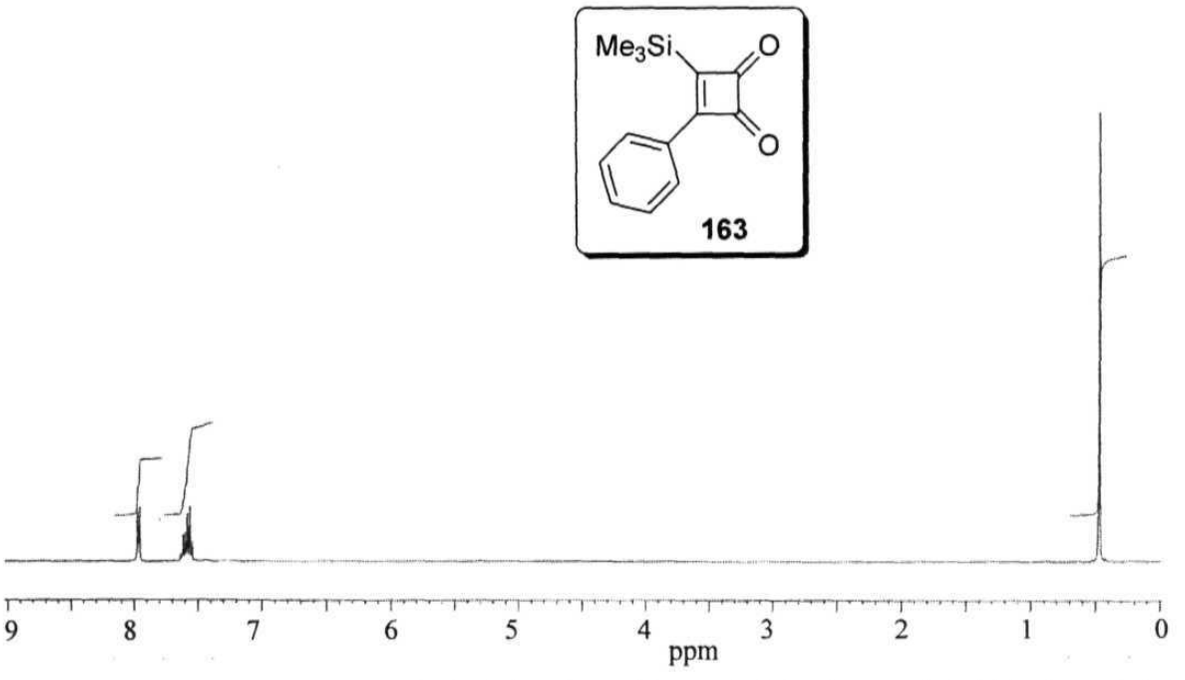
Spectrum No. 9 (Chapter 3, Section 3.4) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



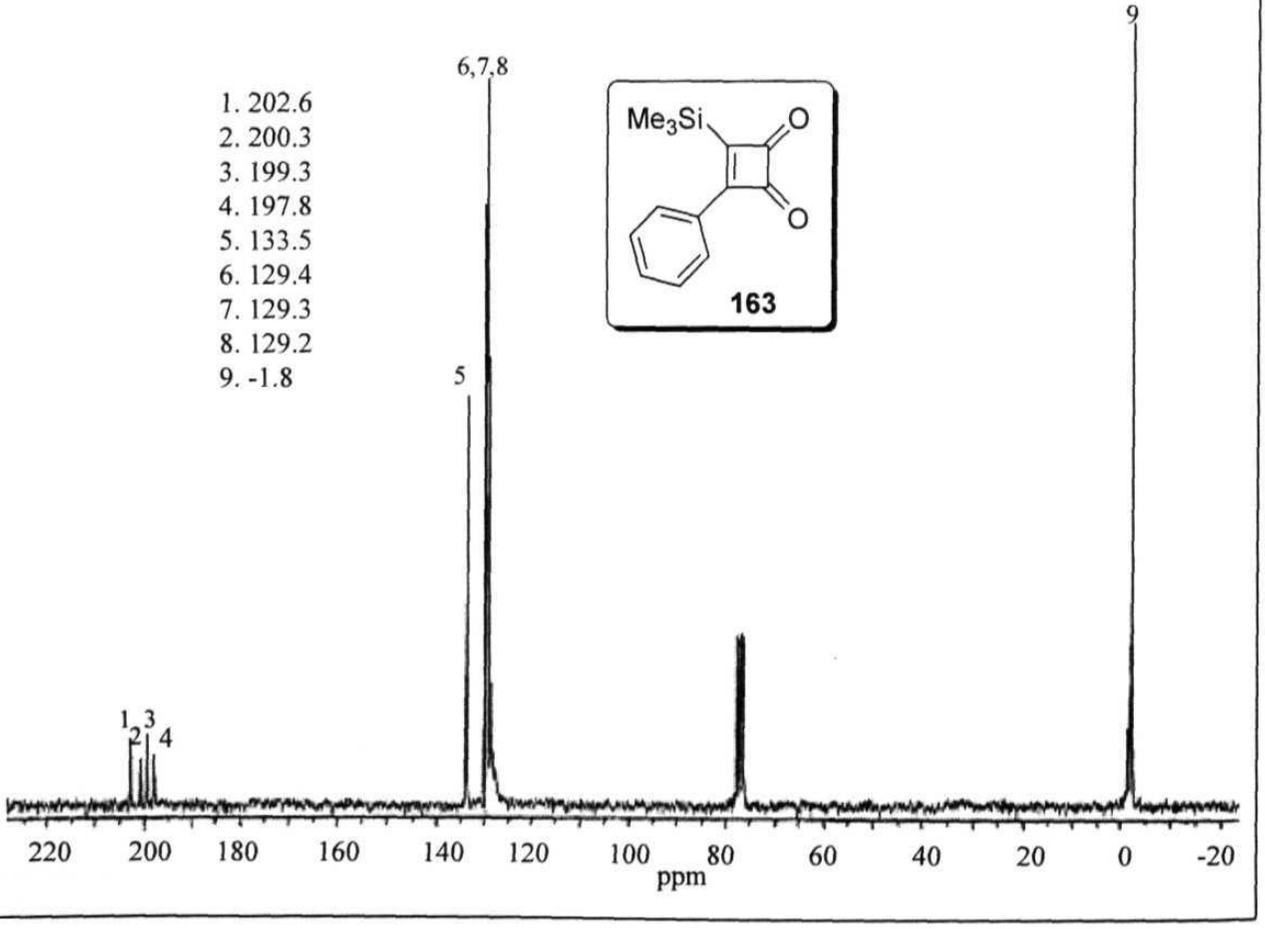
Spectrum No. 10 (Chapter 3, Section 3.4) ^{13}C NMR Spectrum (50 MHz, $CDCl_3$)



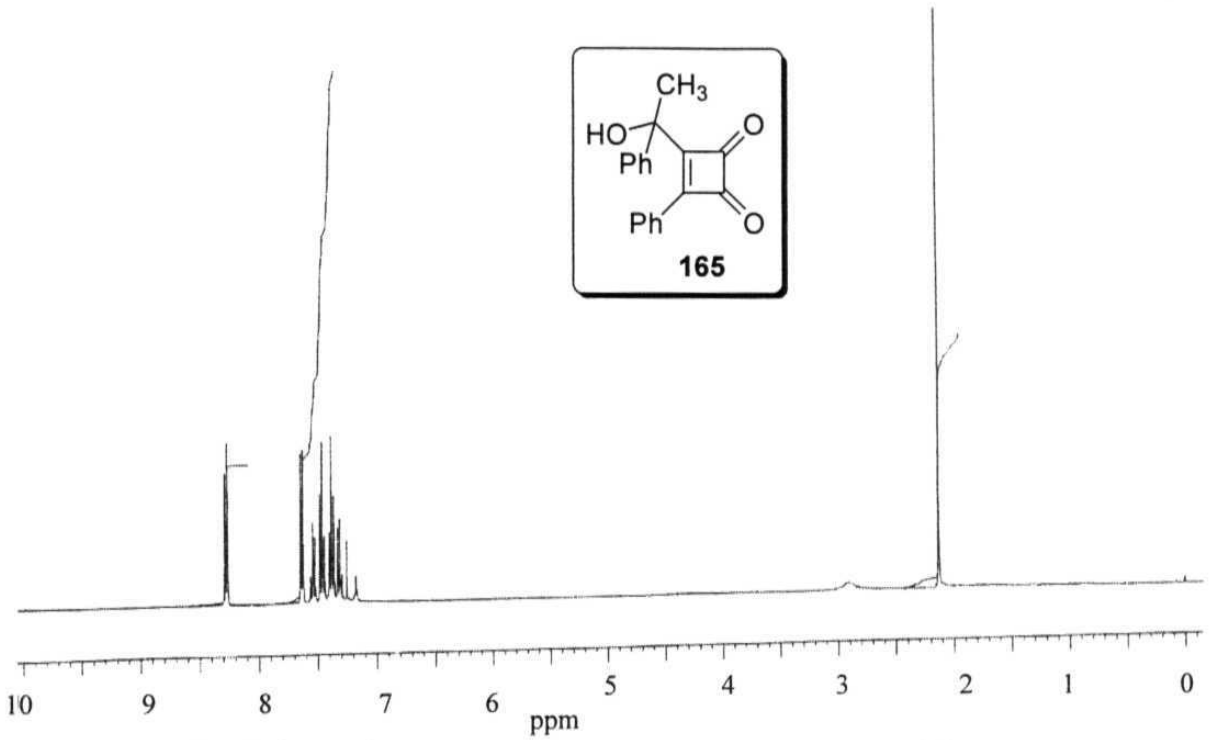
Spectrum No. 11 (Chapter 3, Section 3.7) ^{1} H NMR Spectrum (400 MHz, $CDCl_3$)



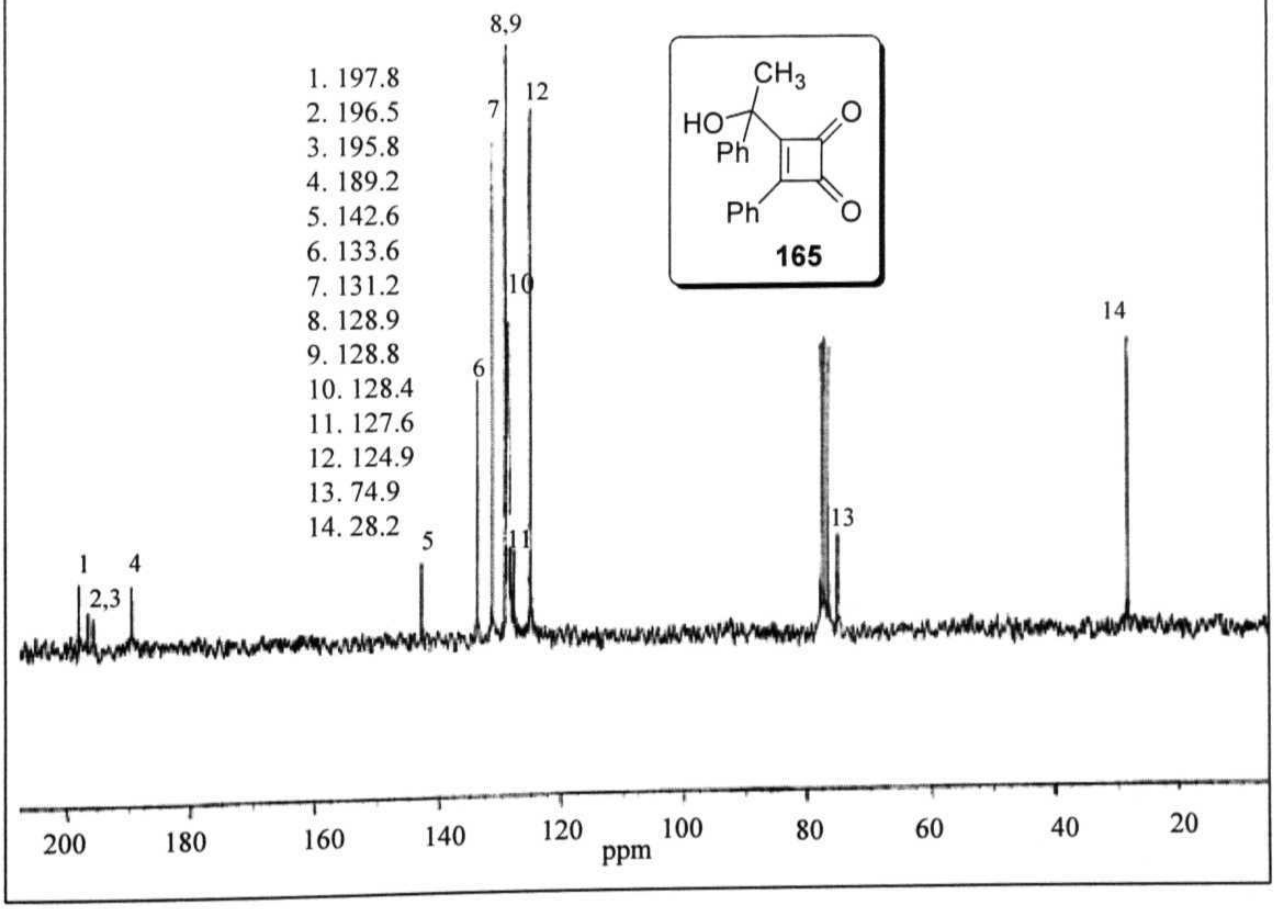
Spectrum No. 12 (Chapter 3, Section 3.7) ^{13} C NMR Spectrum (50 MHz, $CDCl_3$)



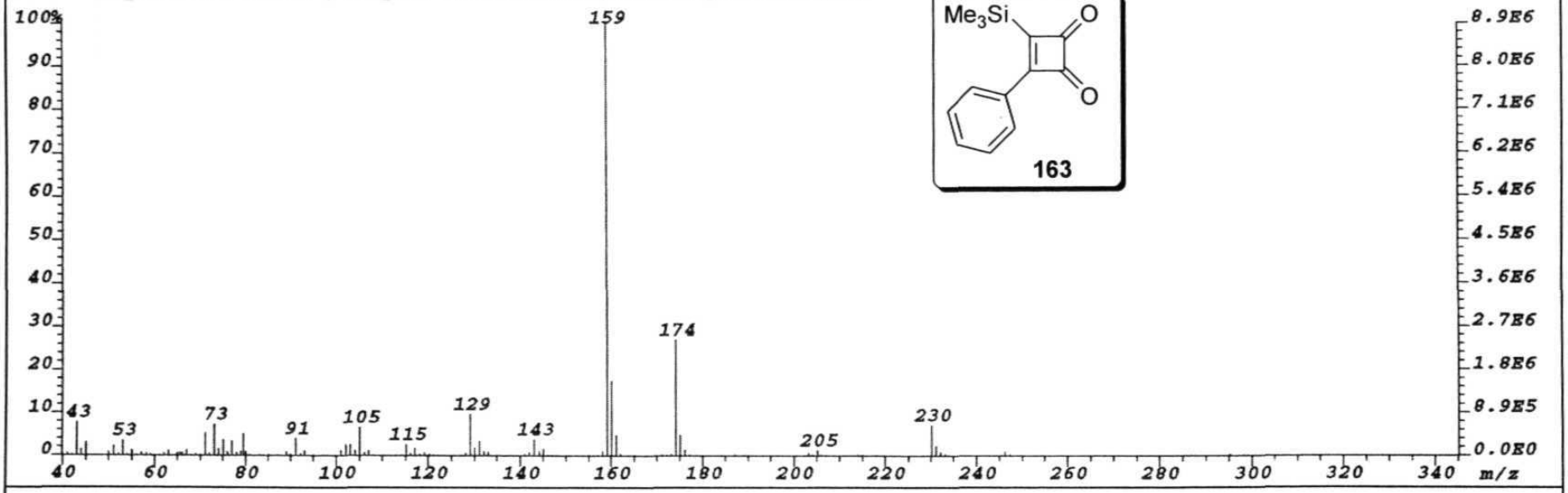
Spectrum No. 13 (Chapter 3, Section 3.7) ^{1} H NMR Spectrum (400 MHz, $CDCl_3$)



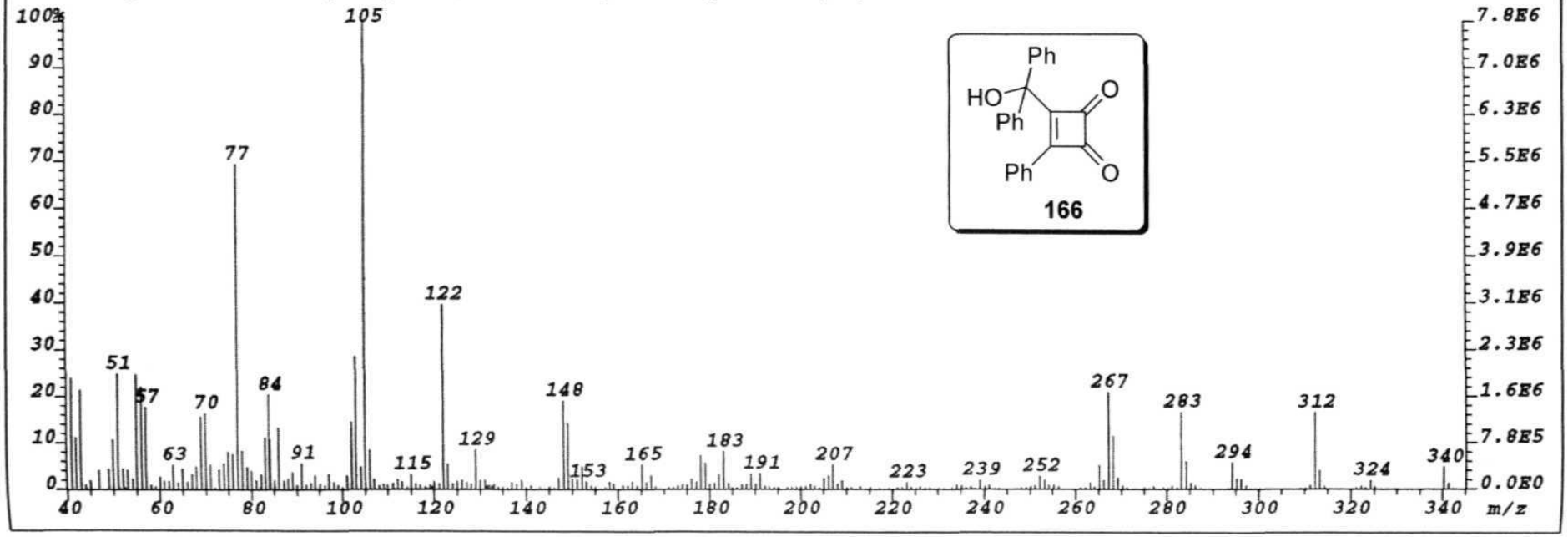
Spectrum No. 14 (Chapter 3, Section 3.7) ^{13} C NMR Spectrum (50 MHz, $CDCl_3$)



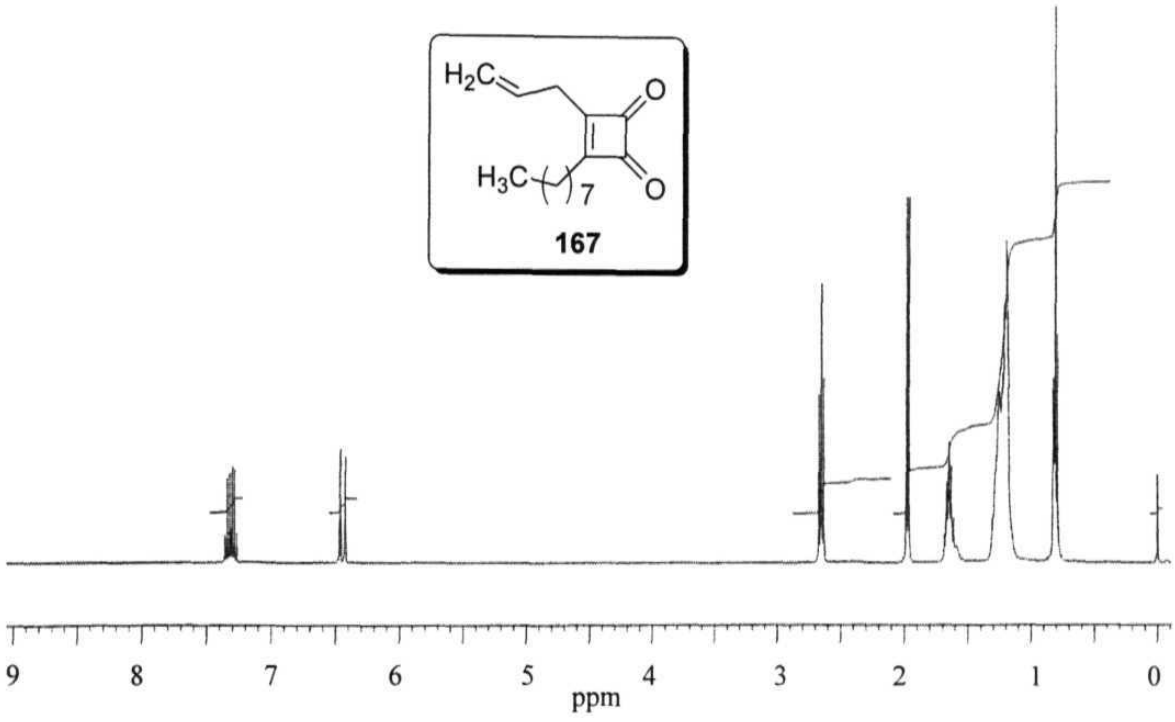
Spectrum No. 15 (Chapter 3, Section 3.7) Mass Spectrum (EI)



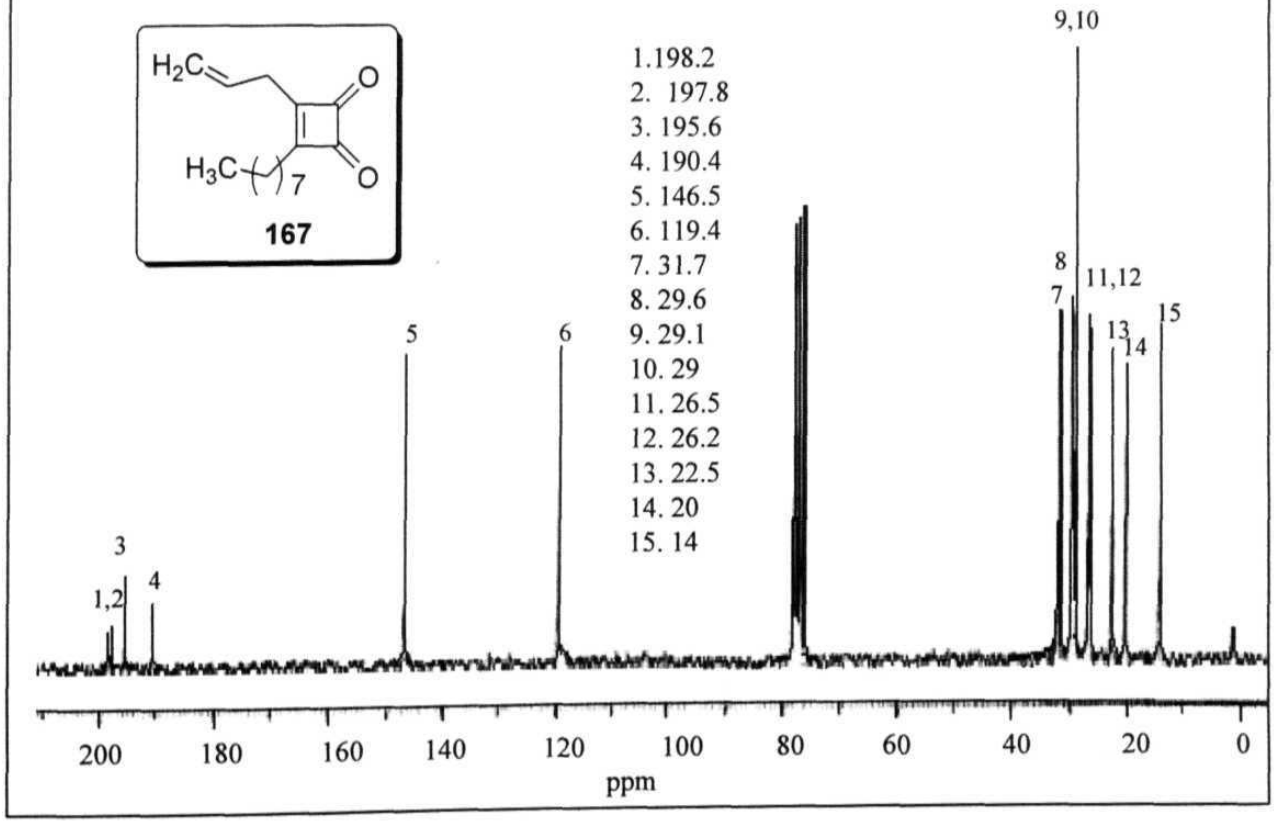
Spectrum No. 16 (Chapter 3, Section 3.7) Mass Spectrum (EI)



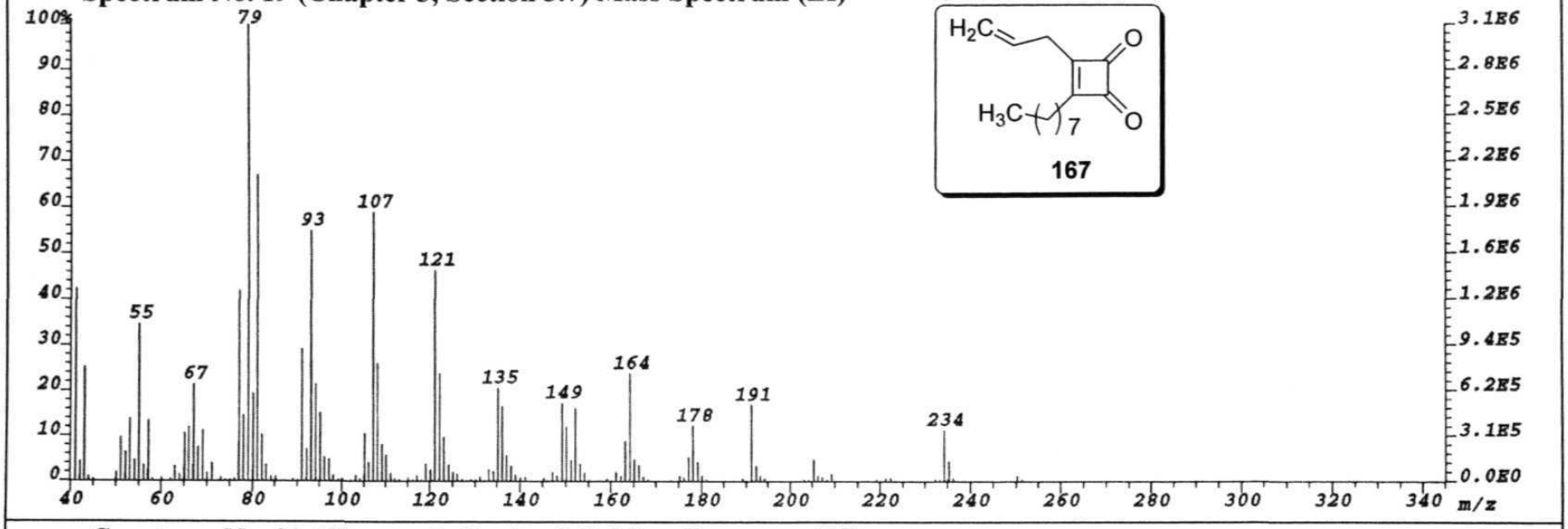
Spectrum No. 17 (Chapter 3, Section 3.7) ^{1} H NMR Spectrum (400 MHz, $CDCl_3$)



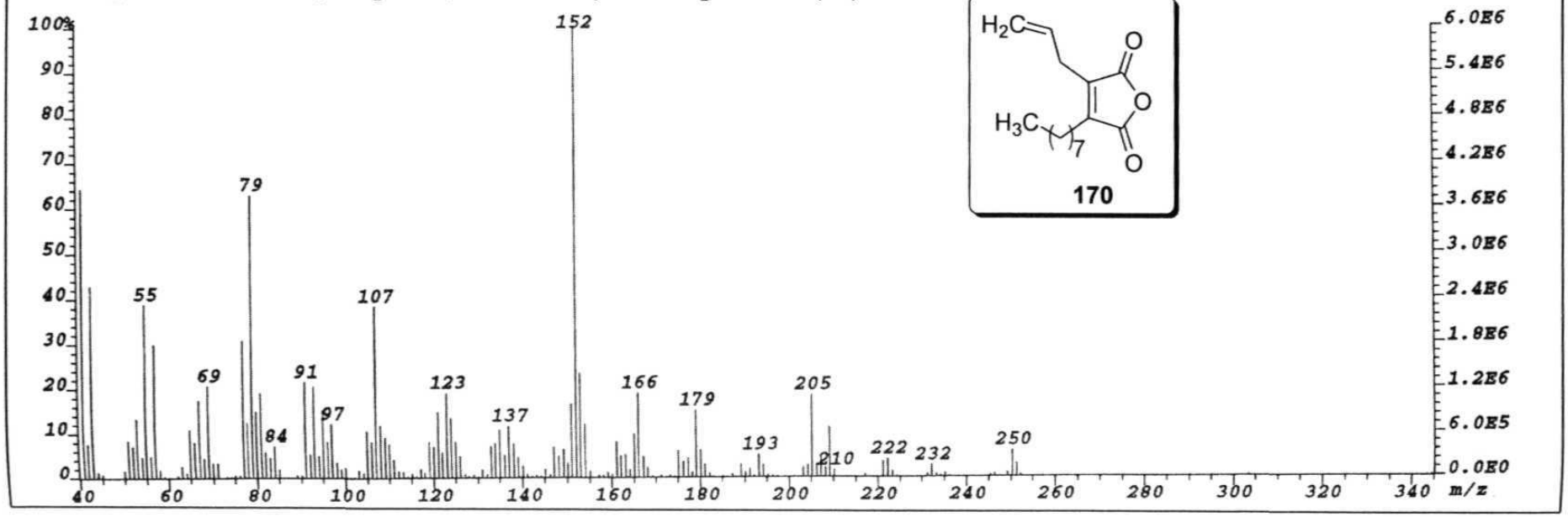
Spectrum No. 18 (Chapter 3, Section 3.7) ^{13} C NMR Spectrum (50 MHz, $CDCl_3$)



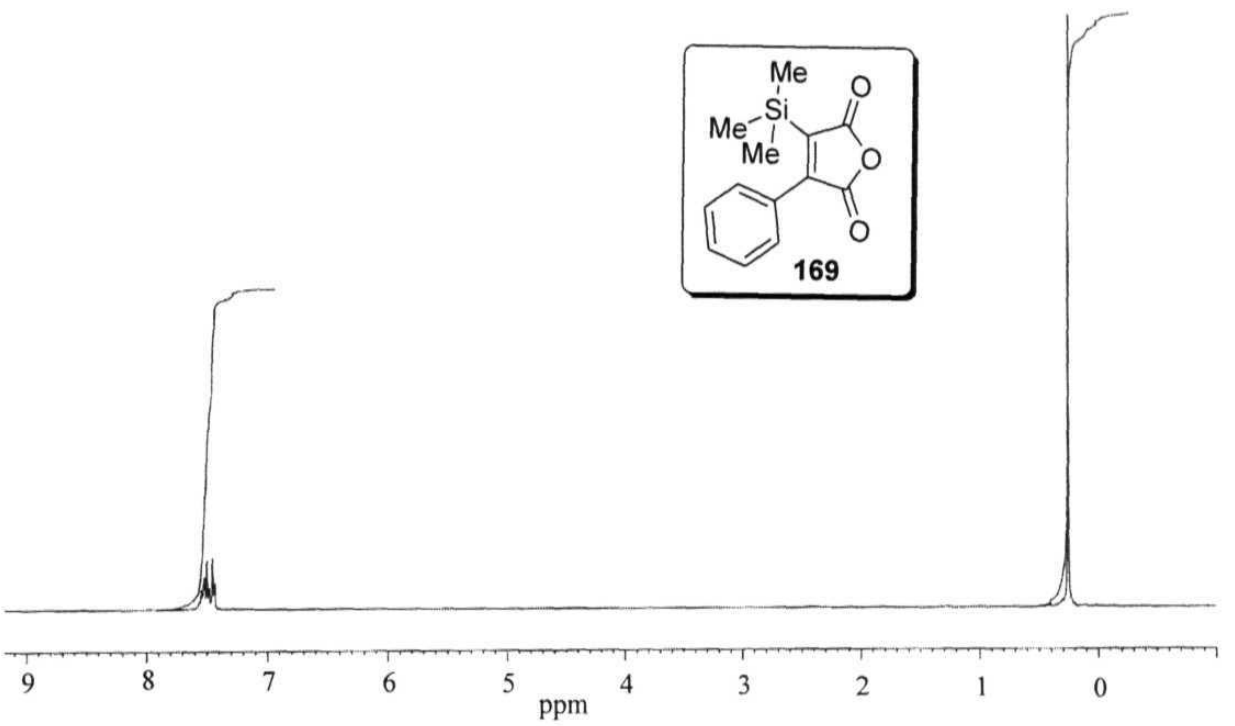
Spectrum No. 19 (Chapter 3, Section 3.7) Mass Spectrum (EI)



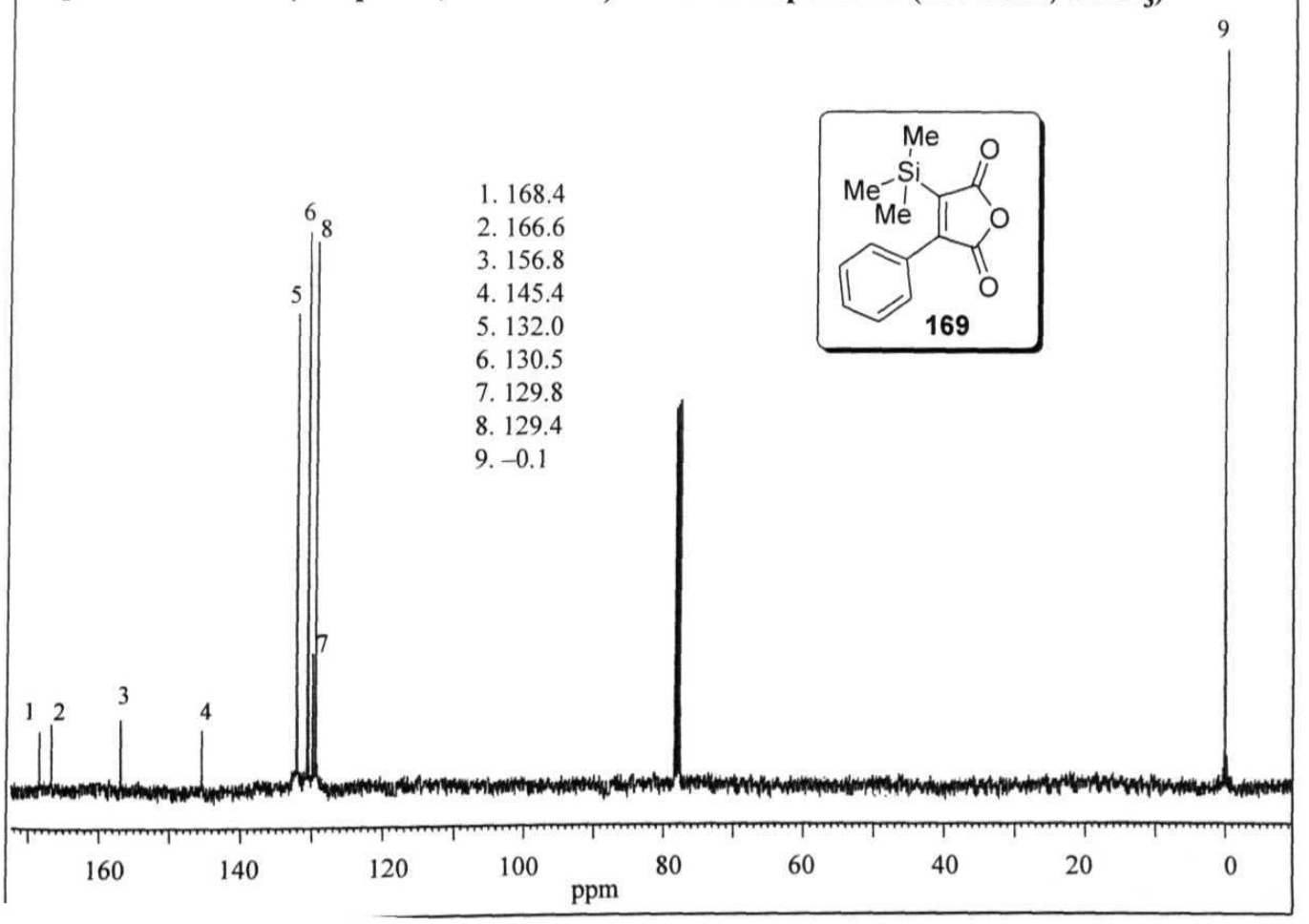
Spectrum No. 20 (Chapter 3, Section 3.8) Mass Spectrum (EI)



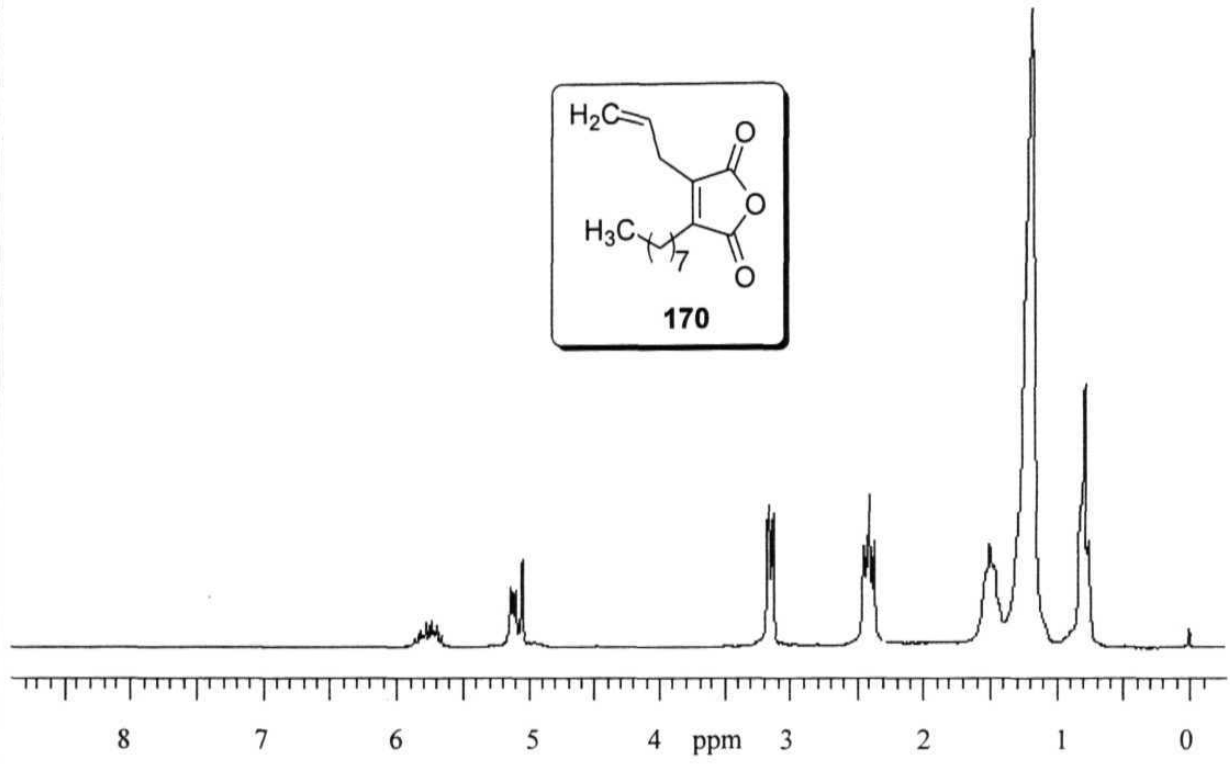
Spectrum No. 21 (Chapter 3, Section 3.8) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



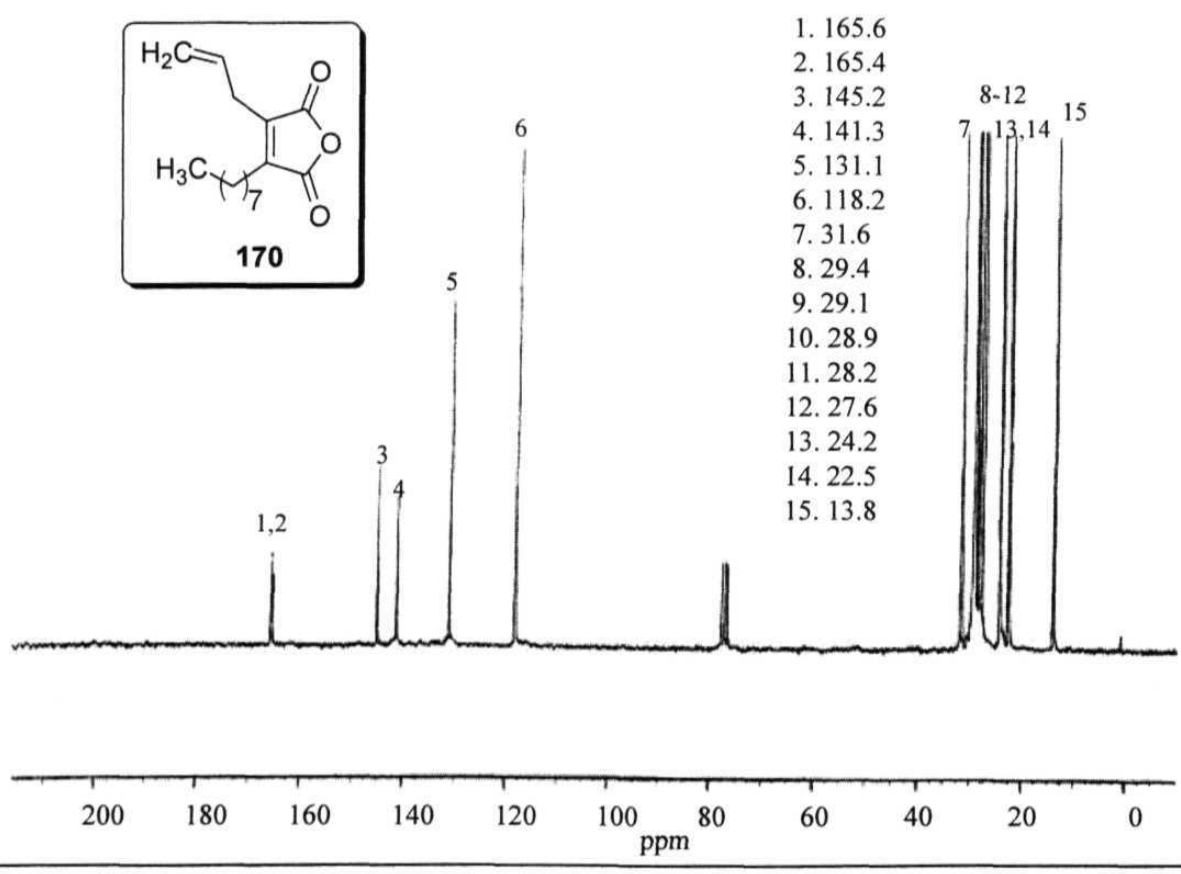
Spectrum No. 22 (Chapter 3, Section 3.8) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



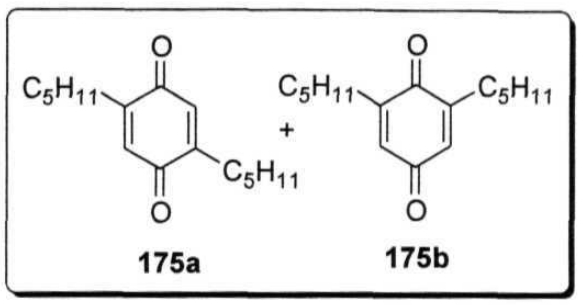
Spectrum No. 23 (Chapter 3, Section 3.8) ^{1} H NMR Spectrum (200 MHz, $CDCl_3$)



Spectrum No. 24 (Chapter 3, Section 3.8) ^{13} C NMR Spectrum (50 MHz, $CDCl_3$)

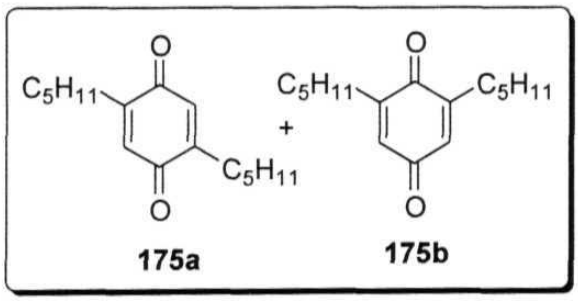


Spectrum No. 25 (Chapter 3, Section 3.10) ^{1} H NMR Spectrum (200 MHz, $CDCl_3$)



175a **175b**

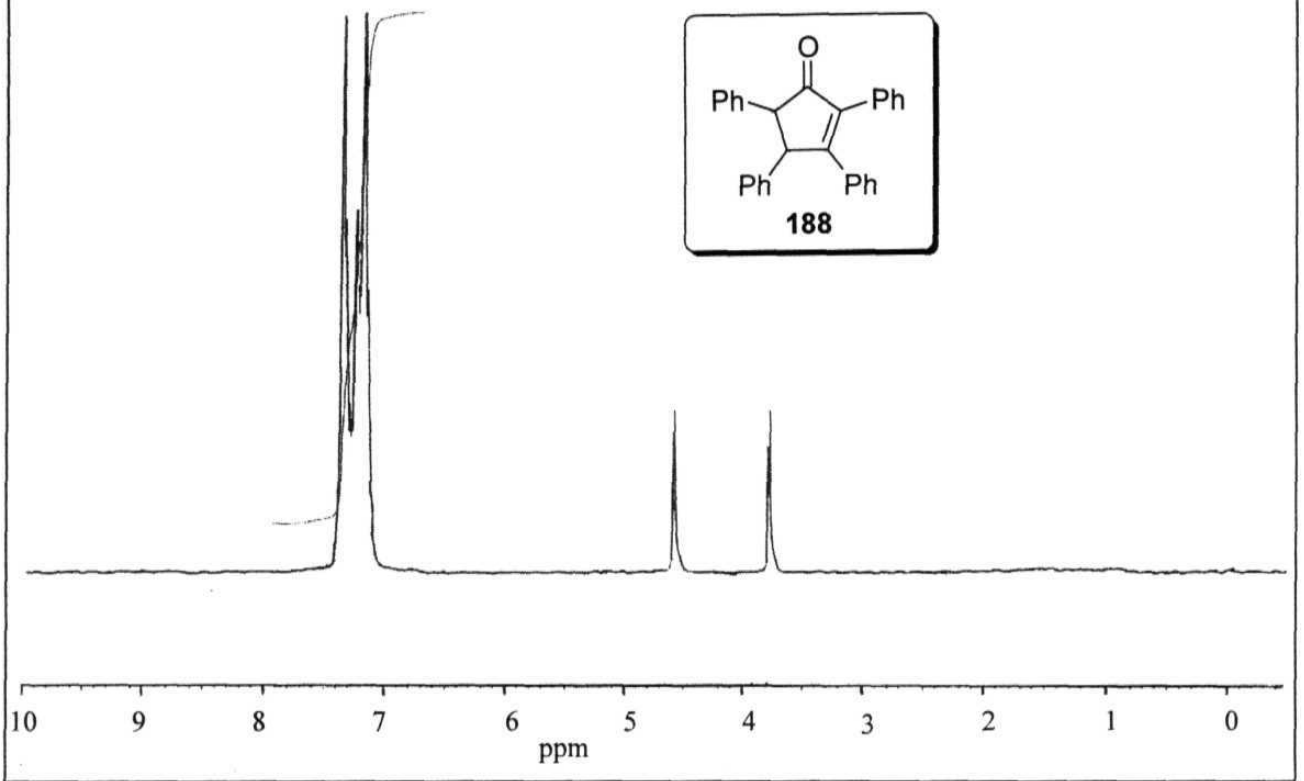
Spectrum No. 26 (Chapter 3, Section 3.10) ^{13} C NMR Spectrum (50 MHz, $CDCl_3$)



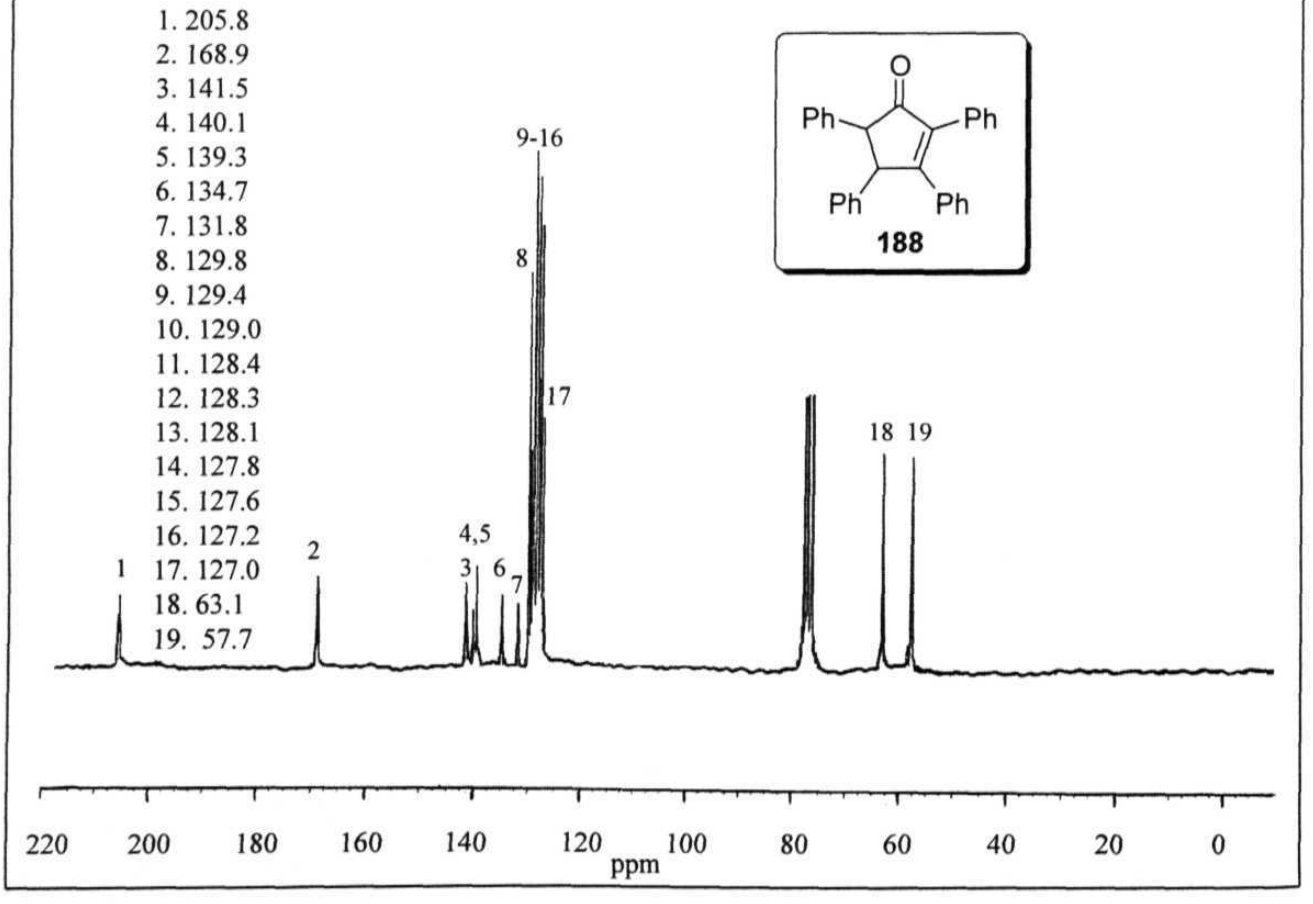
175a **175b**

1. 187.9
2. 187.6
3. 149.7
4. 149.2
5. 132.5
6. 132.0
7. 31.4
8. 29.0
9. 28.5
10. 27.5
11. 22.3
12. 13.8

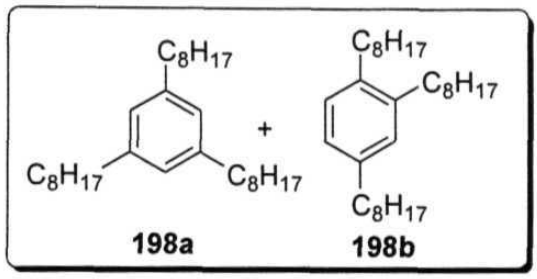
Spectrum No. 27 (Chapter 3, Section 3.11) ^{1}H NMR Spectrum (200 MHz, $CDCl_3$)



Spectrum No. 28 (Chapter 3, Section 3.11) ^{13}C NMR Spectrum (50 MHz, $CDCl_3$)

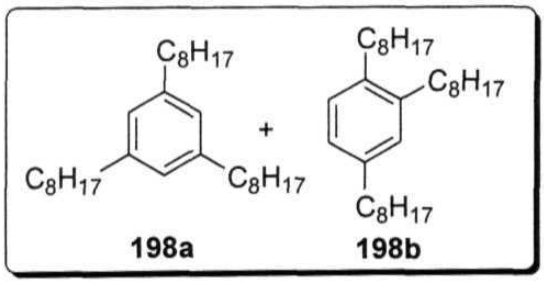


Spectrum No. 29 (Chapter 3, Section 3.12) ^{1}H NMR Spectrum (200 MHz, $CDCl_3$)



198a **198b**

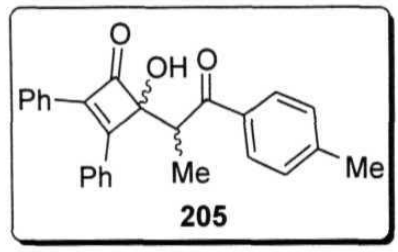
Spectrum No. 30 (Chapter 3, Section 3.12) ^{13}C NMR Spectrum (50 MHz, $CDCl_3$)



198a **198b**

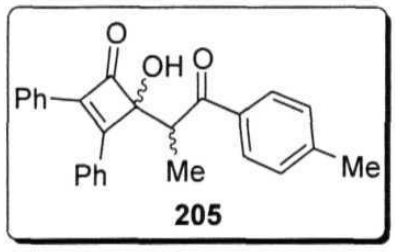
(198a)	**(198a)&(198b)**
1. 142.7	9. 36.3
8. 125.9	10 36.1
(198b)	11. 35.7
2. 140.3	12. 32.8
3. 140.1	13. 32.4
4. 137.7	14. 32.0
5. 129.3	15. 31.6
6. 129.0	16. 315
7. 125.8	17. 29.9
	18. 29.6
	19. 29.4
	20. 22.7
	21. 14.1

Spectrum No. 31 (Chapter 3, Section 3.13) ^{1} H NMR Spectrum (200 MHz, $CDCl_3$)



205

Spectrum No. 32 (Chapter 3, Section 3.13) ^{13} C NMR Spectrum (50 MHz, $CDCl_3$)



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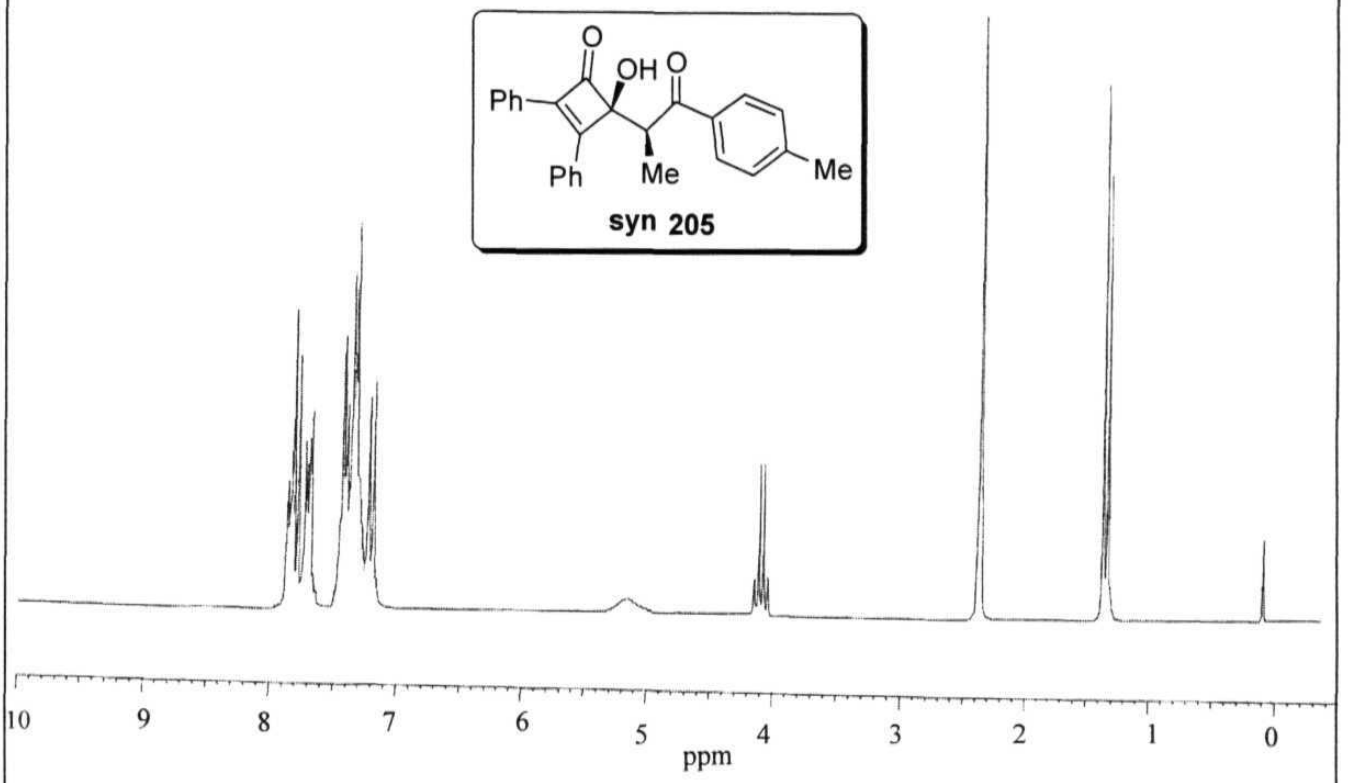
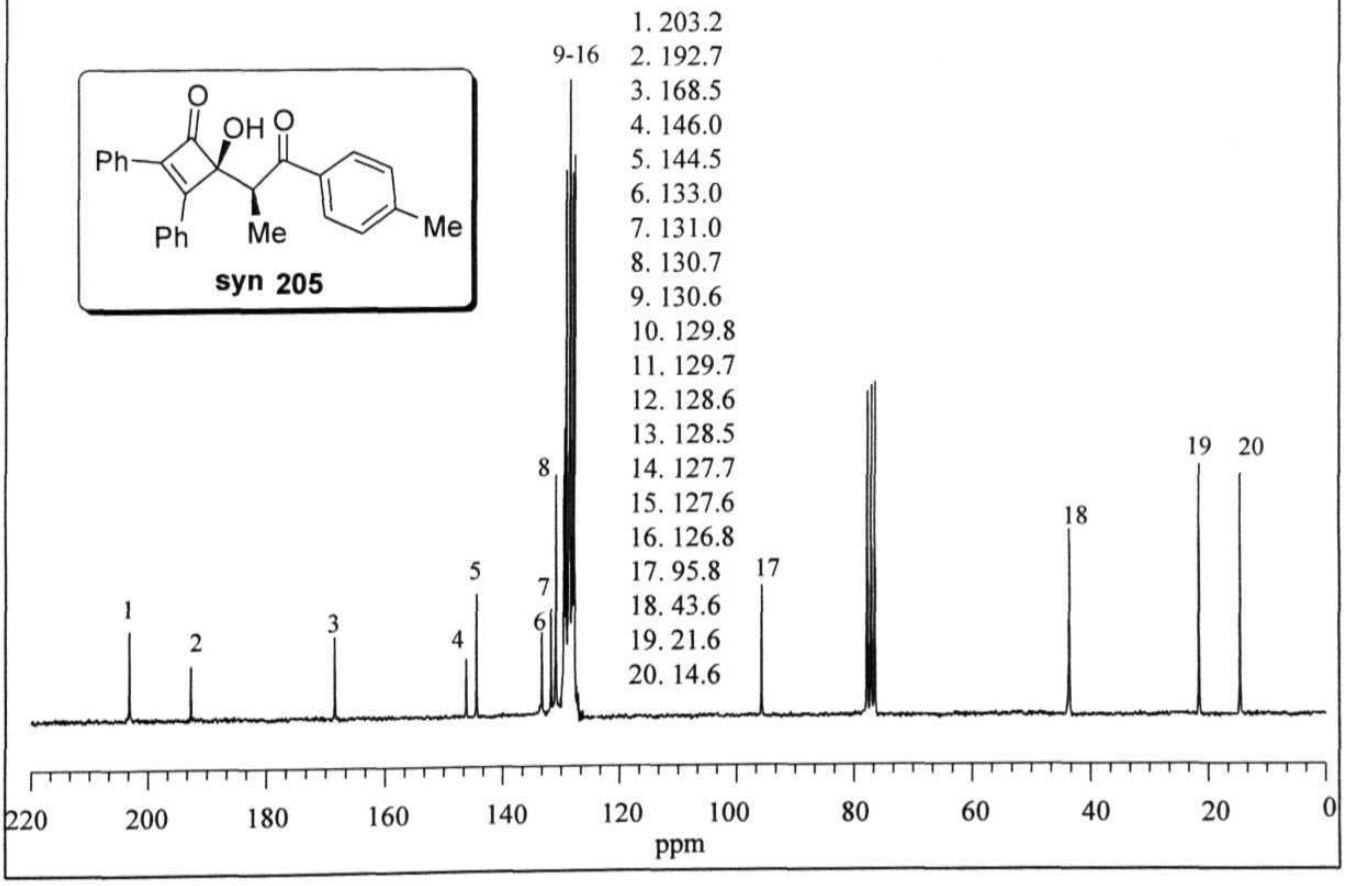
	Major (Syn)	Minor (Anti)
1	203.2	203.5
2	192.7	189.6
3	168.5	169.6
4	146.0	145.9
5	144.5	144.3
6	133.0	132.8
7	131.0	96.2
8	130.7	42.9
9	130.6	14.8
10	129.8	
11	129.7	
12	128.6	
13	128.5	
14	127.7	
15	127.6	
16	126.8	
17	95.8	
18	43.6	
19	21.6	
20	14.6	

Spectrum No. 33 (Chapter 3, Section 3.13) ^{1}H NMR Spectrum (200 MHz, $CDCl_3$)

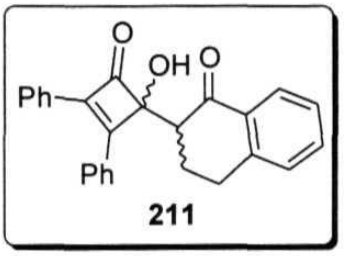


Spectrum No. 34 (Chapter 3, Section 3.13) ^{13}C NMR Spectrum (50 MHz, $CDCl_3$)



Spectrum No. 35 (Chapter 3, Section 3.13) ^{13} C NMR Spectrum (50 MHz, $CDCl_3$)

Major		Minor
1. 200.8	12. 129.5	201.2
2. 191.8	13. 129.3	190.3
3. 166.4	14. 128.8	167.2
4. 147.1	15. 128.6	147.0
5. 144.2	16. 128.3	144.1
6. 134.5	17. 127.9	134.4
7. 131.9	18. 127.0	97.6
8. 130.8	19. 97.4	48.0
9. 130.6	20. 48.3	25.1
10. 130.3	21. 28.6	
11. 129.8	22. 26.0	



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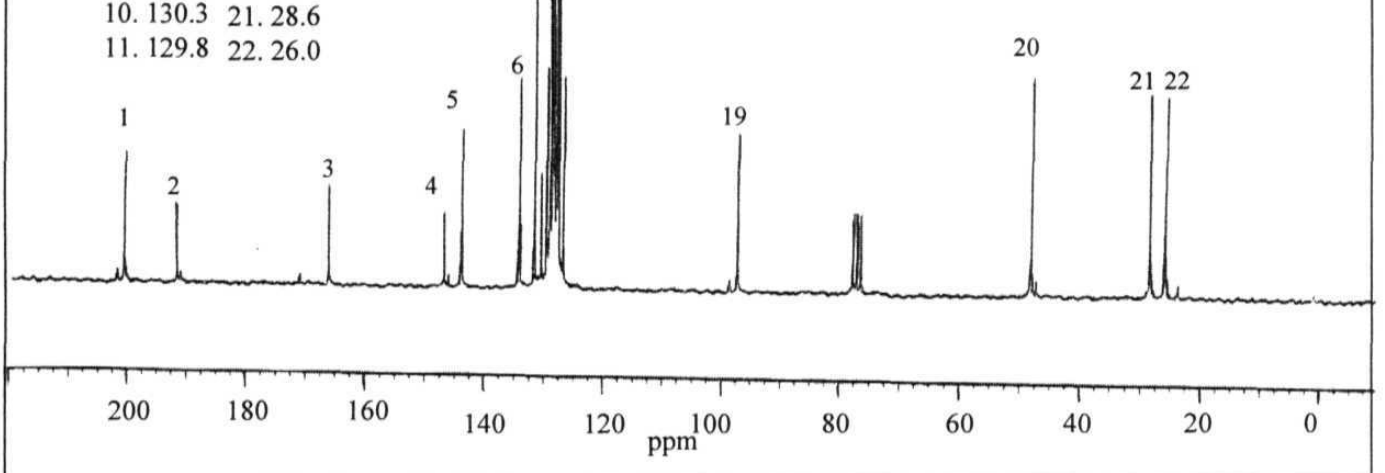
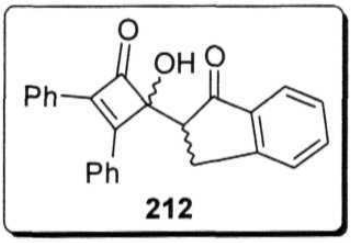


Spectrum No. 36 (Chapter 3, Section 3.13) ^{13} C NMR Spectrum (50 MHz, $CDCl_3$)

Major		Minor
1. 208.0	12. 128.8	207.3
2. 191.6	13. 128.2	191.1
3. 167.5	14. 127.9	170.9
4. 153.5	15. 127.6	153.9
5. 147.1	16. 126.5	147.0
6. 136.2	17. 124.5	136.0
7. 135.7	18. 123.8	135.4
8. 131.8	19. 96.7	131.1
9. 130.8	20. 48.3	130.7
10. 129.9	21. 29.5	129.8
11. 129.4		129.2
		128.7
		96.1
		48.7
		29.8



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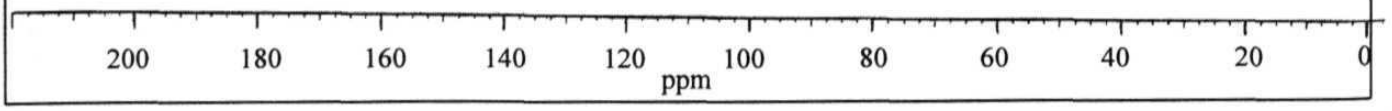
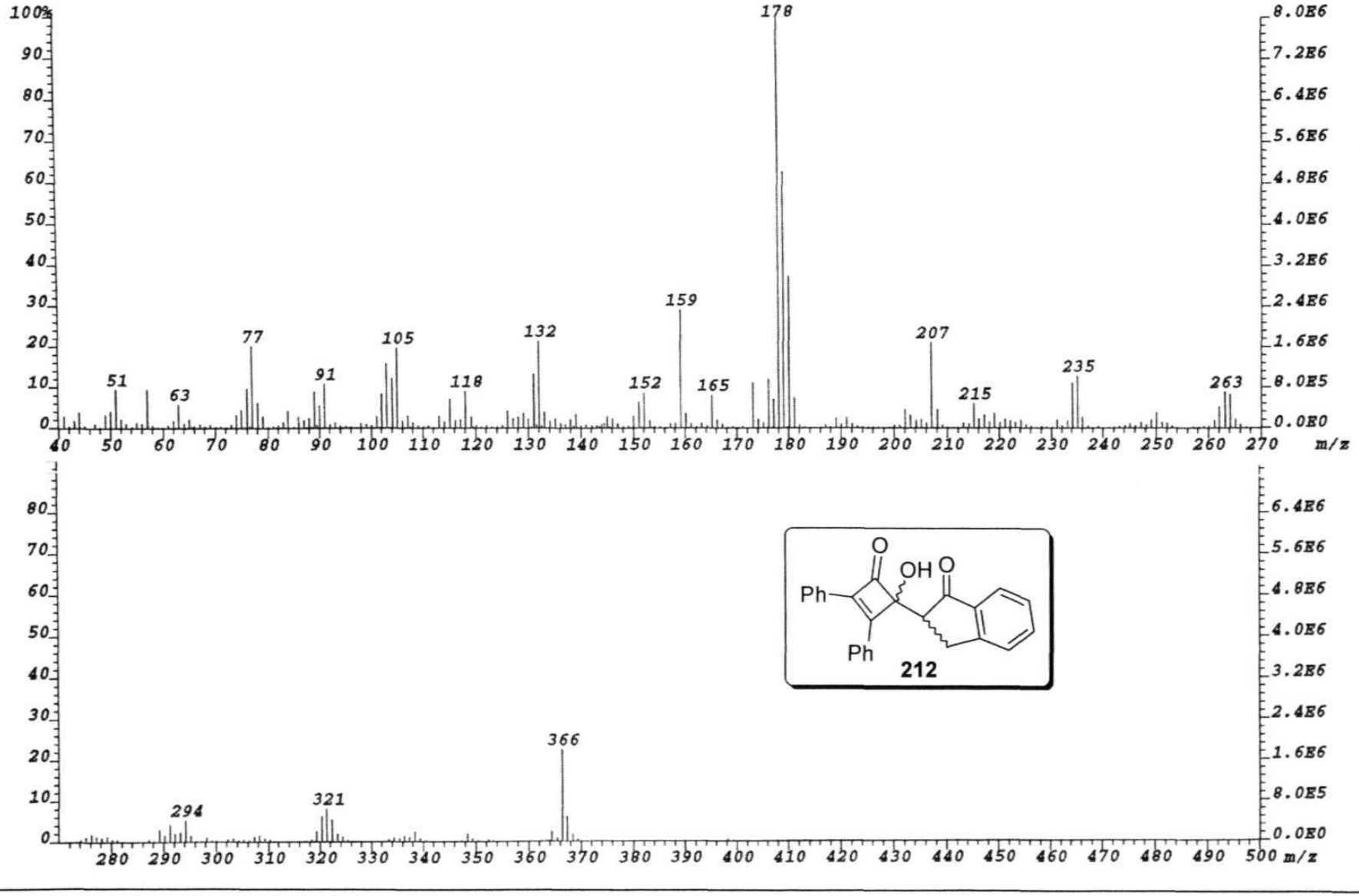


Spectrum No. 37 (Chapter 3, Section 3.13) Mass Spectrum (EI)



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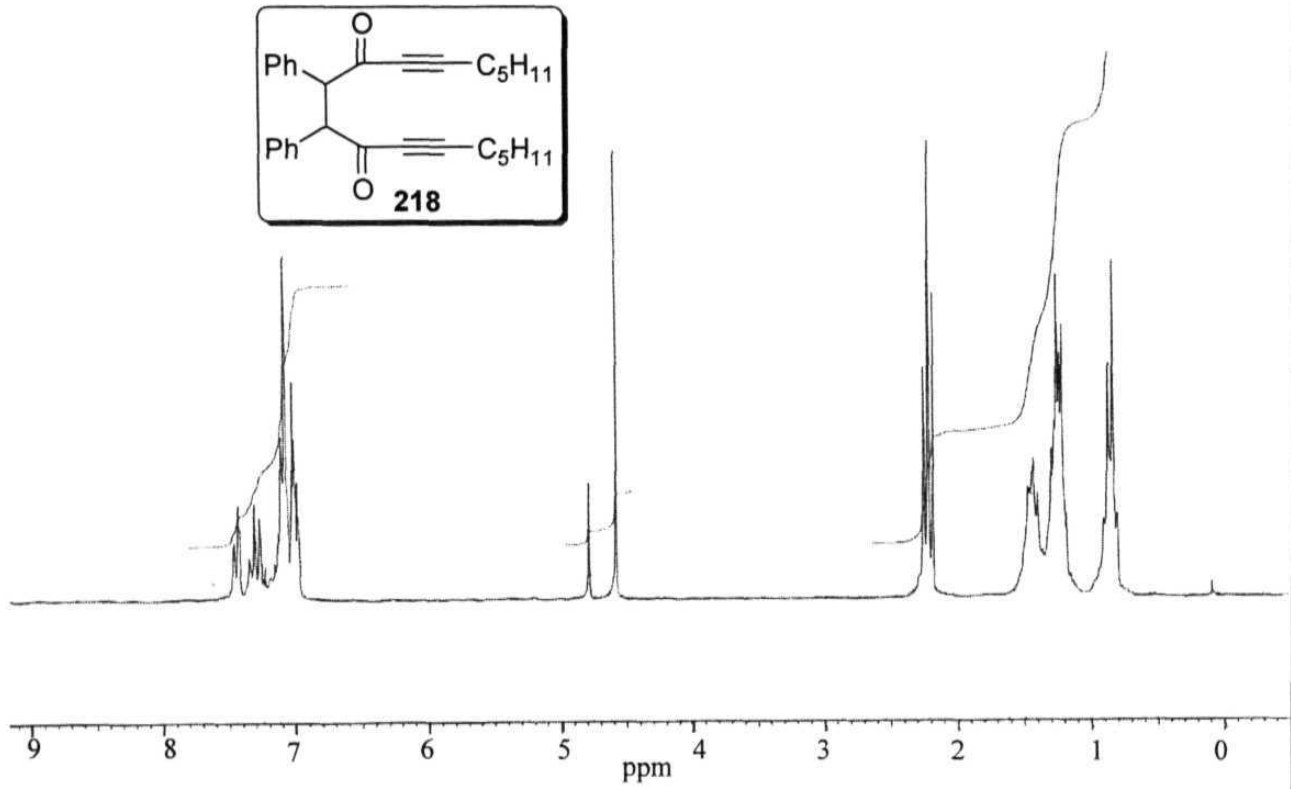
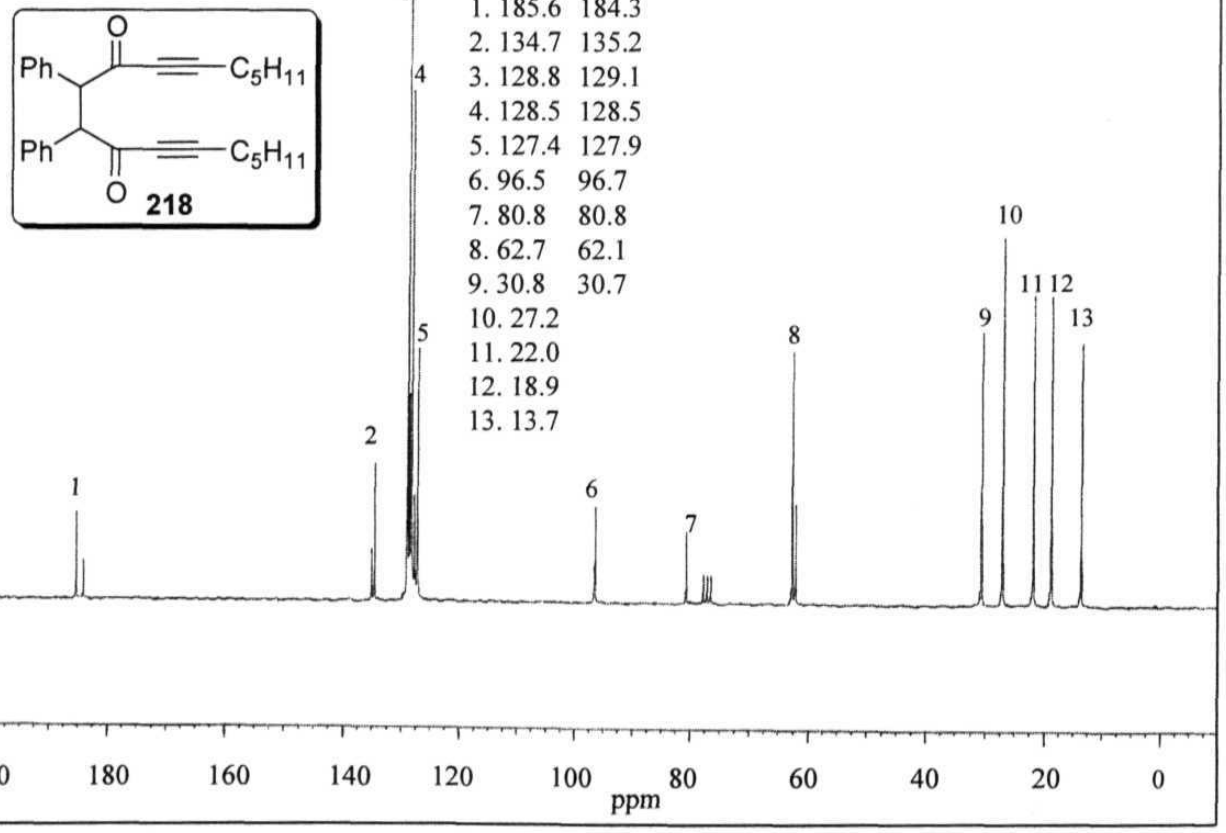
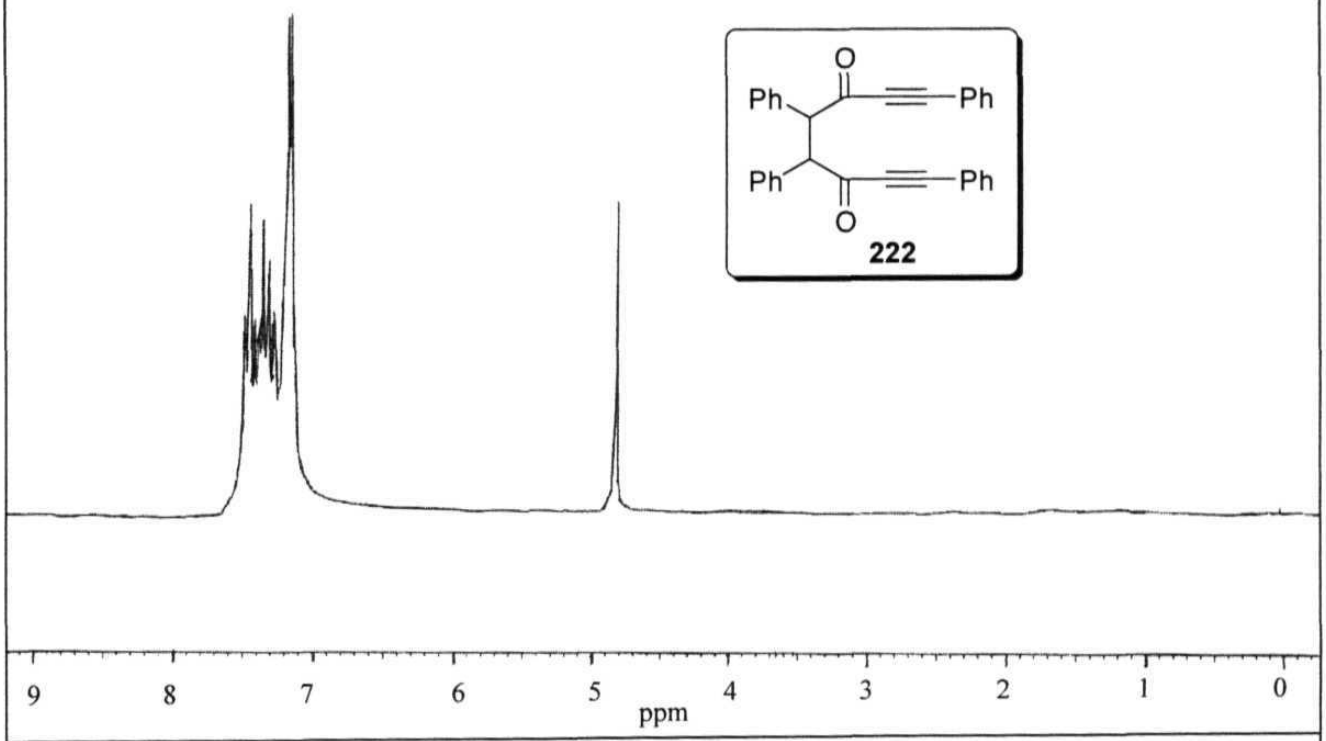
Spectrum No. 38 (Chapter 3, Section 3.14) ^{1}H NMR Spectrum (200 MHz, $CDCl_3$)



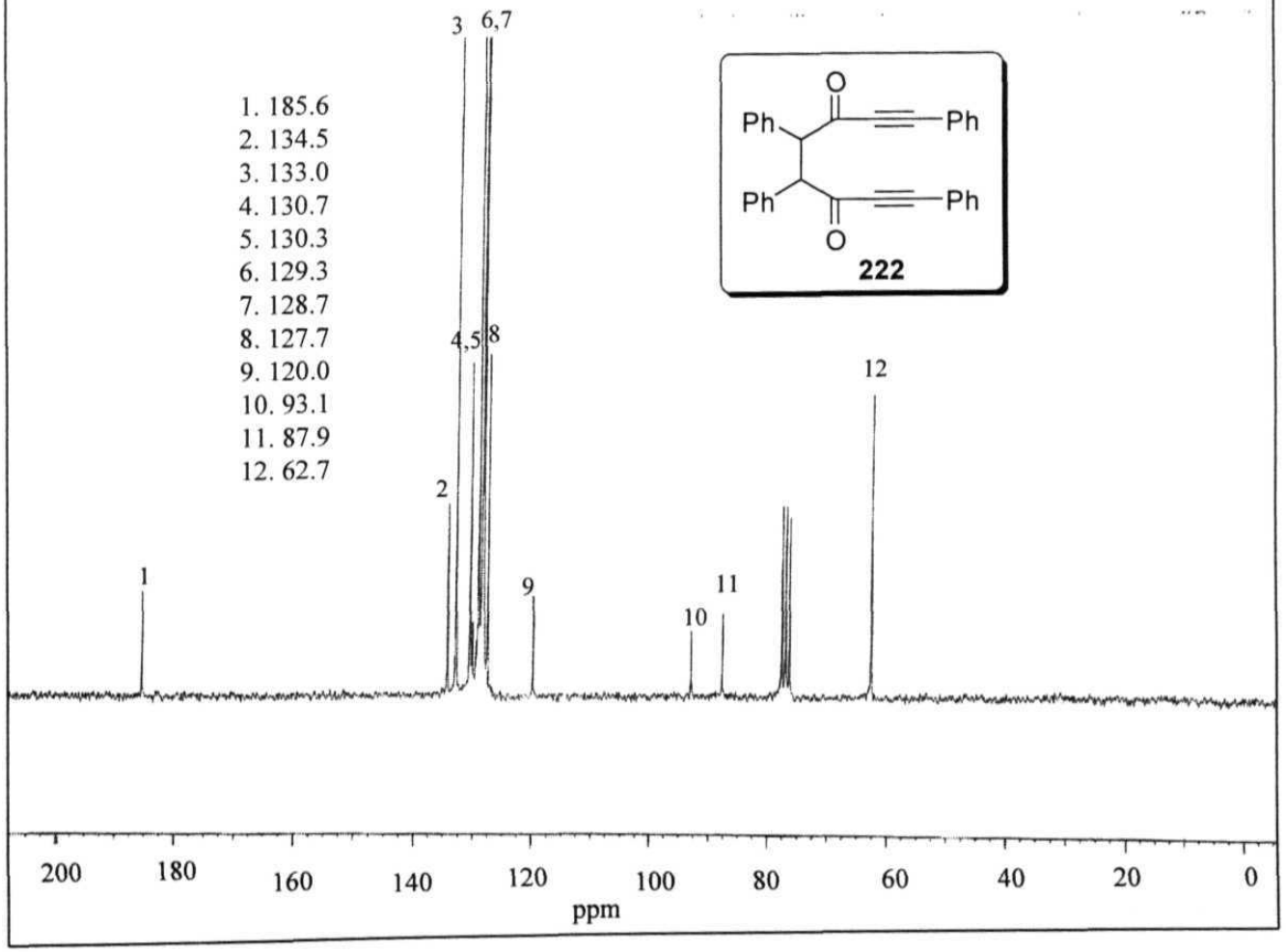
Spectrum No. 39 (Chapter 3, Section 3.14) ^{13}C NMR Spectrum (50 MHz, $CDCl_3$)



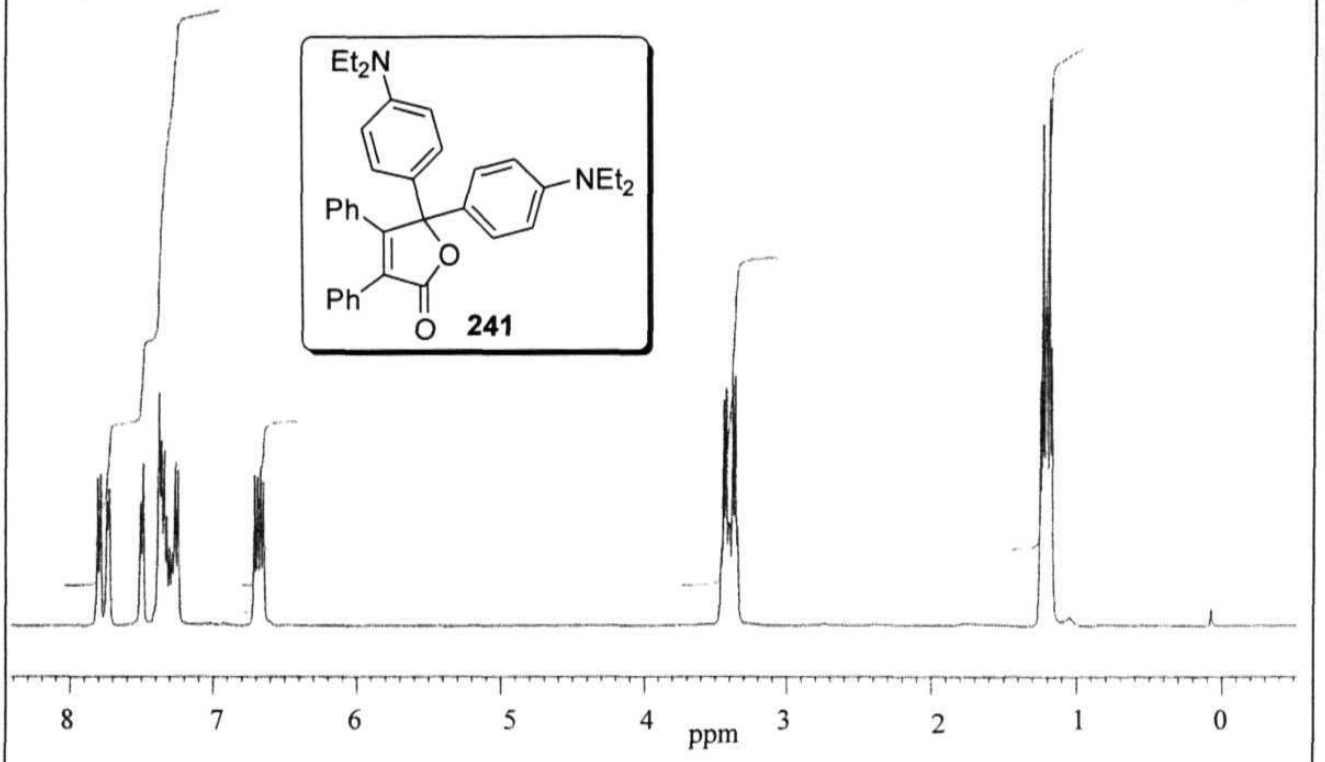
Spectrum No. 40 (Chapter 3, Section 3.14) ^{1} H NMR Spectrum (200 MHz, $CDCl_3$)



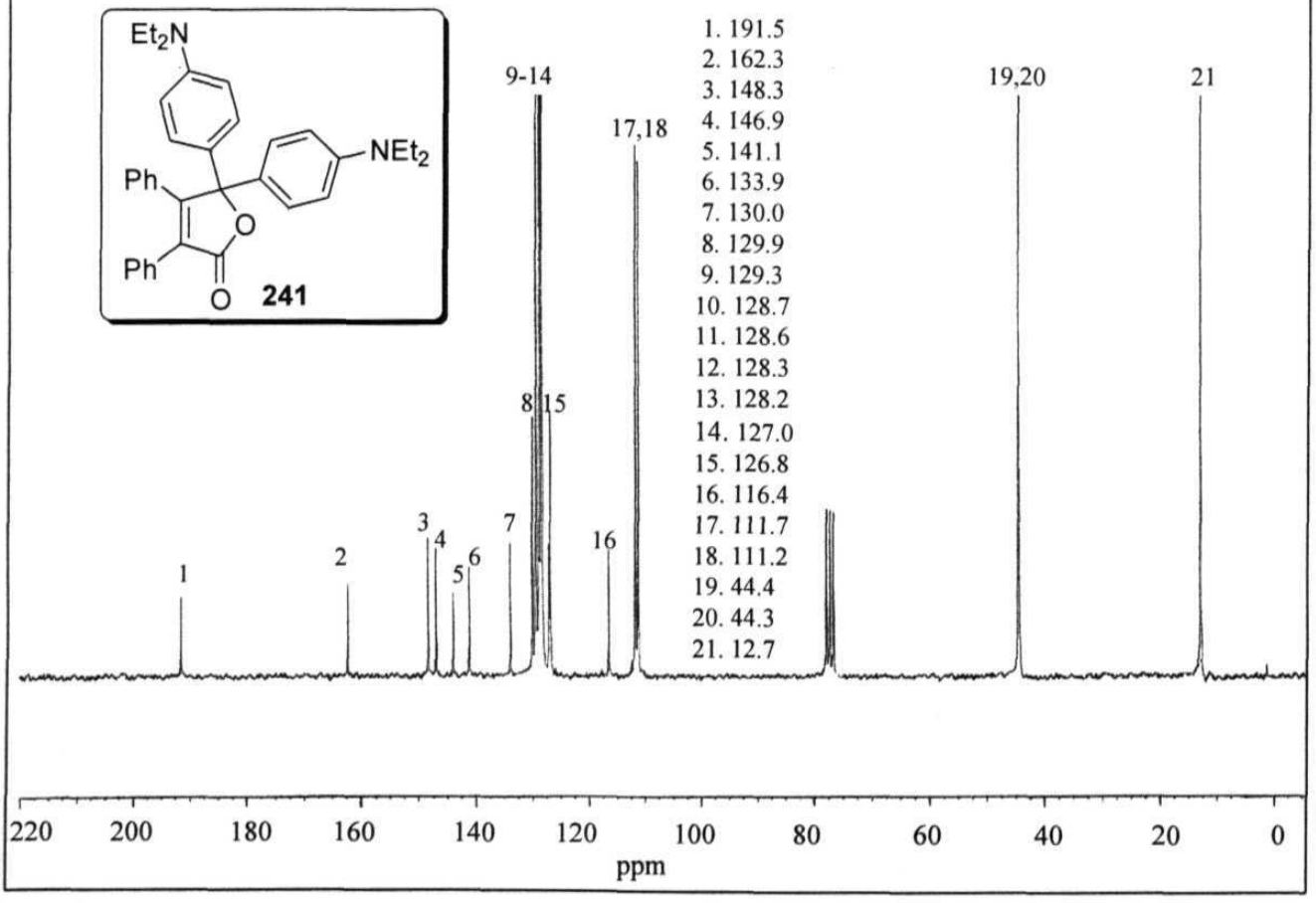
Spectrum No. 41 (Chapter 3, Section 3.14) ^{13} C NMR Spectrum (50 MHz, $CDCl_3$)



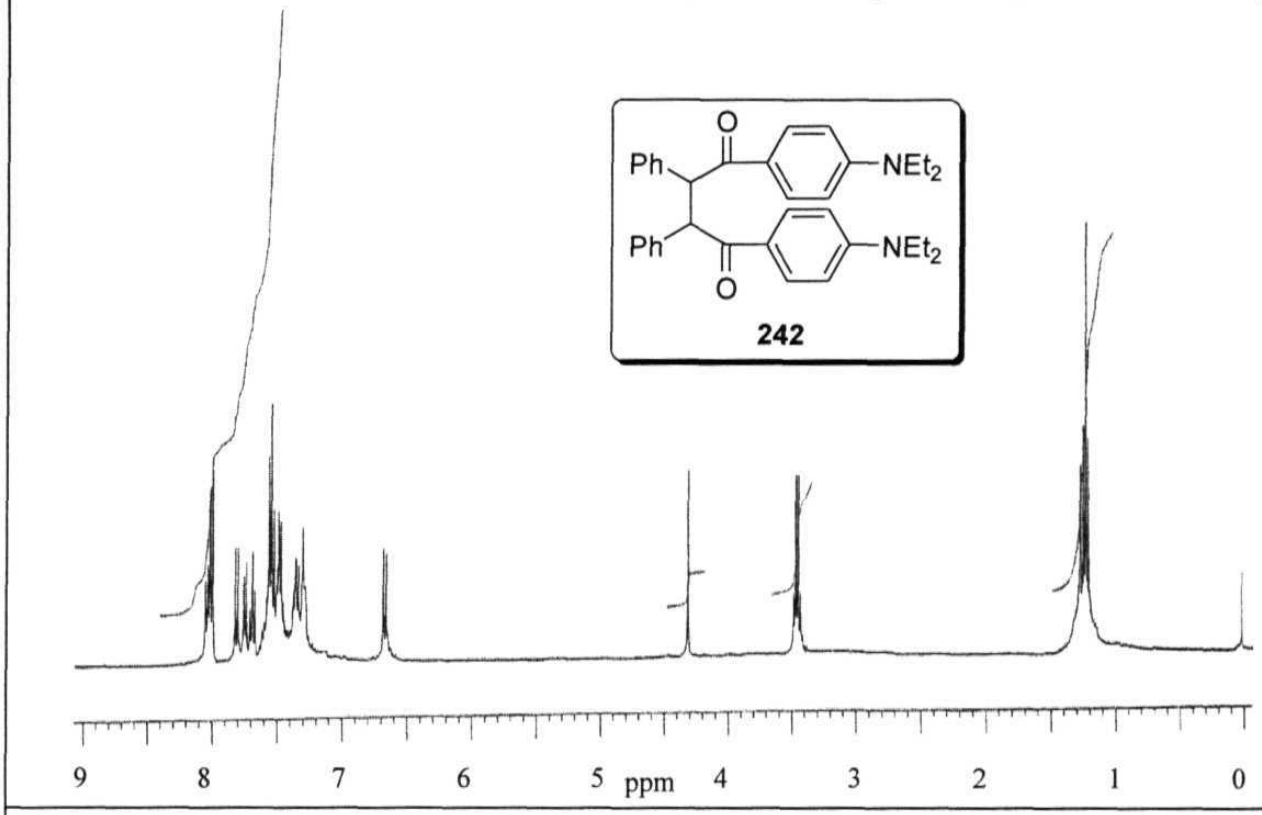
Spectrum No. 42 (Chapter 3, Section 3.15) ^{1} H NMR Spectrum (400 MHz, $CDCl_3$)



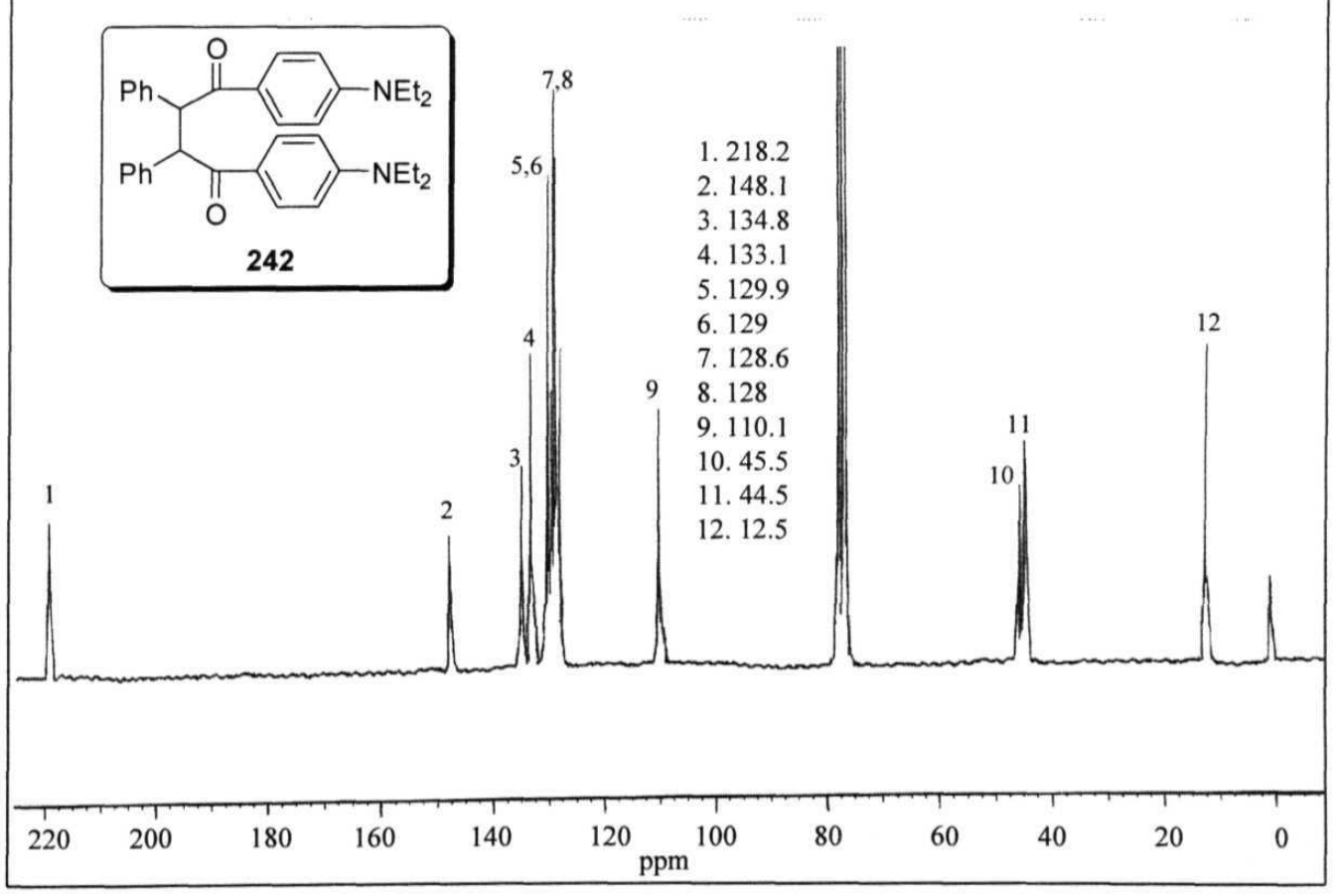
Spectrum No. 43 (Chapter 3, Section 3.15) ^{13} C NMR Spectrum (50 MHz, $CDCl_3$)



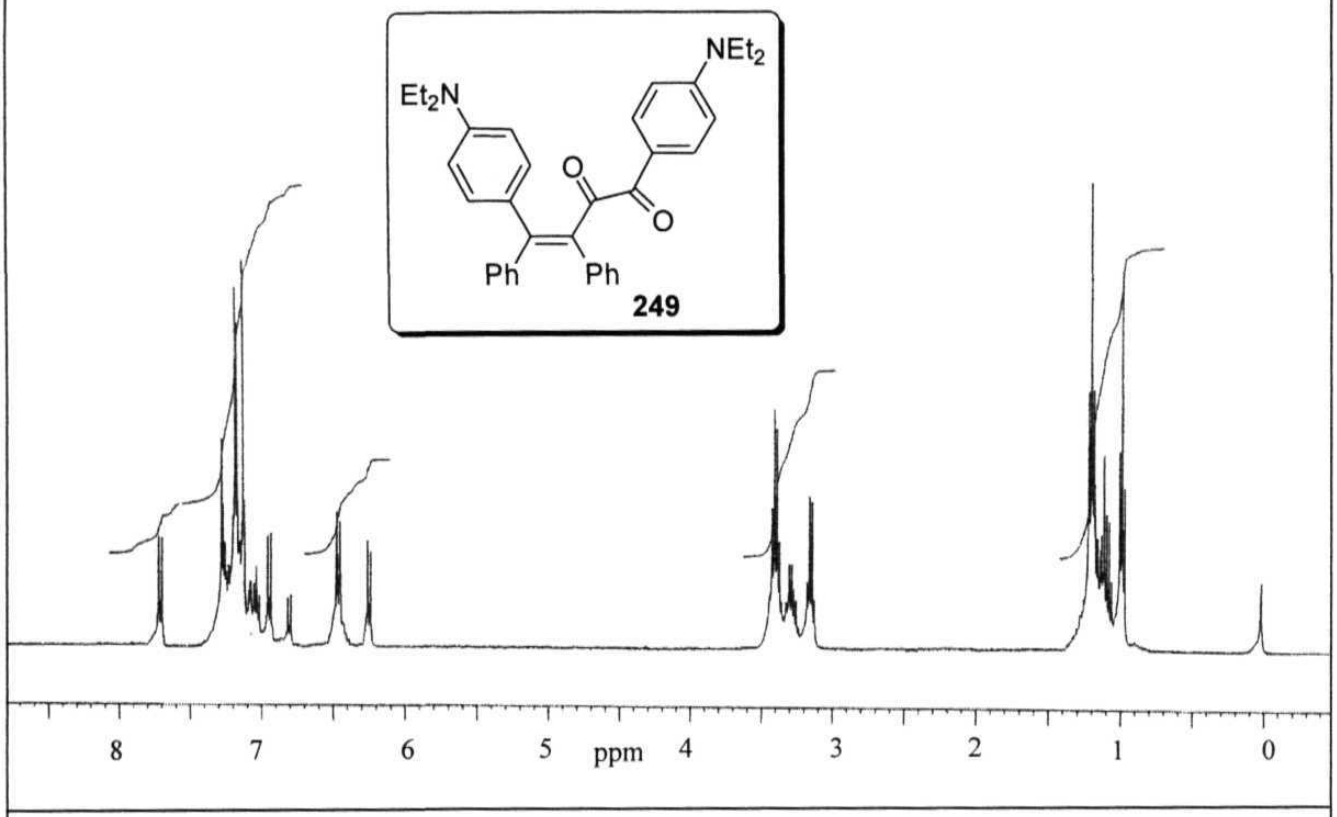
Spectrum No. 44 (Chapter 3, Section 3.15) ^{1} H NMR Spectrum (400 MHz, $CDCl_3$)



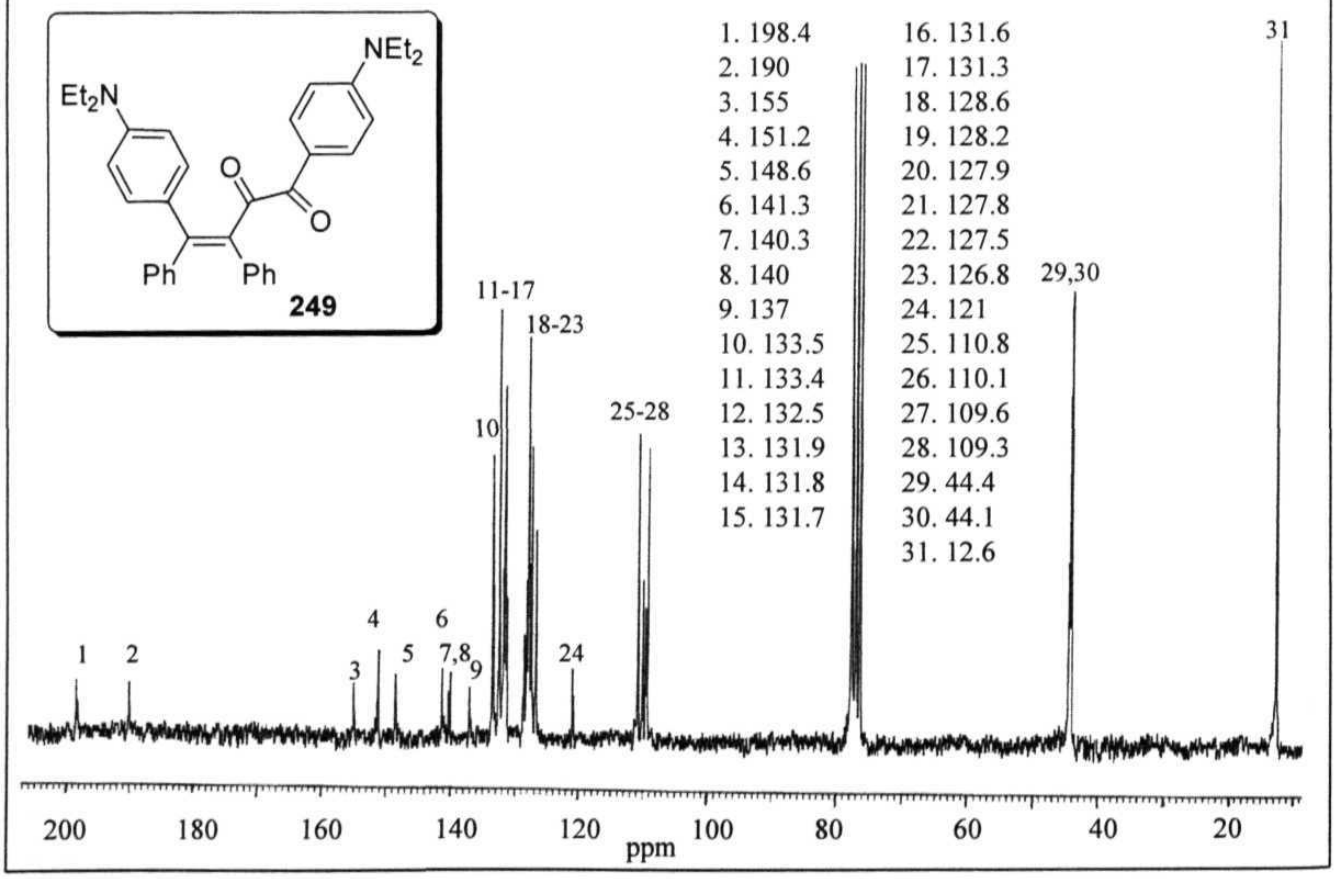
Spectrum No. 45 (Chapter 3, Section 3.15) ^{13} C NMR Spectrum (50 MHz, $CDCl_3$)



Spectrum No. 46 (Chapter 3, Section 3.16) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



Spectrum No. 47 (Chapter 3, Section 3.16) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



Appendix II

X-ray Crystallographic data

Table 1. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å x 10^3) for **142** (**Chapter 3, Section 3.3**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

atom	x	y	z	U(eq)
Fe(1)	7224(1)	-2191(1)	680(1)	35(1)
Fe(2)	7085(1)	739(1)	608(1)	39(1)
O(1)	7804(2)	3123(4)	-40(2)	84(1)
O(2)	7408(3)	2322(5)	2049(2)	105(2)
O(3)	5312(2)	1817(5)	-51(2)	88(1)
O(4)	8209(2)	-4418(5)	1851(2)	89(1)
O(5)	5962(3)	-4540(4)	-135(2)	89(1)
O(6)	6212(2)	-1295(4)	1529(2)	66(1)
O(7)	8745(2)	-396(3)	1752(1)	51(1)
O(8)	9285(2)	1880(5)	1593(2)	92(1)
O(9)	6170(2)	-844(3)	-868(1)	42(1)
O(10)	6536(3)	1153(5)	-1428(2)	87(1)
C(1)	6927(2)	-692(4)	-217(2)	36(1)
C(2)	7634(2)	-1557(4)	-210(2)	34(1)
C(3)	8339(2)	-1417(4)	501(2)	36(1)
C(4)	8136(2)	-441(4)	997(2)	39(1)
C(5)	7518(3)	2212(5)	220(2)	52(1)
C(6)	7283(3)	1703(5)	1501(3)	57(1)
C(7)	5983(3)	1389(5)	202(2)	52(1)
C(8)	6456(3)	-3638(5)	175(2)	52(1)
C(9)	7828(3)	-3560(6)	1396(2)	53(1)

C(10)	6615(2)	-1454(5)	1183(2)	48(1)
C(11)	9271(3)	849(6)	1992(3)	62(1)
C(12)	9814(3)	687(7)	2818(3)	89(2)
C(13)	6058(3)	112(6)	-1461(2)	53(1)
C(14)	5284(3)	-314(7)	-2131(2)	73(2)
C(15)	7674(2)	-2384(4)	-877(2)	41(1)
C(16)	7063(3)	-3431(6)	-1308(3)	65(1)
C(17)	7095(3)	-4047(7)	-1958(3)	86(2)
C(18)	7711(3)	-3644(8)	-2194(3)	78(2)
C(19)	8338(3)	-2625(6)	-1771(3)	66(1)
C(20)	8317(3)	-1990(5)	-1112(2)	53(1)
C(21)	9170(2)	-2216(4)	683(2)	39(1)
C(22)	9894(2)	-1326(5)	854(2)	53(1)
C(23)	10671(3)	-2048(6)	1002(3)	64(1)
C(24)	10726(3)	-3630(6)	994(3)	64(1)
C(25)	10013(3)	-4530(5)	835(2)	55(1)
C(26)	9236(2)	-3831(5)	675(2)	45(1)

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å x 10^3) for **188** (**Chapter 3, Section 3.11**). U (eq) is defined as one third of the trace of the orthogonalized Uij tensor.

atom	**x**	**y**	**z**	**U(eq)**
O	5245(1)	104(1)	8104(1)	85(1)
C(1)	5759(1)	286(1)	8372(1)	64(1)

C(2)	6219(1)	976(1)	8568(1)	62(1)
C(3)	6733(1)	937(1)	8981(1)	59(1)
C(4)	6577(1)	243(1)	8903(1)	58(1)
C(5)	6039(1)	-113(1)	8553(1)	62(1)
C(6)	6481(1)	1399(1)	7979(1)	63(1)
C(7)	6868(2)	1323(2)	7543(1)	81(1)
C(8)	7105(2)	1702(2)	7007(2)	97(1)
C(9)	6966(2)	2170(2)	6887(2)	105(1)
C(10)	6570(2)	2251(2)	7296(2)	113(1)
C(11)	6326(2)	1878(2)	7854(2)	85(1)
C(12)	6726(1)	1097(1)	9683(1)	62(1)
C(13)	7235(2)	1638(2)	9946(1)	89(1)
C(14)	7226(2)	1792(2)	10587(2)	125(2)
C(15)	6707(2)	1402(2)	10966(2)	109(1)
C(16)	6204(2)	856(2)	10719(2)	95(1)
C(17)	6209(2)	702(2)	10072(1)	81(1)
C(18)	6979(1)	28(1)	9243(1)	59(1)
C(19)	7641(1)	413(1)	9265(1)	68(1)
C(20)	8009(2)	224(2)	9608(2)	83(1)
C(21)	7729(2)	-335(2)	9941(2)	89(1)
C(22)	7068(2)	-731(2)	9931(1)	86(1)
C(23)	6695(2)	-552(1)	9578(1)	74(1)
C(24)	5753(2)	-799(1)	8355(1)	71(1)
C(25)	5112(2)	-1229(2)	8426(2)	86(1)
C(26)	4855(2)	-1861(2)	8232(2)	111(1)
C(27)	5245(3)	-2058(2)	7966(2)	120(2)
C(28)	5880(3)	-1645(2)	7891(2)	108(1)

C(29)	6145(2)	-1011(2)	8082(2)	90(1)

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å x 10^3) for **205** (**Chapter 3, Section 3.13**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

atom	x	y	z	U(eq)
C1	3424(1)	1338(1)	1086(1)	50(1)
C2	3138(1)	1341(1)	1694(1)	52(1)
C3	3478(1)	112(1)	1865(1)	50(1)
C4	3641(1)	204(1)	1178(1)	49(1)
C5	3451(1)	2275(1)	616(1)	54(1)
C6	3183(1)	2168(2)	-60(1)	69(1)
C7	3224(1)	3072(2)	-478(1)	83(1)
C8	3522(2)	4094(2)	-233(1)	95(1)
C9	3765(2)	4226(2)	428(1)	114(1)
C10	3737(2)	3326(2)	861(1)	86(1)
C11	3943(1)	-686(1)	812(1)	52(1)
C12	4100(1)	-1778(2)	1086(1)	75(1)
C13	4417(2)	-2625(2)	761(1)	98(1)
C14	4548(1)	-2413(2)	150(1)	97(1)
C15	4395(1)	-1347(2)	-126(1)	86(1)
C16	4102(1)	-484(2)	198(1)	68(1)
C17	4210(1)	43(1)	2445(1)	54(1)
C18	4793(1)	975(1)	2370(1)	53(1)
C19	5517(1)	695(1)	2160(1)	50(1)

C20	5779(1)	-413(1)	2092(1)	63(1)
C21	6461(1)	-610(2)	1898(1)	68(1)
C22	6914(1)	284(2)	1761(1)	61(1)
C23	6664(1)	1396(2)	1840(1)	67(1)
C24	5982(1)	1600(1)	2031(1)	62(1)
C25	4006(1)	160(2)	3116(1)	79(1)
C26	7649(1)	62(2)	1539(1)	82(1)

Table 4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å x 10^3) for **249** (**Chapter 3**, **Section 3.16**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

atom	**x**	**y**	**z**	**U(eq)**
O(1)	-25(8)	1061(2)	5176(8)	76(2)
O(2)	3209(10)	1140(2)	6809(7)	86(3)
N(1)	3874(13)	-611(4)	3786(12)	129(5)
N(2)	5877(12)	794(5)	2276(10)	116(5)
C(1)	2084(15)	-1080(4)	2883(13)	121(5)
C(2)	3082(12)	-789(4)	2510(8)	84(3)
C(3)	5213(13)	-847(4)	4357(16)	153(7)
C(4)	6375(16)	-768(8)	4022(14)	263(14)
C(5)	3507(13)	-238(3)	4261(10)	67(3)
C(6)	4388(13)	-40(4)	5330(10)	79(3)
C(7)	4013(12)	348(3)	4750(11)	71(3)
C(8)	2783(12)	565(3)	5311(9)	54(3)
C(9)	1867(9)	342(3)	4277(9)	50(2)

C(10)	2190(12)	-34(3)	3757(10)	(3)
C(11)	2449(10)	977(3)	5764(9)	55(3)
C(12)	1107(11)	1244(3)	5227(9)	54(3)
C(13)	1191(12)	1724(3)	4976(9)	56(3)
C(14)	26(12)	2000(3)	5135(10)	56(3)
C(15)	-613(12)	1947(3)	6165(12)	75(3)
C(16)	-1768(15)	2178(4)	6367(15)	90(4)
C(17)	-2349(15)	2500(5)	5492(18)	116(5)
C(18)	-1699(17)	2569(4)	4371(15)	(5)
C(19)	-552(14)	2323(4)	4255(12)	86(4)
C(20)	2406(11)	1871(3)	4642(8)	50(2)
C(21)	2847(11)	2359(3)	4806(10)	51(2)
C(22)	3357(12)	2574(3)	3891(11)	66(3)
C(23)	3832(15)	2998(4)	4083(15)	102(5)
C(24)	3894(14)	3204(4)	5203(16)	96(4)
C(25)	3444(14)	2989(4)	6185(11)	87(4)
C(26)	2923(12)	2565(3)	5951(11)	64(3)
C(27)	3328(11)	1588(3)	4046(9)	51(2)
C(28)	4814(11)	1601(3)	4388(9)	56(3)
C(29)	5670(12)	1330(4)	3841(10)	66(3)
C(30)	5038(14)	1047(4)	2877(12)	74(3)
C(31)	3567(12)	1048(3)	2499(10)	60(3)
C(32)	2777(10)	1304(3)	3133(9)	60(3)
C(33)	5192(17)	578(4)	975(16)	230(13)
C(34)	4820(30)	157(5)	1410(16)	183(9)
C (35)	7459(16)	8257)	2539(14)	166(9)
C(36)	8100(20)	1235(8)	1999(19)	205(10)

List of Publications

1. Conversion of Alkynes to Cyclic Imides and Anhydrides Using Reactive Iron Carbonyls Prepared from $Fe(CO)_5$ and $Fe_3(CO)_{12}$, Periasamy, M.; Rameshkumar, C.; **Mukkanti, A.** *J. Organomet. Chem.* **2002**, *649*, 209.
2. Novel Synthesis of Acyloxyferrole Complexes from Alkynes and their Conversion to Cyclobutenediones, Periasamy, M.; **Mukkanti, A.**; Shyam Raj, D. *Organometallics* **2004**, *23*, 619.
3. Convenient Methods of Synthesis of Cyclobutenediones and Anhydrides from Alkynes Using the $Fe(CO)_5/Me_3NO$ Reagent System, Periasamy, M.; **Mukkanti, A.**; Shyam Raj, D. *Communicated.*
4. $TiCl_4$ Promoted Aldol Reaction of Ketones with Cyclobutenediones, Periasamy, M.; **Mukkanti, A.**; Shyam Raj, D. *Communicated.*
5. Methods of Synthesis of Cyclobutenediones, Periasamy, M.; **Mukkanti, A.** *Communicated.*
6. Conversion of 1-Alkynes to Benzoquinones Using the $Fe(CO)_5/TiCl_4$ Reagent System, Periasamy, M.; **Mukkanti, A.**; Shyam Raj, D. *Manuscript under preparation.*
7. Reactions of Alkynyl and Aryltitanium Reagents with Diphenylcyclobutenedione, Periasamy, M.; **Mukkanti, A.**; Shyam Raj, D. *Manuscript under preparation.*