New Reactive Iron Carbonyl Reagents for Double Carbonylation of Alkynes and New Synthetic Methods Using Cyclobutenediones and Aromatic Diketones

A Thesis
Submitted for the Degree of
DOCTOR OF PHILOSOPHY

By

Beesu Mallesh

SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD
HYDERABAD 500 046
INDIA
May 2011

OM SRI SAI RAM

Dedicated to

My Mother Late Smt. Anjamma

And

My Father Sri Chandraiah

And

All My Teachers

Contents

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.

BEESU MALLESH

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

Certificate

Certified that the work embodied in this thesis entitled "**New Reactive Iron Carbonyl Reagents for Double Carbonylation of Alkynes and New Synthetic Methods Using Cyclobutenediones and Aromatic Diketones**" has been carried out by Mr. **Beesu Mallesh** under my supervision and the same has not been submitted elsewhere for a Degree.

PROFESSOR M. PERIASAMY
(THESIS SUPERVISOR)

DEAN
SCHOOL OF CHEMISTRY

ACKNOWLEDGEMENTS

It gives me immense pleasure to express my deep sense of gratitude and profound respect to my research supervisor ***Prof. M. Periasamy*** *for his inspiring guidance, valuable advice and motivation throughout my research work. His constant encouragement boosted to complete my thesis work and I always cherish the human values he has shown. It is always a pleasure for me to be his student. I will be indebted to him for this.*

I thank present and former Deans School of Chemistry, Prof. M. V. Rajasekharan, Prof. D. Basavaiah and Prof M. Periasamy and all the faculty members of the School of Chemistry for their timely help and cooperation.

It is great privilege to express my heartfelt regards to my B. Sc. teachers Sri. T. Sridhar Reddy and Sri. P. Janga Reddy, my M. Sc. teacher Dr. Jayaprakash (JP Sir), my Intermediate teacher Sir Aravida Rayudu and My 10th Class teacher Sri M. Anjaiah for their inspirational teaching, encouragement and motivation towards higher studies and also to all my teachers during the entire tenure of my educational career.

I extend my heartfelt thanks to my colleagues Mr. M. Shanmugaraja and Dr. D. Shyam Raj for their timely help and extreme cooperation for carrying out some of the experiments during my thesis work. I also thank my past and present labmates Dr. G. V. Karunakar, Dr. M. Seenivasaperumal, Dr. M. Narsi Reddy, Dr. S. Suresh, Dr. N. Kishorebabu, Dr. M. Padmaja, Dr. P. Vairaprakash, Dr. G. P. Muthukumara Gopal, Dr. Shaik Anwar, Dr. S. Selva Ganesan, Dr. S. Satish Kumar, Mr. M. Nagaraju, Mr. N. Sanjeeva Kumar, Mrs. Manasi Dalai, Mr. R. Gurubrahamam, Mr. Laxman, Mr. Venkanna, Mr. Obula Reddy, Mr. Suresh, Mr. Raju, Mr. Arif, Mr. Edukondalu, Mr. Yesu and Mr. Srinivas for creating a pleasant work atmosphere.

I would like to express my heartfelt thanks to my friends and research scholars in School of Chemistry G. Durgaprasad (GDP), Dr. Ramakumar, B Rambabu, Madavi Shivaprasad, Madhavachary, M. Swamy, Naveen Kumar, Satish, Krishna Chary, Dr. K. Aravind, Dr. Venu Srinivas, Dr. Phani Pavan, Rama Suresh, Anji, Ramesh, Sajna, Nagarjuna, Dr. Bhuvan, Dr. Ramesh Reddy, Dr. Raju, Dr. Leninbabu, Sekhar Reddy, Santosh, Veeraraghavaiah, Mallikarjunreddy, chandu, Lingaiah, sayanna, Dr. Kishor, Narayana, Rumpa Mondal, Vijay, Sakthidevi, Venky, Shashank, Srinivasa Reddy, Dr. Jagadeesh, Dr. Vikram, Dr. Ramu, T. K. Chaitanya, Sateesh, D. K. Srinivas, Ramesh, Viji, Ganesh, Ravindrababu, Mastan, Vanaja, Srinivas, Manoj, Ramu Yadav, Bhanu, Mallesh, Veeranna, Bharat, Srinu, Kishore, Nagaraju, Ravikumar,

Santosh, G. V. Ramesh, Gupta, Hari, Venu, Sheshadri, Suresh, Rama Krishna, Sekhar reddy, Praveen, Haneesh, Karunakar, Srinu, Nandakishore, Rajesh, Ranjit, Nabakamal nath for their help.

I am very thankful to my friends Dr. Laxmi Narayana (IICT), Y. Srinivas (IICT), Dr. Chandra Mouli (IICT), Narasihma (IICT), Dr. Ramesh, Sudhakar, Surendrachary, Ranjith and Basker for their invaluable moral support and encouragement.

*I express my deepest affection to my **mother** & **father** for their blessings, support and love. I would like to extend my utmost gratitude to elder mothers Smt. Ailamma and Smt. Ahalyamma and my grandfather late Sri Ramalingaiah and my elder father late Sri Dasharadha for their relentless affection, support and encouragement. I would like to express my sincere gratitude to my brother Mr. M. Mallesh and my sister in law Mrs. Sharadha for their constant support, timely help. My special thanks to my brother Mr. L Mahendar for his constant support, timely help and for always being there for me.*

I would like to extend my thanks to my family members and relatives Mr. Nagaraju, Mrs. Padma, Mrs. Ailamma, Mrs. Anuradha, Mrs. Kalavathi, Mrs. Padmanjali, Mr. Srinu, Mr. Basha, Mr. Mallikarjun, Mr. Narshimha, Mr. Mallesh and my Special thanks to Sri Gouraiah and Sri D. Muthyalu for their help and encouragement.

I acknowledge the help and support provided by the technical and non-teaching staff of the School of Chemistry. I also thank Mr. Mallaiah Shetty, Dr. P. Raghavaiah, Mr. Satyanarayana, Mr. Joseph, Mr. Bhaskara Rao, Mr. Syed Thurabuddin, Mr. Venkataramana, Mrs. Asiaperwej, Mrs. Vijaya Laxmi, Mr Prasad, Mr. A. R. Shetty, Mr. Sharma, Mr. Jayaram, Mr. Rangaiah, Mr. Ganesh, Mr. Durgesh and Mr. Chitti Babu for their timely help.

I wish to extend my sincere thanks to the University authorities for providing all the necessary facilities for this work. National Single Crystal X-ray Facility, funded by DST (New Delhi) in School of Chemistry is highly acknowledged. I am thankful to IGM library for providing excellent books and journals.

Finally I would like to thank the CSIR New Delhi for the financial support during my tenure. Also, financial assistance from the research grant of DST-J.C BOSE fellowship of Prof. M. Periasamy is gratefully acknowledged.

Mallesh Beesu

Abbreviations

AcOH	acetic acid
aq.	aqueous
Ar	aryl
Bn	benzyl
Bu	butyl
Cat.	catalytic
cm^{-1}	wavenumber(s)
DCM	dichloromethane
DMF	N,N-dimethylformamide
DMSO	dimethylsulfoxide
d	doublet (in spectroscopy)
de	diastereomeric excess
DME	dimethoxyethane
DIPEA	*N*,*N*-diisopropylethylamine
dr	diastereomeric ratio
eq.	equation
equiv.	equivalent
EI	electron impact
ee	enantiomeric excess
Et	ethyl
EtOH	ethyl alcohol
g	gram (s)
Hz	hertz
h	hour(s)
HFIP	1,1,1,3,3,3-hexafluoro-2-propanol
i	iso
i-Pr	isopropyl
IR	infrared
J	coupling constant (in NMR spectroscopy)
lit.	literature

LVT	low valent titanium
MeOH	methyl alcohol
M	metal
Me	methyl
m	multiplet (in spectroscopy)
min.	minute(s)
mp	melting point
MS	mass spectrum
M.S.	molecular sieves
NMR	nuclear magnetic resonance
n	primary
o	ortho
ORTEP	Oak Ridge Thermal Ellipsoid Plot
Ph	phenyl
ppm	parts per million
Pr	propyl
q	quartet (in spectroscopy)
R	alkyl
rt	room temperature
s	singlet (in spectroscopy)
THF	tetrahydrofuran
t	tertiary
T	temperature
t	triplet (in spectroscopy)
TMS	trimethylsilyl
TMEDA	*N,N,N′,N′*-tetramethylethylenediamine
^{o}C	degree Celsius
δ	chemical shift in parts per million downfield from tetramethyl silane
X	halide

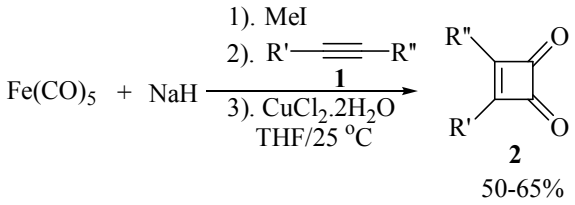
Abstract

This thesis describes the development of "**New Reactive Iron Carbonyl Reagents for Double Carbonylation of Alkynes and New Synthetic Methods Using Cyclobutenediones and Aromatic Diketones**". It comprises of three chapters. Each chapter is subdivided into four parts **Introduction, Results and Discussion, Conclusions** and **Experimental Section** along with **References**. The work described in this thesis is exploratory in nature and the chapters are arranged in the order investigations were executed.

The first chapter describes investigations on the reactions of alkynes with iron carbonyl species, prepared *in situ* using $Fe(CO)_5$/NaH/MeI and $Fe(CO)_5$/*t*-BuOK reagent systems. In the introductory section, a brief review on the cyclocarbonylation reactions of alkynes with various iron carbonyl reagents is presented.

We have observed that the iron carbonyl complexes prepared *in situ* using the $Fe(CO)_5$/NaH/MeI reagent combination and alkynes **1** at 25 ^oC give the corresponding cyclobutenediones **2** in 50-65% yields after $CuCl_2{\cdot}2H_2O$ oxidation (**Scheme 1**).

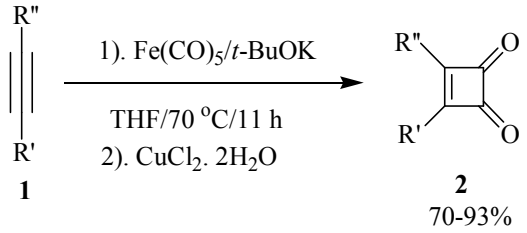
Scheme 1



We have also investigated the use of alkoxides to prepare the coordinatively unsaturated iron carbonyl species from $Fe(CO)_5$. We have observed that *t*-BuOK reacts

with $Fe(CO)_5$ to give reactive iron carbonyl intermediates which in turn reacts with alkynes **1** at 70 ^oC to give the corresponding cyclobutenediones **2** in 70-93% yields after $CuCl_2.2H_2O$ oxidation (**Scheme 2**).

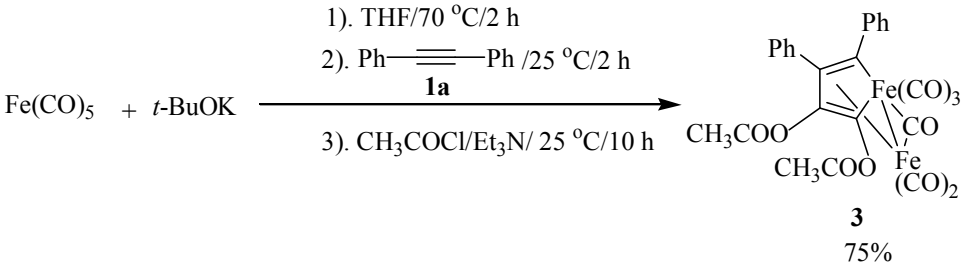
Scheme 2



1 **2**
70-93%

It was observed that addition of Et_3N and acetyl chloride to the alkyne-iron carbonyl complex formed in the reaction of $Fe(CO)_5$ with *t*-BuOK and alkyne **1a** in THF, leads to the formation of the 1,2-acyloxyferrole complex **3** in good yields 75% (**Scheme 3**). The structure of the acyloxyferrole complex **3** was identified by single crystal X-ray analysis.

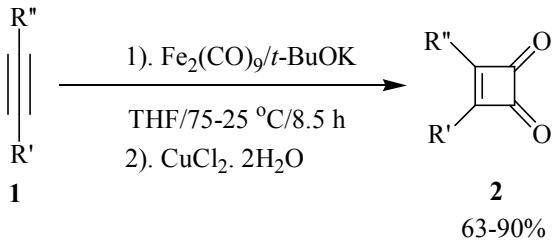
Scheme 3



3
75%

We have found that the $Fe_2(CO)_9$/*t*-BuOK reagent system also reacts with alkynes **1** at 75 ^oC in THF solvent to provide the corresponding cyclobutenediones **2** in 63-90% yields after $CuCl_2.2H_2O$ oxidation (**Scheme 4**).

Scheme 4

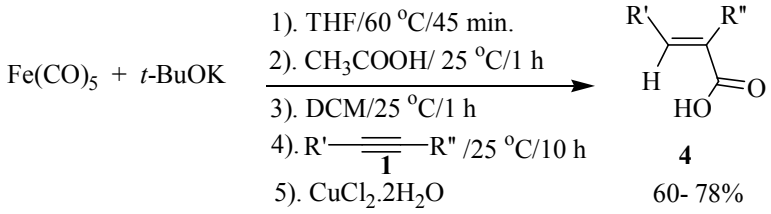


1 **2**

63-90%

We have also observed that the iron carbonyl species prepared *in situ* using the $Fe(CO)_5$/*t*-BuOK/CH_3COOH/CH_2Cl_2 reagent system reacts with alkynes to give α,β-unsaturated carboxylic acids **4** in 60-78% yields after $CuCl_2 \cdot 2H_2O$ oxidation (**Scheme 5**).

Scheme 5

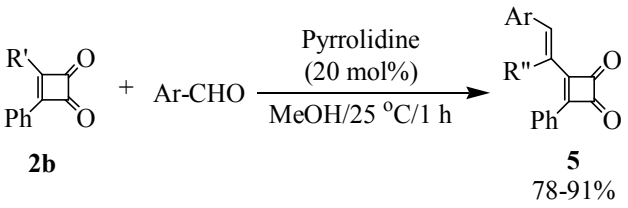


4

60- 78%

Investigations carried out on the methods of functionalization of cyclobutenediones are discussed in chapter **2**. In the introductory section, a brief review on the enamine and iminium ion based secondary amine catalyzed organic transformations are described to facilitate the discussion. We have observed that 3-alkyl-4-phenylcyclobut-3-ene-1,2-diones **2b** undergo stereoselective aldol reaction with various aldehydes in the presence of 20 mol% pyrrolidine to give the alkenyl substituted cyclobutenediones **5** in good yields (**Scheme 6**). The stereochemistry of the aldol adduct **5** was confirmed by single crystal X-ray analysis.

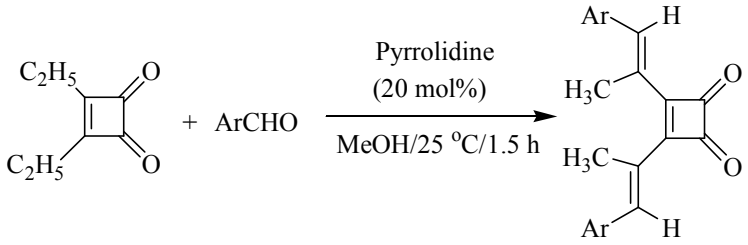
Scheme 6



2b **5**
78-91%

Further, we have found that 3,4-diethylcyclobut-3-ene-1,2-dione **2c** undergoes aldol reaction with various aldehydes in the presence of 20 mol % of pyrrolidine to provide the highly conjugated dialkenyl substituted cyclobutenediones **6** in excellent yields (**Scheme 7**). The structure of **6** was identified by single crystal X-ray analysis.

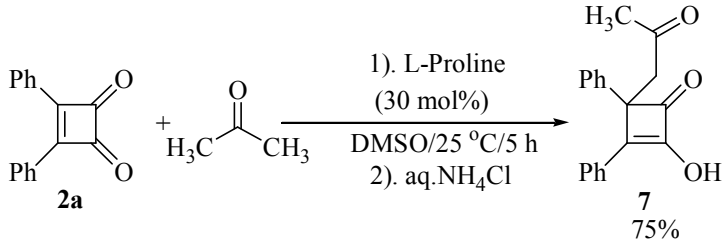
Scheme 7



2c **6**
70-85%

We have observed that acetone undergoes Michael reaction with 3,4-diphenylcyclobut-3-ene-1,2-dione **2a** in the presence of 30 mol% of L-proline to provide the corresponding 1,4-addition product **7** in 75% yield (**Scheme 8**).

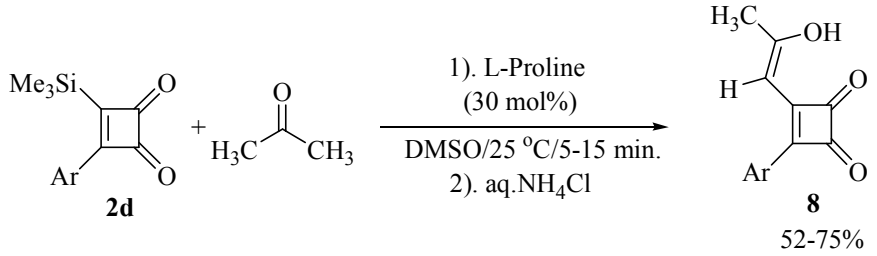
Scheme 8



2a **7**
75%

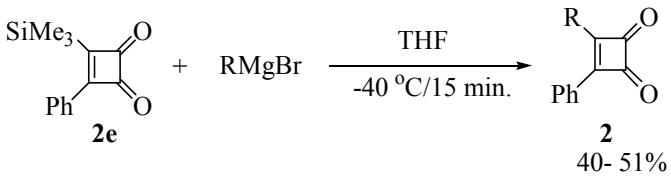
Interestingly, with 3-aryl-4-(trimethylsilyl)cyclobut-3-ene-1,2-diones **2d**, desilylated Michael addition products **8** are formed in 52-75% yields (**Scheme 9**). The structure of **8** was identified by single crystal X-ray analysis.

Scheme 9



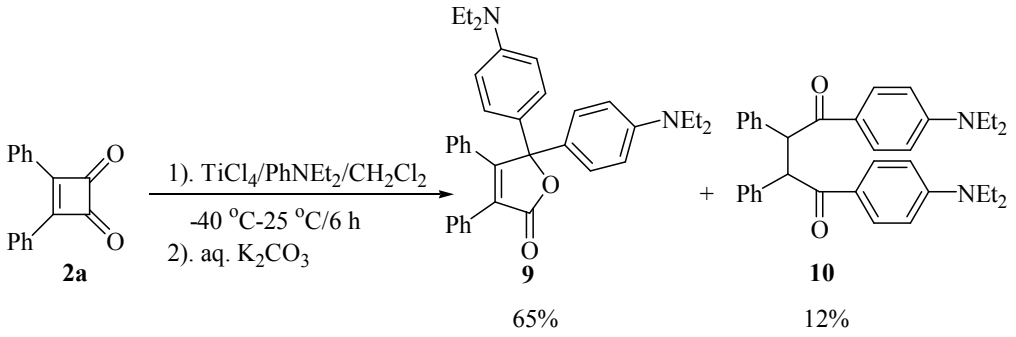
Desilylation is also observed in the reaction of 3-phenyl-4-(trimethylsilyl)cyclobut-3-ene-1,2-dione **2e**, with alkyl magnesium bromides at –40 °C (**Scheme 10**).

Scheme 10



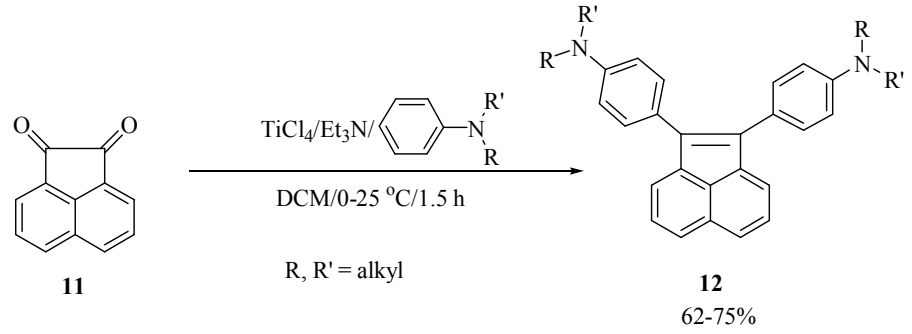
The results on the reactivity pattern of the $TiCl_4$/tertiary amine reagent system with aromatic diketones are discussed in chapter **3**. Previously, it was observed in this laboratory that the 3,4-diphenylcyclobut-3-ene-1,2-dione **2a** reacts with $TiCl_4$/N,N-diethylaniline reagent system to give the corresponding butenolide **9** in 65% yield besides the 1,4-diketone **10** in 12% yield (**Scheme 11**).

Scheme 11



We have examined the reaction of aromatic diketones such as acenaphthenequinone, phenanthrenequinone and anthraquinone. Whereas the phenanthrenequinone and anthraquinone did not react with $TiCl_4$/N,N-dialkylaniline derivatives under ambient conditions, the acenaphthenequinone **11** reacts with N,N-dialkylaniline in the presence of $TiCl_4$ to give the corresponding diarylacenaphthylene **12** in 62-75% yields (**Scheme 12**). The structure of diarylacenaphthylene **12** was confirmed by single crystal X-ray analysis.

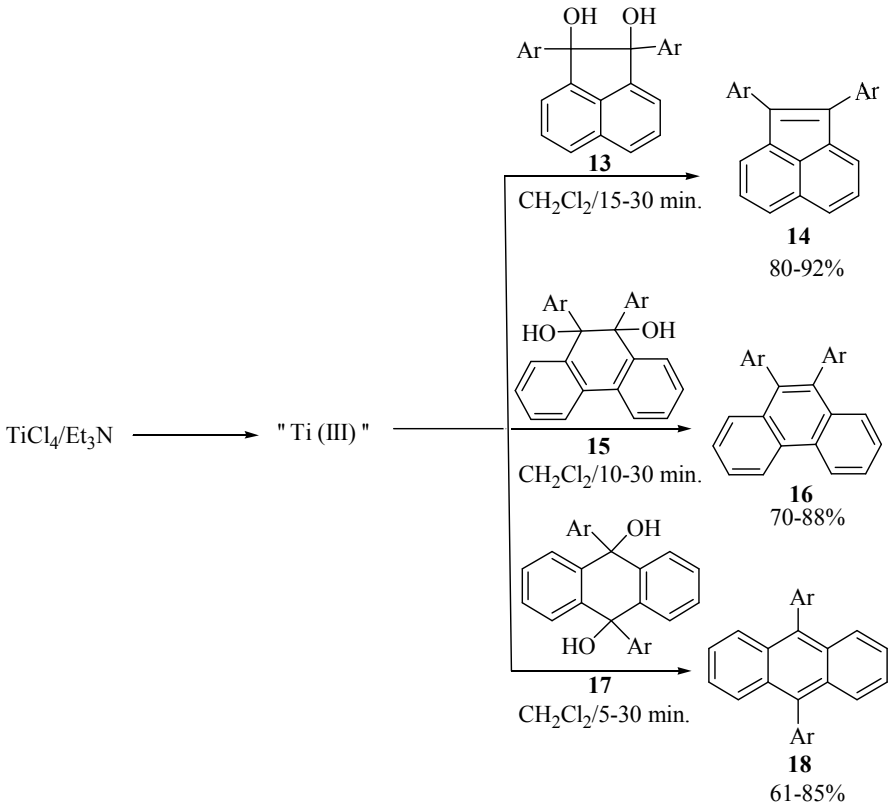
Scheme 12



A general method of conversion of the readily accessible 1,2-diaryl-1,2-dihydroacenaphthylene-1,2-diol **13**, 9,10-dihydroxy-9,10-diarylphenathrene **15** and 9,10-

dihydroxy-9,10-diarylanthracene **17** to the corresponding diarylacenaphthylene **14**, phenanthrene **16** and anthracene **18** derivatives has been developed using low valent titanium species prepared *in situ* using the $TiCl_4/Et_3N$ reagent system (**Scheme 13**).

Scheme 13



The results reported in this thesis are discussed considering mechanisms involved in these transformations and comparison with literature reports.

Note: Scheme numbers and compound numbers given in this abstract are different from those given in the chapters.

Chapter 1

New Reactive Iron Carbonyl Reagents for Double Carbonylation and Hydrocarboxylation of Alkynes

1.1 Introduction

In recent years, the metal carbonyls are increasingly used in organic synthesis. Many transition metals form stable neutral metal carbonyls, anionic metal carbonyls, hydrido metal carbonyls and their derivatives.[1-4] These carbonyl complexes display unique reactivities in isomerization, oligomerization, carbonylation and polymerization processes.[5,6] They have been also used extensively in C-C bond forming reactions.[7-9] Among various transition metal carbonyls, the organoiron complexes have been used in all these processes.[9]

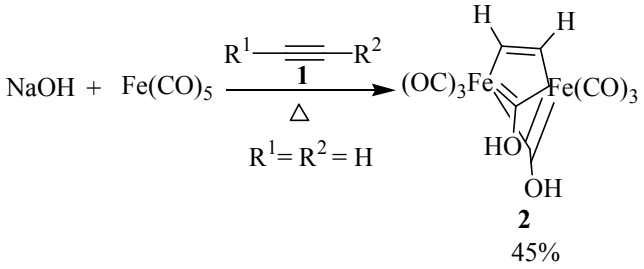
We have undertaken efforts to prepare the reactive iron carbonyl reagents from readily accessible iron carbonyls for developing new organic synthetic methods using alkynes. The results are discussed in this chapter. A brief review on the reactions of alkynes and iron carbonyl reagents will be helpful for the discussion.

1.1.1 Reactions of alkynes with iron carbonyl reagents

Organoiron chemistry was started by the discovery of pentacarbonyliron in 1891 independently by Mond [10] and Berthelot.[11] Another milestone was the discovery of the organometalic complex ferrocene in 1951 by Kealy and Pauson.[12] Since this thesis mainly deals with synthesis and applications of cyclobutenediones prepared by the reaction of alkynes and iron carbonyls, a review on various reactions reported between iron carbonyl complexes and alkynes will be helpful for the discussion.

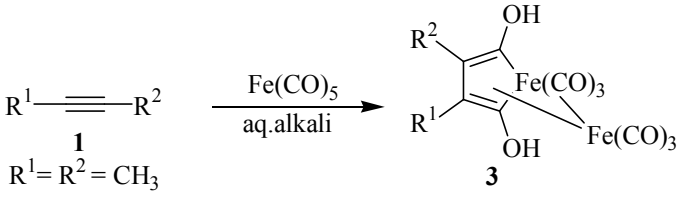
Reppe first reported that, in the presence of NaOH, $Fe(CO)_5$ and acetylene **1** react to give the iron complex of the formula $(HC{=}CH)H_2Fe_2(CO)_8$ **2**.[13] The structure of this iron complex containing two acidic hydrogens was proposed by Steinberg *et al* (**Scheme 1**).[14] An improved method for the preparation of the complex **2** was also reported.[14]

Scheme 1



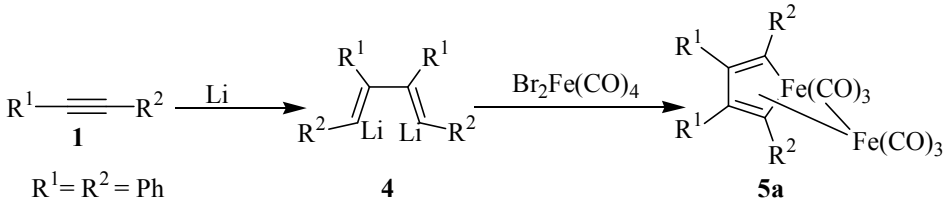
Later, Hock *et al* [15] also studied the organoiron complexes reported by Reppe.[15] They isolated the iron complex **3** in the reaction of but-2-yne **1** with alkaline solution of $Fe(CO)_5$. The structure of the iron complex **3** was determined by X-ray crystallographic data (**Scheme 2**).[15]

Scheme 2



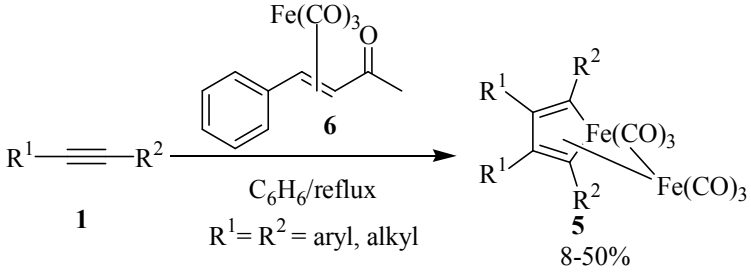
Tetraphenylferrole iron complex **5a** was prepared by the reaction of $Br_2Fe(CO)_4$ with 1,4-dilithio-l,2,3,4-tetraphenylbutadiene **4**. The 1,4-dilithio-l,2,3,4-tetraphenylbuta diene **4** was in turn prepared by the reaction of diphenylacetylene **1** with Li ((**Scheme 3**).[16]

Scheme 3



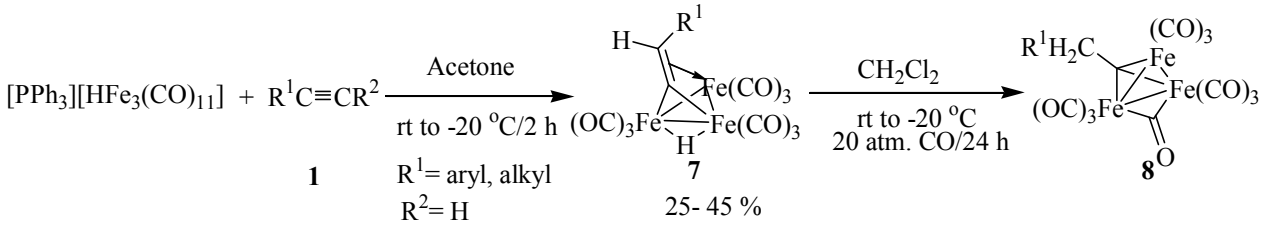
The ferrole derivatives **5** were also prepared by the reaction of alkynes **1** with the benzalacetone iron complex **6** in benzene under refluxing conditions (**Scheme 4**).[17]

Scheme 4



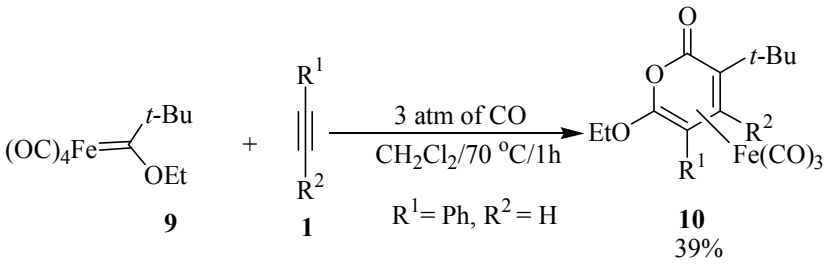
Mono substituted alkynes react with $HFe_3(CO)_{11}^-$ in acetone to give iron carbonyl complexes of the type **7.** The complex **7** is converted to **8** quantitatively under CO pressure in 24 h (**Scheme 5)**.[18]

Scheme 5



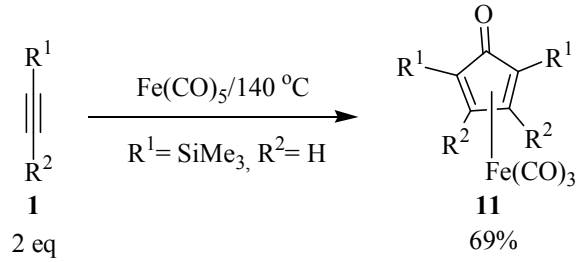
Iron alkoxycarbene **9** reacts with alkynes under slightly elevated CO pressure to give $Fe(CO)_3$-complexed 6-alkoxy-2-pyrones **10** (**Scheme 6**).[19]

Scheme 6



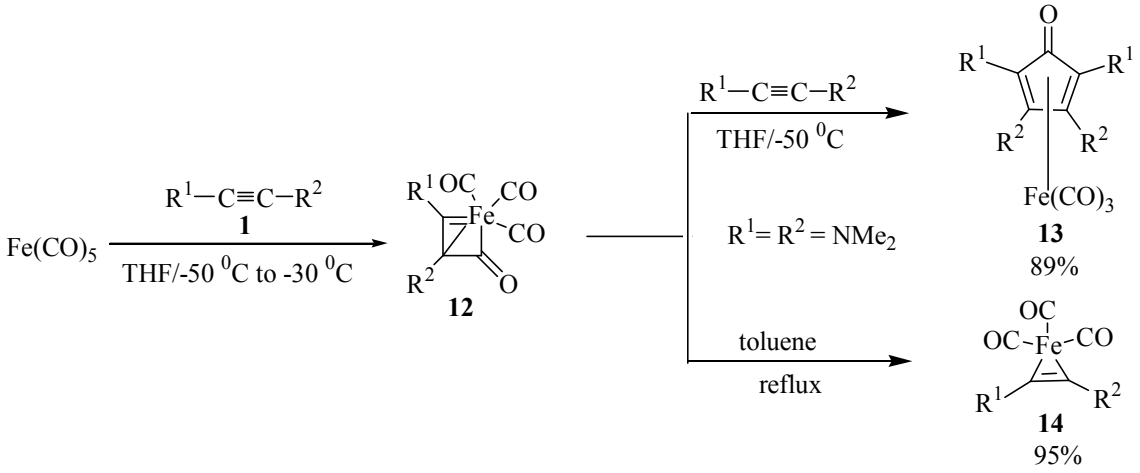
Pentacarbonyliron and two equivalents of trimethylsilylacetylene undergo [2+2+1] cycloaddition reaction to provide the tricarbonyliron complex of 2,5-bis(trimethylsilyl)cyclopentadienone **11** as a single regioisomeric product at 140 °C (**Scheme 7**).[20]

Scheme 7



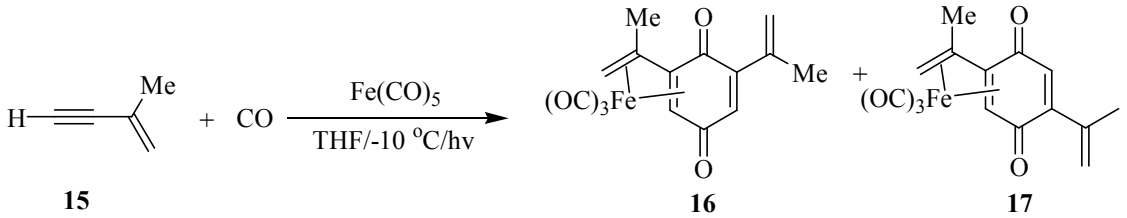
Recently, it was reported that the $Fe(CO)_5$ react with *N,N*-dimethylaminoacetylene to give the ferrabicyclobutenone complex **12**[21] which on further reaction with one more equivalent of *N,N*-dimethylaminoacetylene gives the cyclopentadienone complex **13** at –50 °C in THF.[21] The complex **12** undergoes decorbonylation under refluxing conditions in toluene to give the tricarbonyl iron complex **14** (**Scheme 8**).[21]

Scheme 8



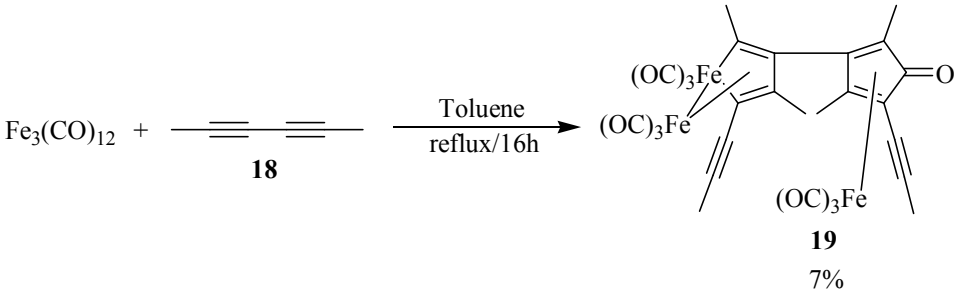
The $Fe(CO)_5$ reacts with eneynes **15** in the presence of CO under photochemical conditions to give the tricarbonyliron benzoquinone complexes **16** and **17** (**Scheme 9**).[22]

Scheme 9



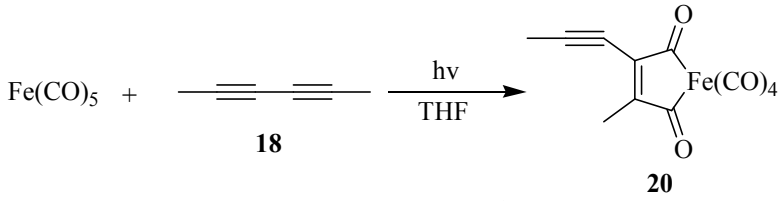
The trimetallic product **19** was obtained in the reaction of 2,4-hexadiyne **18** with $Fe_3(CO)_{12}$ in toluene solvent at refluxing conditions (**Scheme 10**).[23]

Scheme 10



The 2,4-hexadiyne **18** reacts with $Fe(CO)_5$ in THF under photochemical conditions to give the alkynyl substituted maleoyl iron complex **20** (**Scheme 11**).[24]

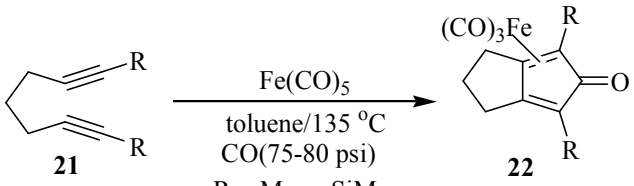
Scheme 11



18 **20**

1,6-Diynes **21** react with $Fe(CO)_5$ at 135 ^oC under CO pressure to give the corresponding cyclopentadienone-$Fe(CO)_3$ complex **22** (**Scheme 12**).[25]

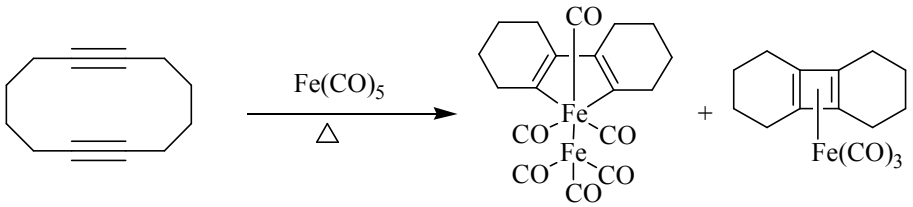
Scheme 12



21 **22**
80-87%

1,7-Cyclododecadiyne **23** reacts with $Fe(CO)_5$ to give the iron carbonyl complexes **24** and **25** (**Scheme 13**).[26]

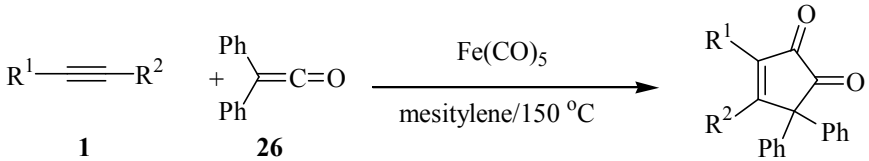
Scheme 13



23 **24**- (major) **25**- (minor)

In the presence of $Fe(CO)_5$, diphenylacetylene and diphenylketene **26** undergo cycloaddition reaction to give the corresponding cyclopentenedione **27** at 150 ^oC (**Scheme 14**).[27]

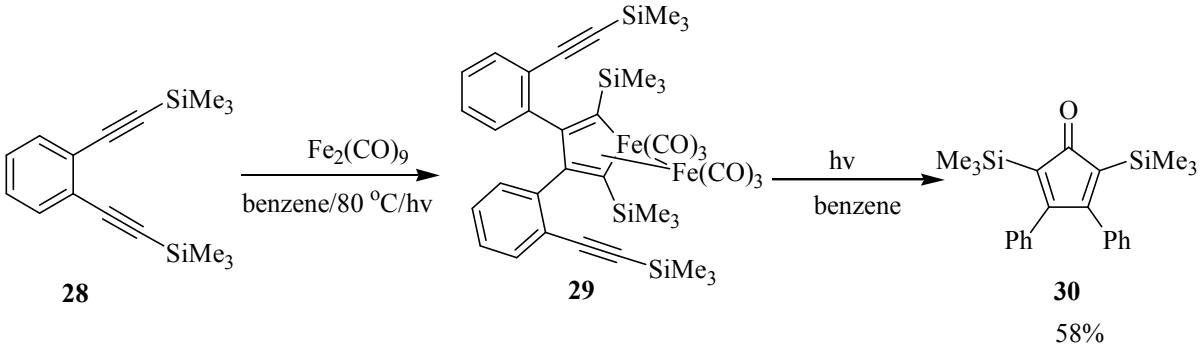
Scheme 14



1 **26** **27**
62%

It has been reported that $Fe_2(CO)_9$ reacts with 1,2-bis((trimethylsilyl)ethynyl)-benzene **28** to give the metallacycle **29** that upon photolysis gives the corresponding metal free cyclopentadienone **30** (**Scheme 15**).[28]

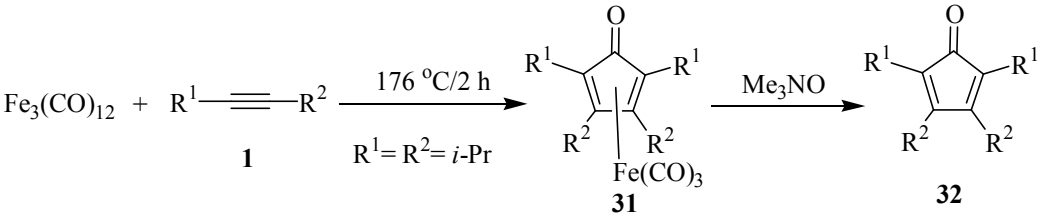
Scheme 15



28 **29** **30** 58%

The $Fe_3(CO)_{12}$ reacts with diisopropylacetylene to give the corresponding tricarbonyliron cyclopentadienone derivative **31** at 176 °C, which on further reaction with trimethylamine *N*-oxide gives the metal-free cyclopentadione **32** in 71% yield (**Scheme 16**).[29]

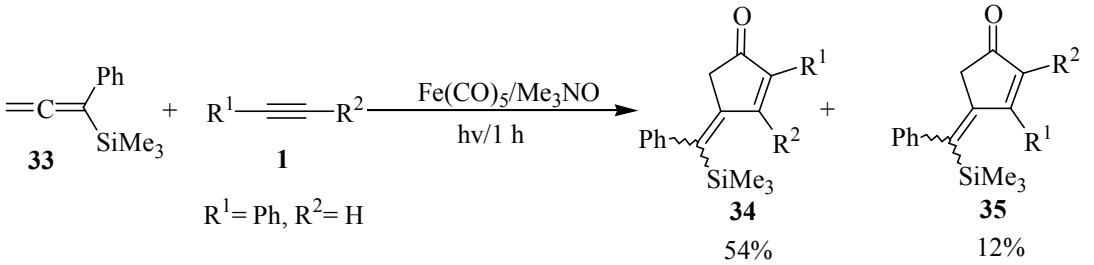
Scheme 16



31 **32** 71%

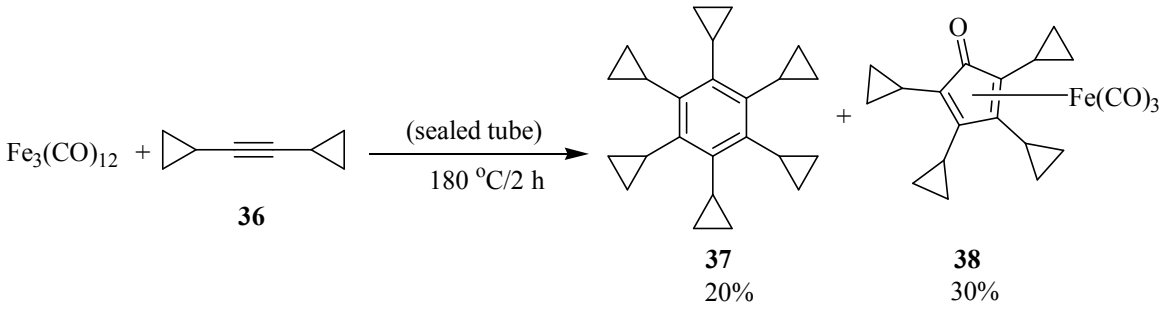
The $Fe(CO)_5/Me_3NO$ reagent system reacts with alkynes and phenylpropadienylsilane **33** under photochemical conditions to give the substituted cyclopentenones **34** and **35**.[30] When the reaction was carried out under thermal conditions, the product mixture was obtained in only 18% yield (**Scheme 17**).[30]

Scheme 17



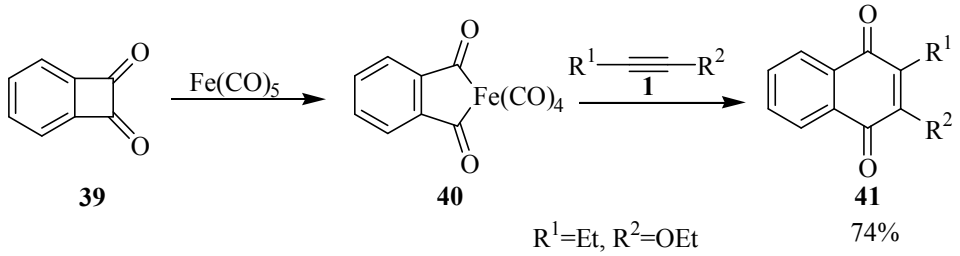
Reaction of dicyclopropylacetylene **36** and $Fe_3(CO)_{12}$ at 180 ^oC gives the corresponding hexacyclopropylbenzene **37** as well as the iron carbonyl derivative of the cyclopentadienone **38** (**Scheme 18**).[31]

Scheme 18



The phthalylironcarbonyl complex **40,** prepared by the reaction benzocyclobut-enedione **39** and $Fe(CO)_5$, reacts with alkyne to give the corresponding naphthoquinone **41** (**Scheme 19**). [9,32]

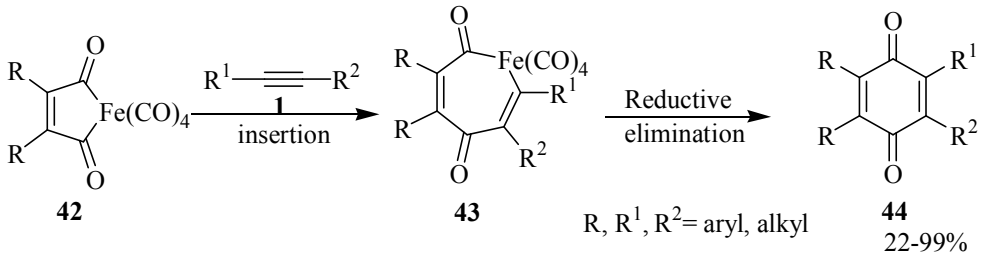
Scheme 19



Also, the maleoyl iron complexes **42**, prepared from their respective cyclobutenediones and iron carbonyls, react with alkynes to give the corresponding

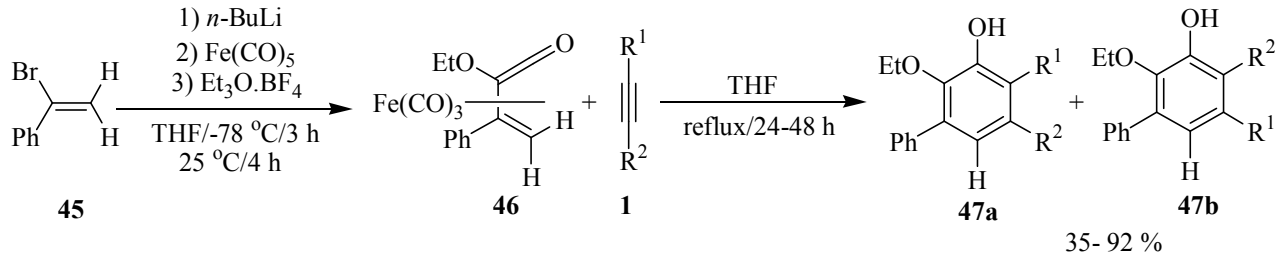
benzoquinones **44** (**Scheme 20**).[32,33] Here, intermediate of the type **43** was postulated to account for the quinone formation. The reaction occurs by insertion of an alkyne to the maleoyl iron complex **42**, giving metallacycle **43** which then undergoes reductive elimination to yield the corresponding benzoquinone **44** (**Scheme 20**).

Scheme 20



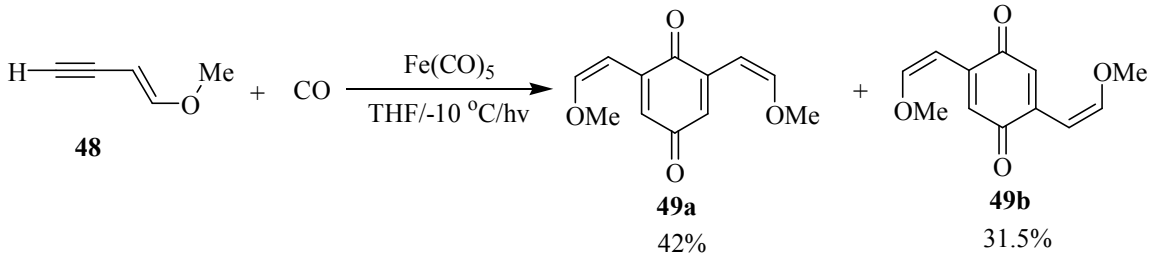
The tricarbonyl[2-ethoxy-3-phenylbuta-1,3-diene-1-one iron (0)] complex **46** obtained in the reaction of $Fe(CO)_5$ with 1-bromophenylethene **45** in the presence of *n*-butyllithium and triethyloxonium tetrafluoroborate reacts with alkynes to give the corresponding catechol derivatives **47a** and **47b** (**Scheme 21**).[34]

Scheme 21



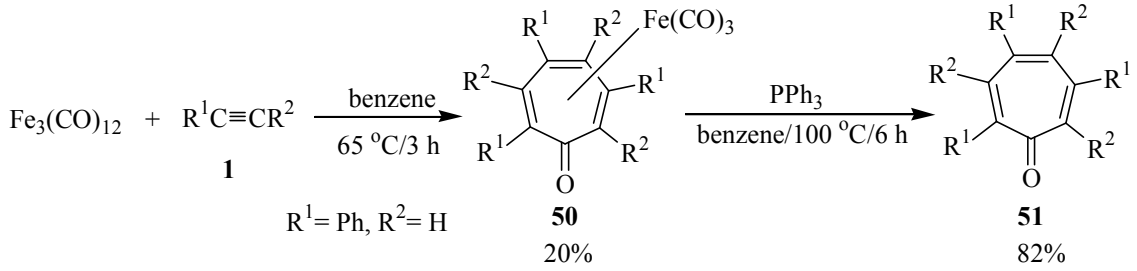
In the presence of $Fe(CO)_5$ and CO, enyne **48** undergoes cyclocarbonylation to give the alkenyl substituted benzoquinone derivatives **49a** and **49b** (**Scheme 22**).[21]

Scheme 22



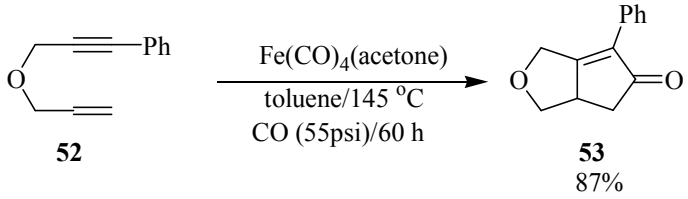
Mono aryl alkynes react with $Fe_3(CO)_{12}$ to give the tricarbonyliron tropone complex **50** at 65 °C which on decomplexation in the presence of PPh_3 affords the corresponding tropone **51** (**Scheme 23**).[35]

Scheme 23



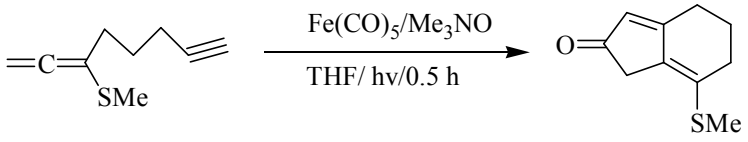
The $Fe(CO)_4$(acetone) complex prepared by the reaction of $Fe_2(CO)_9$ with acetone in toluene undergoes intramolecular Pauson-Khand type reaction to provide the bicyclic cyclopentenone **53** (**Scheme 24**).[36]

Scheme 24



An intramolecular Pauson-Khand type reaction of allenyne **54** using an iron carbonyl complex under photochemical conditions using $Fe(CO)_5/Me_3NO$ was reported. In this reaction, the bicyclic dienone **55** was obtained in 50% yield (**Scheme 25**).[37]

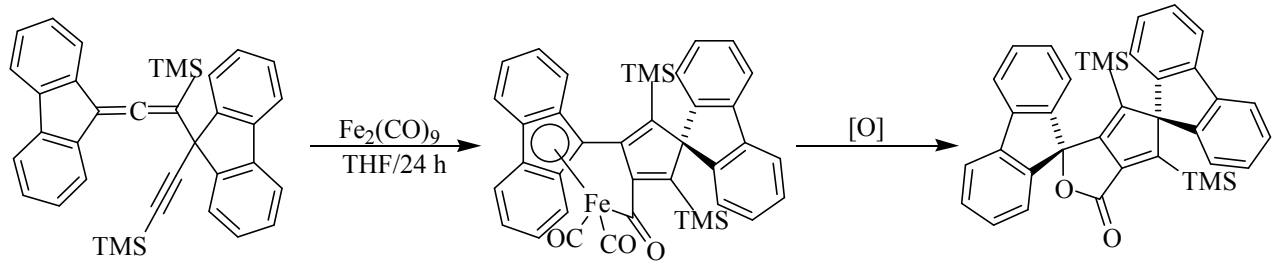
Scheme 25



54 **55**
50 %

Recently, it was reported that the $Fe_2(CO)_9$ reacts with propargyl-allene **56** to give the (η^5-Fluorenyl)Fe complex **57**, which upon oxidation yields the bicyclic lactone **58** (**Scheme 26**).[38]

Scheme 26



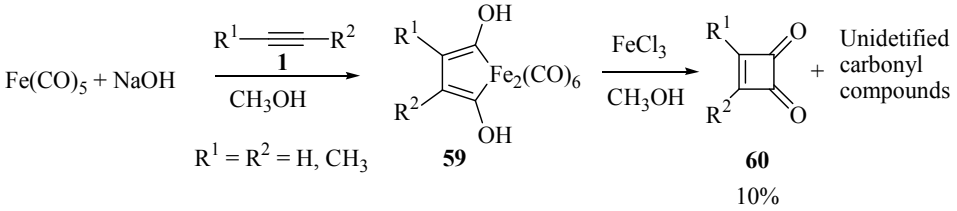
56 **57** **58**
52%

1.1.2 Previous work on the preparation and application of reactive iron carbonyl reagent systems from this laboratory

1.1.2.1 Reaction of $NaHFe(CO)_4$ reagent system with alkynes

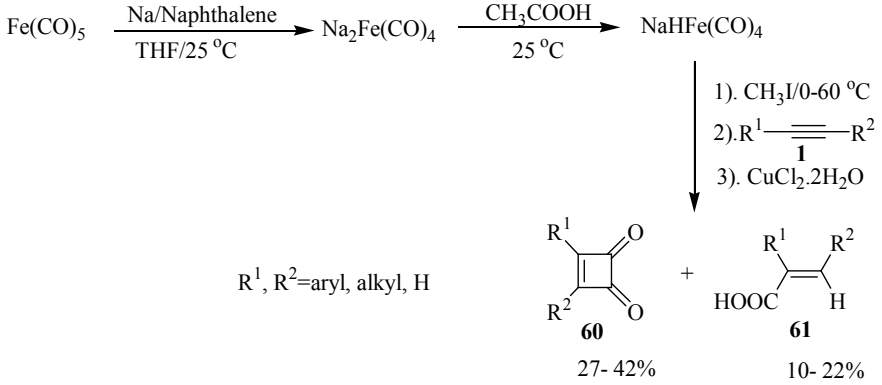
In 1963 Whiting reported that acetylene reacts with the reactive iron carbonyl species, generated from $Fe(CO)_5$/NaOH reagent system to give a ferrole complex **59**. This complex produced the corresponding cyclobutenediones **60** in low yield 10% after $FeCl_3$ oxidation (**Scheme 27**).[39]

Scheme 27



Later, a better method was developed for cyclobutenedione synthesis using the $NaHFe(CO)_4/CH_3I$ reagent system.[40] The iron carbonyl species generated in this way, reacts with alkynes to give the corresponding cyclobutenediones **60** (27-42%) and the α,β-unsaturated carboxylic acids **61** (10-22%) after $CuCl_2.2H_2O$ oxidation (**Scheme 28**).[40] In this reaction, the $NaHFe(CO)_4$ was prepared by acidification of $Na_2Fe(CO)_4$ which in turn was prepared by the reaction of $Fe(CO)_5$ with Na/Naphthalene.

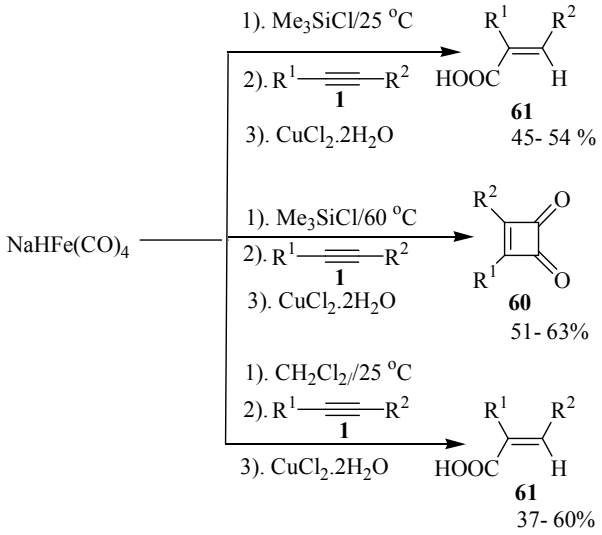
Scheme 28



It was observed that the $NaHFe(CO)_4$ reagent system reacts with alkynes in the presence of Me_3SiCl to give the corresponding α,β-unsaturated carboxylic acids **61** with excellent regio- and stereoselectivities (**Scheme 29**).[41a] When the reaction was carried out at 60 °C, the reactive iron carbonyl species formed from $NaHFe(CO)_4/Me_3SiCl$ reagent system gave the corresponding cyclobutenediones **60** with improved yields. Also, it was

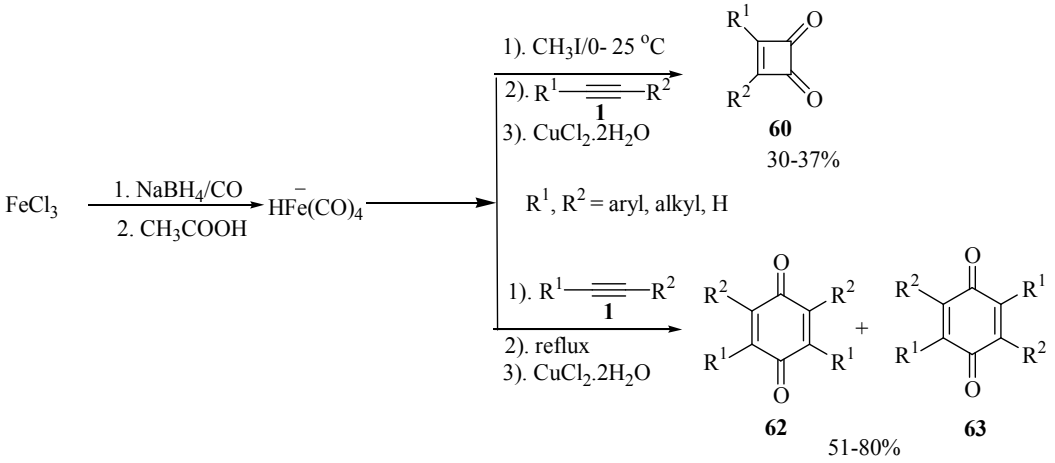
found that the $NaHFe(CO)_4$ reacts with alkynes in the presence of CH_2Cl_2 to give the corresponding α,β-unsaturated carboxylic acids in good yields **61**.[41b]

Scheme 29



It was observed that the $NaHFe(CO)_4$ species, generated using the $FeCl_3/NaBH_4/CO$ combination reacts with alkynes to give a complex that yields the corresponding cyclobutenediones **60** after $CuCl_2.2H_2O$ oxidation at 25 °C (**Scheme 30**).[42] Interestingly, it was observed that the same reagent system converts the alkynes to the corresponding benzoquinones **62** and **63** when the above reaction was carried out at refluxing conditions.

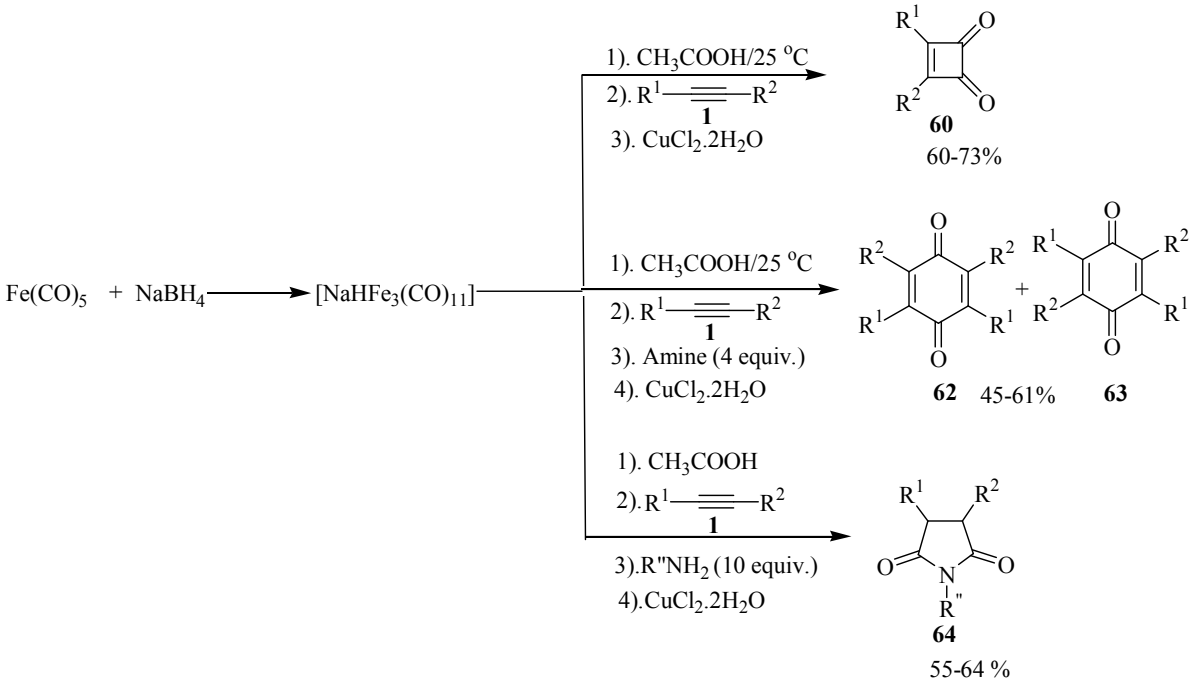
Scheme 30



1.1.2.2 Reaction of $Fe(CO)_5/NaBH_4$ reagent system with alkynes

The $Fe(CO)_5/NaBH_4$ reagent system reacts with alkynes in the presence of CH_3COOH to afford the cyclobutenediones **60** in good yields (60-73%) after $CuCl_2.2H_2O$ oxidation (**Scheme 31**).[43] When the above reaction was carried out in the presence of 4 equiv. of amine, the corresponding disubstituted benzoquinones **62** and **63** were obtained in moderate to good yields. It was also observed that the $Fe(CO)_5/NaBH_4$ reagent system gives the cyclic imide **64** from alkynes when the reaction was carried out using large excess of primary amine (10 mol equiv.)

Scheme 31

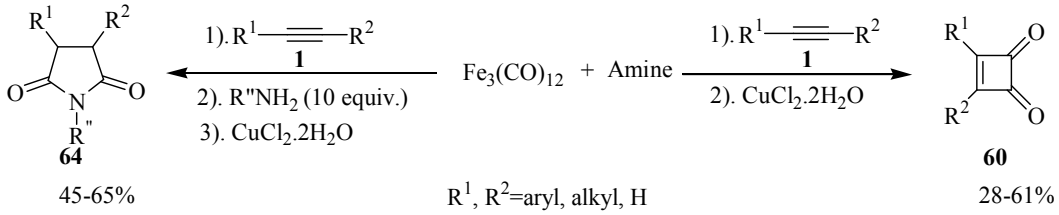


1.1.2.3 Reaction of alkyne with $Fe_3(CO)_{12}$/Amine reagent system

Whereas coordinatively unsaturated iron carbonyl species, prepared using $Fe_3(CO)_{12}$/amine, react with alkynes under ambient conditions to afford cyclobutenediones

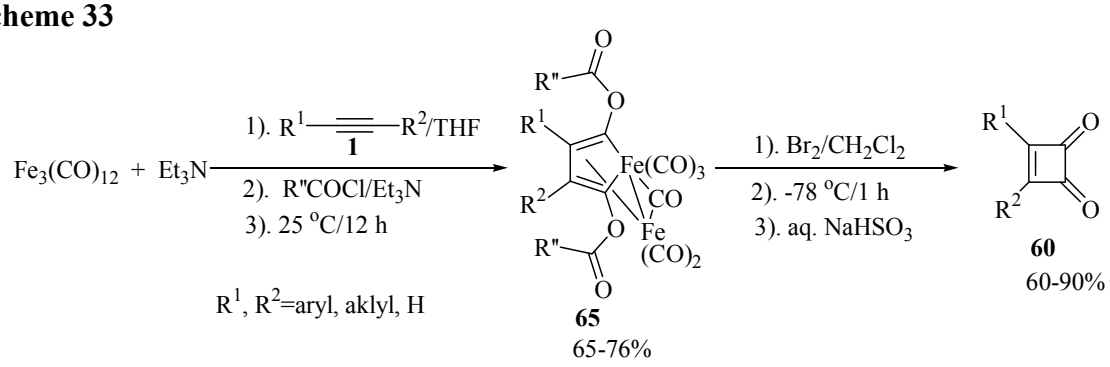
60 (**Scheme 32**),[44] in the presence of excess of amine (10 equiv.), the corresponding cyclic imides **64** (45-65%) were obtained.[45]

Scheme 32



Alkyne iron carbonyl complexes, prepared using the $Fe_3(CO)_{12}$ and amine in THF react with Et_3N and acid chlorides give the acyloxyferrole complexes of the type **65,** which afford the corresponding cyclobutenediones **60** in 60-90 % yields upon reaction with bromine (**Scheme 33**).[46]

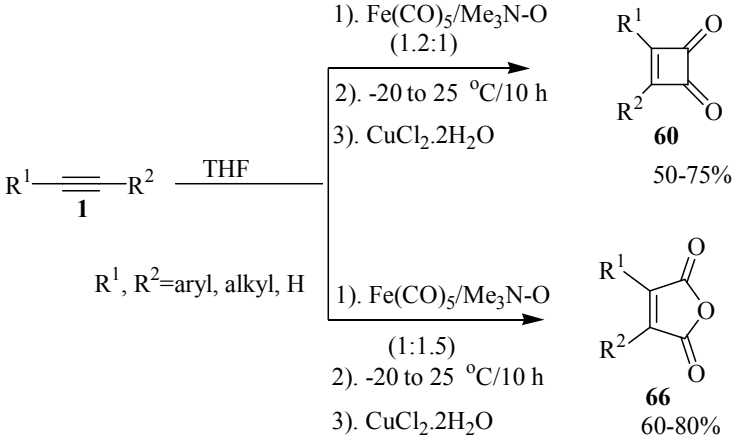
Scheme 33



1.1.2. 4 Reaction of alkyne with the $Fe(CO)_5/Me_3NO$ reagent system

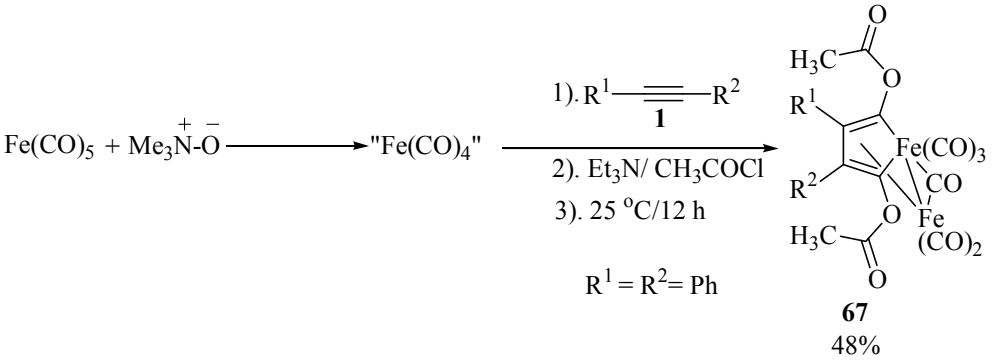
The $Fe(CO)_5/Me_3NO$ reagent system reacts with alkynes at 25 °C to give the corresponding cyclobutenediones **60** in moderate to good yields (50-75%) or the corresponding cyclic anhydrides **66** in good yields after $CuCl_2.2H_2O$ oxidation (**Scheme 34**). [47]

Scheme 34



The alkyne-iron carbonyl complex, prepared using $Fe(CO)_5/Me_3NO$ and diphenylacetylene in THF, gives the acyloxyferrole complex **67** (48%) in the presence of Et_3N and CH_3COCl (**Scheme 35**).[47]

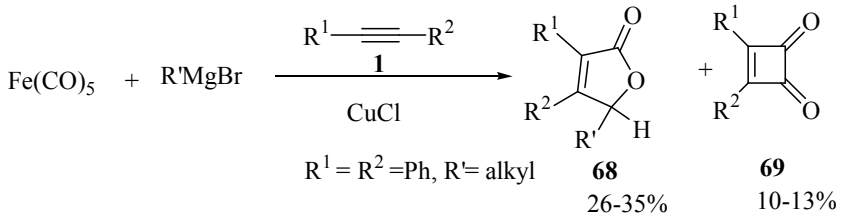
Scheme 35



1.1.2. 5 Other reactions of alkynes with iron carbonyls in the presence of additives

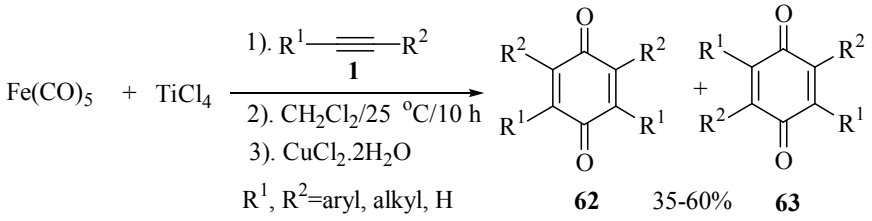
The iron carbonyl species generated from $Fe(CO)_5$ and RMgBr reacts with alkynes to give the corresponding butenolide **68** and cyclobutenediones **69** in moderate yields (**Scheme 36**).[48]

Scheme 36



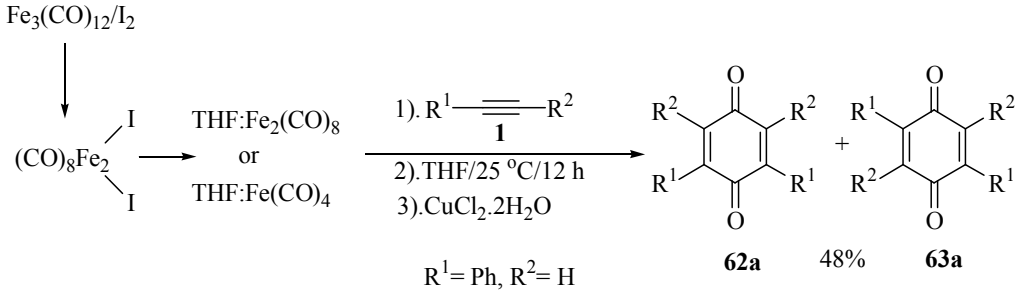
It was observed that the iron carbonyl species obtained from $Fe(CO)_5$ and $TiCl_4$ combination react with alkyne at 25 °C in dichloromethane to give a mixture of benzoquinones **62** and **63** after $CuCl_2.2H_2O$ oxidation (35-60%) (**Scheme 37**). Several 1-alkynes were converted to the corresponding 2,5- and 2,6-dialkylbenzoquinones.[49]

Scheme 37



The iron carbonyl species obtained using the $Fe_3(CO)_{12}/I_2$ reagent system also gives a mixture of benzoquinones (**62a** and **63a)** in 48% yield with phenylacetylene after $CuCl_2.2H_2O$ oxidation (**Scheme 38).**[49]

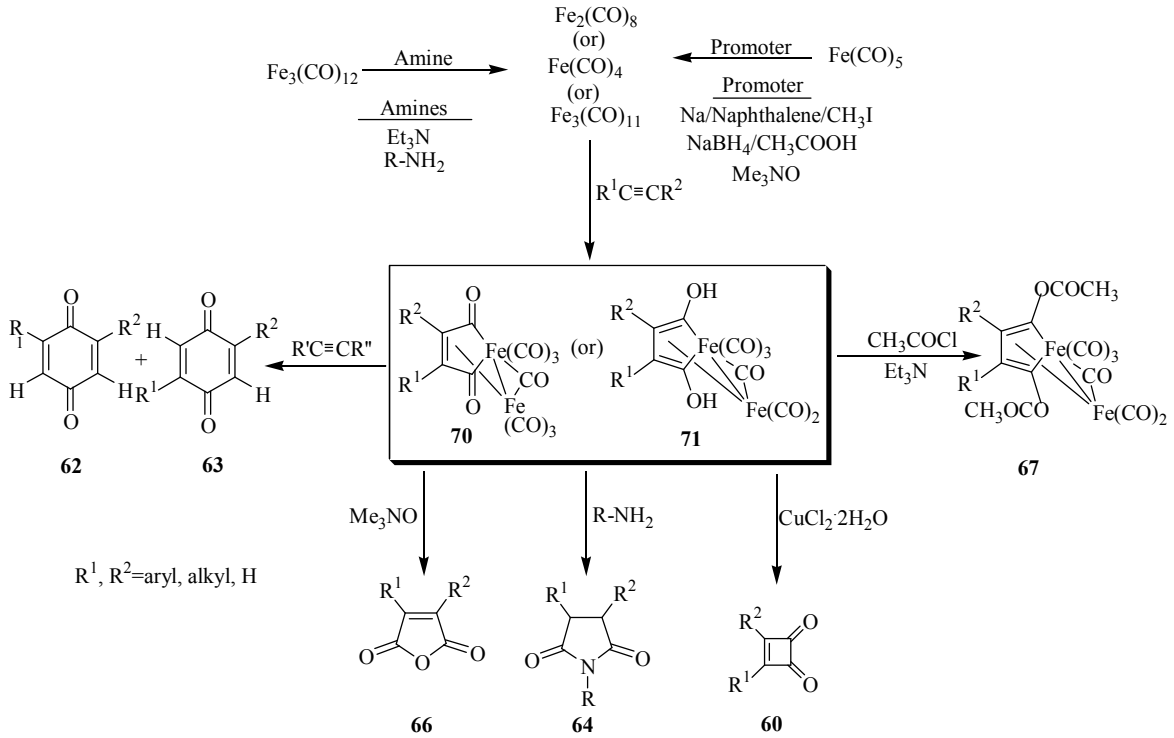
Scheme 38



The formation of various cyclocarbonylation products from alkynes and iron carbonyl reagent systems can be explained by considering the mechanistic pathway

depicted in **Scheme 39**. The iron carbonyls $Fe(CO)_5$ and $Fe_3(CO)_{12}$ would first undergo reaction with promoters to give the reactive unsaturated iron carbonyls like $Fe(CO)_4$ or $Fe_2(CO)_8$ or $Fe_3(CO)_{11}$. These species could undergo further reaction with alkynes to give the maleoyl complex of the type **70** or ferrole complex of the type **71** which could afford the cyclobutenediones, benzoquinones and cyclic imides under various reaction conditions. Such intermediate complexes could be also converted to acyloxyferrole complex **67** in the presence of CH_3COCl and Et_3N.[46,47]

Scheme 39



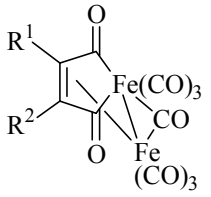
We have investigated the reactions of $Fe(CO)_5$ with the readily accessible NaH and *t*-BuOK reagents to prepare reactive iron carbonyl reagents for developing new synthetic methods. The results are described in the next section.

1.2 Results and Discussion

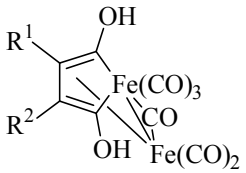
1.2.1 Reaction of alkynes with the $Fe(CO)_5/NaH/CH_3I$ reagent system

As outlined in the introductory section, iron carbonyls undergo carbonylative cyclization with alkynes to provide various cyclic products under different reaction conditions. Among these, we have been interested on the dicarbonylation reaction of alkynes which provides the 4-membered ring quinones which are known as cyclobutenediones. The cyclobutenedione **60** and its derivatives have been widely used in organic synthesis.[50- 54] In recent years, cyclobutenedione derivatives were used not only to synthesize organic molecules with biological relevance like growth regulators, potassium channel openers, drug molecules, sensors[55b-e] but also for preparation of organic materials like NLO materials,[55a] anion recognition systems[56] and chiral ligands.[57] The cyclobutenediones are also versatile starting materials for the synthesis of multifunctional molecules.[58]

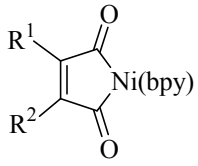
Even though various approaches are available for the synthesis of cyclobutenedione and its derivatives,[59] the use of transition metal reagents is obviously most successful because these complexes can lead to the formation of several bonds in a single pot operation. Formation of cyclobutenediones from alkynes and transition metal reagents involve the intermediacy of metal complexes such as **70**, **71** and **72**.



70



71

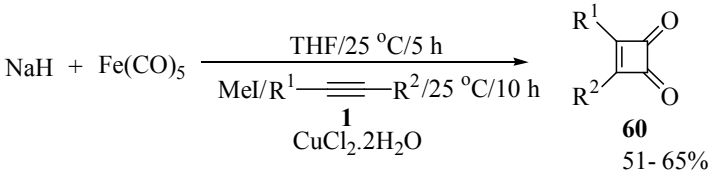


72

Accordingly, it is of interest to examine the preparation of such complexes using readily accessible reagents. Previously, it was reported from this laboratory that the $NaHFe(CO)_4$ reagent converts the alkynes to the corresponding complexes of type **70** or **71** in the presence of various additives like MeI or TMSCl. In this conversion, the $NaHFe(CO)_4$ was prepared using the $Na_2Fe(CO)_4$ which in turn needs to be prepared using the $Fe(CO)_5$/Na/Naphthalene reagent system (**Scheme 28**).[40]

In continuation of these efforts, we have examined the possibility of the preparation of reactive iron carbonyl species using the NaH, $Fe(CO)_5$ and MeI reagent system. We have observed that the reactive iron carbonyl species prepared *in situ* in this way further reacts with alkynes to give an intermediate that can be converted to the corresponding cyclobutenediones after oxidation with $CuCl_2{\cdot}2H_2O$ (**Scheme 40**).[60]

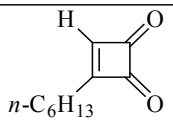
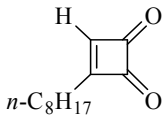
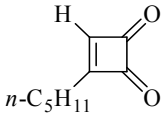
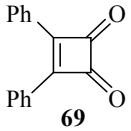
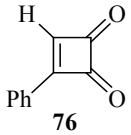
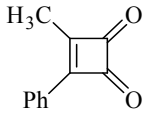
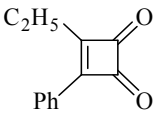
Scheme 40



It has been reported that the $Fe(CO)_5$ reagent reacts with NaH to give the $Na[HFe(CO)_4]$ species.[61] Subsequent reaction with MeI is expected to produce the coordinatively unsaturated iron carbonyl species which could react with alkynes **1** to give the corresponding cyclobutenediones after oxidation with $CuCl_2{\cdot}2H_2O$ (**Scheme 40**).

Several alkynes were converted to the corresponding cyclobutenediones following this procedure. The yields of this transformation are moderate to good (50-65%). The results are summarized in **Table 1.**

Table 1. Synthesis of Cyclobutenediones with $Fe(CO)_5$/NaH/MeI reagent system[a]

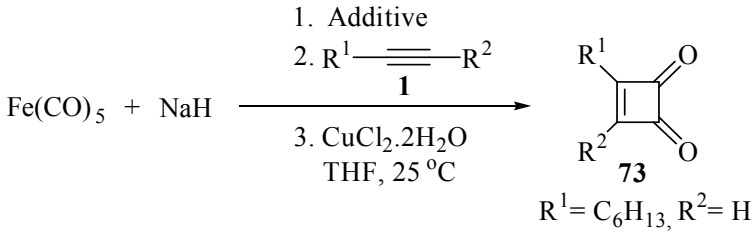
Entry	Alkyne R^1	Alkyne R^2	Product[b]	yield[c] %
1	H	*n*-C_6H_{13}	 **73**	65
2	H	*n*-C_8H_{17}	 **74**	55
3	H	*n*-C_5H_{11}	 **75**	50
4	Ph	Ph	 **69**	52
5	Ph	H	 **76**	55
6	Ph	CH_3	 **77**	56
7	Ph	C_2H_5	 **78**	51

[a] All the reactions were carried out using $Fe(CO)_5$ (7.5 mmol), NaH-55% (15 mmol) , MeI (7.5 mmol) and alkyne (1.25 mmol) in THF (35 mL). [b] The product was identified by spectral data (IR, ^{1}H-NMR, ^{13}C-NMR

and Mass) and comparison with reported data.[47] [c] Yields reported are for the isolated products and based on the amount of alkynes used.

We have examined the use of other reagents like $PhCH_2Cl$, CH_3COOH and Me_3SiCl in the place of MeI. In these cases also, the cyclobutenedione **73** was obtained after $CuCl_2{\cdot}2H_2O$ oxidation but in lesser yields (10-55%) (**Scheme 41).**

Scheme 41



Additive	Yield (%)
1. MeI	65
2. Me_3SiCl	55
3. CH_3COOH	15
4. $PhCH_2Cl$	10

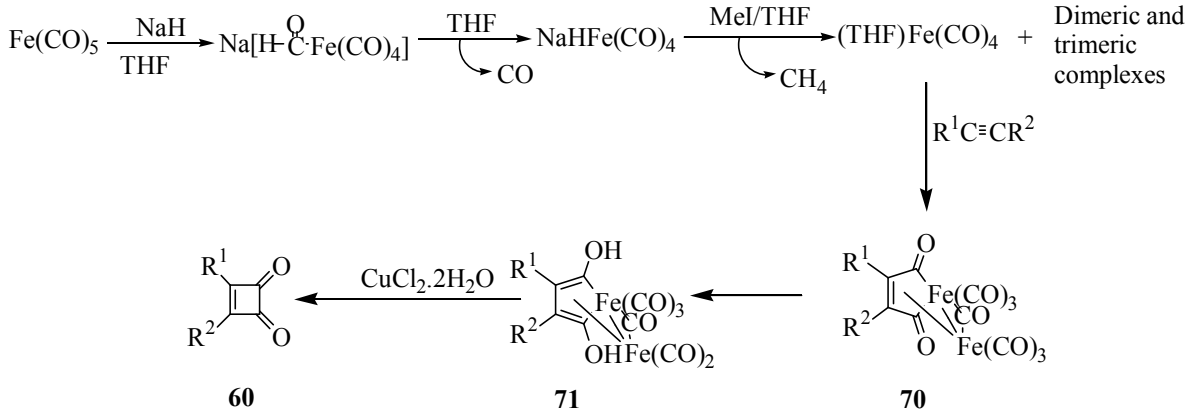
Though, THF was found to be a suitable solvent, CH_3CN also gave comparable results. However, the use of solvents like $CHCl_3$ and CH_2Cl_2 gave unidentified mixture of iron carbonyl products. Presumably, the coordinating solvents may form weak complexes with the unsaturated species like monomeric $Fe(CO)_4$ or dimeric $Fe_2(CO)_9$ or $Fe_2(CO)_8$ or trimeric $Fe_3(CO)_{11}$ that help in realizing cleaner reaction.[62]

In these reactions, the NaH (6 equiv.), $Fe(CO)_5$ (6 equiv.) and MeI (6 equiv.) were used in larger quantities than the alkynes as the initially formed "$Fe(CO)_4$" would also form dimeric and trimeric iron carbonyl species.

The formation of cyclobutenediones from the $NaHFe(CO)_4$ and alkynes can be explained by considering a mechanistic pathway depicted in **Scheme 42**. Addition of the

NaH to the $Fe(CO)_5$ in THF would give the $NaHFe(CO)_4$ species which on reaction with MeI could generate the $THF:Fe(CO)_4$ along with dimeric and trimeric iron carbonyl spices that can further react with alkynes followed by CO insertion to give the ferrole complex of the type **71** or maleoyl complex of the type **70**. Such complexes could give the cyclobutenediones **60** after $CuCl_2{\cdot}2H_2O$ oxidation (**Scheme 42**).

Scheme 42



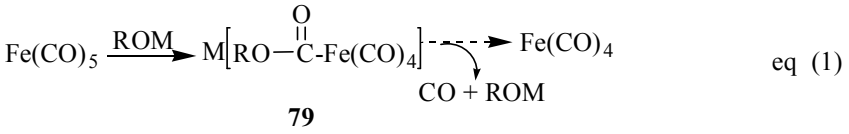
It may be of interest to point out that the present *in situ* method of preparation of coordinatively unsaturated iron carbonyl species has advantages over the erstwhile known methods since this method avoids the use of $Fe_3(CO)_{12}$ or $Fe_2(CO)_9$ which are in turn to be prepared from $Fe(CO)_5$.[62]

1.2.2 Synthesis of cyclobutenediones using the $Fe(CO)_5$/*t*-BuOK reagent system

As outlined in the introductory section, it was reported from this laboratory that the amine oxides and amines react with iron carbonyls to facilitate the formation of reactive

iron carbonyls species which on further reaction with alkynes give the corresponding cyclobutenediones after $CuCl_2.2H_2O$ oxidation (**Scheme 32** and **34**).[44-47]

Previously, it was reported that the $Fe(CO)_5$ reacts with metal alkoxides (*t*-BuOK or CH_3ONa) to give the corresponding $[(CO)_4Fe(COOR)]^-$ species at 0 ^oC.[63] Such species could decompose to give coordinatively unsaturated "$Fe(CO)_4$" species as noted earlier using amine oxides and amines (**Scheme 32** and **34**).[44-47]

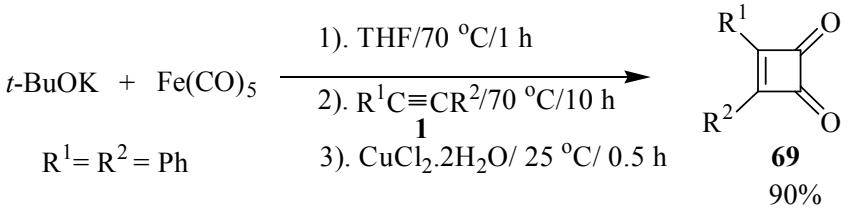


79 eq (1)

Accordingly, we have examined the reaction of $Fe(CO)_5$ using metal alkoxides. We have observed that the reactive iron carbonyl species generated *in situ* from the *t*-BuOK and $Fe(CO)_5$ regent system at 70 ^oC react with alkynes to give an intermediate which on $CuCl_2.2H_2O$ oxidation gives the corresponding cyclobutenediones in 70-93% yields.[64] There was no reaction when this transformation was carried out at room temperature.

The reaction of diphenylacetylene with the $Fe(CO)_5$/*t*-BuOK reagent system at 70 ^oC, gave the corresponding diphenylcyclobutenedione **69** in 90% yield after $CuCl_2.2H_2O$ oxidation (**Scheme 43**).

Scheme 43



69
90%

A variety of aryl, alkyl, silyl and alkynyl substituted, non-symmetrical and symmetrical cyclobutenediones could be synthesized following this method (**Scheme 44**). The results are summarized in **Table 2**. It should be pointed out that under these conditions the reactive iron carbonyl species are generated without using any electrophile (like MeI, TMSCl and CH_3COOH) and the products were obtained in higher yields (70-93%) compared to previously reported methods (25-75%).[40-48]

Scheme 44

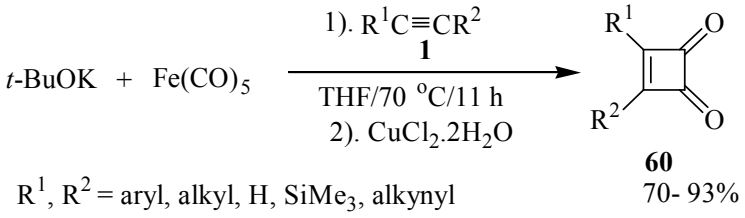
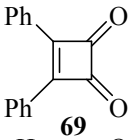
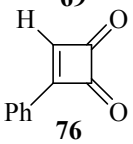
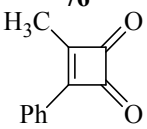
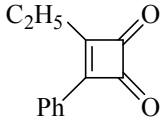
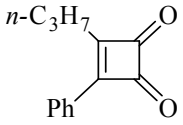
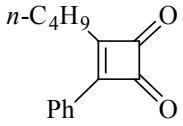
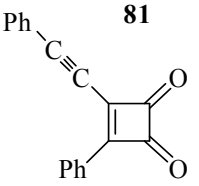
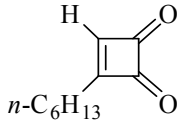
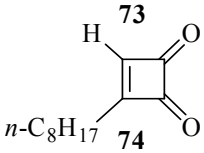
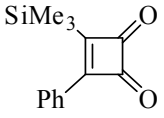
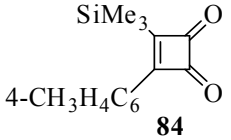
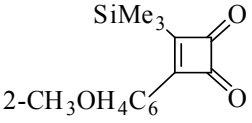


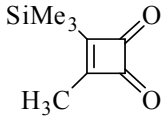
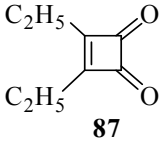
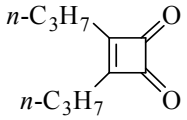
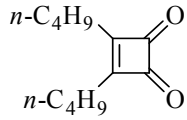
Table 2. Synthesis of cyclobutenediones with the $Fe(CO)_5$/*t*-BuOK reagent system[a]

Entry	Alkyne R^1	Alkyne R^2	Product[b]	yield[c] %
1	C_6H_5	C_6H_5	 **69**	90
2	C_6H_5	H	 **76**	78
3	C_6H_5	CH_3	 **77**	93
4	C_6H_5	C_2H_5	 **78**	85

(Table **2** continued…)

Entry	Alkyne R^1	Alkyne R^2	Product[b]	yield[c] %
5	C_6H_5	*n*-C_3H_7	 **80**	82
6	C_6H_5	*n*-C_4H_9	 **81**	84
7	C_6H_5	$C{\equiv}CC_6H_5$	 **82**	70
8	H	*n*-C_6H_{13}	 **73**	73
9	H	*n*-C_8H_{17}	 **74**	71
10	Me_3Si	C_6H_5	 **83**	75
11	Me_3Si	4-$CH_3C_6H_4$	 **84**	80
12	Me_3Si	2-$CH_3OC_6H_4$	 **85**	85

(Table **2** continued…)

Entry	Alkyne R^1	R^2	Product[b]	yield[c] %
13	Me_3Si	CH_3	 **86**	70[d]
14	C_2H_5	C_2H_5	 **87**	72[d]
15	n-C_3H_7	*n*-C_3H_7	 **88**	82
16	*n*-C_4H_9	C_4H_9	 **89**	88

[a] All the reactions were carried out using $Fe(CO)_5$ (15 mmol, 6 equiv.), *t*-BuOK (15 mmol, 6 equiv.) and alkyne (2.5 mmol, 1 equiv.) in THF (70 mL). [b] The products were identified by spectral data (IR, ^{1}H-NMR, ^{13}C-NMR and Mass) and comparison with the reported data.[40-47] Compound **82** has been also characterized by single crystal X-ray analysis. [c] Yields reported are based on the amount of alkynes used. [d] In entries **13** and **14** experiments, after acetylene addition, the reaction temperature was maintained at 25 ^{o}C for 2 h and 60 ^{o}C for 8 h.

The formation of silyl substituted cyclobutenediones indicates that this reagent system tolerates the silyl functional group (**Table 1**, **entries 10-13**). The formation of alkynyl substituted cyclobutenedione **82** (**Table 1**, **entry 7**) from 1,3-diynes reveals that this reagent system reacts with only one alkyne group without affecting the other alkyne group. This may be due to steric hindrance of the iron carbonyl intermediate for reaction at the adjacent alkyne moiety. However, the presence of an alkynyl moiety on the cyclobutenedione **82** would give an additional handle for further synthetic exploitations.

Such multifunctional derivatives have been previously used in a number of organic transformations.[65, 66]

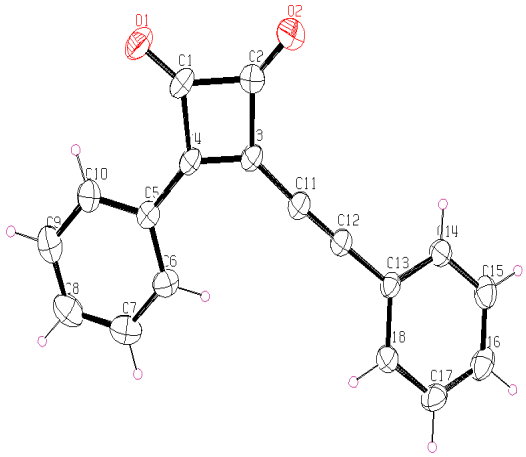


Figure 1. ORTEP diagram of compound **82**

The THF was found to be a good solvent for this transformation. Other solvents such as CH_3CN and acetone also give comparable results. However, use of solvents like $CHCl_3$ and CH_2Cl_2 gave unidentified mixture of iron carbonyl products. Presumably, the coordinating solvents may form weak complexes with the coordinatively unsaturated species like mononuclear $Fe(CO)_4$ or binuclear $Fe_2(CO)_9$ or $Fe_2(CO)_8$ or trinuclear $Fe_3(CO)_{11}$ which could help in realizing cleaner reaction.[62] We have carried out this reaction with diphenyl acetylene using different ratios of $Fe(CO)_5$ and *t*-BuOK, 1:1, 1:1/2 and 1:1/3, respectively. In these cases, the cyclobutenedione **69** was obtained in 90%, 75% and 65% yields, respectively. We also studied the effect of temperature on the reaction and found that optimum results were obtained at 70 °C. When the reaction was carried out at 25 °C, no cyclobutenedione product was obtained even after 20 h.

Table 3. X-ray data collection and structure refinement for **82**

Empirical formula	$C_{18}H_{10}O_2$
Fw	258.26
Temp., wavelength	298(2), 0.71073 Å
Cryst. syst., space group	monoclinic, P2(1)/c
Unit cell dimensions	a=11.7943(8) Å, α=90˚
	b=15.0340(11) Å, β=97.6640˚ (10)
	c=7.5926(5) Å, γ =90˚
Volume	1334.26(16) $Å^3$
Z, calcd. density	4, 1.286 mg/m^3
Abs. coeff.	0.083 mm^{-1}
F(000)	536
Cryst. size	0.50×0.48×0.46 mm
θ range for data collection	1.74 to 25.95˚
Limiting indices	-14≤h≤13, -18≤k≤18, -9≤l≤9
Reflns. collected, unique	10070, 2596[R(int)=0.0251]
Refinement method	full-matrix least-square on F^2
Data/restraints/params	2596/0/221
Goodness-of-fit on F^2	1.020
Final *R* indices[I> 2σ (I)]	R_1=0.0507, wR_2=0.1327
R indices (all data)	R_1= 0.0790, wR_2=0.1519
Largest diff. peak and hole	0.337, -0.141 e. $Å^{-3}$

When the first step of the reaction (i.e. reaction of *t*-BuOK with $Fe(CO)_5$) was carried out at 70 °C for 2 h and the second step of the reaction (i.e. reaction with alkyne) at 25 °C for 10 h, the cyclobutenedione **69** was obtained in 75% yield. We have also carried out experiments using the NaOEt and NaOMe bases. These reagents also react with diphenyl acetylene to give the corresponding cyclobutenedione **69** in 50% and 70% yields, respectively, after $CuCl_2.2H_2O$ oxidation. The results are summarized in **Table 4**.

Table 4. Formation of cyclobutenedione **(69)** from $Fe(CO)_5$/ROM and diphenyl-acetylene in different reaction conditions[a]

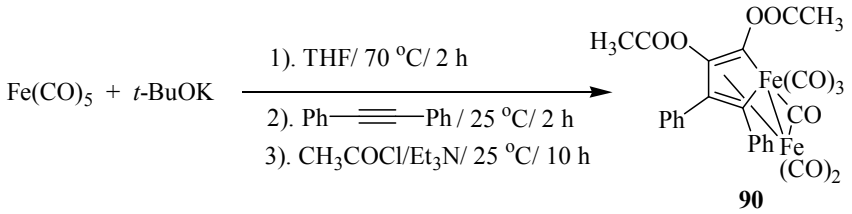
Entry	ROM	$Fe(CO)_5$: *t*-BuOK	Solvent	Temperature	yield[b](%)
1	*t*-BuOK	1: 1	THF	70 °C	90
2	*t*-BuOK	1: 1/2	THF	70 °C	75
3	*t*-BuOK	1: 1/3	THF	70 °C	65
4	*t*-BuOK	1: 1	CH_3CN	70 °C	81
5	*t*-BuOK	1: 1	Acetone	70 °C	70
6	MeONa	1:1	THF	70 °C	70
7	EtONa	1:1	THF	70 °C	50
8	*t*-BuOK	1:1	THF	70 °C to 25 °C	75[c]

[a] All the reactions were carried out using $Fe(CO)_5$ (15 mmol, 6 equiv.), ROM (R = Me, Et, *t*-Bu; M = Na, K) and diphenylacetylene (2.5 mmol, 1 equiv.) in 70 mL solvent. [b] Yields reported are based on the amount of alkyne used. [c] The reaction of *t*-BuOK with $Fe(CO)_5$ was carried out at 70 °C for 2 h and the reaction of alkyne was carried out at 25 °C for 10 h

We have also made efforts to identify the intermediate species involved in the above transformation using Et_3N and CH_3COCl to trap the intermediates. We have observed that

the corresponding 1,2-diacyloxyferrole complex **90** is formed in 75% yield in this experiment (**Scheme 45**).

Scheme 45



90

The structural assignment of the acyloxyferrole complex **90** was confirmed by single crystal X-ray analysis**.** It contains a semi-bridged carbonyl group between Fe(1)-Fe(2), which was previously considered as stabilizing factor in such complexes.[67]

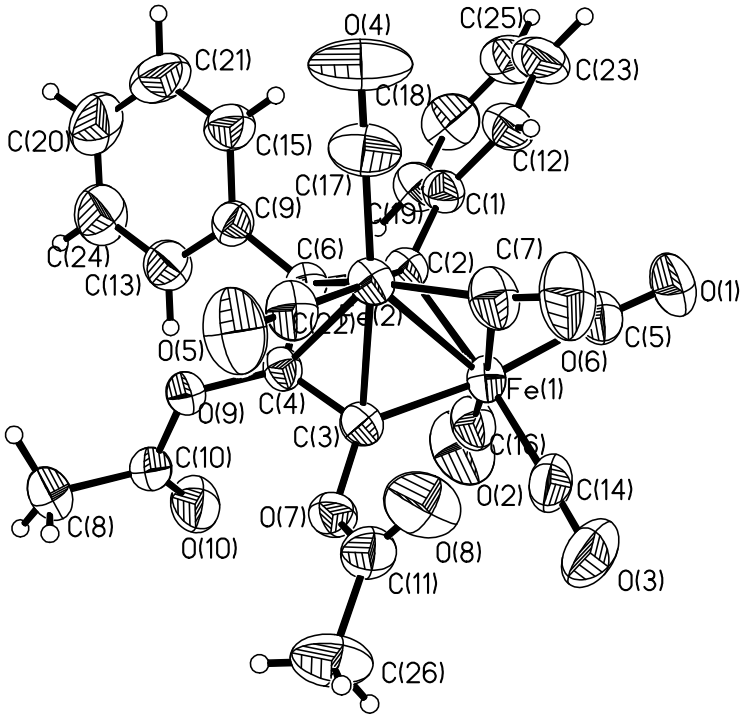


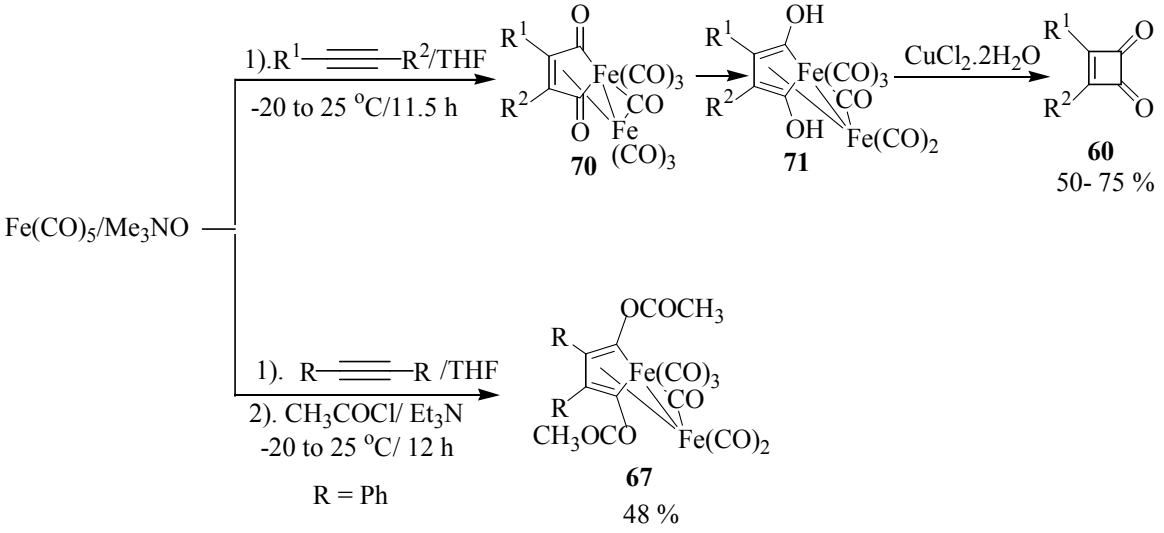
Figure 2. ORTEP diagram of acyloxyferrole complex **90**

Table 5. X-ray data collection and structure refinement for **90**

Empirical formula	$C_{26}H_{16}Fe_2O_{10}$
Fw	600.09
Temp., wavelength	298(2), 0.71073 Å
Cryst. syst., space group	monoclinic, P-21/c
Unit cell dimensions	a=16.411(3) Å, α=90˚
	b=18.877(4) Å, β=96.75˚ (3)
	c=8.4637(17) Å, γ =90˚
Volume	2603.8(9) $Å^3$
Z, calcd. density	4, 1.531 mg/m^3
Abs. coeff.	1.170 mm^{-1}
F(000)	1216
Cryst. size	0.62×0.56×0.46 mm
θ range for data collection	1.65 to 25.94˚
Limiting indices	-20≤h≤20, -23≤k≤23, -10≤l≤10
Reflns. collected, unique	26466, 5076 [R(int)=0.035]
Refinement method	full-matrix least-square on F^2
Data/restraints/params	5076/0/345
Goodness-of-fit on F^2	1.038
Final *R* indices[I> 2σ (I)]	R_1=0.0366, wR_2=0.0915
R indices (all data)	R_1=0.0440, wR_2=0.0959
Largest diff. peak and hole	0.496, -0.215 e. $Å^{-3}$

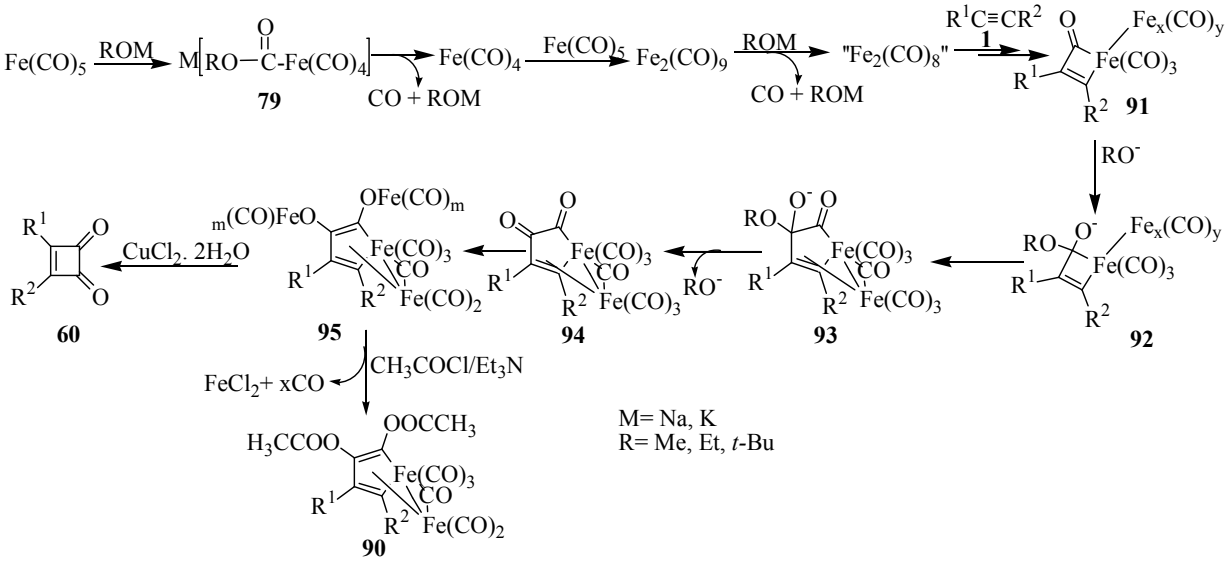
Previously, the acyloxyferrole complex **67** was isolated when the reaction of $Fe(CO)_5/Me_3NO$ with diphenylacetylene was run in the presence of Et_3N and CH_3COCl (**Scheme 46**). Accordingly, the formation cyclobutenediones **60** was rationalized considering the intermediacy of maleoyl complex of the type **70** or ferrole complex of the type **71** (**Scheme 46**).[47]

Scheme 46



Since the 1,2-diacyloxyferrolecomplex **90** is formed in the present transformation using *t*-BuOK/$Fe(CO)_5$, probably the reaction would go through a different type of double carbonylation of alkynes with sequential insertion of carbon monoxide at only one end of the acetylenic carbon in contrast to erstwhile reported methods, in which the carbonylation takes place at both ends of the acetylenic carbons leading to intermediate of the type **70**. Clearly, the mechanism and the intermediate species proposed in the erstwhile methods are not tenable for the present transformation. Therefore, the mechanism outlined in the **Scheme 47** may be considered to rationalize this difference.

Scheme 47



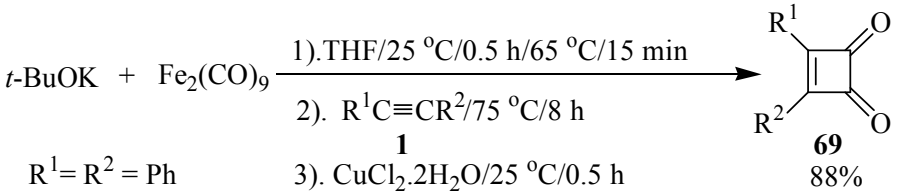
Previously, it was reported that $Fe(CO)_5$ reacts with metal alkoxides (*t*-BuOK or CH_3ONa) to give the corresponding $[(CO)_4Fe(COOR)]^-$ species at 0 ^oC.[67] We have envisaged that such species could decompose to give unsaturated iron carbonyl species as observed earlier using amine oxides and amines.[44- 47, 68] Accordingly, in the present case, addition of ROM to the $Fe(CO)_5$ in THF would give the "$Fe(CO)_4$" species through such a decarbonylation (**Scheme 47**). These species could further undergo reaction with $Fe(CO)_5$ to give species like $Fe_2(CO)_8$ via $Fe_2(CO)_9$. Such species could further react with alkynes followed by CO insertion to give the ferracyclopentenedione of the type **94** or ferrole complex of the type **95** which could give the corresponding cyclobutenediones after $CuCl_2.2H_2O$ oxidation. The formation 1,2-diacyloxyferrole complexes **90** here in contrast to 1,4-diacyloxyferrole complexes **67 (Scheme 46)** could be due to the presence of strong

base leading to the nucleophilic intermediate **92** favoring another CO insertion in the adjacent carbon to give the intermediate species **93** (**Scheme 47**).

1.2.3 Synthesis of cyclobutenediones by the reaction of $Fe_2(CO)_9$/*t*-BuOK reagent system with alkynes

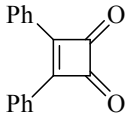
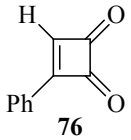
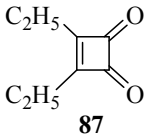
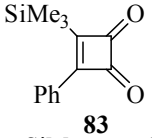
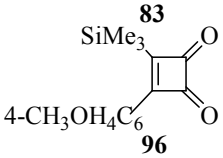
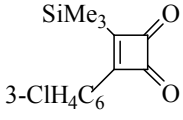
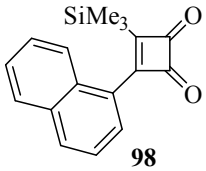
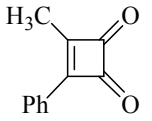
In the mechanism outlined in **Scheme 47**, the formation of $Fe_2(CO)_9$ is visualized. Accordingly, we have examined the reactivity of *t*-BuOK with $Fe_2(CO)_9$. Indeed, we have observed that the $Fe_2(CO)_9$/*t*-BuOK reagent system also converts the alkynes to the corresponding cyclobutenediones in 63-90% yields under similar reaction conditions. When the reaction of diphenylactylene was carried out with the $Fe_2(CO)_9$/*t*-BuOK reagent system, the corresponding diphenylcyclobutenedione **69** was obtained in 88% yield (**Scheme 48**).

Scheme 48

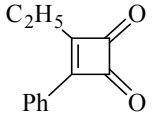
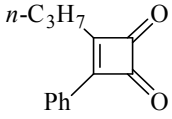
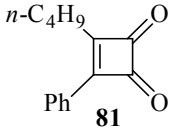


Again, a variety of aryl, alkyl, and silyl substituted, non-symmetrical and symmetrical alkynes are converted to the corresponding cyclobutenediones following this method. The products were obtained here in comparable yields (63-90%) but in shorter reaction times compared to the $Fe(CO)_5$/*t*-BuOK reagent system. The results are summarized in **Table 6**.

Table 6. Synthesis of cyclobutenediones with the $Fe_2(CO)_9$/*t*-BuOK reagent system[a]

Entry	Alkyne R^1	Alkyne R^2	Product[b]	yield[c] %
1	C_6H_5	C_6H_5	 **69**	88
2	C_6H_5	H	 **76**	63
3	C_2H_5	C_2H_5	 **87**	65[d]
4	Me_3Si	C_6H_5	 **83**	72
5	Me_3Si	4-$CH_3OC_6H_4$	 **96**	70
6	Me_3Si	3-ClC_6H_4	 **97**	71
7	Me_3Si	1-naphthyl	 **98**	69
8	C_6H_5	CH_3	 **77**	86

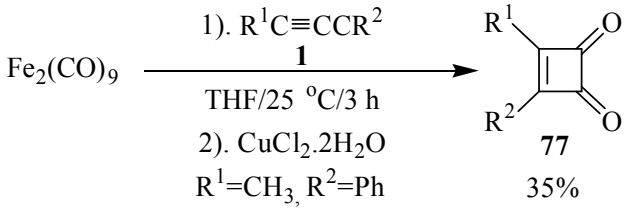
(Table **6** continued…)

Entry	Alkyne R^1	Alkyne R^2	Product[b]	yield[c] %
9	C_6H_5	C_2H_5	 **78**	83
10	C_6H_5	*n*-C_3H_7	 **80**	85
11	C_6H_5	*n*-C_4H_9	 **81**	90

[a] All the reactions were carried out using $Fe_2(CO)_9$ (6 mmol, 3 equiv.), *t*-BuOK (8 mmol, 4 equiv.) and alkyne (2 mmol, 1 equiv.) in THF (50 mL). [b] The products were formed after $CuCl_2.2H_2O$ Oxidation, identified by spectral data (IR, ^{1}H-NMR, ^{13}C-NMR and Mass) and comparison with the reported data.[40-47] [c] Yields reported are based on the amount of alkynes used. [d] In entry **3** experiment, after alkyne addition, the reaction temperature was maintained at 25 ^oC for 1 h and 65 ^oC for 7 h.

It was reported that the $Fe_2(CO)_9$ undergoes disproportion in THF to give the reactive iron carbonyl species $Fe(CO)_4$ and $Fe(CO)_5$.[69] However, when the reaction of 1-phenyl-1-propyne was carried out using $Fe_2(CO)_9$ in THF then the corresponding cyclobutenedione **77** was obtained only in 35% yield after $CuCl_2.2H_2O$ oxidation (**Scheme 49)**.

Scheme 49

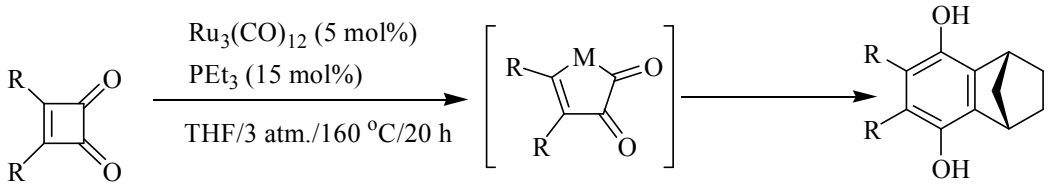


Presumably, the reactive species formed are not the same under the $Fe_2(CO)_9$/THF and $Fe_2(CO)_9$/*t*-BuOK reagent systems.

The simple, convenient and easily scalable synthetic routes described here for the cyclobutenediones synthesis using the readily accessible and inexpensive $Fe(CO)_5$, $Fe_2(CO)_9$ and *t*-BuOK reagents, should make the method useful for further synthetic exploitations.

Further, in the present case, the cyclobutenediones were obtained via a new pathway involving a novel 1,2-dicarbonyliron intermediate **94 (Scheme 47).** Previously, formation of such complexes were reported only in transformations using Ru and Pt complexes **(Scheme 50)**.[70]

Scheme 50



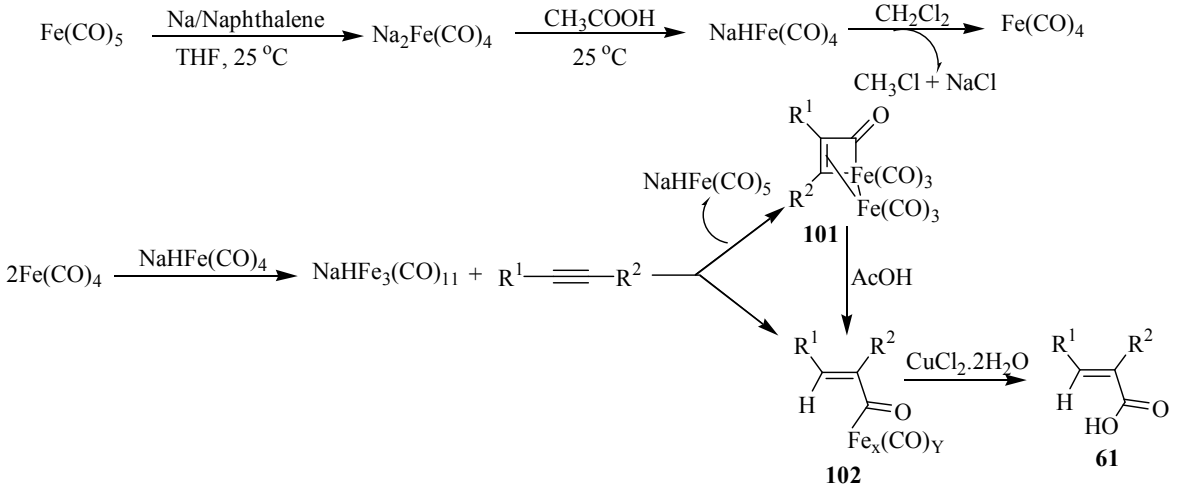
Accordingly, the reactive iron carbonyl species generated using the $Fe(CO)_5$/*t*-BuOK and $Fe_2(CO)_9$/*t*-BuOK reagent system are expected to stimulate further research efforts in this area.

1.2.4 Stereoselective hydrocarboxylation of alkynes using the $Fe(CO)_5$/*t*-BuOK/AcOH reagent system

As discussed in the previous section, the $Fe(CO)_5$/*t*-BuOK reagent system converts the alkynes to the corresponding cyclobutenediones [64] and the reaction goes

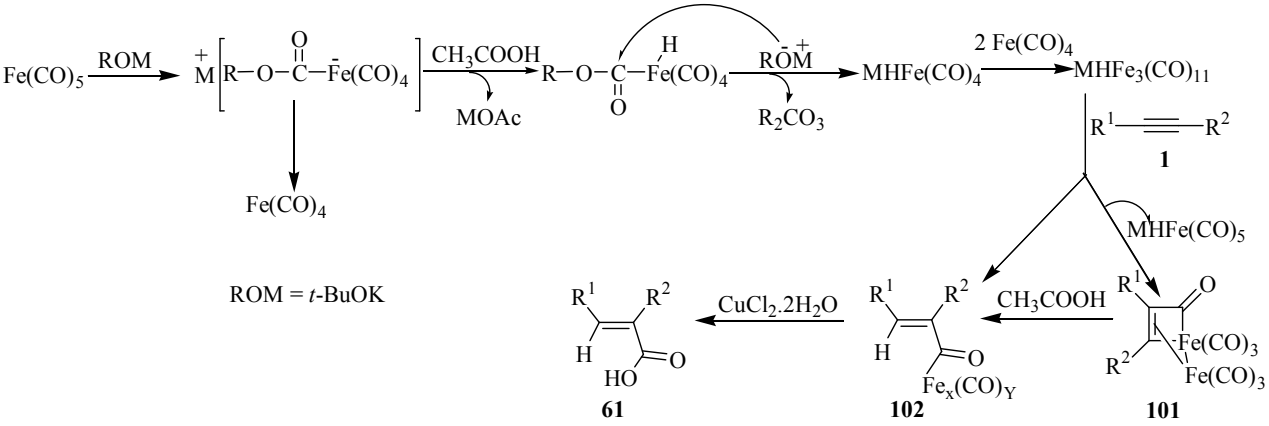
through the intermediacy of α,β-unsaturated carbonyl complex **91** as envisaged in **Scheme 47**. Previously, such intermediates were considered in the hydrocarboxylation of alkynes to explain the results (**Scheme 51**).

Scheme 51



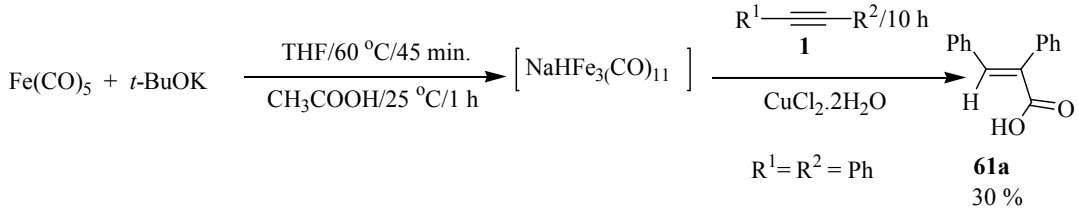
Formation of intermediates of the type **101** could be also envisioned in reaction using the $Fe(CO)_5$/ROM reagent system as outlined in **Scheme 52**.

Scheme 52



In order to examine this possibility, we have carried out the reaction of diphenylacetylene with $Fe(CO)_5$/*t*-BuOK reagent system in the presence of CH_3COOH. Under these conditions, the corresponding α,β-unsaturated carboxylic acid **61a** was obtained in 30% yield.

Scheme 53



However, when the reaction was carried out using CH_2Cl_2 and CH_3COOH, the α,β-unsaturated carboxylic acids were obtained in 60-78% yield (**Scheme 54**). The results are summarized in **Table 7.**

Scheme 54

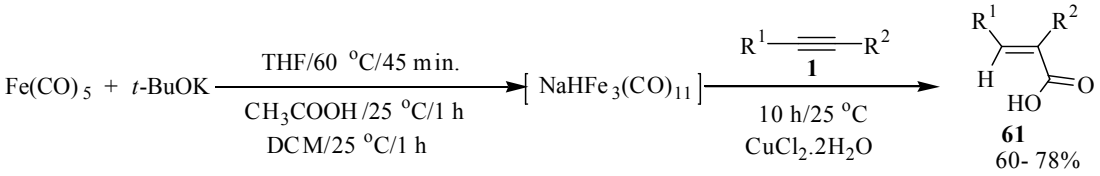
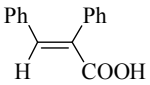
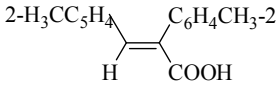
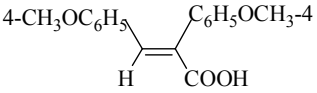
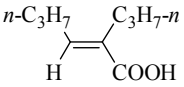
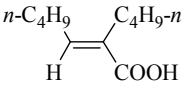
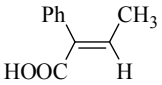
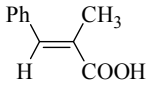
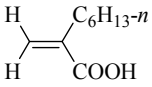
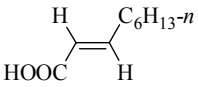


Table 7. Regio and stereoselective hydrocarboxylation of alkynes using novel $Fe(CO)_5$/*t*-BuOK/AcOH/CH_2Cl_2 reagent system[a]

Entry	Alkyne R^1	Alkyne R^2	Product[b]	yield[c] %
1	Ph	Ph	 **61a**	75
2	2-$CH_3C_6H_5$	2-$CH_3C_6H_5$	 **61b**	65
3	4-$CH_3OC_6H_5$	4-$CH_3OC_6H_5$	 **61c**	60
4	*n*-C_3H_7	*n*-C_3H_7	 **61d**	65
5	*n*-C_4H_9	*n*-C_4H_9	 **61e**	68
6	Ph	CH_3	 **61f** (71%)  **61g** (29%)	78[d]
7	H	*n*-C_6H_{13}	 **61h** (75%)  **61i** (25%)	62[d]

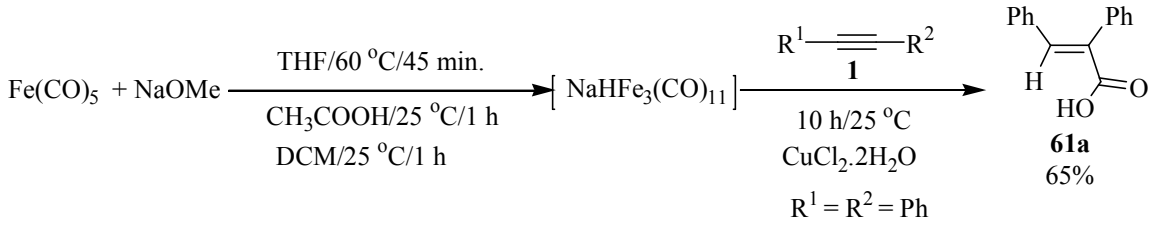
[a] All the reactions were carried out using $Fe(CO)_5$ (7.5 mmol, 6 equiv.), *t*-BuOK (7.5 mmol, 6 equiv.) and alkyne (1.25 mmol, 1 equiv.) in THF (25 mL). [b] The products were formed after $CuCl_2.2H_2O$ oxidation, identified by spectral data (IR, ^{1}H-NMR, ^{13}C-NMR and Mass) and comparison with the reported data.[40,41,79]

[c] Yields reported are for the isolated products and based on the amount of alkynes used. [d] The regio isomers ratio was determined by ^{1}H NMR analysis of the crude product mixture.

Symmetrical alkynes undergo stereoselective hydrocarboxylation to give the (*E*)-α,β-unsaturated carboxylic acids (**entries 1-5**). In the case of 1-phenyl-1-propyne (**entry 6**), the (*E*)-2-phenylbut-2-enoic acid **61f** and (*E*)-2-methyl-3-phenylacrylic acid **61g** are formed in 71:29 ratio. In the case of 1-octyne, the 2-methyleneoctanoic acid **61h** and (*E*)-non-2-enoic acid **61i** were obtained in 75:25 ratio. Clearly, in the case of unsymmetrical alkynes, the carbonylation occurs at the highly substituted acetylenic carbon to more extent. In all these cases, along with α,β-unsaturated carboxylic acids the corresponding cyclobutenediones were also isolated as side products (< 5%).

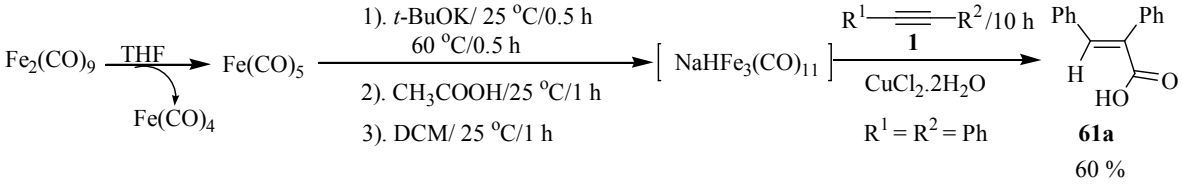
We have also examined the reactivity of diphenylacetylene with the $Fe(CO)_5/NaOMe/CH_3COOH/CH_2Cl_2$ reagent system. In this case, the (*E*)-2,3-diphenyl acrylic acid **61a** was obtained in 65% yield (**Scheme 55**).

Scheme 55



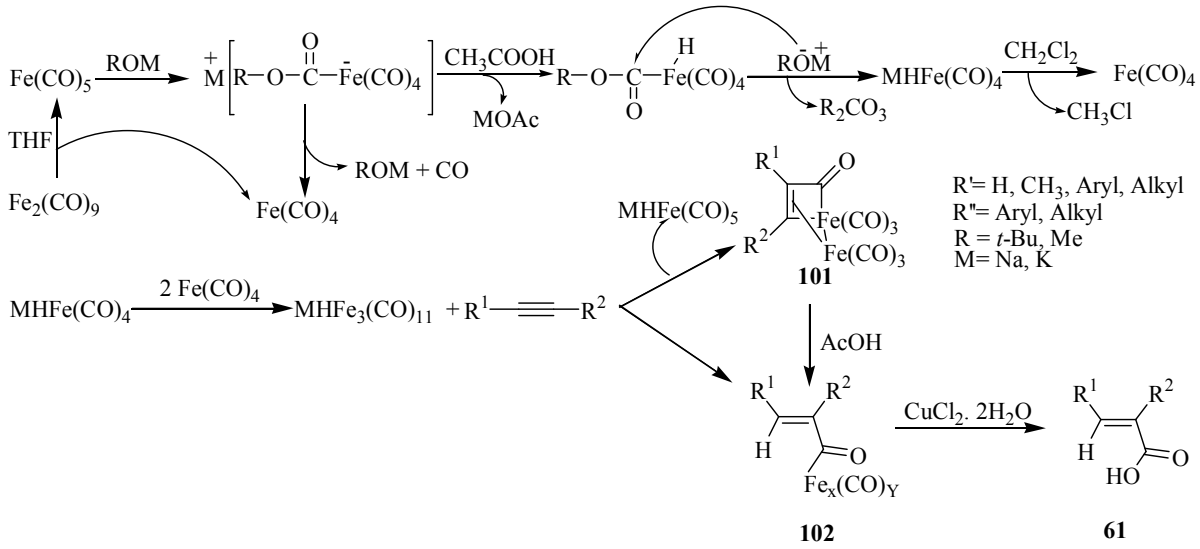
We have also observed that the $Fe_2(CO)_9/t$-BuOK/CH_3COOH/CH_2Cl_2 reagent system react with diphenylacetylene to give the (*E*)-2,3-diphenylacrylic acid **61a** in 60 % yield (**Scheme 56**).

Scheme 56



The mechanism for the formation of α,β-unsaturated carboxylic acids **61** from alkynes and $Fe_2(CO)_9$/ROM/AcOH/CH_2Cl_2 reagent system may be considered as envisaged in **Scheme 57**.

Scheme 57



The $Fe(CO)_5$ or the $Fe(CO)_5$ obtained from $Fe_2(CO)_9$/THF reagent system would undergo reaction with alkoxide followed by CH_3COOH and CH_2Cl_2 to provide the $Fe(CO)_4$. Which could react with $MHFe(CO)_4$ to give the $[HFe_3(CO)_{11}]^-$ species. These species after reaction with alkynes would provide the hydrometallation product **102** or iron complex **101** (**Scheme 57**). These complexes could give the α,β-unsaturated carboxylic

acids after $CuCl_2.2H_2O$ oxidation. However, the formation of other metal carbonyl species such as **101** cannot be ruled out.

We have developed a simple, one-pot method for the stereoselective synthesis of α, β-unsaturated carboxylic acids by using *in situ* generated reactive iron carbonyl species. This method of generation of reactive iron carbonyl species by using the readily accessible reagents *t*-BuOK, AcOH and CH_2Cl_2 is expected to be useful for further synthetic exploitations. Transition metal mediated hydrocarboxylation reaction are of immense interest in organic synthesis.[71] Hydrocarboxylation of alkynes is an industrially important reaction for large scale production of acrylic acid derivatives.[72] The (*E*)-α,β-ethylenic carboxylic acids are not only versatile synthons, but also exist widely in natural products, for example honeybee,[73] caffeir acid[74] and in several biologically active molecules.[75] Therefore, the method described here for the hydrocarboxylation of alkynes have good synthetic potential.

1.3 Conclusions

The iron carbonyl species $HFe_3(CO)_{11}^-$ prepared using the $Fe(CO)_5$/NaH and CH_3I reagent system at 25 °C, reacts with alkynes in THF, to give the corresponding cyclobutenediones in good yield (50-65%) after $CuCl_2.2H_2O$ oxidation. Also, alkoxides facilitate the double carbonylation reaction of alkynes using $Fe(CO)_5$. The reaction of iron carbonyl species, prepared in THF using the $Fe(CO)_5$ and *t*-BuOK at 70 °C, with various alkynes gives the corresponding cyclobutenediones in good yields (70-93%). The nature of intermediate alkyne-iron carbonyl complexes involved in the reaction of alkynes with the $Fe(CO)_5$/*t*-BuOK reagent system was identified through isolation of the corresponding acyloxyferrole complex by carrying out the reaction in the presence of CH_3COCl/Et_3N. The 1,2-acyloxyferrole complex was obtained in this transformation in contrast to the 1,4-acyloxyferrole complex obtained in the hitherto reported methods.

The $Fe_2(CO)_9$/*t*-BuOK reagent system is also useful for the double carbonylation of alkynes, giving the corresponding cyclobutenediones in good yields (63-90%) in a short reaction time (8.5 h).

We have also found that the $Fe(CO)_5$/*t*-BuOK/CH_3COOH/CH_2Cl_2 and $Fe_2(CO)_9$/*t*-BuOK/CH_3COOH/CH_2Cl_2 reagent systems are useful for stereo and regio selective hydrocarboxylation with alkynes and the corresponding α,β-unsaturated carboxylic acids were obtained in good yields (60-78%).

1.4 Experimental Section

1.4.1 General information:

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on Bruker-Avance-400, respectively in $CDCl_3$ and TMS was used as reference (δ = 0 *ppm*). IR (KBr) spectra and IR (neat) spectra were recorded on JASCO FT-IR spectrophotometer model 5300 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. 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 (3x10 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 ^{o}C in an air oven for 4 h, 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 vented inside the fume hood. 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.

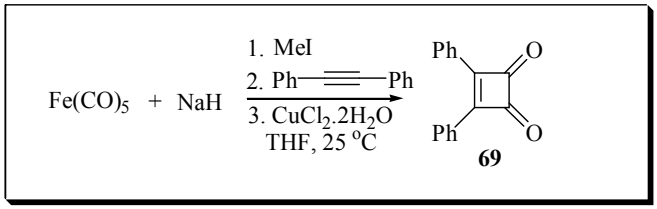
The $Fe(CO)_5$ and $Fe_2(CO)_9$ reagents were supplied by Fluka, Switzerland and Aldrich, USA respectively. Aliphatic alkynes supplied by Aldrich, USA, silyl substituted and diaryl alkynes were prepared following a reported procedure.[76] THF was distilled over sodium benzophenone ketyl system. Et_3N supplied by Spectrochem Ltd., India, was distilled and stored over KOH. DCM was distilled over calcium hydride and stored over molecular sieves.

The X-ray diffraction measurements for compounds **82** and **90** 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).

1.4.2 Preparation of cyclobutenedione 69 using the $Fe(CO)_5$/NaH/MeI reagent system

The $Fe(CO)_5$ (1.0 mL, 7.5 mmol) was added dropwise to the NaH (0.33 g, 7.5 mmol) in THF (35 mL) at 25 ^oC under dry nitrogen and stirred for another 5 h at same

temperature. The above reaction mixture was treated with CH_3I (0.46 mL, 1.06 g, 7.5 mmol) at 0 ^oC under dry N_2 atmosphere. After 10 min. diphenylacetylene (0.22 g, 1.25 mmol) was added and the contents were further stirred for 10 h at room temperature. The metal carbonyl complexes were oxidized using $CuCl_2.2H_2O$ (2.5 g, 15 mmol) in acetone (10 mL). Saturated NaCl solution was added and the contents were extracted with ether (2x40 mL). The combined ether extracts were washed successively with saturated $Na_2S_2O_3$ solution and brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to column chromatography (silica gel, hexane-EtOAc). Ethyl acetate (2%) in hexane eluted the 3,4-diphenyl-3-cyclobutene-1,2-dione **69**.



69

Yield : 0.152 g (52%)

mp : 95-96 ^oC (Lit.[77a,b] mp 97 ^oC)

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

^{1}H NMR : (400 MHz) δ = 8.01-8.04 (m, 4H), 7.61-7.51 (m, 6H) *ppm*

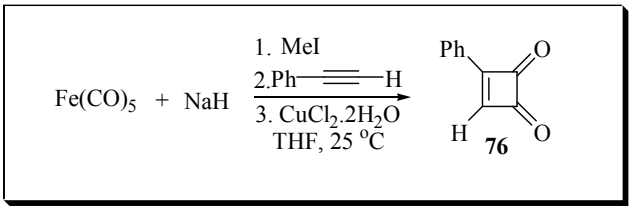
(Spectrum No. 1)

^{13}C NMR : (100 MHz) δ = 195.9, 187.2, 133.3, 129.2, 128.1, 127.9 *ppm*

(Spectrum No. 2)

MS (EI) : *m/z* 235 (M+1)

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



Yield **:** 0.108 g (55%)

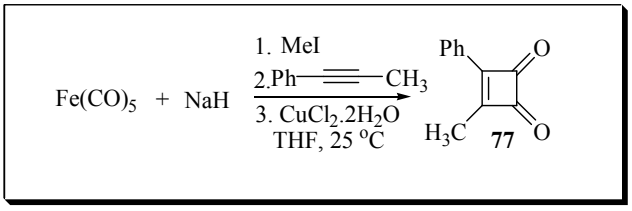
mp **:** 152-153 °C (Lit.[77a,b] mp 152-153 °C)

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

^{1}H NMR **:** (400 MHz) δ = 9.56 (s, 1H), 8.02-7.52 (m, 5H) *ppm*

^{13}C NMR **:** (100 MHz) δ = 197.8, 196.0, 195.5, 178.3, 134.7, 129.6, 129.4, 127.3 *ppm*

MS (EI) **:** *m/z* 159 (M+1)



Yield **:** 0.120 g **(**56%)

mp **:** 98-100 °C (Lit.[77c] mp 98-100 °C)

IR (KBr) **:** 1782, 1765 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 8.03-8.01 (m, 2H), 7.61-7.55 (m, 3H), 2.66 (s, 3H) *ppm* **(Spectrum No. 3)**

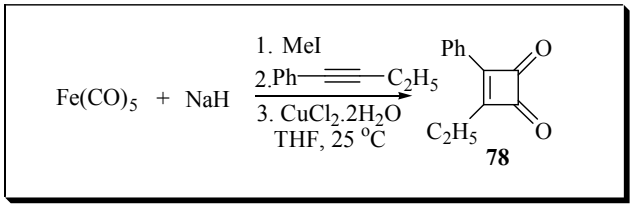
^{13}C NMR **:** (100 MHz) δ = 198.4, 196.9, 193.7, 191.3, 133.5, 129.5, 128.6, 128.5, 12.5 *ppm* **(Spectrum No. 4)**

MS (EI) **:** *m/z* 173 (M+1)

Analysis **:** for $C_{11}H_8O_2$

Calculated: C, 76.73%; H, 4.68%

Found: C, 76.66%; H, 4.70%



78

Yield **:** 0.118 g (51%)

mp **:** 64-66 ^{o}C (Lit.[77d] mp 62 ^{o}C)

IR (KBr) **:** 1778, 1755 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 8.01-7.99 (m, 2H), 7.62-7.54 (m, 3H), 3.08 (q, J = 7.6 Hz, 2H), 1.43 (t, J = 7.6 Hz, 3H) *ppm*

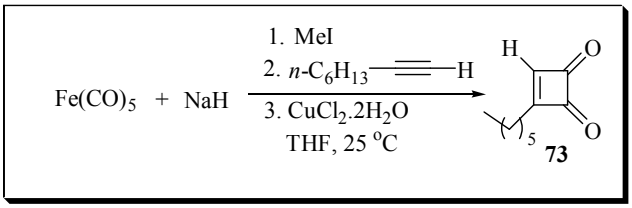
^{13}C NMR **:** (100 MHz) δ = 198.7, 198.3, 197.5, 190.3, 133.5, 129.5, 128.5, 128.4, 21.1, 10.3 *ppm*

MS (EI) **:** *m/z* 187 (M+1)

Analysis **:** for $C_{12}H_{10}O_2$

Calculated: C, 77.40%; H, 5.41%

Found: C, 77.51%; H, 5.42%



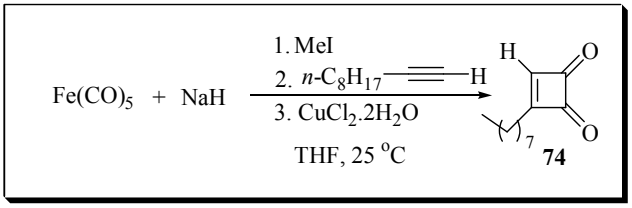
Yield **:** 0.135 g (65%)

IR (neat) **:** 1784 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 9.24 (s, 1H), 2.73 (t, *J* = 7.2 Hz, 2H), 1.68-1.61 (m, 2H), 1.34-1.23 (m, 6H), 0.80 (t, *J* = 7.2 Hz, 3H) *ppm* **(Spectrum No. 5)**

^{13}C NMR **:** (100 MHz) δ = 208.3, 200.0, 196.7, 184.9, 31.1, 28.8, 27.4, 25.7, 22.2, 13.8 *ppm* **(Spectrum No. 6)**

MS (EI) **:** *m/z* 167 (M+1)



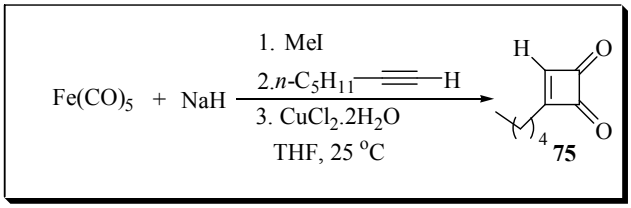
Yield **:** 0.133 g (55%)

IR (neat) **:** 1784 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 9.29 (s, 1H), 2.80 (t, *J* = 7.6 Hz, 2H), 1.76-1.69 (m, 2H), 1.40-1.28 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 3H) *ppm*

^{13}C NMR **:** (100 MHz) δ = 208.3, 200.0, 196.6, 184.8, 31.5, 29.1, 28.9, 28.8, 27.4, 25.8, 22.4, 13.9 *ppm*

MS (EI) : *m/z* 195 (M+1)



Yield : 0.095 g (50%)

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

^{1}H NMR : (400 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*

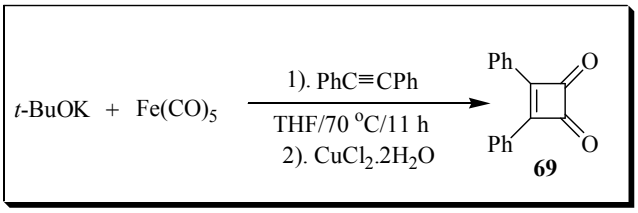
^{13}C NMR : (100 MHz) δ = 208.3, 199.9, 196.6, 184.8, 31.2, 27.1, 25.6, 22.1, 13.7 *ppm*

MS (EI) : *m/z* 151 (M-1)

1.4.3 Preparation of cyclobutenedione 69 using the $Fe(CO)_5$/*t*-BuOK reagent system

The $Fe(CO)_5$ (2.0 mL, 15 mmol) was added dropwise to a solution of anhydrous *t*-BuOK (1.68 g, 15 mmol) in THF (70 mL) at 25 °C under dry nitrogen. The colour of the reaction mixture immediately changes from yellow to dark brown. The reaction mixture was stirred for another 1 h at 70 °C and brought slowly to 25 °C. Diphenylacetylene (0.445 g, 2.5 mmol) was added and further stirred for 10 h at 70 °C. The mixture was brought slowly to 25 °C. The metal carbonyl complexes were oxidised using $CuCl_2.2H_2O$ (5.1 g, 30 mmol) in acetone (20 mL). Saturated NaCl solution was added and the contents were

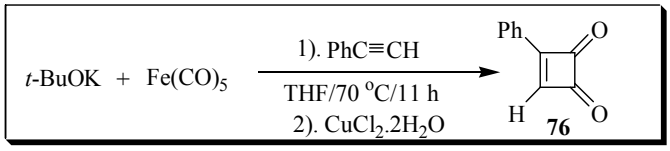
extracted with ether (2x75 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to column chromatography (silica gel, hexane-EtOAc). Ethyl acetate (2%) in hexane eluted the 3,4-diphenyl-3-cyclobutene-1,2-dione **69**.



Yield **:** 0.526 g (90%)

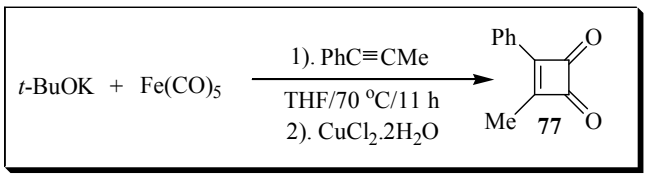
The IR, ^1H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound previously obtained in reaction using the $Fe(CO)_5$/NaH/MeI reagent system.

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



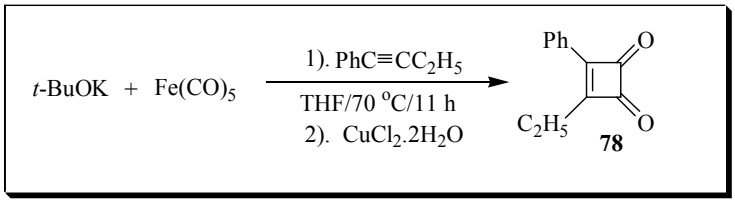
Yield **:** 0.308 g (78%)

The IR, ^1H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound previously obtained in reaction using the $Fe(CO)_5$/NaH/MeI reagent system.



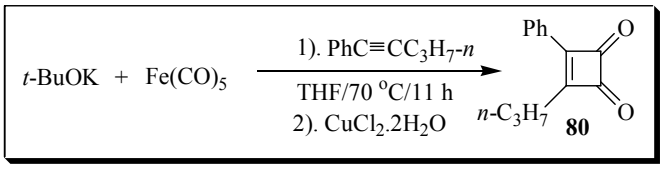
Yield **:** 0.400 g (93%)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound previously obtained in reaction using the $Fe(CO)_5$/NaH/MeI reagent system.



Yield : 0.395 g (85%)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound previously obtained in reaction using the $Fe(CO)_5$/NaH/MeI reagent system.



Yield : 0.41 g (82%)

mp : 60-62 ^{0}C

IR (KBr) : 1766 cm^{-1}

^{1}H NMR : (400 MHz) δ = 8.03-8.01 (m, 2H), 7.61-7.55 (m, 3H), 3.05 (t, J = 7.2 Hz, 2H), 1.95-1.89 (m, 2H), 1.08 (t, J = 7.6 Hz, 3H) *ppm*

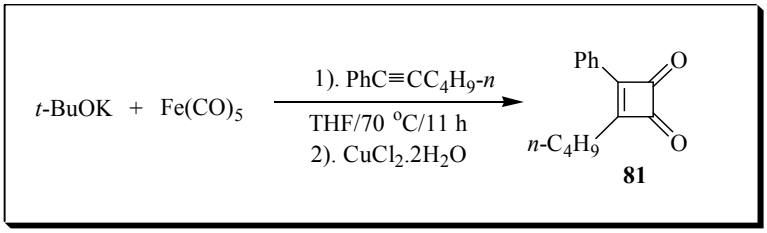
^{13}C NMR : (100 MHz) δ = 198.5, 197.9, 197.4, 190.8, 133.5, 129.5, 128.5, 128.4, 29.7, 19.7, 14.5 *ppm*

MS (EI) : *m/z* 201 (M+1)

Analysis : for $C_{13}H_{12}O_2$

Calculated: C, 77.98%; H, 6.04%.

Found: C, 77.96%; H, 6.03%



Yield : 0.45 g (84%)

mp : 49-51 ^{0}C

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

^{1}H NMR : (400 MHz) δ = 8.01-7.99 (m, 2H), 7.57-7.55 (m, 3H), 3.04 (t, J = 7.2 Hz, 2H), 1.86-1.81 (m, 2H), 1.50-1.44 (m, 2H), 0.97 (t, J = 6.8 Hz, 3H) *ppm*

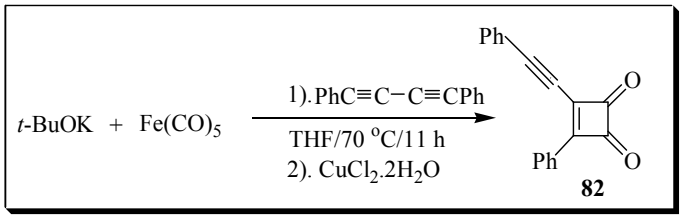
^{13}C NMR : (100 MHz) δ = 198.5, 198.1, 197.4, 190.6, 133.5, 129.5, 128.5, 128.4, 28.1, 27.5, 23.1, 13.7 *ppm*

MS (EI) : *m/z* 215 (M+1)

Analysis : for $C_{14}H_{14}O_2$

Calculated: C, 78.48%; H, 6.59%

Found: C, 78.48%; H, 6.55%



Yield : 0.451 g (70%)

mp : 116-118 ^{0}C

IR (KBr) : 2189, 1778, 1765 cm^{-1}

^{1}H NMR : (400 MHz) δ = 8.29-7.45 (m, 10 H) *ppm*

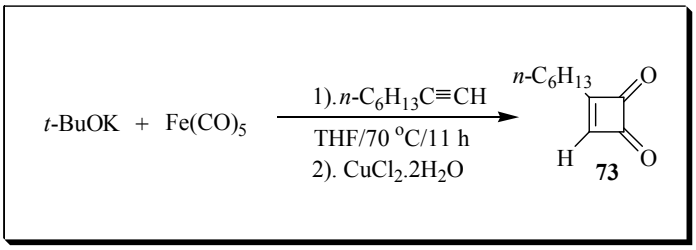
^{13}C NMR : (100 MHz) δ = 198.1, 192.8, 187.9, 172.9, 134.6, 132.4, 131.4, 130.9, 129.4, 129.1, 128.8, 124.7, 120.7, 78.3 *ppm*

MS (EI) : *m/z* 259 (M+1)

Analysis : for $C_{18}H_{10}O_2$

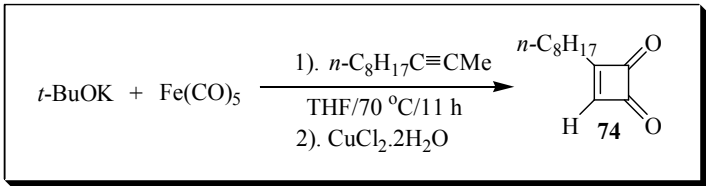
Calculated: C, 83.71%; H, 3.90%

Found: C, 83.63%; H, 3.92%



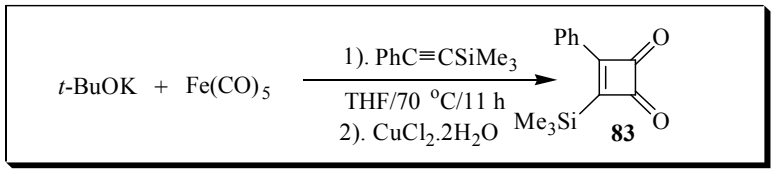
Yield : 0.303 g (73%)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound previously obtained in reaction using the $Fe(CO)_5$/NaH/MeI reagent system.



Yield : 0.344 g (71%)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound previously obtained in reaction using the $Fe(CO)_5$/NaH/MeI reagent system.



Yield : 0.431 g **(**75%)

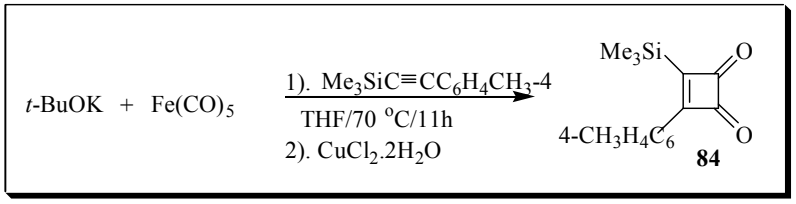
mp : 101-102 ^{0}C (Lit.[40] mp 102.8-103.2 ^{0}C)

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

^{1}H NMR : (400 MHz) δ = 7.96-7.94 (m, 2H), 7.60-7.55 (m, 3H), 0.46 (s, 9H) *ppm*

^{13}C NMR : (100 MHz) δ = 202.6, 200.4, 199.3, 197.9, 133.6, 129.5, 129.3, 129.1, -1.83 *ppm*

MS (EI) : *m/z* 231 (M+1)



Yield : 0.488 g (80%)

mp : 80-82 ^{0}C, (Lit.[78] mp 89-90 ^{o}C)

IR (KBr) : 1761 cm^{-1}

^{1}H NMR : (400 MHz) δ = 7.88 (d, *J* = 8 Hz, 2H), 7.37 (d, *J* = 8 Hz, 2H), 2.46 (s, 3H), 0.46 (s, 9H) *ppm* **(Spectrum No. 7)**

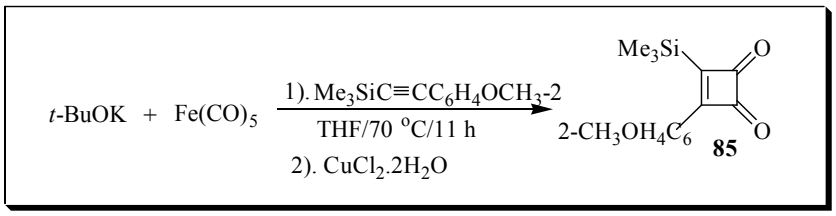
^{13}C NMR **:** (100 MHz) δ = 201.1, 200.5, 199.0, 198.2, 144.9, 130.1, 129.7, 126.5, 22.01, -1.8 *ppm* **(Spectrum No. 8)**

MS (EI) **:** *m/z* 243 (M-1)

Analysis **:** for $C_{14}H_{16}O_2Si$

Calculated: C, 68.81%; H, 6.60%.

Found: C, 68.81%; H, 6.60 %.



Yield **:** 0.552 g (85%)

mp **:** 99-101 ^{o}C

IR (KBr) **:** 1763 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 7.92-7.89 (m, 1H), 7.57-7.52 (m, 1H), 7.13-7.09 (m, 1H), 7.02 (d, J = 8.4 Hz, 1H), 3.89 (s, 3H), 0.34 (s, 9H) *ppm*

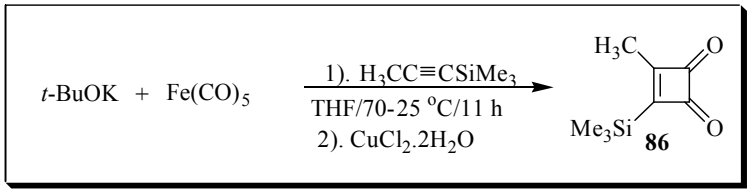
^{13}C NMR **:** (100 MHz) δ = 205.4, 201.4, 198.3, 196.8, 156.4, 134.7, 130.3, 120.9, 118.5, 111.2, 55.2, -1.72 *ppm*

MS (EI) **:** *m/z* 261 (M+1)

Analysis **:** for $C_{14}H_{16}O_3Si$

Calculated: C, 64.58 %; H, 6.19 %

Found: C, 64.51%; H, 6.22 %



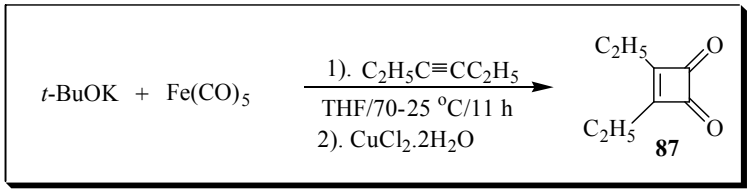
Yield **:** 0.294 g (70%)

IR (neat) **:** 1779 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 2.42 (s, 3H), 0.33 (s, 9H) *ppm* **(Spectrum No.11)**

^{13}C NMR **:** (100 MHz) δ = 208.7, 207.2, 201.2, 200.1, 13.1, -2.31 *ppm* **(Spectrum No.12)**

MS (EI) **:** *m/z* 169 (M+1)



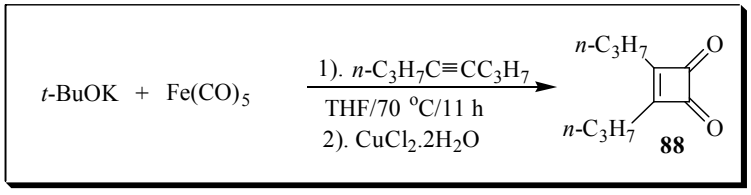
Yield **:** 0.248 g (72%)

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

^{1}H NMR **:** (400 MHz) δ = 2.69 (q, J = 7.6 Hz, 4H), 1.22 (t, J = 7.6 Hz, 6H) *ppm*

^{13}C NMR **:** (100 MHz) δ = 203.1, 199.5, 19.9, 10.3 *ppm*

MS (EI) **:** *m/z* 139 (M+1)



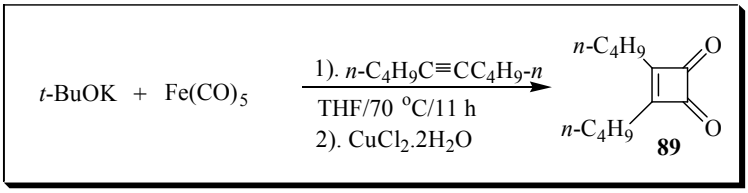
Yield : 0.340 g (82%)

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

^{1}H NMR : (400 MHz) δ = 2.61 (t, J = 7.6 Hz, 4H), 1.68-1.62 (m, 4H), 0.89 (t, J = 8 Hz, 6H) *ppm* **(Spectrum No.13)**

^{13}C NMR : (100 MHz) δ = 202.7, 199.5, 28.2, 19.4, 13.9 *ppm* **(Spectrum No.14)**

MS (EI) : *m/z* 167 (M+1)



Yield : 0.427 g (88%)

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

^{1}H NMR : (400 MHz) δ = 2.67 (t, J = 7.2 Hz, 4H), 1.67-1.62 (m, 4H), 1.36-1.31 (m, 4H), 0. 89 (t, J = 6.4 Hz, 6H) *ppm*

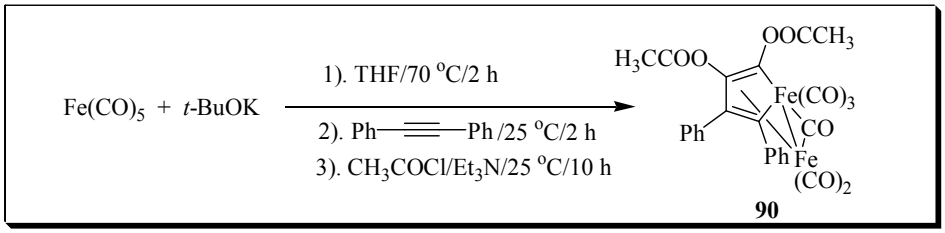
^{13}C NMR : (100 MHz) δ = 202.9, 199.7, 28.0, 26.2, 22.7, 13.5 *ppm*

MS (EI) : *m/z* 193 (M-1)

1.4.4 Preparation of acyloxyferrole complex 90

The $Fe(CO)_5$ (2.0 mL, 15 mmol) was added dropwise to a solution of anhydrous *t*-BuOK (1.68 g, 15 mmol) in THF (70 mL) at 25 °C under dry nitrogen. Then the reaction mixture was stirred for another 2 h at 70 °C and brought slowly to room temperature.

Diphenylacetylene (0.445 g, 2.5 mmol) was added and the contents were further stirred for 2 h at room temperature. Then, Et_3N (2.1 mL, 15 mmol) and CH_3COCl (1 mL, 15 mmol) were added and the contents were further stirred for 10 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 (2.5%) in hexane eluted the ferrole complex **90**. This complex is relatively stable but on long time standing or exposure to atmosphere leads to decomposition.



90

Yield : 1.125 g (75%)

mp : 140-142 °C (dec.)

IR (KBr) : 2077, 2038, 2000, 1780 cm^{-1}

^{1}H NMR : (400 MHz) δ = 7.21-6.83 (m, 10H), 2.20 (s, 3H), 2.09 (s, 3H) *ppm* **(Spectrum No.15)**

^{13}C NMR : (100 MHz) δ = 212.1, 209.0, 204.5, 204.2, 178.5, 167.4, 167.0, 159.4, 147.1, 134.3, 131.6, 129.6, 128.5, 128.0, 127.7, 127.5, 126.2, 125.1, 21.0, 20.3 *ppm* **(Spectrum No.16)**

MS (EI) : *m/z* 601 (M+1), 602 (M+2)

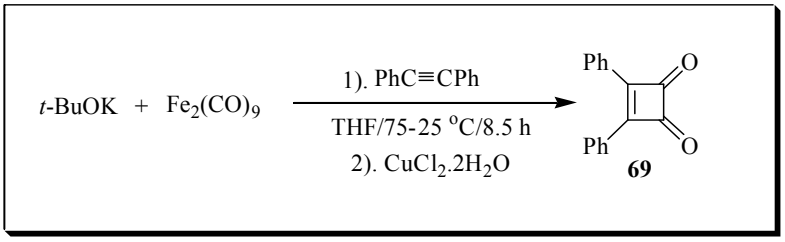
Analysis : for $C_{26}H_{16}O_{10}Fe_2$

Calculated: C, 52.04 %; H, 2.69 %

Found: C, 52.02%; H, 2.69 %

1.4.5 Preparation of cyclobutenedione 69 using the $Fe_2(CO)_9$/*t*-BuOK reagent system

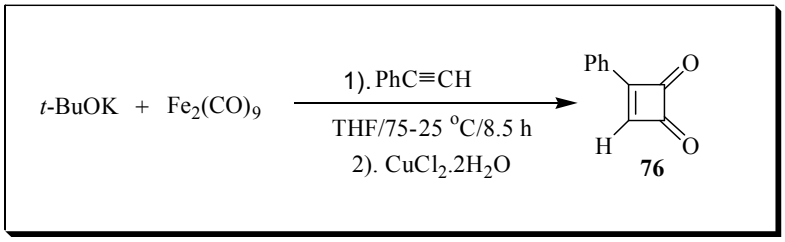
THF (50 mL) was added to the mixture of $Fe_2(CO)_9$ (2.20 g, 6 mmol) and *t*-BuOK (0.89 g, 8 mmol) at 25 °C under dry nitrogen. The reaction mixture was stirred for 0.5 h at 25 °C and another 15 min. at 65 °C. Diphenylacetylene (0.356 g, 2.0 mmol) was added and the contents were further stirred for 8 h at 75 °C. The mixture was brought slowly to 25°C. The metal carbonyl complexes were oxidized using $CuCl_2.2H_2O$ (5.1 g, 30 mmol) in acetone (20 mL). Saturated NaCl solution was added and the contents were extracted with ether (2x60 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 (2%) in hexane eluted the 3,4-diphenylcyclobutene-1,2-dione **69**.



Yield **:** 0.412 g (88%)

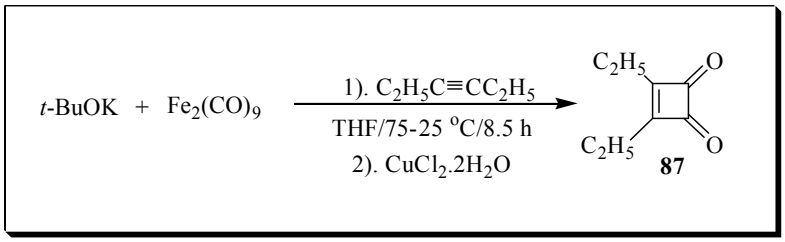
The IR, ^1H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound previously obtained in reaction using the $Fe(CO)_5$/NaH/MeI reagent system.

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



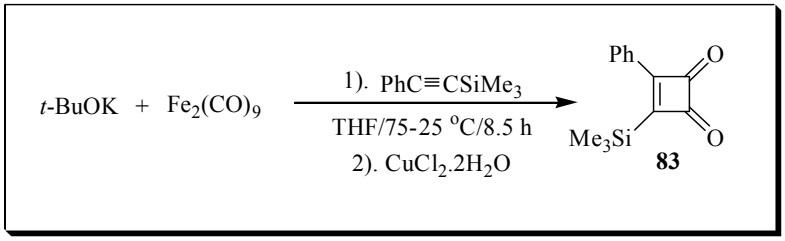
Yield **:** 0.199 g (63%)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound previously obtained in reaction using the $Fe(CO)_5$/NaH/MeI reagent system.



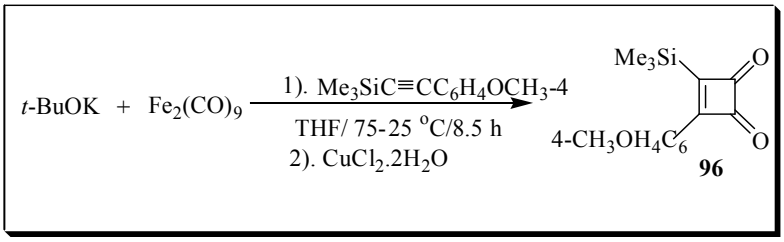
Yield **:** 0.179 g (65%)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound previously obtained in reaction using the $Fe(CO)_5$/*t*-BuOK reagent system.



Yield **:** 0.331 g (72%)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound previously obtained in reaction using the $Fe(CO)_5$/*t*-BuOK reagent system.



Yield : 0.364 g (70%)

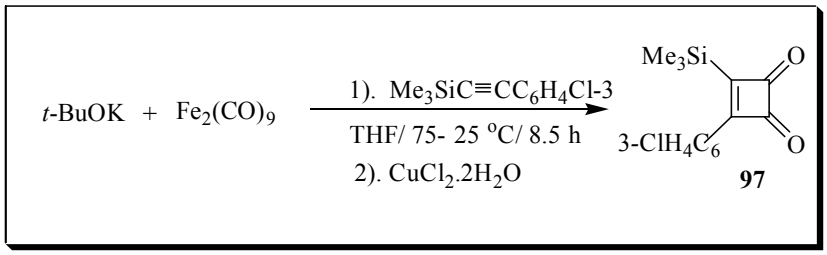
mp : 102-104 ^{0}C (Lit.[78] mp 114-115 ^{o}C)

IR (KBr) : 1768, 1751 cm^{-1}

^{1}H NMR : (400 MHz) δ = 7.97 (d, *J* = 8 Hz, 2H), 7.04 (d, *J* = 8 Hz, 2H), 3.90 (s, 3H), 0.45 (s, 9H) *ppm*

^{13}C NMR : (100 MHz) δ = 200.2, 198.9, 198.4, 197.7, 164.1, 131.9, 121.9, 114.8, 55.6, -1.79 *ppm*

MS (EI) : *m/z* 261 (M+1)



Yield : 0.375 g (71%)

mp : 96-98 ^{o}C

IR (KBr) : 1759 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 7.93 (s, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8 Hz, 1H), 7.52-7.48 (m, 1H), 0.47 (s, 9H) *ppm*

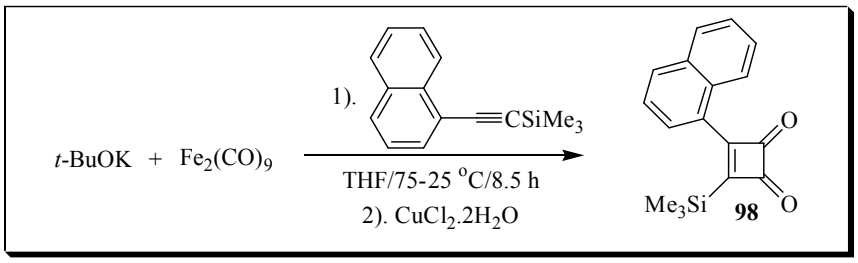
^{13}C NMR **:** (100 MHz) δ = 204.1, 199.9, 197.8, 197.1, 135.4, 133.2, 130.6, 130.5, 129.1, 127.3, -1.84 *ppm*

MS (EI) **:** *m/z* 265 (M+1)

Analysis **:** for $C_{13}H_{13}ClO_2Si$

Calculated: C, 58.97 %; H, 4.95 %

Found: C, 58.85%; H, 4.91 %



Yield **:** 0.386 g (69%)

mp **:** 100-102 ^oC

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

^{1}H NMR **:** (400 MHz) δ = 8.05-7.80 (m, 3H), 7.62-7.53 (m, 4H), 0.34 (s, 9H) *ppm* **(Spectrum No.9)**

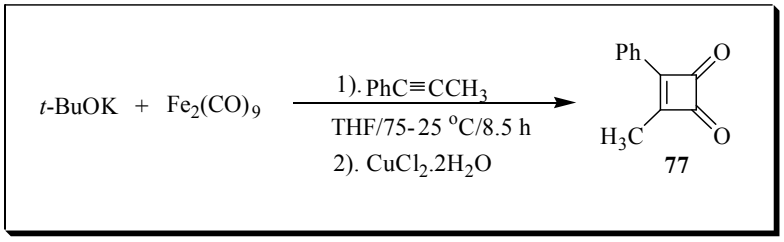
^{13}C NMR **:** (100 MHz) δ = 207.9, 203.8, 200.6, 197.4, 133.6, 132.5, 129.6, 128.7, 127.4, 127.1, 127.0, 126.9, 125.4, 124.9, -2.0 *ppm* **(Spectrum No.10)**

MS (EI) **:** *m/z* 281 (M+1)

Analysis : for $C_{17}H_{16}O_2Si$

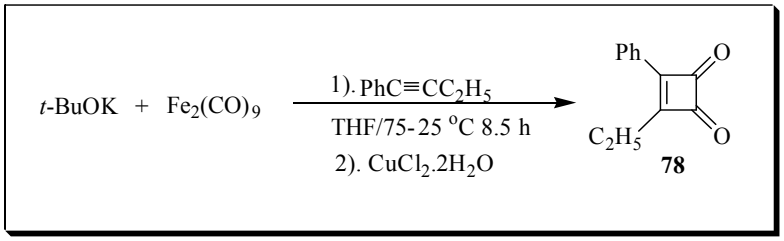
Calculated: C, 72.82 %; H, 5.75 %

Found: C, 72.88 %; H, 5.71 %



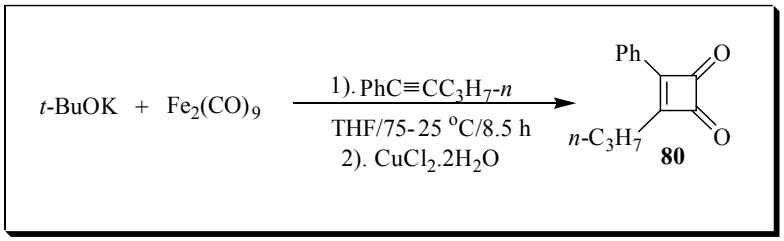
Yield : 0.296 g (86%)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound previously obtained in reaction using the $Fe(CO)_5$/NaH/MeI reagent system.



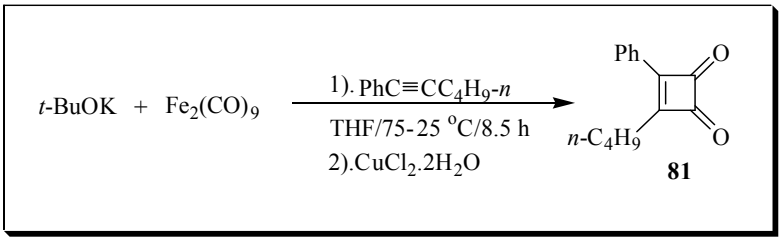
Yield : 0.309 g (83%)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound previously obtained in reaction using the $Fe(CO)_5$/NaH/MeI reagent system.



Yield : 0.340 g (85%)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound previously obtained in reaction using the $Fe(CO)_5$/*t*-BuOK reagent system.



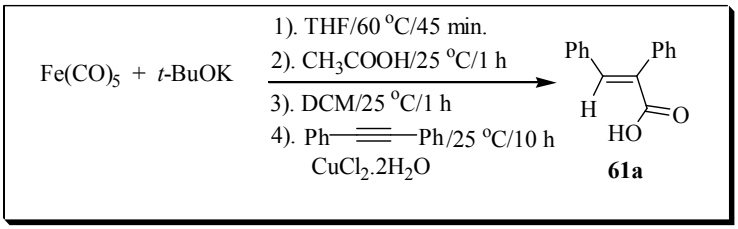
Yield **:** 0.385 g (90%)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound previously obtained in reaction using the $Fe(CO)_5$/*t*-BuOK reagent system.

1.4.6 Synthesis of (*E*)-2,3-diphenylacrylic acid 61a by using the $Fe(CO)_5$/*t*-BuOK/AcOH/CH_2Cl_2 reagent system

The $Fe(CO)_5$ (1.0 mL, 7.5 mmol) was added drop wise to a solution of anhydrous *t*-BuOK (0.84 g, 7.5 mmol) in THF (25 mL) at 25 °C under dry nitrogen. The contents were stirred for 45 min. at 60 °C and brought slowly to 25 °C. Acetic acid (0.43 mL, 7.5 mmol) was added and the contents were stirred for 1 h at 25 °C. Dichloromethane (5 mL) was added and the contents were stirred for another 1 h. Then diphenylacetylene (0.22 g, 1.25 mmol) was added and further stirred for 10 h. The metal carbonyl complexes were oxidized using $CuCl_2.2H_2O$ (2.55 g, 15 mmol) in acetone (10 mL). Saturated NaCl solution was added and the contents were extracted with ether (2x40 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 (10%) in hexane eluted the (*E*)-2,3-diphenylacrylic acid **61a.**



Yield : 0.210 g (75%)

mp : 168-170 °C (Lit.[40] mp 172-173 °C)

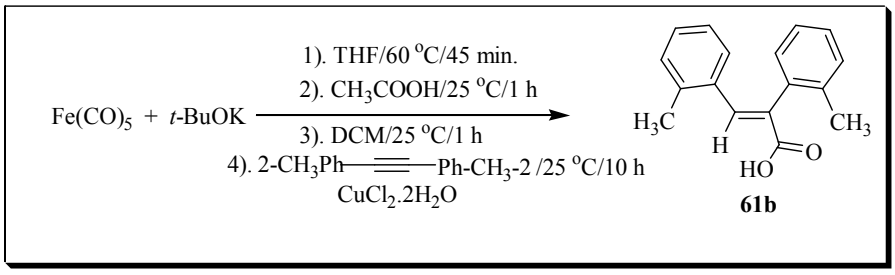
IR (KBr) : 1678 cm^{-1}

^{1}H NMR : (400 MHz) δ = 7.95 (s, 1H), 7.35-7.05 (m, 10H) *ppm*

^{13}C NMR : (100 MHz) δ = 173.2, 142.5, 135.3, 134.3, 131.7, 130.9, 129.8, 129.5, 128.7, 128.3, 128.1 *ppm*

MS (EI) : *m/z* 225 (M+1)

The above procedure was followed for the conversion of other alkynes to the corresponding α,β-unsaturated carboxylic acids.



Yield : 0.204 g (65%)

mp : 164-165 °C

IR (KBr) **:** 1674 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 8.16 (s, 1H), 7.20-6.60 (m, 8H), 2.38 (s, 3H), 2.09 (s, 3H) *ppm*

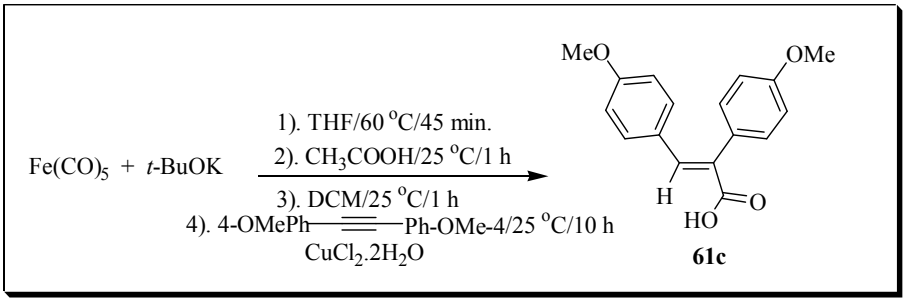
^{13}C NMR **:** (100 MHz) δ = 172.9, 140.8, 138.1, 136.7, 134.8, 133.5, 131.6, 130.3, 130.2, 130.0, 129.2, 128.9, 128.1, 125.9, 125.6, 20.1, 19.6.*ppm*

MS (EI) **:** *m/z* 253 (M+1)

Analysis **:** for $C_{17}H_{16}O_2$

Calculated: C, 80.93%; H, 6.39%

Found: C, 80.85%; H, 6.32%



Yield **:** 0.213 g (60%)

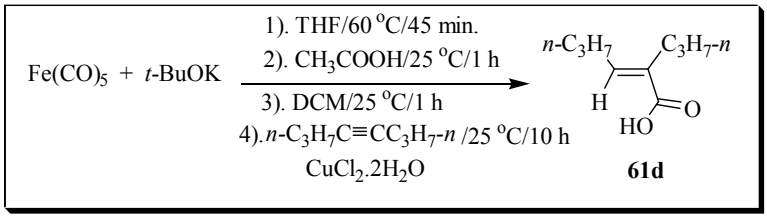
mp **:** 204-206 °C (Lit.[79a] mp 213-214 °C)

IR (KBr) **:** 1666 cm^{-1}

^{1}H NMR **:** (400 MHz, ($(CD_3)_2SO$)) δ = 7.66 (s, 1H), 7.06 (d, *J* = 8.8 Hz, 2H). 7.02 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 3.69 (s, 3H) *ppm* **(Spectrum No.17)**

^{13}C NMR **:** (100 MHz, $((CD_3)_2SO)$) δ = 168.9, 159.9, 158.6, 138.6, 132.0, 130.8, 130.4, 128.7, 127.1, 114.1, 113.9, 55.2, 55.1.*ppm* **(Spectrum No.18)**

MS (EI) **:** *m/z* 283 (M-1)



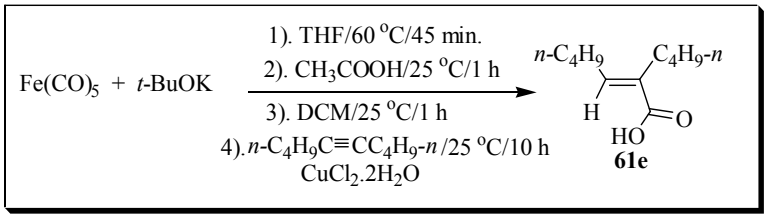
Yield **:** 0.127 g (65%)

IR (neat) **:** 1682 cm^{-1}

^{1}H NMR **:** (400 MHz) δ= 6.90 (t, *J* = 7.2 Hz, 1H), 2.26 (t, *J* = 8 Hz, 2H), 2.20-2.15 (m, 2H), 1.51-1.39 (m, 4H), 0.94 (t, *J* = 7.6 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H) *ppm*

^{13}C NMR **:** (100 MHz) δ = 173.9, 145.5, 131.8, 30.8, 28.4, 22.4, 21.9, 13.9, 13.8 *ppm*

MS (EI) **:** *m/z* 155 (M-1)



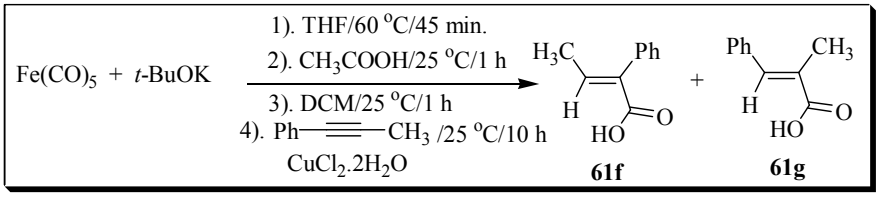
Yield **:** 0.156 g (68%)

IR (neat) **:** 1682 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 6.90 (t, J = 7.2 Hz, 1H), 2.28 (t, J = 7.2 Hz, 2H), 2.23-2.17 (m, 2H), 1.43-1.31 (m, 8H), 0.92 (t, J = 3.6 Hz, 3H), 0.89 (t, J = 3.6 Hz, 3H) *ppm* **(Spectrum No.19)**

^{13}C NMR **:** (100 MHz) δ = 173.8, 145.4, 131.9, 31.5, 30.8, 28.4, 26.2, 22.7, 22.4, 13.9, 13.8.*ppm* **(Spectrum No.20)**

MS (EI) **:** *m/z* 185 (M+1)



Compound 61f

Yield **:** 0.112 g (55.4%)

mp **:** 135-137 °C (Lit.[79b] mp 138-139 °C)

IR (KBr) **:** 1684 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 7.46-7.25 (m, 6H), 1.84 (d, J = 6.8 Hz, 3H) *ppm* **(Spectrum No.21)**

^{13}C NMR **:** (100 MHz) δ = 172.7, 142.8, 134.4, 134.2, 129.8, 128.0, 127.6, 15.7 *ppm* **(Spectrum No.22)**

Compound 61g

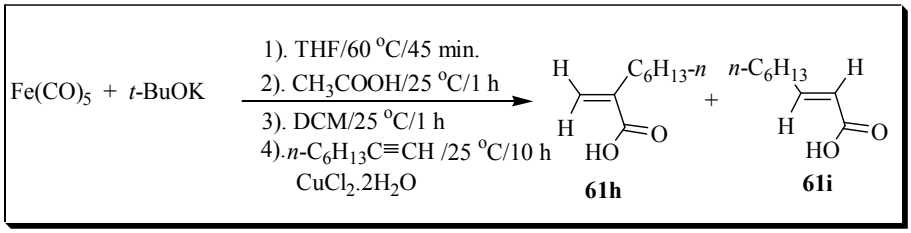
Yield **:** 0.046 g (22.6%)

mp **:** 70-72 °C (Lit.[79c] mp 76-80 °C)

^{1}H NMR **:** (400 MHz) δ = 7.85 (s, 1H), 7.46-7.36 (m, 5H), 2.12 (s, 3H) *ppm* **(Spectrum No.23)**

^{13}C NMR **:** (100 MHz) δ = 174.4, 141.1, 135.6, 129.9, 128.7, 128.5, 127.6, 13.7 *ppm* **(Spectrum No.24)**

MS (EI) **:** *m/z* 163 (M+1)



Compound 61h

Yield **:** 0.091 g (46.5%)

IR (neat) **:** 1697 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 6.27 (d, *J* = 1.2 Hz, 1H), 5.64 (d, *J* = 1.2 Hz, 1H). 2.30 (t, *J* = 7.2 Hz, 2H), 1.50-1.44 (m, 2H), 1.34-1.26 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H) *ppm*

^{13}C NMR **:** (100 MHz) δ = 173.1, 140.3, 126.9, 31.6, 31.5, 28.9, 28.3, 22.6, 14.1*ppm*

Compound 61i

Yield **:** 0.030 g (15.5%)

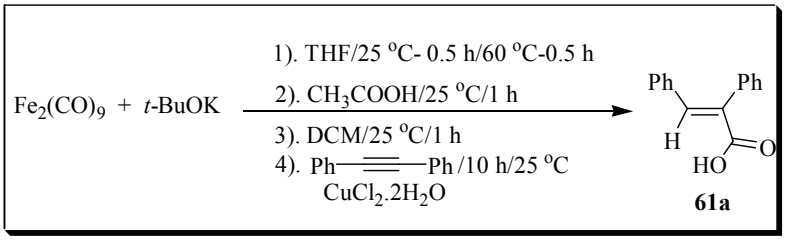
^{1}H NMR **:** (400 MHz) δ = 7.11 (dt, *J* = 15.6, 7.2 Hz, 1H), 5.84 (d, *J* = 15.6 Hz, 1H), 2.25 (m, 2H), 1.50-1.45 (m, 2H), 1.36-1.28 (m, 6H), 0.90 (t, *J* = 6.8 Hz, 3H) *ppm*

^{13}C NMR **:** (100 MHz) δ = 172.3, 152.6, 120.6, 32.3, 31.6, 28.8, 27.8, 22.5, 14.1 *ppm*

MS (EI) **:** *m/z* 155 (M-1)

1.4.7 Synthesis of (*E*)-2,3-diphenylacrylic acid 61a by using novel $Fe_2(CO)_9$/*t*-BuOK/AcOH/CH_2Cl_2 reagent system.

To a solution of $Fe_2(CO)_9$ (1.10 g, 3 mmol) in THF (25 mL), *t*-BuOK (0.67 g, 6 mmol) was added under dry nitrogen and stirred for 0.5 h at 25 ^oC and for 0.5 h at 60 $^\circ C$. The contents were brought slowly to 25 $^\circ C$ and acetic acid (0.34 mL, 6.0 mmol) was added and stirred for 1 h. Then dichloromethane (5 mL) was added and stirred for 1 h. Diphenylacetylene (0.178 g, 1.0 mmol) was added and the contents were further stirred for 10 h. The metal carbonyl complexes were oxidized using $CuCl_2.2H_2O$ (2.55 g, 15 mmol) in acetone (10 mL). Saturated NaCl solution was added and the contents were extracted with ether (2x40 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 (10%) in hexane eluted the (*E*)-2,3-diphenylacrylic acid **61a.**



Yield **:** 0.134 g (60%)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound previously obtained in reaction using the $Fe(CO)_5$/*t*-BuOK/AcOH/CH_2Cl_2 reagent system.

1.5 References

1. Wender, I.; Pino, P. *Organic Syntheses via Metal Carbonyls*, Wiley Interscience, New York, **1977**, vol. 1 & 2.
2. Haidue, I.; Zukerman, J. J., *Basic Principles in Organometallic Chemistry* (ed. Watter De Gruyter), New York, **1985**.
3. Beck, I. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 168.
4. Ellis, J. E.; Chi, K. M.; DiMaio, A. J.; Frerichs, S. R.; Stemzel, J. R.; Rheingol, L.; Haggerty, B. S. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 194.
5. Liebeskind, L. S.; Baysdon, S. L.; Souht, M. S.; Iyer, S.; Leeds, J. P. *Tetrahedron* **1985,** *41,* 5839.
6. (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. (Eds), *Principles and Applications of Organotransition Metal Chemistry,* University Science Books, Mill Valley, California, **1987**. **(**b) Khumtaveeporn, K.; Alper, H. *Acc. Chem. Res.* **1995**, *28,* 414. (c) Brunet, J. J. *Chem. Rev.* **1990,** *90,* 1041.
7. (a) Wilkinson, G.; Stone, F. G. A.; Abel, E. W. (Eds) *Comprehensive Organometallic Chemistry,* Pergamon Press, Oxford, New York, **1982**, Vol. 1-8.
8. Gustorf, E. A. K. V.; Grevels, F. -W.; Fischler, I. (Eds) *The Organic Chemistry of Iron,* Academic Press, New York, Vol. 1, **1978** and Vol. 2**, 1981.**
9. Schore, N. E. *Chem. Rev.* **1988**, *88,* 1081.
10. Mond, L.; Quincke, F. *J. Chem. Soc.* **1891**, *59*, 604.

11. Berthelot, M.; Hebd. C. R. *Seances Acad. Sci.* **1891**, *112*, 1343.

12. Kealy, T. J.; Pauson, P. L. *Nature* **1951**, *168*, 1039.

13. Reppe, W.; Vetter, H. *Justus Liebigs Ann. Chem*. **1953**, *582*, 133.

14. Sternberg, H. W.; Friedel, R. A.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1956**, *78*, 3621.

15. Hock, A. A.; Mills, O. S. *Acta Cryst.* **1961**, *14,* 139.

16. Efraty, A. *Chem. Rev.* **1977**, *77,* 691.

17. King, R**.** B.; Ackermann, M. N. *J. Organomet. Chem.* **1973**, *60,* C57.

18. (a) Suades, J.; Mathieu, R. *J. Organomet. Chem.* **1986**, *312,* 335. (b) Lourdichi, M.; Mathieu, R. *Organometallics* **1986**, *5,* 2067.

19. Semmelhack, M. F.; Tamura, R.; Schnatter, W.; Springer, J. *J. Am. Chem. Soc.* **1984**, *106***,** 5363.

20. Knolker, H. J.; Heber, J.; Mahler, C. H. *Synlett* **1992**, 1002.

21. Filippou, A. C.; Rosenauer, T. *Angew. Chem., Int. Ed*. **2002**, *41*, 2393.

22. Mathur, P.; Avasare, V. D.; Mobin, S. M. *Tetrahedron* **2008**, *64*, 8943.

23. King, R. B.; Eavenson, C. W. *J. Organomet. Chem.* **1972**, *42*, C95.

24. Pettersen, R. C.; Cihonski, J. L.; Young, F. R. III; Levenson. R. A. *J. Chem. Soc., Chem. Commun.* **1975**, 370.

25. Pearson, A. J.; Dubbert, R. A. *J. Chem. Soc.,Chem. Commun.* **1991**, 202.

26. Chin, H. B.; Bau, R. *J. Am. Chem. Soc.* **1973**, *95,* 5068.

27. (a) Sigman, M. S.; Kerr, C. E.; Eaton, B. E. *J. Am. Chem. Soc.* **1993**, *115,* 7545. (b). Sigman, M. S.; Eaton, B. E.; Heise, J. D.; Kubiak, C. P. *Organometallics* **1996**, *15,* 2829.

28. Noyori, R.; Hayakawa, Y.; Takaya, H.; Murai, S.; Kobayashi, R.; Sonoda, N. *J. Am. Chem. Soc.* **1978**, *100,* 1759.

29. Wilcox, C.; Breslow, R. *Tetrahedron Lett.* **1980**, *21,* 3241.

30. Shibata, T.; Koga, Y.; Narasaka, K. *Bull. Chem. Soc., Jpn*. **1995**, *68*, 911.

31. Usieli, V.; Victor, R.; Sarel, S. *Tetrahedron Lett.* **1976**, 2705.

32. Liebeskind, L. S. *Tetrahedron* **1989**, *45,* 3053.

33. Liebeskind, L. S.; Baysdon, S. L.; South, M. S. *J. Am. Chem. Soc.* **1980,** *102,* 7397.

34. Darbasie, N. D.; Schnatter, W. F. K.; Warner, K. F.; Manolache, N. *Tetrahedron Lett*. **2006**, *47*, 963.

35. (a) Braye, E. H.; Hubel, W. *J. Organomet. Chem.* **1965**, *3,* 25. (b) Neumann, M. F.; Martina, D. *Tetrahedron Lett.* **1977**, 2293. (c) Klimes, J.; Weiss, E. *Chem. Ber.* **1982**, *775*, 2175.

36. Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21,* 711.

37. Narasaka, K.; Shibata, T. *Chem. Lett.* **1994**, 315.

38. Banide, E. V.; Oulie, P.; Muller-Bunz, H.; McGlinchey, M. J. *Organometallics* **2008,** *27,* 5657.

39. Whiting, M. C. *Chem. Weekblad* **1963**, *53*, 119.

40. Periasamy, M.; Radhakrishnan, U.; Brunet, J. J.; Chauvin, R.; Elzaizi, A. J. *Chem. Commun.* **1996**, 1499.

41. (a) Periasamy, M.; Rameshkumar, C.; Radhakrishnan, U.; Brunet. J. J. *J. Org. Chem.* **1998**, *63,* 4930. (b). Periasamy, M.; Radhakrishnan, U.; Rameshkumar, C.; Brunet. J. J. *Tetrahedron Lett.* **1997**, *38,* 1623.

42. Rameshkumar, C.; Periasamy, M. *Organometallics* **2000**, *19*, 2400.

43. Periasamy, M.; Rameshkumar, C.; Radhakrishnan, U. *Tetrahedron Lett*. **1997**, *38,* 7229.

44. Rameshkumar, C.; Periasamy, M. *Tetrahedron Lett.* **2000**, *41*, 2719.

45. Periasamy, M.; Rameshkumar, C.; Mukkanti, A. *J. Organomet. Chem.* **2002***, 649,* 209.

46. Periasamy, M.; Mukkanti, A.; Shyam Raj, D. *Organometallics* **2004**, *23*, 619.

47. Periasamy, M.; Mukkanti, A.; Shyam Raj, D. *Organometallics* **2004**, *23*, 6323.

48. Radhakrishnan, U.; Periasamy, M. *Organometallics* **1997**, *16*, 1800.

49. Mukkanti, A. Ph. D. Thesis, **2004**, University of Hyderabad, Hyderabad, India.

50. (a) Jewell, C. F. Jr.; Liebeskind, L. S.; Williamson, M. *J. Am. Chem. Soc*. **1985**, *107*, 6715. (b) Liebeskind, L. S.; Iyer, S.; Jewell, C. F. Jr. *J. Org. Chem.* **1986**, *51*, 3065. (c) Liebeskind, L. S.; Bombrum, A. *J. Org. Chem*. **1994**, *59*, 6856.

51. (a) Shi, X.; Amin, R.; Liebeskind, L. S. *J. Org. Chem*. **2000**, *65,* 1650. (b) Shi, X.; Liebeskind, L. S. *J. Org. Chem*. **2000**, *65*, 1665. (c) Pena-Cabrera, E.; Liebeskind,

L. S. *J. Org. Chem*. **2002,** *67*, 1689. (d) Aguilar-Aguilar, A. L.; Liebeskind, L. S.; Pena-Cabrera, E. *J. Org. Chem.* **2007**, *72*, 8539.

52. (a) Karlsson, J. O.; Nguyen, N. V.; Foland, L. D.; Moore, H. W. *J. Am. Chem. Soc*. **1985**, *107*, 3392. (b) Moore, H. W.; Decker, O. H. *Chem. Rev*. **1986**, *86*, 821. (c) Lee, K. H.; Moore, H. W. *J. Org. Chem.* **1995**, *60*, 735. (d) Taing, M.; Moore, H. W. *J. Org. Chem*. **1996***, 61*, 329.

53. (a) Negri, J. T.; Morwick, T.; Doyon, J.; Wilson, P. D.; Hickey, E. R.; Paquette, L. A. *J. Am. Chem. Soc*. **1993**, *115*, 12189. (b) Paquette, L. A.; Morwick, T. M. *J. Am. Chem. Soc*. 1**997**, *119*, 1230. (c) Paquette, L. A.; Kuo, L. H.; Tae, J. *J. Org. Chem*. **1998**, *63*, 2010. (d) Geng, F.; Liu, J.; Paquette, L. A. *Org. Lett.* **2002,** *4*, 71.

54. (a) Danheiser, R. L.; Gee, S. K.; Sard, H. *J. Am. Chem. Soc*. **1982**, *104,* 7670. (b) Danheiser, R. L.; Gee, S. K. *J. Org. Chem*. **1984**, *49*, 1672. (c) Danheiser, R. L.; Gee, S. K.; Perez, J. J. *J. Am. Chem. Soc*. **1986**, *108*, 806.

55. (a) Law, K. Y.; Bailey, F. C. *J. Org. Chem*. **1992**, *57*, 3278. (b) Kinney, W. A.; Abou-Gharbia, M.; Garrison, D. T.; Schmidt, J.; Kowal, D. M.; Bramlett, D. R.; Miller, T. L.; Tasse, R. P.; Zaleska, M. M.; Moyer, J. A. *J. Med. Chem*. **1998**, *41,* 236. (c) Bang-Andersen, B.; Ahmadian, H.; Lenz, S. M.; Stensbøl, T. B.; Madsen, U.; Bogeso, K. P.; Krogsgaard-Larsen, P. *J. Med. Chem*. **2000**, *43*, 4910. (d) Kinney, W. A. *Tetrahedron Lett*. **1993**, *34*, 2715. (e) Xie, J.; Comeau, A. B.; Seto, C. T. *Org. Lett*. **2004**, *6,* 83.

56. (a) Tomas, S.; Rotger, M. C.; Gonzalez, J. F.; Deya, P. M.; Ballester, P.; Costa, A. *Tetrahedron Lett*. **1995**, *36,* 2523. (b) Tomas, S.; Prohens, R.; Deslongchamps, G.; Ballester, P.; Costa, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2208. (c) Prohens, R.; Martorell, G.; Ballester, P.;Costa, A. *Chem. Commun*. **2001**, 1456.

57. Zhang, J.; Zhou, H.-B.; Lu, S.-M.; Luo, M.-M.; Xie, R. G.; Choi, M. C. K.; Zhou, Z.-Y.; Chan, S. C.; Yang, T. K. *Tetrahedron: Asymmetry* **2001**, *12*, 1907.

58. (a) Zhang, S.; Liebeskind, L. S. *J. Org. Chem*. **1999**, *64*, 4042. (b) Mingo, P.; Zhang, S.; Liebeskind, L. S. *J. Org. Chem*. **1999**, *64,* 2145. (c) Wipf, P.; Hopkins, C. R. *J. Org. Chem***. 1999**, *64*, 6881. (d) Tiedemann, R.; Turnbull, P.; Moore, H. W. *J. Org. Chem*. **1999**, *64*, 4030.

59. Mukkanti, A.; Periasamy, M. *ARKIVOC* **2005**, (*xi*), 48 and references therein.

60. Periasamy, M.; Beesu, M.; Shyam Raj, D. *J. Organomet. Chem*. **2008**, *693*, 2843.

61. Bricker, J. C.; Martin, W. P.; Shore, S. G. *Organometallics* **1987**, *6*, 2545.

62. (a) Shvo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun*. **1975**, 829. (b) Elzinga, J.; Hogeveen, H. *J. Chem. Soc., Chem. Commun*. **1977**, 705.

63. (a) Salaun, J. Y.; le Gall, G.; Laurent. P.; des Abbayes, H. *J. Organomet. Chem*. **1992***, 441*, 99. (b) Cabon, P.; Rumin, R.; Salaun, J. Y.; Triki, S.; des Abbayes, H. *Organometallics*. **2005**, *24*, 1709.

64. Beesu, M.; Periasamy, M. *J. Org. Chem*. **2011**, *76*, 543.

65. (a) Liebeskind, L. S.; Richard, W. F. *J. Org. Chem*. **1990**, *55*, 5359. (b) Liebeskind, L. S.; Richard, W. F.; Kevin, R. W.; Thomas T. S.; *J. Org. Chem*. **1990**, *55*, 2482.

(c) Michael, W. R.; Daniel, J. P.; Steven, T. P.; Lafayette, D. F.; Harold, W. M. *J. Org. Chem*. **1988**, *53*, 2477.

66. (a) Sharad, K. V.; Everly, B. F.; Harold, W. M. *J. Org. Chem.* **2000**, *65*, 8564. (b) Leo, A. P.; Tina, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 1607. (c) Steven, T. P.; Harold, W. M. *J. Am. Chem. Soc*. **1990**, *112*, 1897. (d) Michael, W. R.; Harold, W. M. *J. Org. Chem.* **1988**, *53*, 4166. (e) Michael, W. R.; Harold, W. M. *J. Org. Chem*. **1987**, *52,* 3491.

67. (a) Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc*. **1974**, *96*, 1233. (b) Casarin, M.; Ajo, D.; Granozzi, G.; Tondello, E.; Aime, S. *Inorg. Chem*. **1985**, *24*, 1241.

68. (a) Rajesh, T.; Periasamy, M. *Tetrahedron Lett.* **1998**, *39*, 117. (b) Sugihara, T.; Yamada, M.; Ban, H.; Yamaguchi, M.; Kaneko, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2801.

69. Cotton, F. A.; Troup, J. M. *J. Am. Chem. Soc.* **1974**, *96,* 3438.

70. Kondo, T.; Nakamura, A.; Okada, T.; Suzuki, N.; Wada, K.; Mitsudo, T. *J. Am. Chem. Soc.* **2000,** *122,* 6319.

71. (a) Derien, S.; Clinet, J.-C; Duiiach, E.; Perichon. J. *J. Org. Chem.* **1993,** *58***,** 2578**.** **(**b) Scrivanti, A.; Matteoli, U. *Tetrahedron Lett*. **1995,** *36,* 9015. (c) Brunet, J. J.; Passelaigue, E. *Organometallics* **1990,** *9*, 1711. (d) Kim, I. S.; Krische, M. J**.** *Org. Lett.* **2008,** *10*, 513. (e) Ojima, I. *Chem. Rev*. **1988**, *88*, 1011. (f) Zargarian, D.; Alper, H. *Organometallics* **1991,** *10*, 2914. (g) Al-Masum, M.; Yamamoto, Y. *J.*

Am. Chem. Soc. **1998,** *120,* 3809. (h) Williams, C. M.; Johnson, J. B.; Rovis, T. *J. Am. Chem. Soc*. **2008**, *130*, 14936.

72. Pino, P.; Braca, G. *Organic Syntheses via Metal Carbonyls;* John Wiley and sons: New York, **1977**, *2*, 419.

73. Callow, R. K.; Johnston, N. C. *Bee World* **1960**, *41*, 152.

74. Cho, H.; Ueda, M.; Tamaoka, M.; Hamaguchi, M.; Aisaka, K.; Kiso, Y.; Inoue, T.; Ogino, R.; Tatsaoka, T.; Ishihara, T.; Noguchi, T.; Morita, I.; Murota, S. *J. Med. Chem*. **1991**, *34*, 1503.

75. Watanabe, T.; Hayashi, K.; Yoshimatsu, S.; Sakai, K.; Takeyma, S.; Takashima, K. *J. Med. Chem.* **1980**, *23*, 50.

76 Mio, M. J.; Kopel, L. C.; Braun, J. B.; Gadzikwa, T. L.; Hull, K. L; Brisbois, R. G.; Markworth, C. J.; Grieco. P. A. *Org. Lett.* **2002**, *4*, 3199. (b). Elangovan, A.; Wang, Y. H.; Ho, T. I. Org. Lett. **2003**, *5*, 1841.

77 (a) Liebeskind, L. S.; Baysdon, S. L. *Tetrahedron Lett*. **1984**, *25*, 1747. (b) Parker, M. S. A.; Rizzo, C. J. *Syn. Commun.* **1995**, *25*, 2781. (c) Liebeskind, L. S. *Tetrahedron Lett*. **1990**, *31*, 4293. (d) Ried, W. Liebigs *Annalen der Chemie*. **1982**, *2*, 355.

78. Ronghua, L.; Thomas T. *J. Chem. Soc., Perkin Trans. 2***, 1996**, 2757.

79. (a) Oh, K.; Kim, S.; Lee, J.; Cho, W.; Lee, T.; Kim, S. *J. Med. Chem.* **2004**, *47*, 2418. (b) Palmer, F. N.; Lach, F.; Poriel, C.; Pepper, A. G.;Bagley, M. C; Slawin, A. M. Z.; Moody. C. J**.** *Org. Biomol. Chem*., **2005**, *3*, 3805. (c) Dalcanale, E. *J. Org . Chem***. 1986,** *51***,** 567.

Chapter 2

Conversion of Cyclobutenediones to New Functionalized Organic Compounds

2.1 Introduction

2.1 Reactions of carbonyl compounds catalyzed by L-proline and secondary amines

In recent years, organocatalysis has been widely used in organic synthesis.[1,2] Organocatalysis offers many advantages for synthetic organic chemistry. In contrast to many metal catalysts, most organocatalysts are stable to air and water, easily handled experimentally, relatively nontoxic and readily separated from the crude reaction mixture.

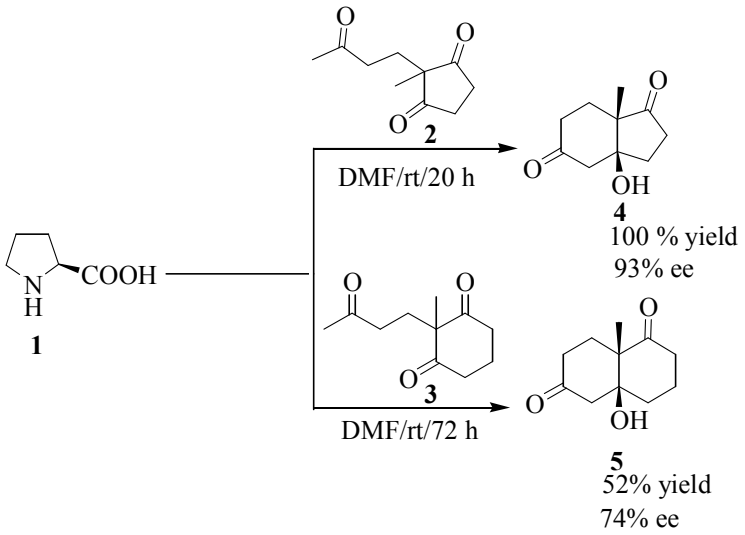
Among various organic catalysts, L-proline and secondary amines have been widely used.[3] As discussed in chapter **1**, methods have been developed for cyclobutenedione synthesis using iron carbonyls and alkynes. We became interested to examine the reactivity pattern of cyclobutenediones in the presence of L-proline and pyrrolidine reagents. Organocatalysts with secondary amine functionality are useful in either enamine catalysis through forming catalytic quantities of an active enamine nucleophile or iminium catalysis by forming catalytic quantities of an activated iminium electrophile. A brief review on L-proline and secondary amines catalyzed organic transformations will be helpful for the discussion.

2.1.1 L-Proline catalyzed aldol reactions

2.1.1.1 L-Proline catalyzed intramolecular aldol reactions

One of the extensively studied organocatalyzed reaction is the aldol condensation of aldehydes and ketones. The aldol reaction is among the most commonly applied C-C bond forming reactions.[4] The versatility of this reaction stems from its utility in constructing chiral building blocks via the stereoselective formation of C-C bonds for the synthesis of structurally complex molecules, namely natural products or non-natural drug molecules. For example, in the presence of L-proline **1** the triketones **2** and **3** undergo intra molecular aldol reaction to furnish the corresponding aldols **4** and **5** in good yields with high enantioselectivity (**Scheme 1**).[5,6]

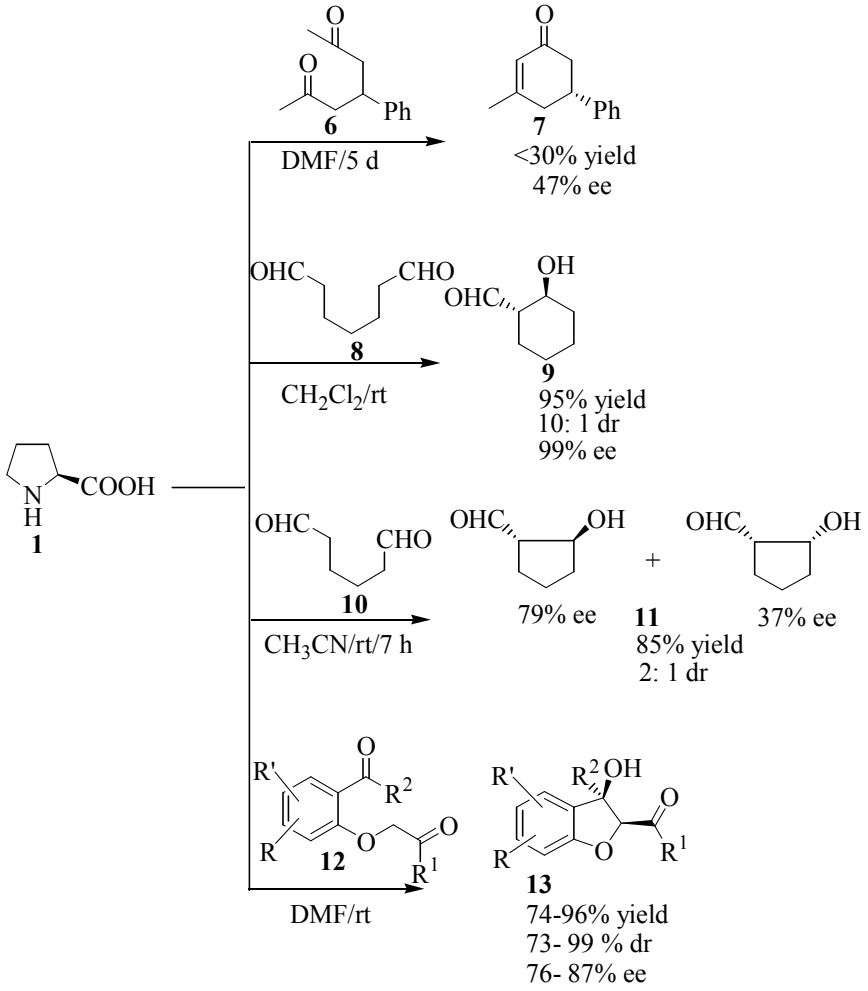
Scheme 1



It was reported that the acylic 4-substituted 2,6-heptandiones **6**, achiral heptanedials **8,** hexanedial **10**, dicarbonyl compounds **12** undergo intramolecular aldol reaction in the

presence of L-proline catalyst to provide the corresponding cyclohexenone derivative **7,** *anti*-aldols **9**, 5-enolexo aldols **11** and 2,3-dihydrobenzofuranols **13** (**Chart 1**).[7-11]

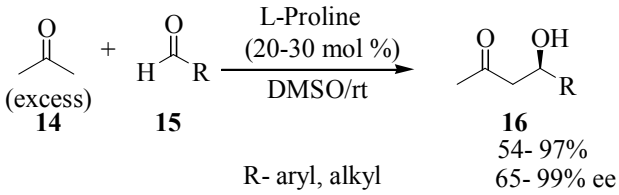
Chart 1



2.1.1.2 L-Proline catalyzed intermolecular aldol reactions

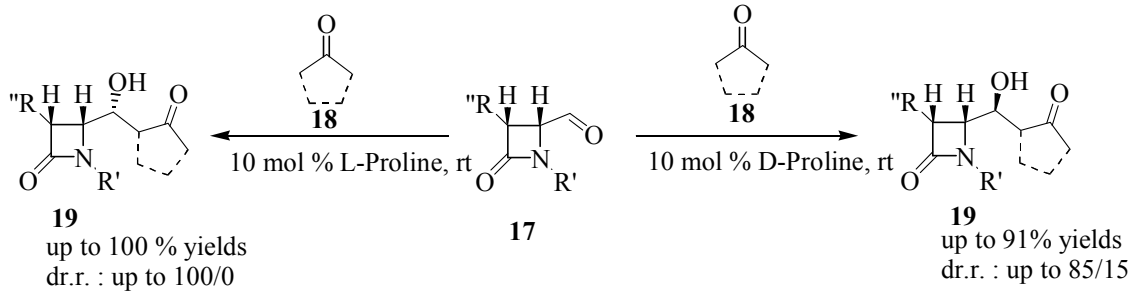
In the presence of a catalytic amounts of L-proline (typically 20-30 mol %) in DMSO, acetone undergoes aldol reaction with aromatic and α-branched aldehydes, to provide the corresponding aldols **16** in good yields and enantioselectivities (**Scheme 2**).[12]

Scheme 2



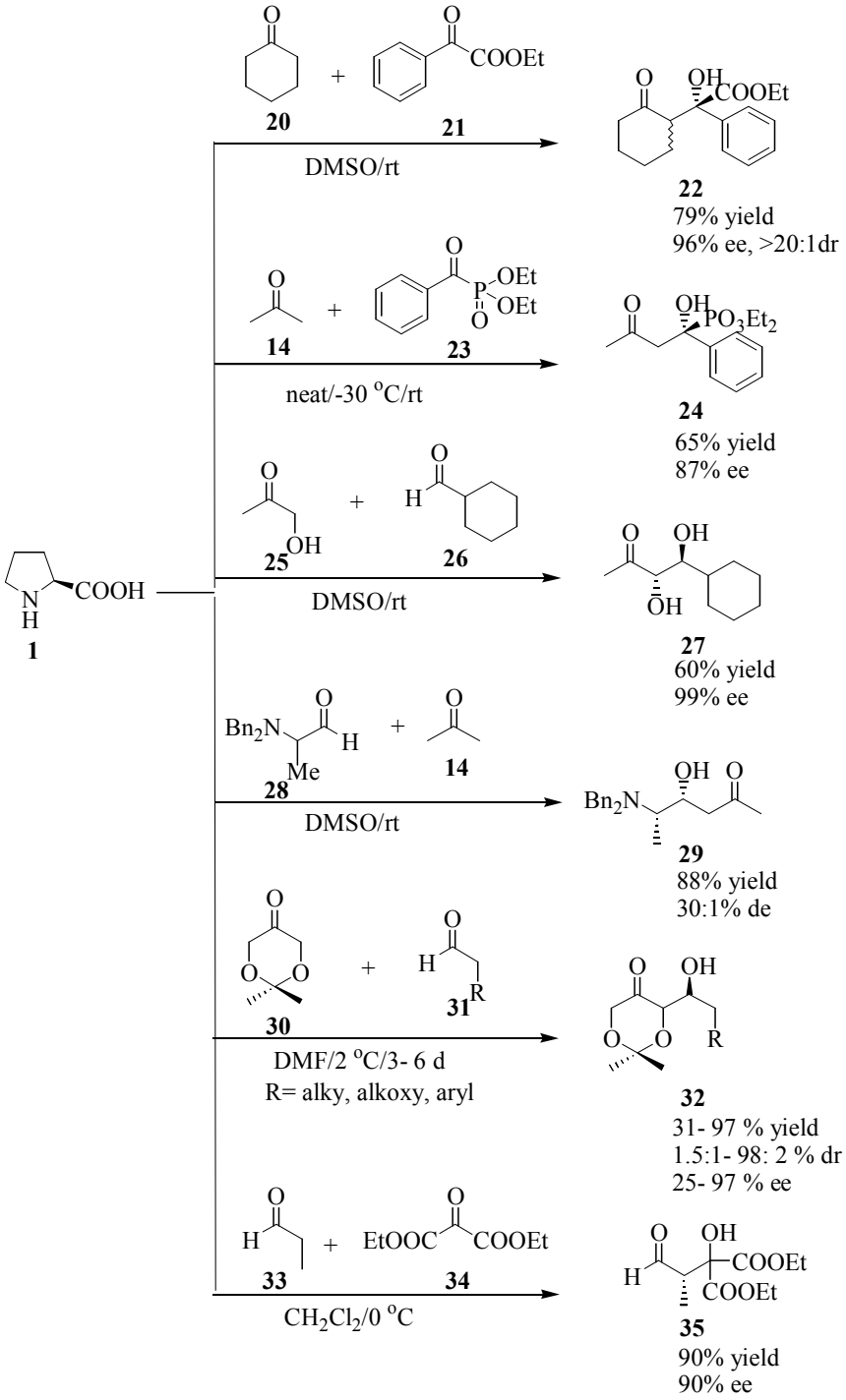
Unmodified ketones undergo aldol reaction with 4-oxoazetidine-2-carbaldehydes **17** in the presence of catalytic amount of L-proline or D-proline, to give the corresponding *γ*-amino-*α*-hydroxy ketones **19** with good yields and diastereoselectivities (**Scheme 3**).[22]

Scheme 3



Several other intermolecular asymmetric transformations have been reported (**Chart 2**).[13-17, 20]

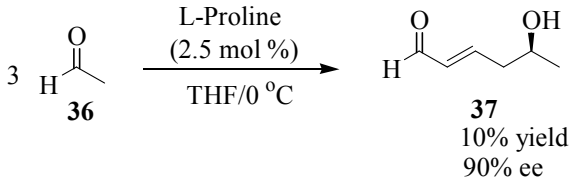
Chart 2


COOH
N
H
1
20
21
COOEt
DMSO/rt
22
79% yield
96% ee, >20:1dr
14
23
OEt
OEt
neat/-30 °C/rt
24
65% yield
87% ee
25
OH
26
DMSO/rt
27
60% yield
99% ee
Bn2N
Me
28
14
DMSO/rt
29
88% yield
30:1% de
30
31
R
DMF/2 °C/3- 6 d
R= alky, alkoxy, aryl
32
31- 97 % yield
1.5:1- 98: 2 % dr
25- 97 % ee
33
EtOOC
COOEt
34
CH2Cl2/0 °C
35
90% yield
90% ee

2.1.1.3 L-Proline catalyzed self aldol reactions

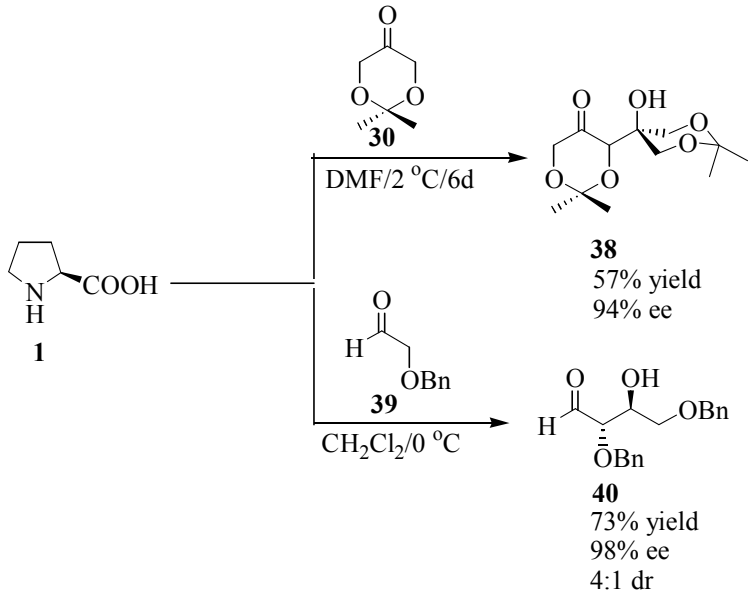
In the presence of catalytic amount of L-proline, acetaldehyde **36** undergoes enantioselective self-aldolization reaction to provide the 5-hydroxy-(2*E*)-hexenal **37**, an aldol trimer of acetaldehyde, with up to 90% ee in low yield (**Scheme 4**).[19]

Scheme 4



The 2,2-dimethyl-1,3-dioxan-5-one (DHA) **30** and α-oxyaldehyde **39** undergo self-aldolization to afford the corresponding aldol adduct **38** and **40** in better yields under L-proline catalysis (**Scheme 5**).[18, 21]

Scheme 5

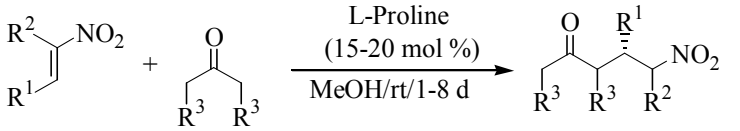


2.1.2 L-Proline and secondary amine catalyzed Michael reactions

The C-C bond formation by conjugate addition of nucleophiles to the *β*-position of α,*β*-unsaturated carbonyl compounds (Michael reaction) are frequently used in organic synthesis.[23] In the case of carbonyl compounds, in organocatalytic Michael addition reactions, the donors are activated via formation of enamine or enol intermediates and the acceptors are activated via formation of iminium ion intermediates. Among different Michael acceptors, nitroalkenes, alkylidene malonate and vinyl ketones are the most commonly used because of their high reactivity and the possible further conversion of the product to other useful functionalities.

The unactivated symmetric ketones **42** react with nitroolefins **41** to furnish the γ-nitro ketones **43** in high yields and good diastereoselectivities but only with low enantioselectivities (**Scheme 6**).[24]

Scheme 6

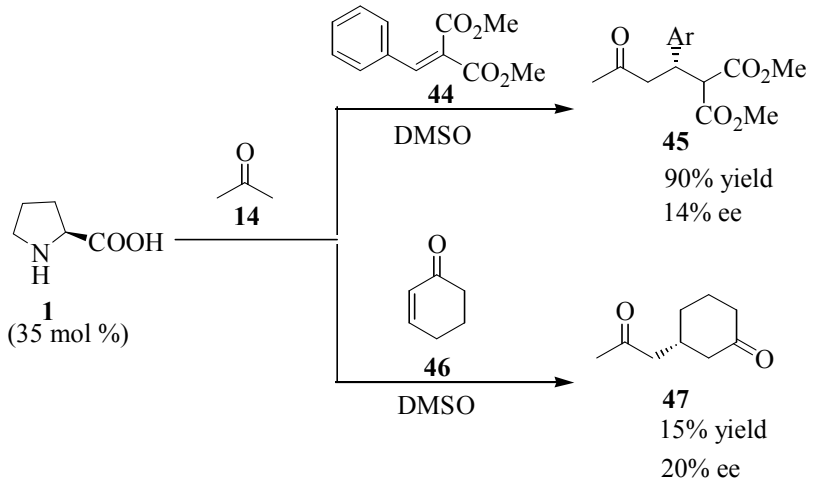


41 **42** **43**

74-97 % yield
0-76% ee
10:1- 20:1 dr

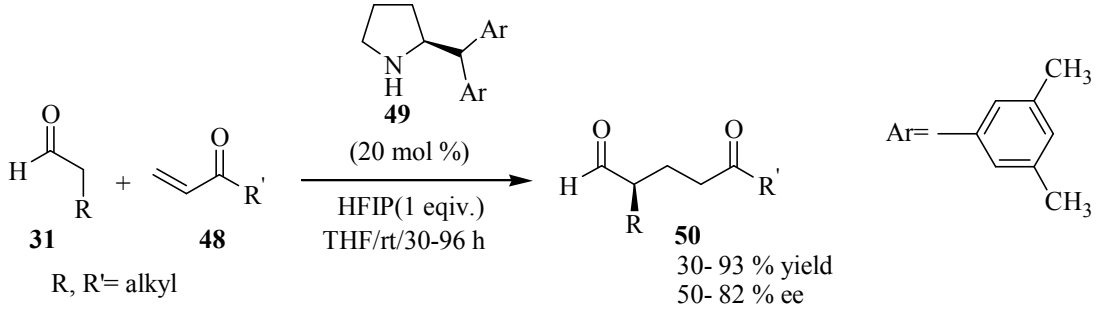
It has been reported that acetone **14** undergoes proline catalyzed Michael addition reaction with aromatic alkylidene malonate **44** and cyclohexenone **46** in DMSO solvent. The corresponding Michael adducts **45** and **47** were formed respectively in 90% (14% ee) and 15% (20% ee) yields (**Scheme 7**).[25]

Scheme 7



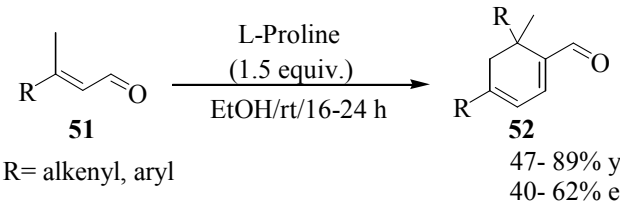
Simple aldehydes **31** undergo Michael addition reaction with vinyl ketones **48** in the presence of (*S*)-2-[bis(3,5-dimethylphenyl) methyl]pyrrolidine catalyst **49** to give the 5-keto aldehydes **50** in good yields and good enantioselectivity (**Scheme 8).**[26]

Scheme 8



α,β-Unsaturated aldehydes **51** undergo self-condensation to give the trisubstituted cyclohexadienes **52** in good yields and moderate enantioselectivity under proline catalysis (**Scheme 9**).[27]

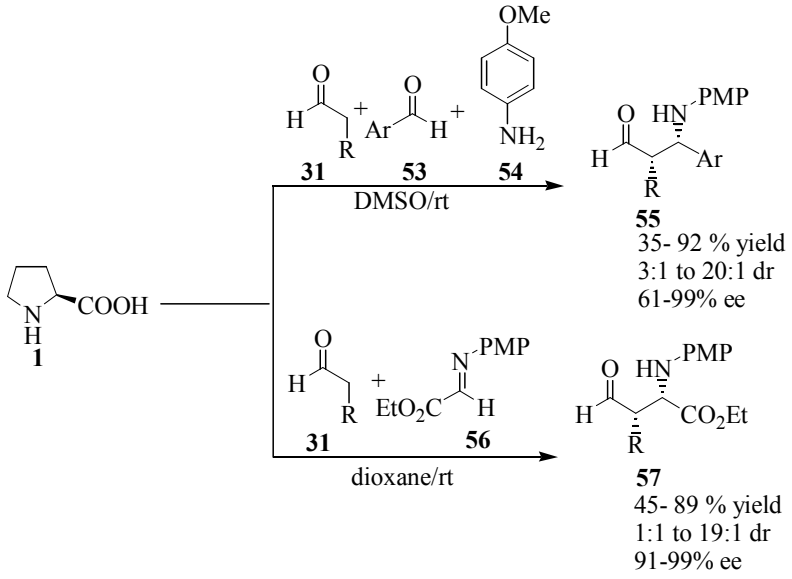
Scheme 9



2.1.3 L-Proline catalyzed Mannich reaction

Aliphatic **31** and aromatic aldehydes **53** and amines **54** and *N*-PMP-protected α-imino glyoxylates **56** undergo Mannich reactions to afford the *β*-amino carbonyl compounds **55** and **57** in the presence of L-proline catalyst (**Scheme 10**).[28,29]

Scheme 10

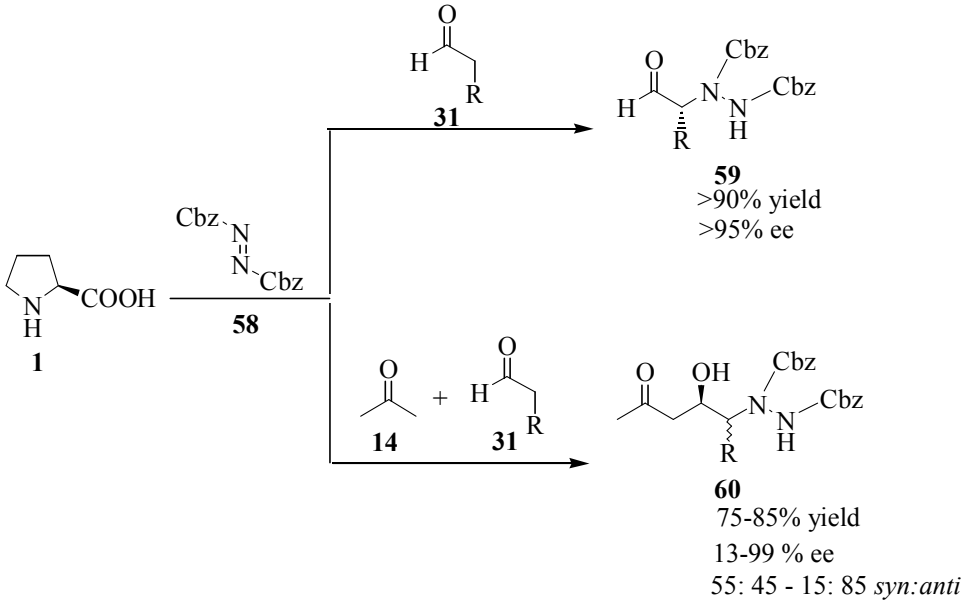


2.1.4 Other organocatalytic transformations

It has been reported that L-proline is also useful as a catalyst for α-amination of aldehydes. Simple aldehydes **31** and a mixture of acetone and aldehydes undergo reaction

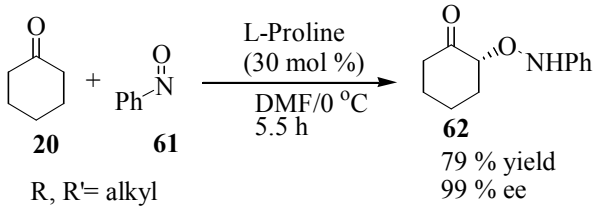
with azodicarboxylates **58** to give the corresponding α-hydrazino aldehydes **59** and β-amino alcohols **60** (**Scheme 11**).[30, 31]

Scheme 11



Cyclohexanone **20** reacts with nitrosobenzene **61** in the presence of L-proline in DMF solvent to give the α-aminoxylated ketone **62** with good yields and enatioselectivity (**Scheme 12**).[32]

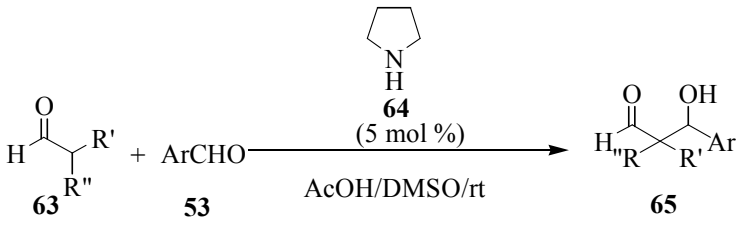
Scheme 12



In the presence of catalytic quantities of pyrrolidine **64** (5 mol %) and acetic acid, α, α-dialkylaldehydes **63** undergo aldol reaction with aryl aldehydes (**Scheme 13**).[33] The

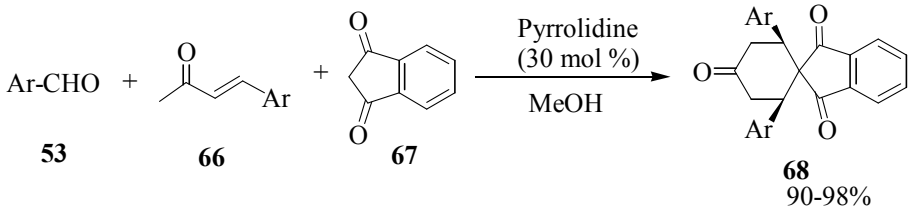
corresponding quaternary carbon containing aldol products **65** were obtained in good yields. It was observed that L-proline is a poor catalyst for this reaction.[33]

Scheme 13



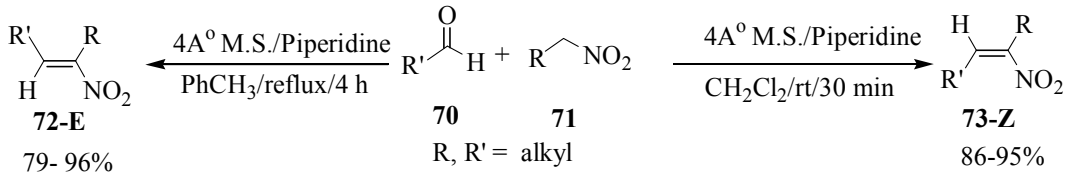
The 1,3-indandione **67** reacts with aromatic aldehydes and α,β-unsaturated ketones **66** in the presence of pyrrolidine **64** to give the corresponding spiro compounds **68** in excellent yields with *syn*-selectivity (**Scheme 14**).[34]

Scheme 14



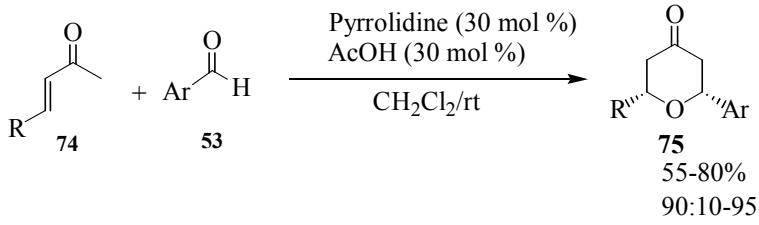
In the presence of catalytic amounts of piperidine **69** and 4Å molecular sieves, aliphatic aldehydes **70** reacts with nitro alkanes **71** to give the (*E*)- or (*Z*)-nitro alkenes (**72** or **73**) in good yields.[35] Simply by changing reaction conditions (solvent and temperature), it is possible to control the stereochemical outcome of the reaction (**Scheme 15**).[35]

Scheme 15



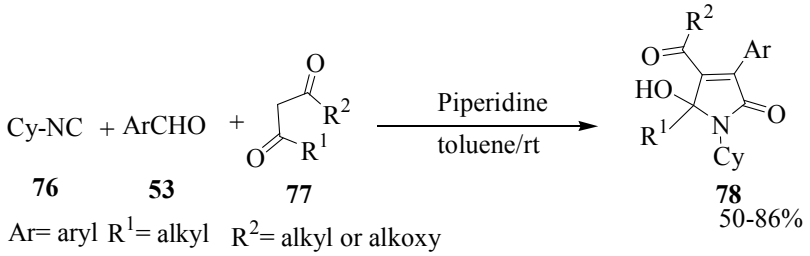
Acyclic α,β–unsaturated ketones **74** undergo oxa-Diels–Alder reaction with aldehydes in the presence of 30 mol % pyrrolidine **64** and AcOH to give the substituted tetrahydropyran-4-ones **75** in good yields with >95% diastereoselectivity (**Scheme 16**).[36]

Scheme 16



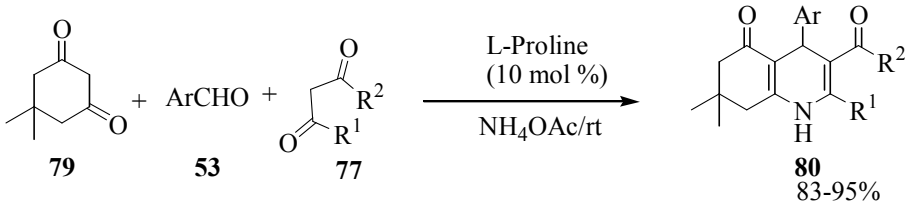
In the presence catalytic quantity of piperidine **69**, cyclohexyl isocyanide **76** react with various aldehydes and 1,3-dicarbonyl compounds **77** to give the 5-hydroxy-2H-pyrrol-2-one **78** derivatives in moderate to good yields (**Scheme 17**). [37]

Scheme 17



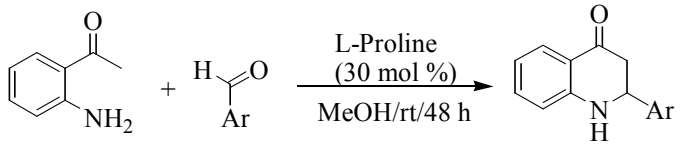
Polyhydroquinoline derivatives **80** were obtained in good yields from aldehyde, dimedone **79**, acetoacetate ester or acetylacetone **77** and ammonium acetate in the presence of L-proline **1** catalyst (**Scheme 18**).[38]

Scheme 18



2-Aminoacetophenone **81** reacts with aryl aldehyde in the presence of 30 mol % of L-proline to give the substituted 2-aryl-2,3-dihydroquinolin-4(1H)-ones **82** in good yields. The efficiency of the catalyst was established using a variety of electron-deficient to electron-rich aryl aldehyde substrates (**Scheme 19**).[39]

Scheme 19

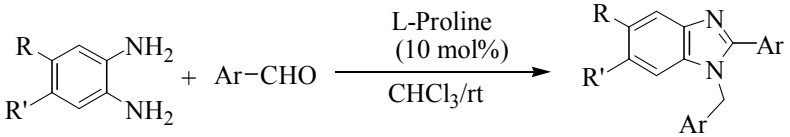


81 **53** **82**

79-93 %

In the presence of L-proline **1**, *o*-phenylenediamines **83** and aryl aldehydes **53** undergo condensation in chloroform solvent at ambient temperature to give the 2-aryl-1-arylmethyl-benzimidazoles **84** in moderate to excellent yields via the corresponding iminium ion intermediate (**Scheme 20**).[40]

Scheme 20

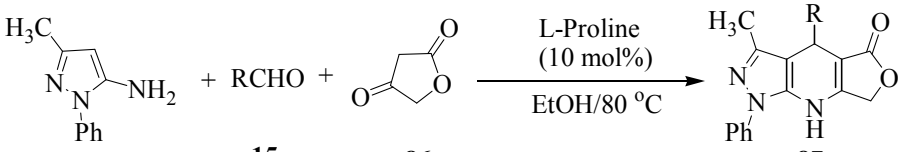


83 **53** **84**

32-95%

5-Amino-1-phenyl-3-methylpyrazole **85** and aldehydes **15** undergo reaction with tetronic acid **86** in the presence of catalytic amount of L-proline to give the 3-methyl-1-phenyl-4-substituted-4,8-dihydrofuro[30,40:5,6]pyrido[2,3-c]pyrazole derivatives **87** in ethanol and the products were obtained in moderate to good yields (**Scheme 21**).[41]

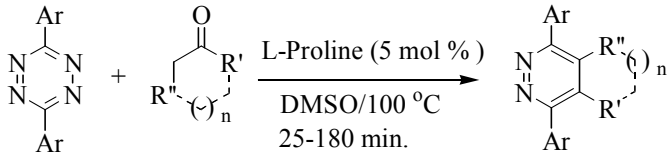
Scheme 21



85 **15** **86** **87**
59-97%

Cyclic and acyclic ketones participate in Diels–Alder reaction with 1,2,4,5-tetrazines **88** in the presence of catalytic amount of L-proline, to give the corresponding adducts **90** in high yields. The transformation was explained via formation of an enamine intermediate (**Scheme 22**).[42]

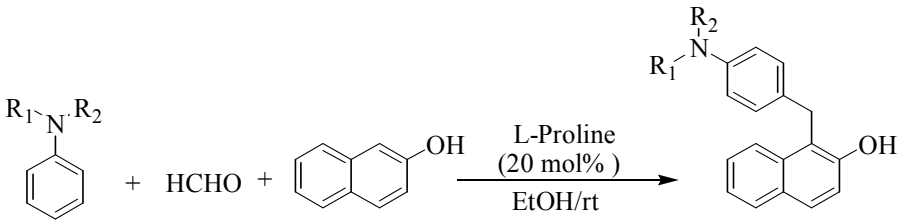
Scheme 22



88 **89** **90**
75-98 %

Tertiary aromatic amines **91**, formaldehyde **92** and 2-naphthols **93** undergo Mannich type reactions in the presence of 20 mol % of L-proline to produce the corresponding diarylmethane derivatives **94** in moderate to good yields (**Scheme 23**).[43]

Scheme 23

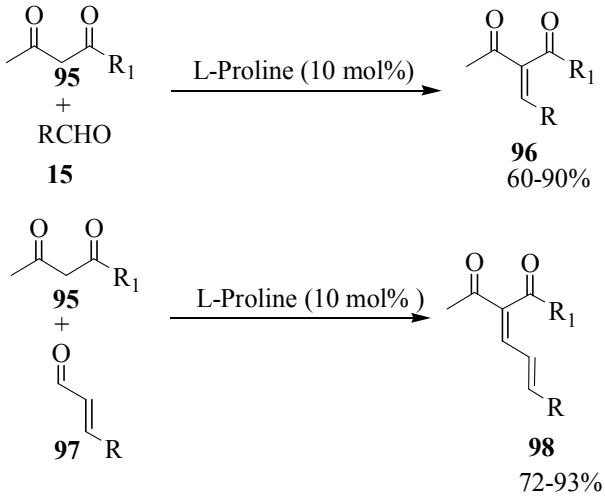


91 **92** **93** **94**
74-82%

Aldehydes undergo aldol condensation reaction with 1,3-dicarbonyl compounds **95** in the presence of catalytic amount of L-proline to give the corresponding conjugated

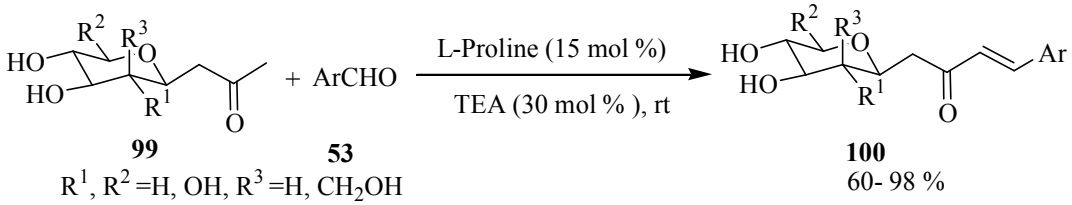
enones **96** and dienones **98**. In these reactions, only one isomer was obtained with most of the 1,3-dicarbonyl compounds and aldehydes (**Scheme 24**).[44]

Scheme 24



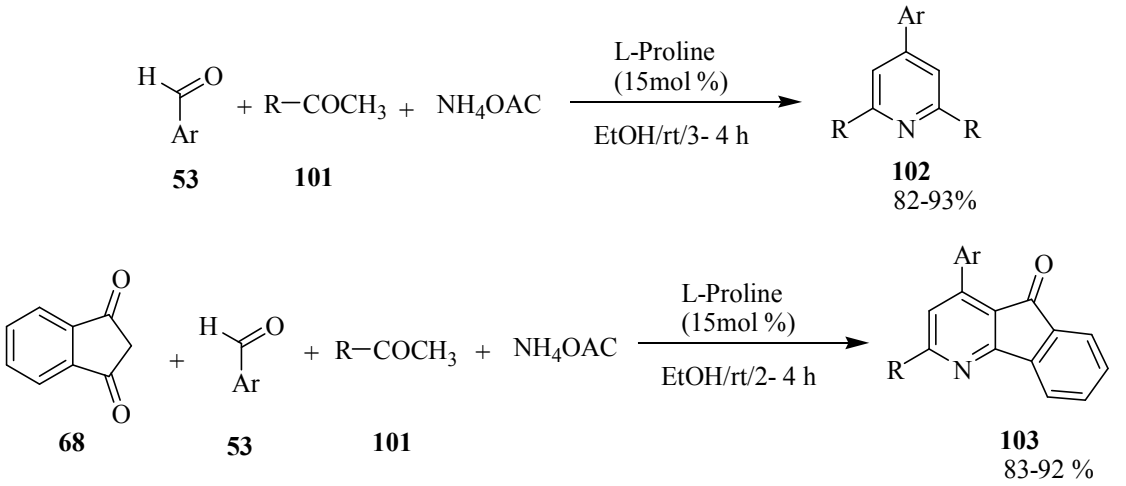
In the presence of catalytic quantities of L-proline and triethylamine (TEA), various ketones and a wide range of aldehydes undergo aldol condensation to produce the corresponding (*E*)-α,β-unsaturated ketones **100** in excellent yields (**Scheme 25**).[45]

Scheme 25



In the presence of 15 mol % of L-proline, aryl aldehydes **53,** aryl methyl ketone **101** and NH_4OAc undergo condensation reaction to give the symmetrically substituted pyridine derivatives **102**. When this reaction was carried out in the presence of indan-1,3-dione **68**, highly substituted pyridine derivatives **103** were obtained (**Scheme 26**).[47]

Scheme 26

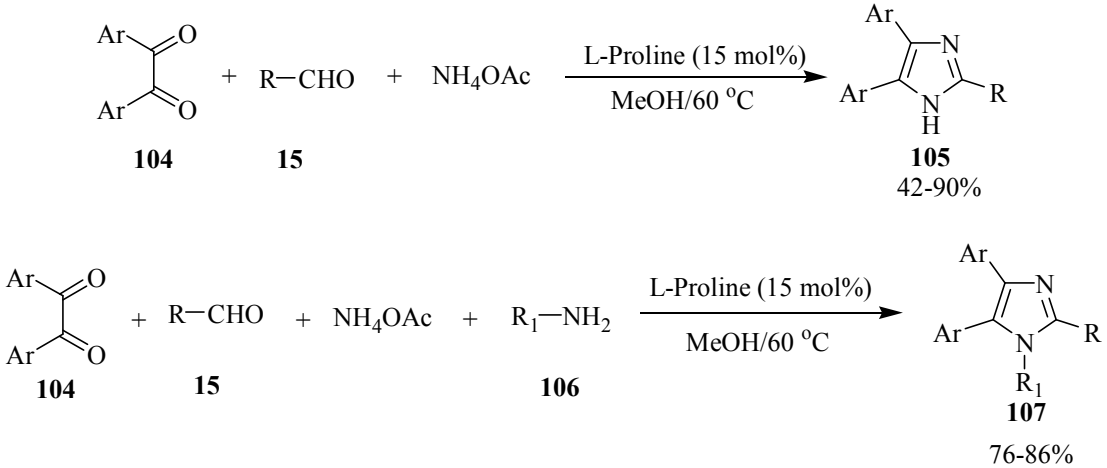


53 **101** **102** 82-93%

68 **53** **101** **103** 83-92 %

2,4,5-Trisubstituted imidazoles **105** were obtained in the three component cyclocondensation of 1,2-dicarbonyl compound **104**, aldehyde **15** and ammonium acetate in the presence of 15 mol % of L-proline in methanol solvent. In this process, the products were obtained in high yields and purified by non-chromatographic methods. When the above reaction was carried out in the presence of primary amine **106**, the N-substituted imidazole derivatives **107** were obtained in good yields (**Scheme 27**).[46]

Scheme 27



104 **15** **105** 42-90%

104 **15** **106** **107** 76-86%

The results of our studies using the readily accessible cyclobutenedione derivatives in organocatalytic transformations are presented in the next section.

2.2 Results and Discussion

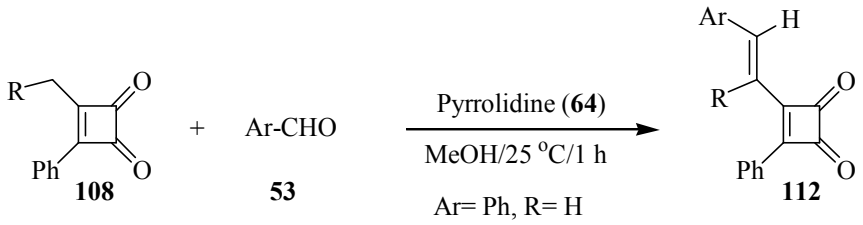
2.2.1 Stereoselective synthesis of alkenyl cyclobutenediones

As outlined in chapter **1**, cyclobutenediones and its derivatives are important synthons, useful in the synthesis of compounds for medicinal chemistry and material science applications.[48,49] A large number of cyclobutenedione derivatives and related compounds have been prepared in order to synthesize novel bioactive agents with improved pharmacological properties.[50,51] As discussed in chapter **1,** we have developed several methods to access cyclobutenediones using iron carbonyl reagents and alkynes. In continuation of these efforts, we have explored the development of new organic transformations using cyclobutenediones in the presence of organic catalysts.

As discussed in the introductory section, various aldehydes and ketones undergo aldol reaction in the presence of amine catalysts. However, there has been no report on organo catalytic aldol reaction involving cyclobutenediones. Therefore, we have examined aldol condensation reaction of cyclobutenediones with aromatic aldehyde catalyzed by pyrrolidine.

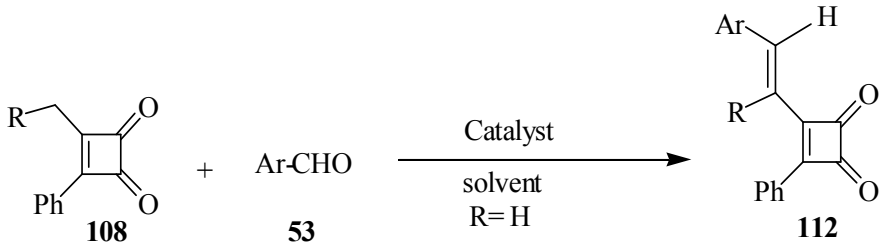
Initially, the aldol condensation reaction of 3-methyl-4-phenylcyclobutenedione **108** and benzaldehyde in MeOH solvent was investigated. We have observed that catalytic amount of pyrrolidine **64** (20 mol %) catalyzes the reaction to give the desired condensation product in 88% yield at 25 ^{o}C (**Table 1**, **entry 1**).

Scheme 28



The reaction was carried out in various solvents like CH_3OH, C_2H_5OH, DMSO, CH_2Cl_2, $CHCl_3$ and THF. In all the cases, the products were obtained in comparable yields **(Table 1**, **entries 1-6**). To optimize the catalyst loading, the conversion was carried out using 10 mol %, 20 mol %, and 30 mol % of pyrrolidine. The results are summarized in **Table 1**. A 20 mol % loading of pyrrolidine was sufficient to push the reaction forward. Use of higher amount of catalyst did not lead to significant change in the product yield. We have also examined the transformation using other organic catalysts like piperidine **69**, morpholine **111** and L-proline **1**. In all the cases, the products were obtained in similar yields (**Table 1**, **entries 1**, **9**, **10** and **11**). However, in the case of pyrrolidine (20 mol %), the products were obtained in good yields in shorter reaction time in methanol. The results are summarized in **Table 1**.

Table1. Stereoselective olefination on 3-methyl-4-phenyl-cyclobutene-1,2-dione **108** using various organic catalysts in different solvents.[a]



108 **53** **112**

Entry	Catalyst	Solvent	mol (%)	Time	yield[b](%)
1	Pyrrolidine(**64**)	MeOH	20	1h	88
2	Pyrrolidine	EtOH	20	1h	86
3	Pyrrolidine	DMSO	20	1h	82
4	Pyrrolidine	THF	20	1.5h	85
5	Pyrrolidine	CH_2Cl_2	20	1.5h	83
6	Pyrrolidine	$CHCl_3$	20	1.5h	85
7	Pyrrolidine	MeOH	10	2h	80
8	Pyrrolidine	MeOH	30	1h	88
9	Piperdine(**69**)	MeOH	20	1h	80
10	Morpholine**(111)**	MeOH	20	1h	75
11	L-Proline**(1)**	MeOH	20	8h	78

[a] All the reactions were carried out using cyclobutenedione **108** (0.5 mmol) aldehyde **53 (**1.5 mmol), 3 equiv.) and catalyst at 25 ^{o}C. [b] Yields reported are for the isolated products and based on the amount of cyclobutenedione (**108**) used.

After establishing the optimal reaction conditions required, the generality of this condensation reaction was examined. A number of alkenyl substituted cyclobutenediones derivatives were synthesized in good yields (**Table 2**). A variety of functional groups such as alkoxy, halide and amine are tolerated in this transformation. The results are summarized in **Table 2.** The substituted benzaldehyde derivatives having electron donating and withdrawing groups afforded the products in good yields (**Table 2**, **entries 9** and **10**). The structures of the condensation products **112** and **122** were confirmed by single crystal x-ray analysis.

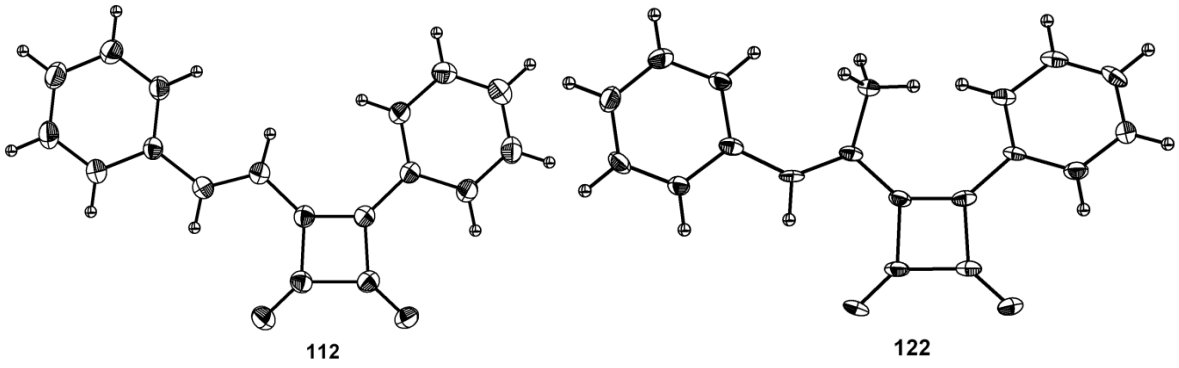


Figure 1. ORTEP diagrams of compounds **112** and **122**

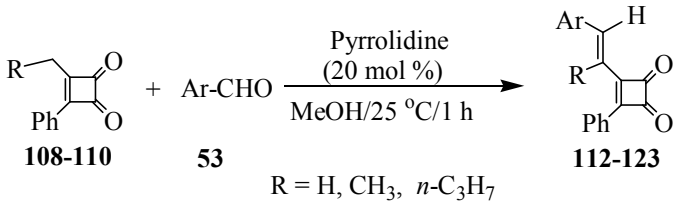
Table 2. X-ray data collection and structure refinement for **112**

Empirical formula	$C_{18}H_{12}O_2$
Fw	260.28
Temp., wavelength	298(2), 0.71073 Å
Cryst. syst., space group	orthorhombic, pbca
Unit cell dimensions	a=14.163(3) Å, α=90˚
	b=8.1161(17) Å, β=90˚
	c=23.806(5) Å, γ =90˚
Volume	2736.6(10) $Å^3$
Z, calcd. density	8, 1.263 mg/m^3
Abs. coeff.	0.082 mm^{-1}
F(000)	1088
Cryst. size	0.40×0.32×0.24 mm
θ range for data collection	1.71 to 25.94˚
Limiting indices	-17≤h≤13, -9≤k≤9, -29≤l≤28
Reflns. collected, unique	14223, 2660 [R(int)=0.0507]
Refinement method	full-matrix least-square on F^2
Data/restraints/params	2660/0/181
Goodness-of-fit on F^2	1.017
Final *R* indices[I> 2σ (I)]	R_1=0.0531, wR_2=0.1023
R indices (all data)	R_1=0.0992, wR_2=0.1191
Largest diff. peak and hole	0.121, -0.095 e. $Å^{-3}$

Table 3. X-ray data collection and structure refinement for **122**

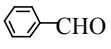
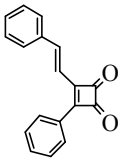
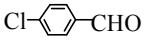
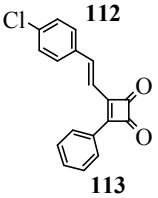
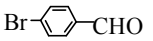
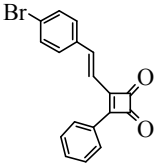
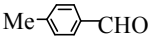
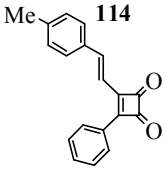
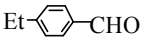
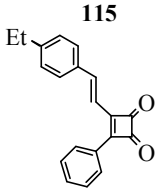
Empirical formula	$C_{19}H_{14}O_2$
Fw	274.30
Temp., wavelength	100(2), 0.71073 Å
Cryst. syst., space group	monoclinic, P-21/c
Unit cell dimensions	a=12.878(2) Å, α=90˚
	b= 14.943(3) Å, β= 93.491˚ (3)
	c= 7.2161(12) Å, γ =90˚
Volume	1386.0(4) $Å^3$
Z, calcd. density	4, 1.315 mg/m^3
Abs. coeff.	0.084 mm^{-1}
F(000)	576
Cryst. size	0.40×0.12×0.08 mm
θ range for data collection	1.58 to 25.00˚
Limiting indices	-15≤h≤15, -17≤k≤17, -8≤l≤8
Reflns. collected, unique	12898, 2448[R(int)=0.0726]
Refinement method	full-matrix least-square on F^2
Data/restraints/params	2448/0/191
Goodness-of-fit on F^2	1.210
Final *R* indices[I> 2σ (I)]	R_1= 0.0785, wR_2= 0.1635
R indices (all data)	R_1= 0.0955, wR_2= 0.1715
Largest diff. peak and hole	0.321, -0.331 e. $Å^{-3}$

Table 4. Stereoselective synthesis of alkenyl cyclobutenediones using pyrrolidine catalysts in methanol solvent [a]

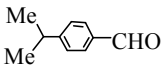
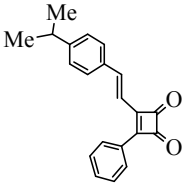
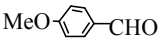
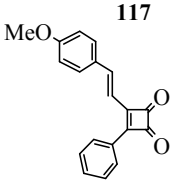
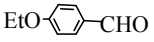
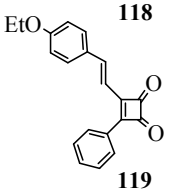
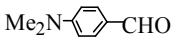
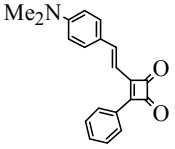
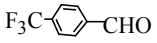
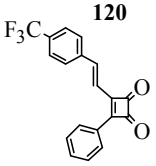
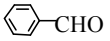
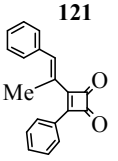
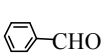
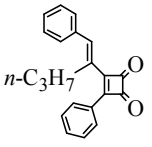


108-110 **53** **112-123**

R = H, CH_3, n-C_3H_7

Entry	R	Ar-CHO	Product[b]	yield[c] %
1	H **108**		 **112**	88
2	H		 **113**	85
3	H		 **114**	82
4	H		 **115**	83
5	H		 **116**	85

(Table **4** continued…)

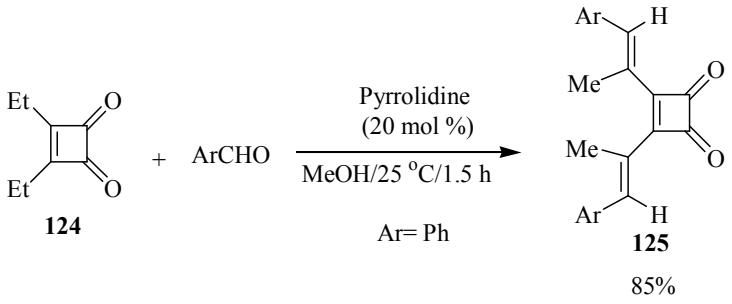
Entry	R	Ar-CHO	Product[b]	yield[c] %
6	H		 **117**	78
7	H		 **118**	82
8	H		 **119**	80
9	H		 **120**	90
10	H		 **121**	91
11	CH_3 **109**		 **122**	85
12	*n*-C_3H_7 **110**		 **123**	80

[a] All the reactions were carried out using cyclobutenedione (0.5 mmol) aldehyde (1.5 mmol, 3 equiv.) and pyrrolidine (20 mmol %) in MeOH (2.5 mL) at 25 ^{o}C for 1 h. [b] The products were identified by spectral

data (IR, ^{1}H-NMR, ^{13}C-NMR and Mass). [c] Yields reported are for the isolated products and based on the amount of cyclobutenedione used.

This transformation is also successful with dialkyl cyclobutenedione **124**. In these experiments, highly conjugated dialkenyl substituted cyclobutenediones are obtained in excellent yields. Initially, we have carried out this reaction using 3,4-diethylcyclobutenedione **124** (0.5 mmol) and benzaldehyde (2 mmol) with 20 mol % of pyrrolidine. The corresponding 3,4-distyrylcyclobutene-1,2-dione **125** was obtained in 85% yield (**Scheme 29**).

Scheme 29



The structure of 3,4-bis((*E*)-1-phenylprop-1-en-2-yl)cyclobutene-1,2-dione **125** was also confirmed by single crystal x-ray analysis.

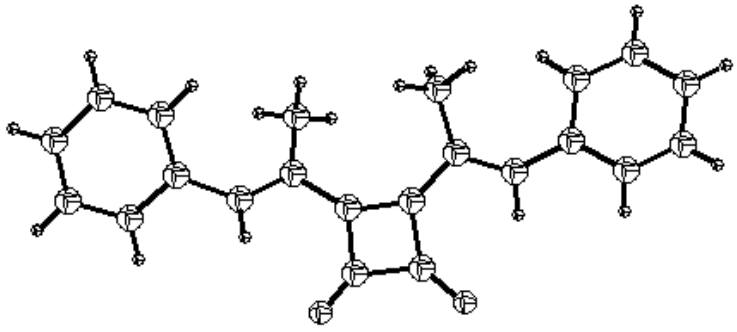


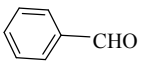
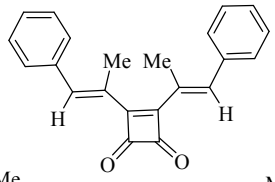
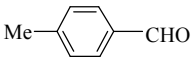
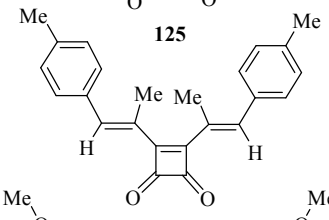
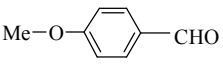
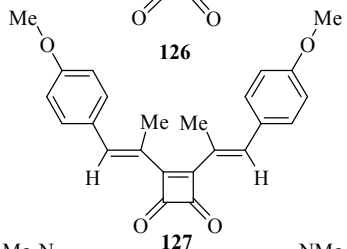
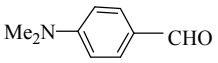
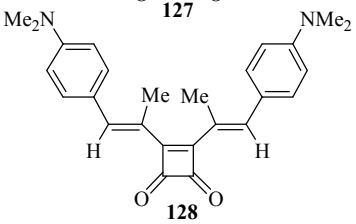
Figure 2. ORTEP diagram of compound **125**.

Table 5. X-ray data collection and structure refinement for **125**

Empirical formula	$C_{22}H_{18}O_2$
Fw	314.36
Temp., wavelength	100(2), 0.71073 Å
Cryst. syst., space group	orthorhombic , pbca
Unit cell dimensions	a= 12.851(4) Å, α=90˚
	b= 13.648(5) Å, β= 90˚
	c= 18.969(6) Å, γ =90˚
Volume	3327.0(19) $Å^3$
Z, calcd. density	8, 1.255 mg/m^3
Abs. coeff.	0.079 mm^{-1}
F(000)	1328
Cryst. size	0.42×0.34×0.24 mm
θ range for data collection	2.15 to 26.01˚
Limiting indices	-15≤h≤15, -16≤k≤16, -23≤l≤23
Reflns. collected, unique	32135, 3251 [R(int)=0.0610]
Refinement method	full-matrix least-square on F^2
Data/restraints/params	3251/0/219
Goodness-of-fit on F^2	1.174
Final *R* indices[I> 2σ (I)]	R_1= 0.0614, wR_2= 0.1391
R indices (all data)	R_1= 0.0691, wR_2= 0.1441
Largest diff. peak and hole	0.232, -0.218 e. $Å^{-3}$

We have also carried out this reaction with various aldehydes. The corresponding substituted 3,4-distyrylcyclobutene-1,2-diones were obtained in good yields (**Scheme 29**). The results are summarized in **Table 6**.

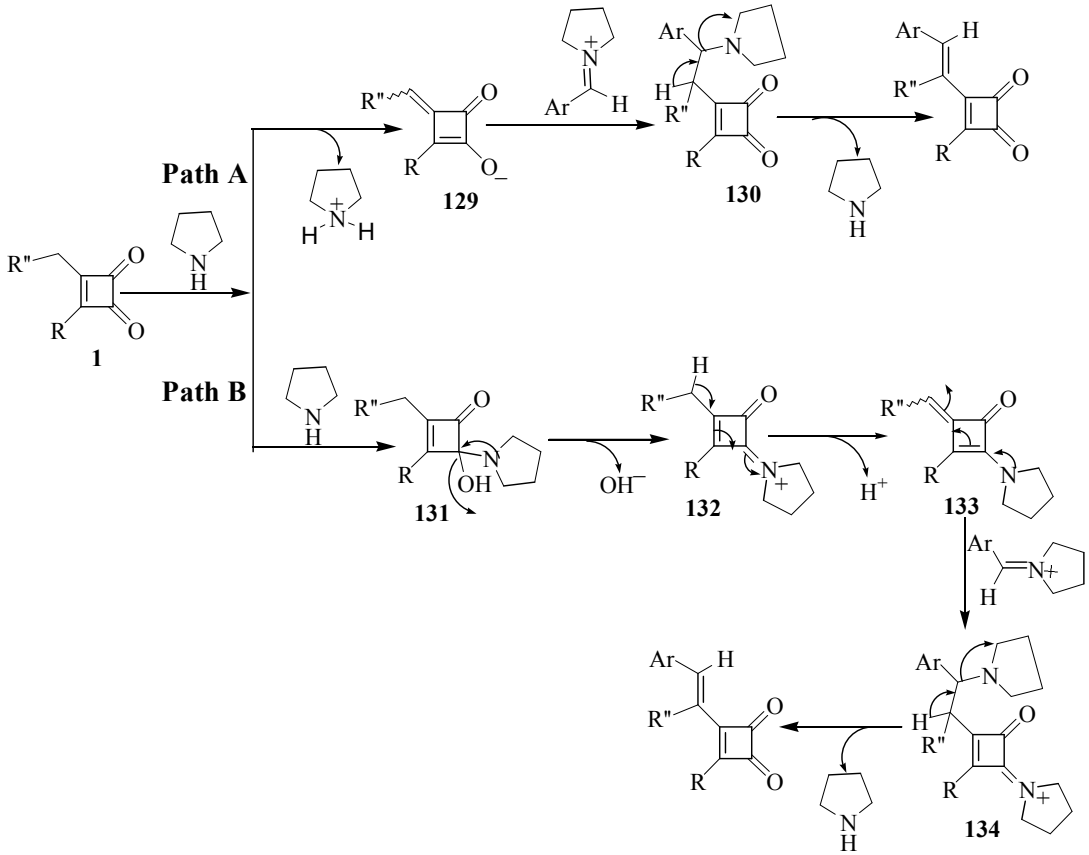
Table 6. Synthesis of 3,4-distrylcyclobut-3-ene-1,2-diones using pyrrolidine catalyst[a]

Entry	ArCHO	Product[b]	yield[c] %
1		 **125**	85
2		 **126**	82
3		 **127**	75
4		 **128**	70

[a] All the reactions were carried out using cyclobutenedione **124 (**0.5 mmol) aldehyde (2 mmol, 4 equiv.) and pyrrolidine (20 mmol %) in MeOH (3 mL) at 25 ^{o}C for 1.5 h. [b] The products were identified by spectral data (IR, ^{1}H-NMR, ^{13}C-NMR and Mass). [c] Yields reported are for the isolated products and based on the amount of cyclobutenedione (**124**) used.

The γ-olefination of cyclobutenediones (**Scheme 28** and **29**) can be explained by considering a tentative mechanism outlined in **Scheme 30.** The reaction of the dienolate intermediate **129** with the iminium ion derived from aldehyde to give the product **(112-123)** via the intermediate **130** may be considered (**path A**, **Scheme 30**). However, the alternative mechanism as outlined in **Path B** involving the reaction of the intermediate **133** to give the product **(112-123)** via the intermediate **134** cannot be also ruled out (**Scheme 30**).

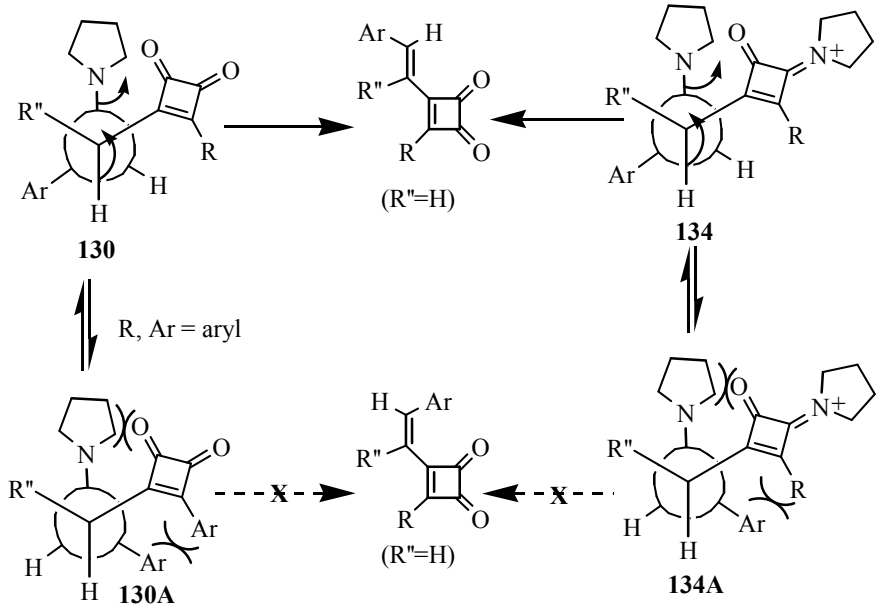
Scheme 30



The stereoselectivity of the present transformation is excellent and only one isomer was obtained in all cases. This observation may be rationalized considering the transition

states **130** or **130A** and **134** or **134A** (**Scheme 31**). Thus, the intermediates **130** and **134** are favored over the intermediates **130A** and **134A**, leading to compounds **112-123** as the only products (**Scheme 31**). It is of interest to note that such condensation reactions of aldehydes with certain 1,3-dicarbonyl compounds gave only one geometrical isomer (**Scheme 24**).

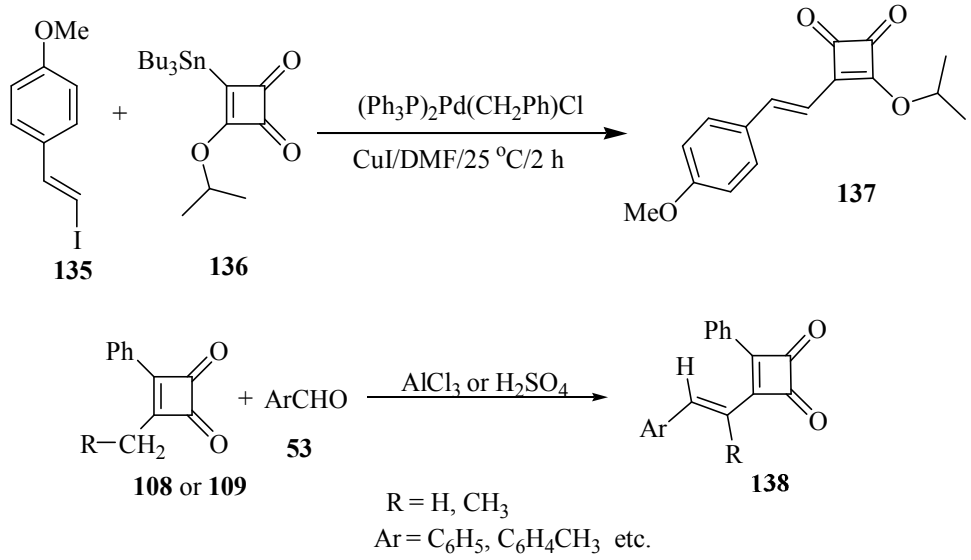
Scheme 31



The mild and efficient methods for the preparation of highly conjugated mono- and di-alkenyl substituted cyclobutenediones using aldehydes and cyclobutenediones under amine catalysis have good synthetic potential. The mildness of the reaction conditions allows rapid and easy preparation of functionalized cyclobutenediones in high yields under very benign reaction conditions.

The derivates of alkenyl substituted cyclobutenediones are of interest in medicinal chemistry [52] and some of these cyclobutenedione derivatives have also proven application as organic optical materials.[53] Accordingly, the method described here has considerable potential for the synthesis of bioactive molecules and donor-acceptor cyclobutenedione derivates for material science applications. Previously, such cyclobutenedione derivatives were prepared using palladium reagents[52] and through methods employing strong Lewis or bronsted acids (**Scheme 32**).[54]

Scheme 32



These reported methods suffer from harsh reaction conditions, long reaction times, expensive reagents and lower yields compared to the organocatalytic methods described here.

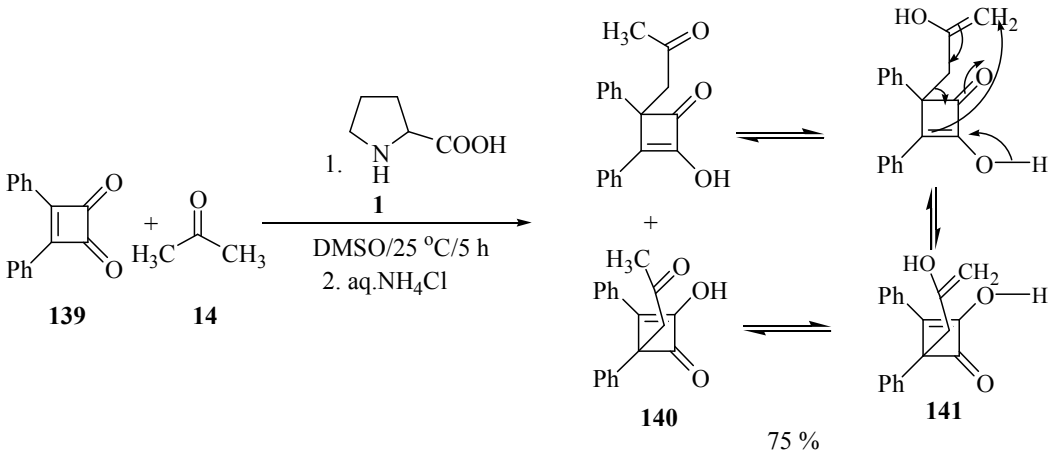
2.2.2 New Cyclobutenediones via Michael Reaction

The Michael addition is one of the most useful carbon-carbon bond-forming reactions widely used in organic synthesis.[23,55] Direct Michael-type conjugate addition reactions are amongst the most simple, efficient and atom-economical process in organic synthesis. Generally, these reactions are carried out using stoichiometric amounts of inorganic bases such as sodium ethoxide, potassium tert-butoxide, potassium hydroxide, sodium metal, LDA, sodium hydride or *n*-butyllithium.[56] Strong basic conditions can, however, lead to side reactions. Recently, excellent enantioselective Michael reactions have been developed using transition metal catalysts and these procedures are also not free from disadvantages.[57] Organocatalysis has been recognized as having special features such as being environmentally benign and having atom economy and convenient synthetic operation. As discussed in the introductory section, several Michael addition reactions were reported using L-proline catalyst. However, to the best of our knowledge, there has been no report on organocatalytic Michael addition reaction involving cyclobutenediones. We have examined L-proline catalyzed Michael addition reaction of cyclobutenedione derivatives.

Initially, we have carried the reaction of acetone and diphenylcyclobutenedione **139** in the presence of L-proline (30 mol %) catalyst in DMSO solvent at room temperature. The corresponding 1,4-addition product **140** that exists in enol form was isolated. Unfortunately, compound **140** was obtained as recemic mixture, presumably, because of

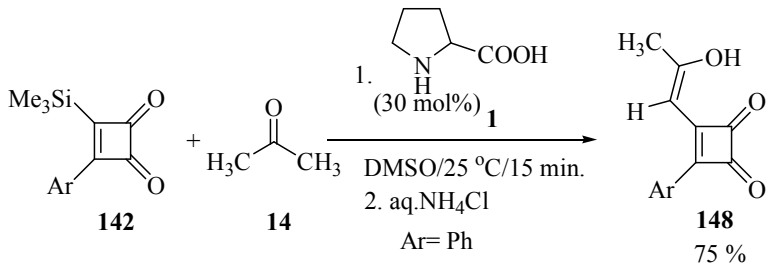
formation of 1:1 ratio two enantiomers (**Scheme 33**). Also, recemization due to rearrangements of the corresponding enols **141** cannot be ruled out (**Scheme 33**).

Scheme 33



Conjugate addition is one of the most important bond forming strategies available to synthetic organic chemists. This is mainly due to the broad spectrum of donors and acceptors that can be employed in this reaction. Therefore, we have further examined the reactivity of substituted cyclobutenediones with acetone in the presence of L-proline (30 mol %). Surprisingly, in the case of silyl substituted cyclobutenedione, the Michael addition takes place with concomitant desilylation. Interestingly, the Michael addition products obtained exists in an enol form (**Scheme 34**).

Scheme 34



This product **148** was also characterized by single crystal X-ray analysis. It exists in enol form and there is a strong intramolecular hydrogen bonding interactions (-O-H…..O distance 1.852 A^{o}).

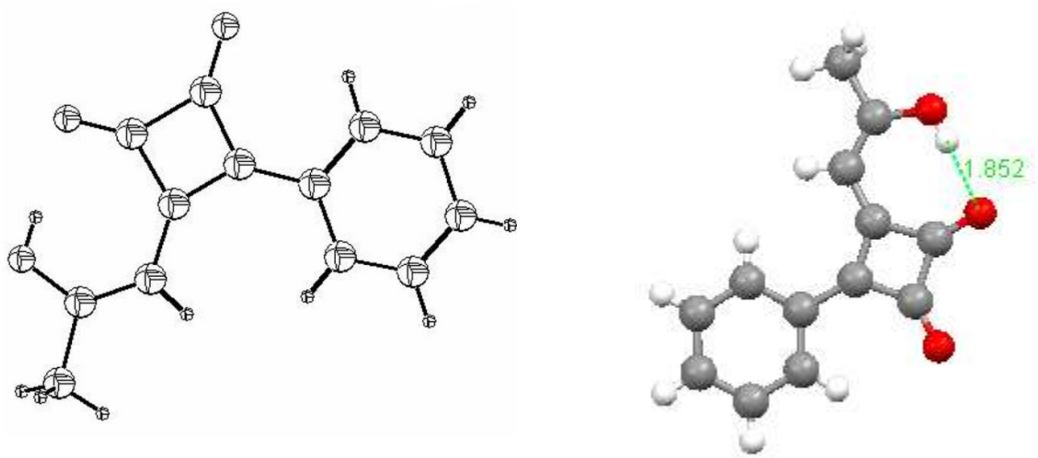


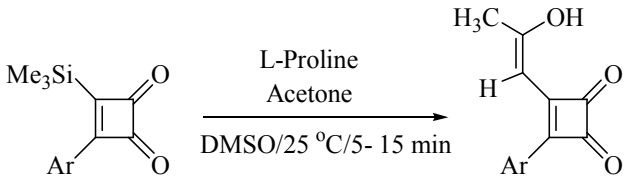
Figure 3. ORTEP diagram of compound **148**

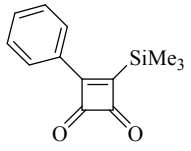
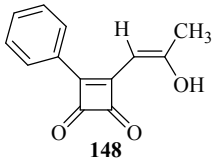
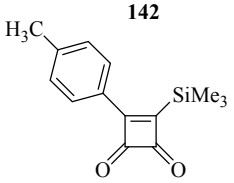
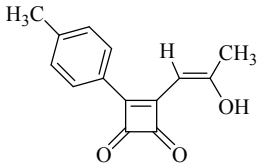
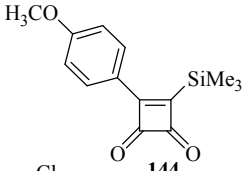
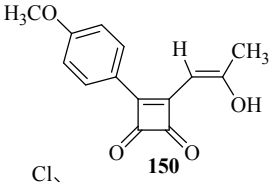
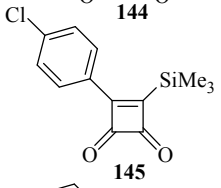
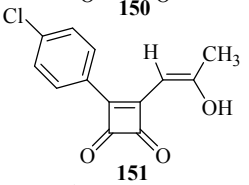
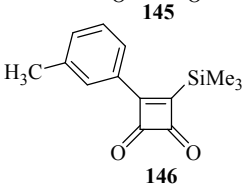
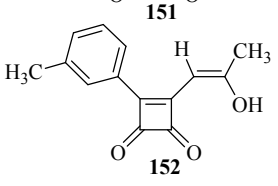
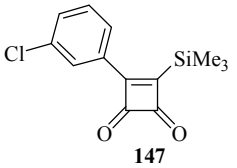
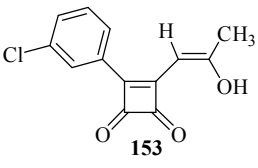
We have also examined this reaction using DMF solvent in place of DMSO. In this case, the corresponding desilylated cyclobutenedione derivative was obtained only in 45% yield. Runs using other catalysts like pyrrolidine, piperidine in the place of L-proline gave only unidentifiable mixture of products. We have also carried out this reaction using 20 mol % L-proline, but 30 mol % of L-proline gave better results. After establishing the optimal reaction conditions, the reaction was carried out using different silyl substituted cyclobutenediones. The corresponding enolic cyclobutenedione derivatives were obtained in moderate to good yields (**Table 8**). In the case of chloro substituted cyclobutenediones (**entries 4** and **6**) the reaction was completed in 5 min. after adding the cyclobutenedione to the reaction mixture.

Table 7. X-ray data collection and structure refinement for **148**

Empirical formula	$C_{13}H_{10}O_3$
Fw	214.21
Temp., wavelength	298(2), 0.71073 Å
Cryst. syst., space group	orthorhombic , Pna2(1)
Unit cell dimensions	a= 8.4940(9) Å, α=90˚
	b= 21.048(2) Å, β= 90˚
	c= 5.9259(6) Å, γ =90˚
Volume	1059.43(19) $Å^3$
Z, calcd. density	4, 1.343 mg/m^3
Abs. coeff.	0.096 mm^{-1}
F(000)	448
Cryst. size	0.40×0.28×0.20 mm
θ range for data collection	1.94 to 25.95˚
Limiting indices	-10≤h≤10, -25≤k≤25, -5≤l≤7
Reflns. collected, unique	5664, 1720 [R(int)=0.0276]
Refinement method	full-matrix least-square on F^2
Data/restraints/params	1720/1/147
Goodness-of-fit on F^2	1.060
Final *R* indices[I> 2σ (I)]	R_1= 0.0423, wR_2= 0.0955
R indices (all data)	R_1= 0.0569, wR_2= 0.1018
Largest diff. peak and hole	0.133, -0.159 e. $Å^{-3}$

Table 8. Reaction of acetone with cyclobutenediones in the presence of L-proline [a]

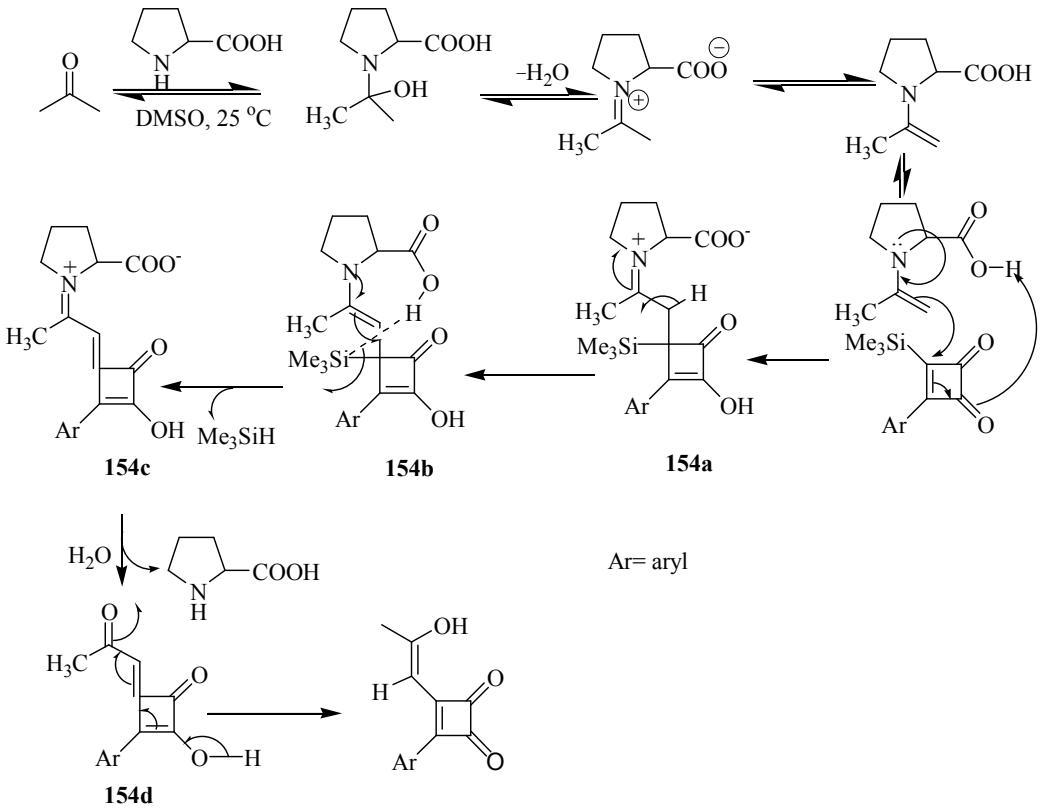


Entry	dione	Product[b]	yield[c] %
1	 **142**	 **148**	75
2	 **143**	 **149**	60
3	 **144**	 **150**	65
4	 **145**	 **151**	52
5	 **146**	 **152**	58
6	 **147**	 **153**	55

[a] All the reactions were carried out using cyclobutenedione (0.5 mmol), acetone (0.3 mL) and L-Proline (30 mmol %) in DMSO (4 mL) at 25 °C. [b] The products were identified by spectral data (IR, ^{1}H-NMR, ^{13}C-NMR and Mass). [c] Yields reported are for the isolated products and based on the amount of cyclobutenedione used.

The 1,4-addition of acetone to silylcyclobutenedione in the presence L-proline can be explained by considering a tentative mechanism outlined in **Scheme 35.**

Scheme 35

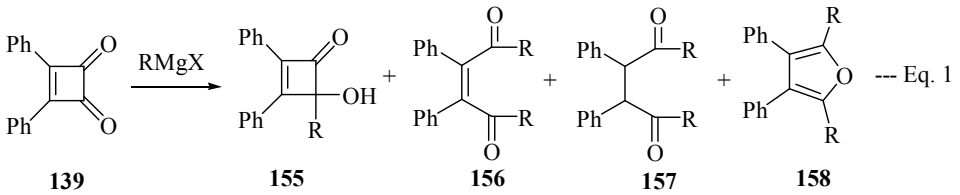


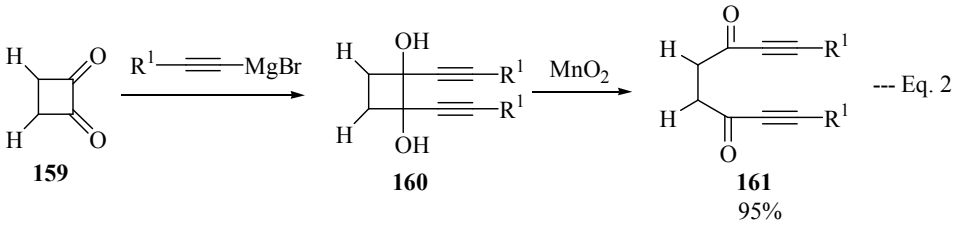
The use of enamines in Michael addition reactions is well established. Accordingly, the enamine generated from acetone and L-proline is expected to react with cyclobutenedione at the silyl substituted carbon to give the intermediate species **154a**. This on further rearrangement could give the intermediate **154b**, which could undergo desilylation followed by hydrolysis to give the enolic substituted cyclobutenedione derivatives (**Scheme 35**). This enol form may be more stable due to extended conjugation and intramolecular hydrogen bonding.

The new cyclobutenedione derivatives obtained *via* organocatalytic Michael reaction described above have considerable potential for further synthetic exploitations in view of their multifunctional character.

2.2.3 Conversion of silyl substituted cyclobutenediones to alkyl substituted cyclobutenediones by using Grignard reagent

Previously, it was reported that alkynyl magnesium reagents react with diphenylcyclobutenedione **139** to give various addition products (Eq. 1).[58a] Also, addition of alkynyl magnesium compounds to cyclobutanedione **159** yields 1,4-diketones after MnO_2 oxidation (Eq. 2). [58b]





We bacame interested in the reaction of alkyl magnesium reagents with 3-phenyl-4-trimethylsilylcyclobutenedione **142** to compare the reactivity pattern with the above mentioned reactions. Initially, we have carried out this reaction at room temperature and obtained unidentifiable mixture of products. Fortunately, when the reaction was carried out

at -40 ^{o}C, new desilylated cyclobutenedione derivatives **109**, **110**, **162-164** were obtained in moderate yields (**Scheme 36**).

Scheme 36

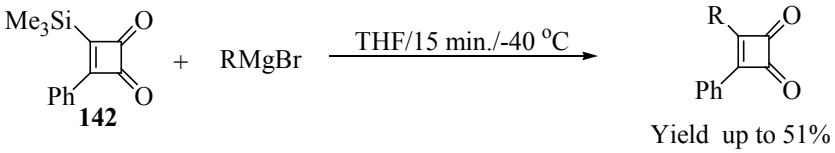
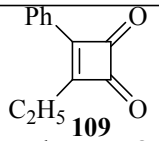
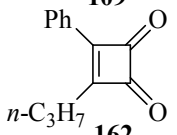
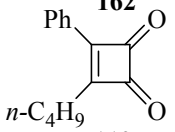
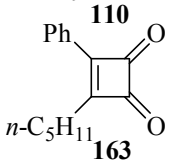
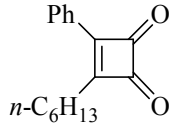


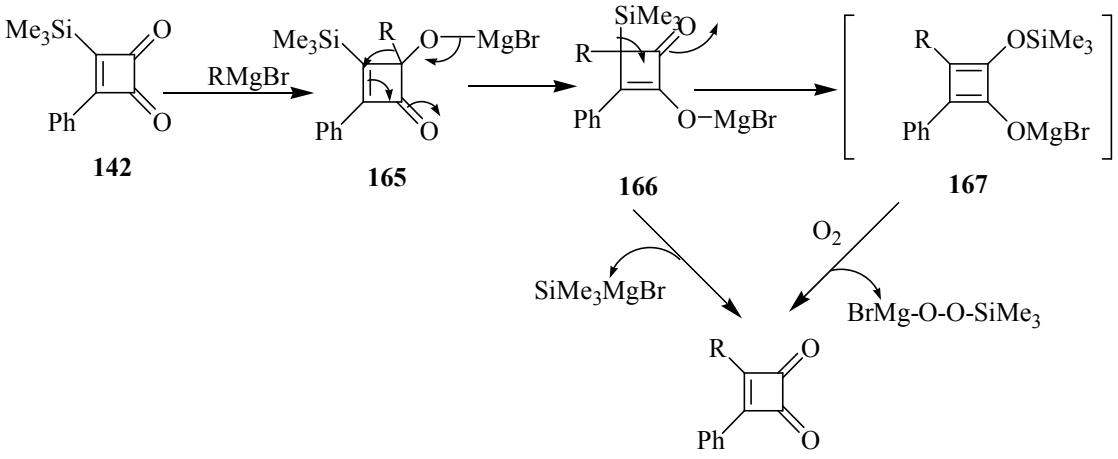
Table 9. Synthesis of phenyl alkyl substituted cyclobutenediones by using Grignard reagent

Entry	Alkyne	Product[b]	yield[c] %
1	C_2H_5MgBr	 **109**	45
2	*n*-C_3H_7MgBr	 **162**	46
3	*n*-C_4H_9MgBr	 **110**	51
4	*n*-$C_5H_{11}MgBr$	 **163**	40
5	*n*-$C_6H_{13}MgBr$	 **164**	42

[a] All the reactions were carried out using cyclobutenedione **142** (1 mmol) Grignard reagent (1 mmol) in THF (15 mL) at –40 ^{o}C. [b] The products were identified by spectral data (IR, ^{1}H-NMR, ^{13}C-NMR and Mass) [c] Yields reported are for the isolated products and based on the amount of cyclobutenedione (**142**) used.

The formation of alkyl phenyl cyclobutenediones from 3-phenyl-4-(trimethylsilyl) cyclobutenedione and Grignard reagent can be explained by considering the mechanism outlined in **Scheme 37**. The Grignard reagent could undergo reaction at the carbonyl carbon followed by rearrangement and desilylation to give the new cyclobutenediones via the intermediates **165** and **166** (**Scheme 37**). The aromaticity of the cyclobutenedione moiety would be driving force for such a transformation.

Scheme 37



However, the intermediacy of the unstable antiaromatic dioxycyclobutadiene **167** cannot be ruled out as it would be expected to react with molecular oxygen to give the aromatic cyclobutenedione along with oxygenated trimethylsilyl magnesium bromide (**Scheme 37**).

2.3 Conclusions

3-Alkyl-4-phenylcyclobutenediones undergo stereoselective aldol condensation reaction with various aldehydes to provide the alkenyl substituted cyclobutenediones in 78-91% yields under ambient reaction conditions. The 3,4-diethylcyclobutenediones undergoes double aldol condensation reaction with various aldehydes under similar reaction conditions to give the dialkenyl substituted cyclobutenedione derivatives in 70-85% yields.

Diphenylcyclobutenedione undergoes Michael addition with acetone in the presence of L-proline catalyst to provide the corresponding 1,4-addition product in 75% yield. The 3-aryl-4-trimethylsilylcyclobutenediones also undergo 1,4-addition reaction to provide the corresponding aryl alkyl substituted cyclobutenediones in 52-75% yields with concomitant desilylation.

Several new functionalized, highly conjugated cyclobutenedione derivatives are accessed through transformations described here. These methods have good potential for further synthetic exploitations, since the products are important class of multifunctional organic synthons.

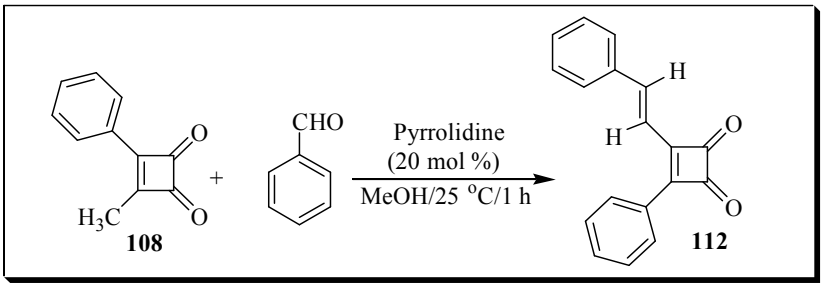
2.4 Experimental Section

2.4.1 General information:

The general information given in the section 1.4 is also applicable to the experiments described in this section. The cyclobutenediones were prepared by following a reported procedure.[59]

2.4.2 Preparation of (*E*)-3-phenyl-4-styrylcyclobut-3-ene-1,2-dione 112

To a mixture of 3-methyl-4-phenyl-cyclobutene-1,2-dione **108** (0.086 g, 0.5 mmol) and benzaldehyde (0.15 mL, 1.5 mmol) in 2.5 mL of MeOH catalytic amount of pyrrolidine (8.2 μL, 20 mol %) was added. The reaction mixture was stirred for 1 h at room temperature. It was treated with 5mL of saturated ammonium chloride solution and extracted with ethyl acetate (3x10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to column chromatography (silica gel, hexane-EtOAc). Ethyl acetate (3%) in hexane eluted the (*E*)-3-phenyl-4-styrylcyclobut-3-ene-1,2-dione **112**.



Yield : 0.114 g (88%)

mp : 148-150 °C (Lit.[54] mp 160 °C)

IR (KBr) : 1759 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 8.30 (d, J = 14.8 Hz, 1H), 8.09-8.07 (m, 2H), 7.68-7.45 (m, 9H) *ppm* **(Spectrum No. 25)**

^{13}C NMR **:** (100 MHz) δ = 196.7, 195.9, 184.2, 183.4, 146.1, 134.9, 133.2, 131.4, 129.4, 129.2, 129.0, 128.7, 128.4, 115.2 *ppm* **(Spectrum No. 26)**

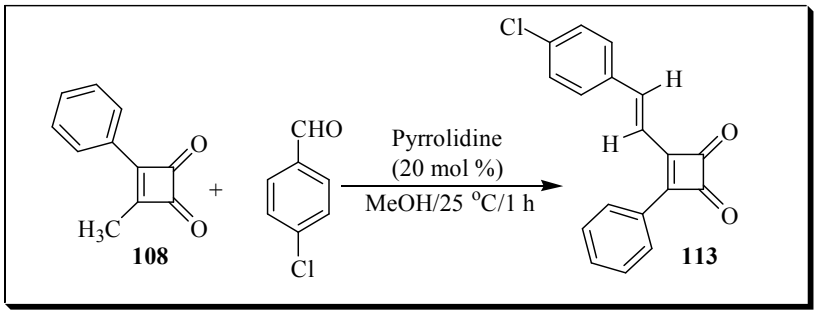
MS (EI) **:** *m/z* 261 (M+1).

Analysis **:** for $C_{18}H_{12}O_2$

Calculated: C, 83.06%; H, 4.65%

Found: C, 83.25%; H, 4.59%

The above procedure was followed for the condensation of other aldehydes with 3-alkyl-4-phenyl-cyclobutene-1,2-dione.



Yield **:** 0.125 g (85%)

mp **:** 171-173 °C (Lit.[54] mp 185 °C)

IR (KBr) **:** 1759 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 8.25 (d, J = 15.6 Hz, 1H), 8.09-8.06 (m, 2H), 7.62-7.56 (m, 5H), 7.48 (d, J = 15.6 Hz, 1H), 7.43-7.41 (m, 2H) *ppm*

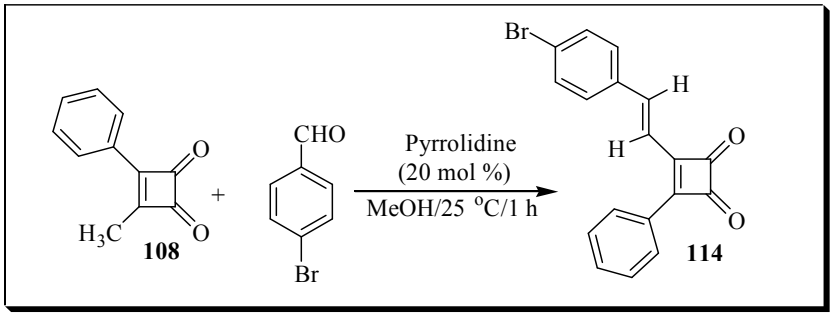
^{13}C NMR **:** (100 MHz) δ = 196.6, 195.8, 183.8, 183.7, 144.4, 137.4, 133.4, 129.8, 129.5, 128.9, 128.4, 115.7 *ppm*

MS (EI) **:** *m/z* 295 (M+1)

Analysis **:** for $C_{18}H_{11}ClO_2$

Calculated: C, 73.35%; H, 3.76%

Found: C, 73.51%; H, 3.71%



Yield **:** 0.138 g (82%)

mp **:** 166-168 ^{o}C

IR (KBr) **:** 1747 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 8.26 (d, *J* = 15.6 Hz, 1H), 8.10-8.08 (m, 2H), 7.62-7.54 (m, 7H), 7.51 (d, *J* = 15.6 Hz, 1H) *ppm* **(Spectrum No. 27)**

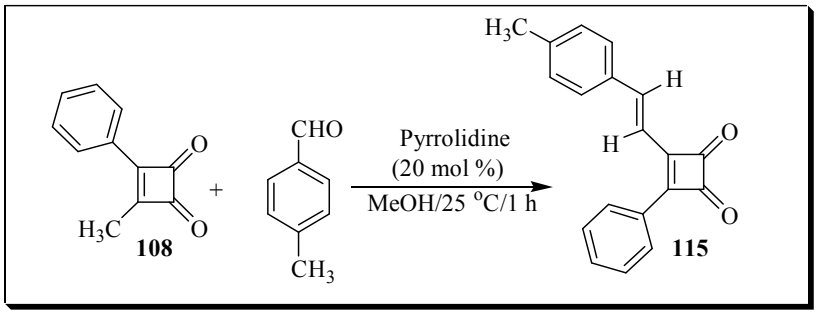
^{13}C NMR **:** (100 MHz) δ = 196.5, 195.8, 183.85, 183.81, 144.5, 133.8, 133.3, 132.5, 129.9, 129.5, 128.9, 128.4, 125.8, 115.7 *ppm* **(Spectrum No. 28)**

MS (EI) **:** *m/z* 339 (M+2)

Analysis **:** for $C_{18}H_{11}BrO_2$

Calculated: C, 63.74%; H, 3.27%

Found: C, 63.85%; H, 3.21%



Yield : 0.114 g (83%)

mp : 156-158 °C (Lit.[54] mp 163 °C)

IR (KBr) : 2914, 1751, 1736 cm^{-1}

^{1}H NMR : (400 MHz) δ = 8.33 (d, J = 15.6 Hz, 1H), 8.12-8.10 (m, 2H), 7.61-7.60 (m, 5H), 7.50 (d, J = 15.6 Hz, 1H), 7.29-7.27 (m, 2H), 2.44 (s, 3H) *ppm* **(Spectrum No. 29)**

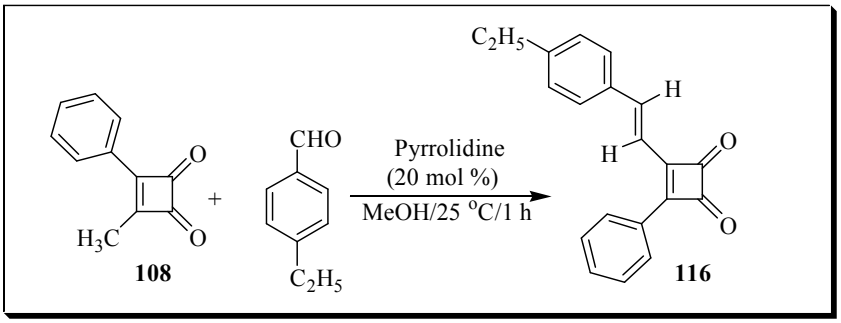
^{13}C NMR : (100 MHz) δ = 196.8, 195.8, 184.4, 182.8, 146.3, 142.2, 133.0, 132.2, 129.9, 129.4, 129.1, 128.8, 128.3, 114.2, 21.6 *ppm* **(Spectrum No. 30)**

MS (EI) : *m/z* 275 (M+1)

Analysis : for $C_{19}H_{14}O_2$

Calculated: C, 83.19%; H, 5.14%

Found: C, 83.31%; H, 5.08%



Yield **:** 0.122 g (85%)

mp **:** 118-120 ^{o}C

IR (KBr) **:** 2966, 2926, 1751cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 8.32 (d, J = 15.6 Hz, 1 H), 8.10-8.08 (m, 2H), 7.63-7.57 (m, 5H), 7.48 (d, J = 15.6 Hz, 1H), 7.30-7.28 (m, 2H), 2.70 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H) *ppm*

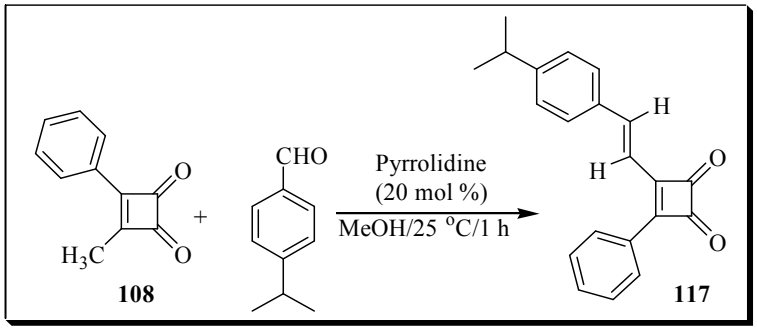
^{13}C NMR **:** (100 MHz) δ = 196.8, 195.8, 184.4, 182.8, 148.5, 146.4, 133.0, 132.5, 129.4, 129.1, 128.9, 128.7, 128.3, 114.3, 28.9, 15.1 *ppm*

MS (EI) **:** *m/z* 289 (M+1)

Analysis **:** for $C_{20}H_{16}O_2$

Calculated: C, 83.31%; H, 5.59%

Found: C, 83.45%; H, 5.51%



Yield : 0.118 g (78%)

mp : 126-128 °C

IR (KBr) : 2959, 2926, 1766 cm^{-1}

^{1}H NMR : (400 MHz) δ = 8.32 (d, *J* = 15.6 Hz, 1H), 8.10-8.08 (m, 2H), 7.63-7.57 (m, 5H), 7.48 (d, *J* = 15.6 Hz, 1H), 7.33-7.31 (m, 2H), 3.01-2.91 (m, 1H), 1.28 (d, *J* = 6.8 Hz, 6H) *ppm*

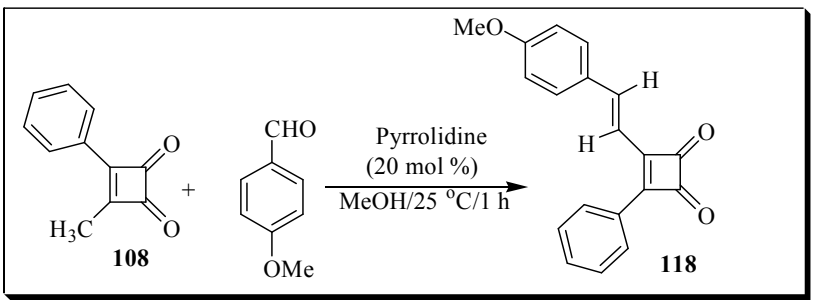
^{13}C NMR : (100 MHz) δ = 196.8, 195.8, 184.4, 182.9, 153.1, 146.4, 133.0, 132.6, 129.4, 129.2, 128.9, 128.3, 127.3, 114.4, 34.2, 23.6 *ppm*

MS (EI) : *m/z* 303 (M+1)

Analysis : for $C_{21}H_{18}O_2$

Calculated: C, 83.42%; H, 6.00%

Found: C, 83.35%; H, 6.12%



Yield : 0.119 g (82%)

mp : 140-142 ^{o}C (Lit.[54] mp 156 ^{o}C)

IR (KBr) : 2978, 1763, 1751 cm^{-1}

^{1}H NMR : (400 MHz) δ = 8.31 (d, J = 15.6 Hz, 1H), 8.09-8.08 (m, 2H), 7.67-7.57 (m, 5H), 7.39 (d, J = 15.6 Hz, 1H), 6.97 (d, J = 8.4 Hz, 2H), 3.87 (s, 3H) *ppm*

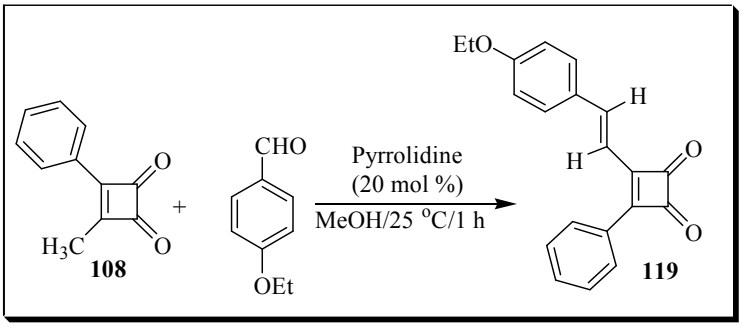
^{13}C NMR : (100 MHz) δ = 197.1, 195.7, 184.5, 182.1, 162.5, 146.2, 132.8, 130.8, 129.4, 129.3, 128.2, 127.7, 114.7, 113.0, 55.5 *ppm*

MS (EI) : *m/z* 291 (M+1)

Analysis : for $C_{19}H_{14}O_3$

Calculated: C, 78.61%; H, 4.86%

Found: C, 78.45%; H, 4.92%



Yield : 0.122 g (80%)

mp : 136-138 ^{o}C

IR (KBr) : 2978, 2924, 1763, 1743 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 8.28 (d, J = 15.6 Hz, 1H), 8.08-8.06 (m, 2H), 7.64-7.55 (m, 5H), 7.36 (d, J = 15.6 Hz, 1H), 6.94 (d, J = 8.4 Hz, 2H), 4.08 (q, J = 7.2 Hz, 2H), 1.44 (t, J = 7.2 Hz, 3H) *ppm* **(Spectrum No. 31)**

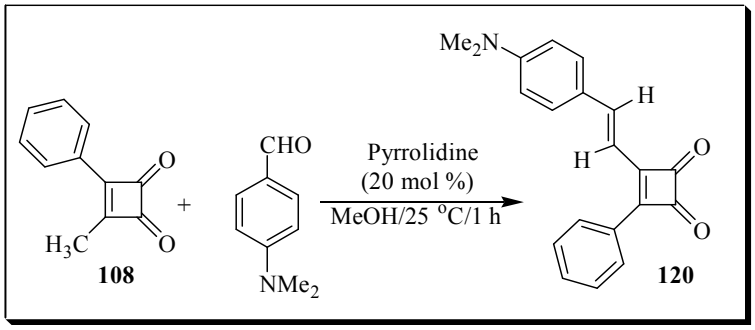
^{13}C NMR **:** (100 MHz) δ = 197.1, 195.7, 184.5, 182.0, 161.9, 146.3, 132.8, 130.8, 129.4, 129.3, 128.2, 127.5, 115.2, 112.8, 63.8, 14.7 *ppm* **(Spectrum No. 32)**

MS (EI) **:** *m/z* 303 (M-1)

Analysis **:** for $C_{20}H_{16}O_3$

Calculated: C, 78.93%; H, 5.30%

Found: C, 78.81%; H; 5.41%



Yield **:** 0.136 g (90%)

mp **:** 215-217 °C (Lit.[54] mp 227 °C)

IR (KBr) **:** 1755, 1728 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 8.28 (d, J = 15.6 Hz, 1H), 8.08-8.06 (m, 2H), 7.58-7.54 (m, 5H), 7.22 (d, J = 15.6 Hz, 1H), 6.67 (d, J =9.2 Hz, 2H), 3.06 (s, 6H) *ppm* **(Spectrum No. 33)**

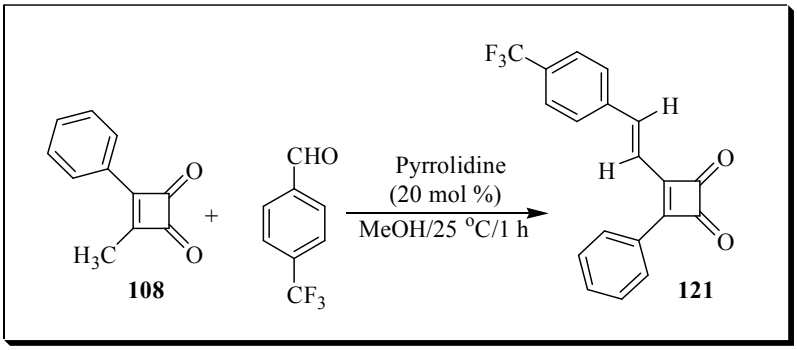
^{13}C NMR **:** (100 MHz) δ = 197.7, 195.3, 184.5, 179.5, 152.6, 147.5, 132.2, 131.2, 129.8, 129.2, 127.9, 122.7, 111.9, 109.8, 40.0 *ppm* **(Spectrum No. 34)**

MS (EI) **:** *m/z* 304 (M+1)

Analysis **:** for $C_{20}H_{17}NO_2$

Calculated: C, 79.19%; H, 5.65%; N, 4.62

Found: C, 79.10%; H, 5.61%; N, 4.75



Yield **:** 0.149 g (91%)

mp **:** 140-142 ^oC

IR (KBr) **:** 1768, 1747 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 8.30 (d, J = 15.6 Hz, 1H), 8.09 (d, J = 8 Hz, 2H), 7.79 (d, J = 8 Hz, 2H), 7.70 (d, J = 8 Hz, 2H), 7.62-7.58 (m, 4H) *ppm*

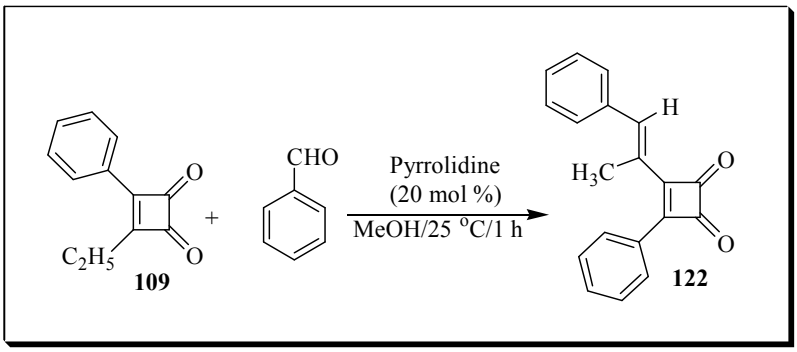
^{13}C NMR **:** (100 MHz) δ = 196.3, 195.8, 184.6, 183.4, 143.6, 138.2, 133.6, 132.3 (q, J = 32 Hz), 129.6, 128.8, 128.7, 128.6, 126.1 (q, J = 4 Hz), 123.7 (q, J = 271 Hz), 117.4 *ppm*

MS (EI) **:** *m/z* 329 (M+1)

Analysis **:** for $C_{19}H_{11}F_3O_2$

Calculated: C, 69.51%; H, 3.38%

Found: C, 69.38%; H, 3.45%



Yield **:** 0.117 g (85 %)

mp **:** 96-98 ^{o}C

IR (KBr) **:** 2968, 1765 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 8.02 (s, 1H), 7.89-7.86 (m, 2H), 7.56-7.36 (m, 8H), 2.31 (s, 3H) *ppm* **(Spectrum No. 35)**

^{13}C NMR **:** (100 MHz) δ = 196.1, 195.7, 190.2, 186.2, 141.6, 135.3, 132.3, 130.3, 129.3, 128.9, 128.8, 128.6, 128.0, 127.1, 16.9 *ppm*

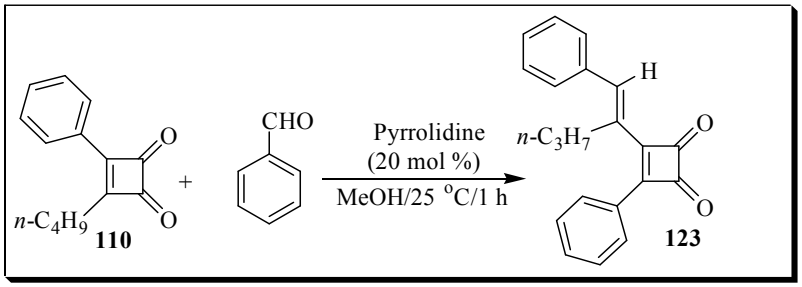
(Spectrum. No. 36)

MS (EI) **:** *m/z* 275 (M+1)

Analysis : for $C_{19}H_{14}O_2$

Calculated: C, 83.19%; H, 5.14%

Found: C, 83.31%; H, 5.08%



Yield : 0.121 g (80 %)

mp : semi solid

IR (KBr) : 2962, 2934, 1786, 1768 cm^{-1}

^{1}H NMR : (400 MHz) δ = 7.96-7.93 (m, 2H), 7.76 (s, 1H), 7.58-7.38 (m, 8H), 2.81 (t, J = 7.6 Hz, 2H), 1.47-1.37 (m, 2H), 0.81 (t, J =7.2 Hz, 3H) *ppm*

^{13}C NMR : (100 MHz) δ = 196.5, 196.0, 191.5, 186.9, 139.2, 135.1, 133.0, 132.6, 129.7, 129.0, 128.7, 128.4, 128.3, 30.4, 22.1, 13.6 *ppm*

MS (EI) : *m/z* 303 (M+1)

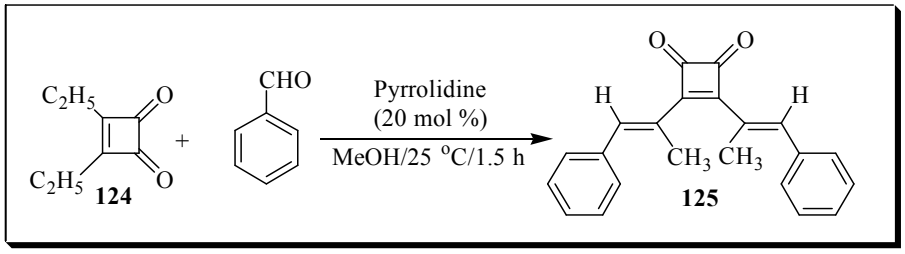
Analysis : for $C_{21}H_{18}O_2$

Calculated: C 83.42%; H, 6.00%

Found: C, 83.31%; H, 5.92%

2.4.3 Preparation of 3,4-bis((*E*)-1-phenylprop-1-en-2-yl)cyclobutene-1,2-dione 125

To a mixture of 3,4-diethylcyclobutenedione **124** (0.069 g, 0.5 mmol) in 3 mL of MeOH solvent and catalytic amount of pyrrolidine (8.2 µL, 20 mol %), benzaldehyde (0.2 mL, 2 mmol) was added. And the reaction mixture was stirred for 1.5 h at room temperature. The reaction mixture was treated with 5 mL of saturated ammonium chloride solution and extracted with ethyl acetate (3x10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was subjected to column chromatography (silica gel, hexane-EtOAc). Ethyl acetate (3%) in hexane eluted the 3,4-bis((*E*)-1-phenylprop-1-en-2-yl)cyclobutene-1,2-dione **125.**



Yield : 0.133 g (85 %)

mp : 118-120 °C

IR (KBr) : 1743 cm^{-1}

^{1}H NMR : (400 MHz) δ = 7.74 (s, 2H), 7.54-7.39 (m, 10H), 2.37 (s, 6H) *ppm*

(Spectrum No. 37)

^{13}C NMR **:** (100 MHz) δ = 196.1, 189.7, 140.7, 135.6, 130.3, 129.2, 128.7, 127.2, 17.4 *ppm* **(Spectrum No. 38)**

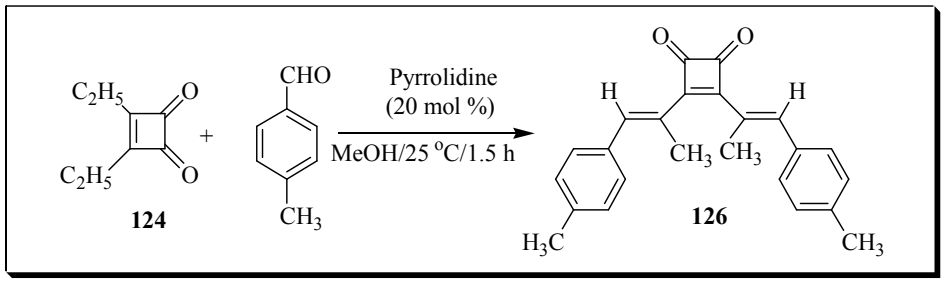
MS (EI) **:** *m/z* 315 (M+1)

Analysis **:** for $C_{22}H_{18}O_2$

Calculated: C, 84.05%; H, 5.77%

Found: C, 84.18%; H, 5.71%

The above procedure was followed for the reaction of other aldehydes with 3,4-diethylcyclobutenedione **124**.



Yield **:** 0.140 g **(**82 %)

mp **:** 156-158 ^{o}C

IR (KBr) **:** 2922, 1745 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 7.74 (s, 2H), 7.46 (d, J = 8 Hz, 4H), 7.27 (d, J = 8 Hz, 4H), 2.42 (s, 6H), 2.38 (s, 6H) *ppm*

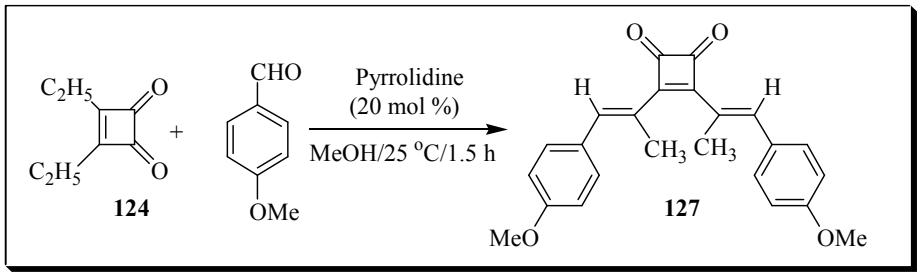
^{13}C NMR **:** (100 MHz) δ = 196.2, 189.3, 140.8, 139.6, 132.8, 130.4, 129.4, 126.3, 21.5, 17.6 *ppm*

MS (EI) **:** *m/z* 343 (M+1)

Analysis **:** for $C_{24}H_{22}O_2$

Calculated: C, 84.18%; H, 6.48%

Found: C, 84.05%; H, 6.55%



Yield : 0.140 g (75 %)

mp : 164-166 °C

IR (KBr) : 2961, 1739 cm^{-1}

^{1}H NMR : (400 MHz) δ = 7.72 (s, 2H), 7.52 (d, J = 8.8 Hz, 4H), 6.96 (d, J = 8.8 Hz, 4H), 3.86 (s, 6H), 2.36 (s, 6H) *ppm* **(Spectrum No. 39)**

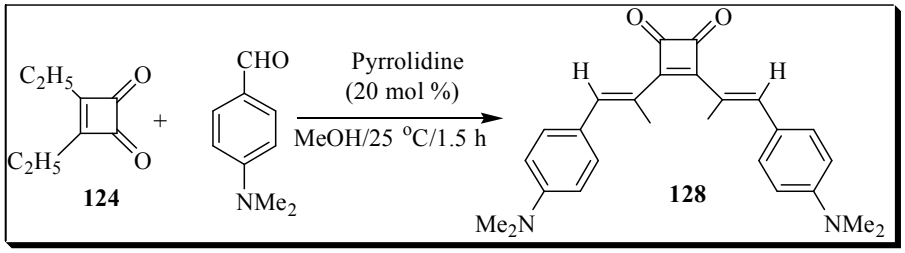
^{13}C NMR : (100 MHz) δ = 196.2, 188.9, 160.4, 140.5, 132.3, 128.5, 125.0, 114.2, 55.4, 17.8 *ppm* **(Spectrum No. 40)**

MS (EI) : *m/z* 373 (M-1)

Analysis : for $C_{24}H_{22}O_4$

Calculated: C, 76.99%; H, 5.92%

Found: C, 76.88%; H, 5.97%



Yield : 0.140 g (70%)

mp : 156-158 ^{o}C

IR (KBr) : 2922, 1743 cm^{-1}

^{1}H NMR : (400 MHz) δ = 7.74 (s, 2H), 7.51 (d, J = 8 Hz, 4H), 6.72 (d, J = 8 Hz, 4H), 3.05 (s, 12H), 2.37 (s, 6H) *ppm*

^{13}C NMR : (100 MHz) δ = 196.4, 187.5, 150.7, 141.3, 132.6, 124.0, 122.7, 111.7, 40.1, 18.2 *ppm*

MS (EI) : *m/z* 401 (M+1)

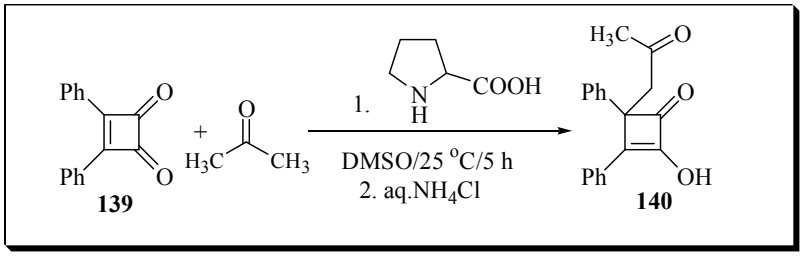
Analysis : for $C_{26}H_{28}N_2O_2$

Calculated: C, 77.97%; H, 7.05%; N, 6.99%

Found: C, 77.91%; H, 7.15%; N, 6.85%

3.4.4 Reaction of acetone with the diphenylcyclobutenedione 139 in the presence of L-proline catalyst

To a solution of L-proline (0.017 g, 30 mol %) in DMSO (1.5 mL), acetone (0.5 mL) was added at 25 ^{o}C and stirred for 15 min. Diphenylcyclobutenedione (0.117 g, 0.5 mmol) in DMSO (1.5 mL) was added dropwise and the contents were stirred for 5 h. The reaction mixture was treated with 5 mL of saturated NH_4Cl solution and extracted with ethyl acetate (3x10 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 subjected to column chromatography (silica gel, hexane-EtOAc). Ethyl acetate (20%) in hexane eluted the 2-hydroxy-4-(2-oxopropyl)-3,4-diphenylcyclobuten-2-one **140.**



Yield : 0.109 g (75%)

mp : 148-150 ^{o}C

IR (KBr) : 3449, 1753, 1712 cm^{-1}

^{1}H NMR : (400 MHz) δ = 9.34 (s, 1H), 7.71-7.24 (m, 10H), 3.45 (s, 2H), 2.1 (s, 3H) *ppm*

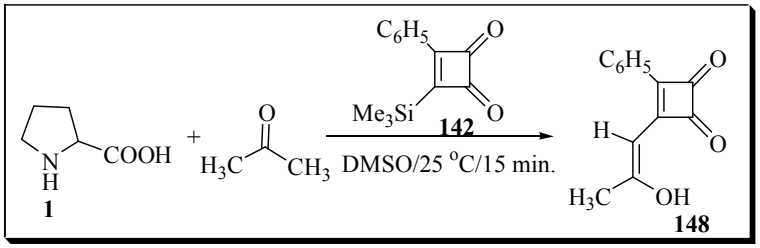
^{13}C NMR : (100 MHz) δ = 206.6, 188.9, 147.9, 144.2, 139.4, 130.9, 130.0, 129.2, 128.9, 128.7, 127.5, 126.5, 62.9, 45.4, 31.5 *ppm*

MS (EI) : *m/z* 293 (M+1)

2.4.5 Reaction of acetone with 3-phenyl-4-(trimethylsilyl)-cyclobutene-1,2-dione 142 in the presence of L-proline catalyst

To a solution of L-proline (0.017 g, 30 mol %) in DMSO (2 mL), acetone (0.3 mL) was added and stirred for 15 min. at 25 ^{o}C. 3-Phenyl-4-(trimethylsilyl)-cyclobut-3-ene-1,2-dione (0.115 g, 0.5 mmol) in DMSO (2 mL) was added dropwise. The contents were stirred for 15 min. The reaction mixture was treated with 5 mL of saturated NH_4Cl solution and extracted with ethyl acetate (3x10 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 subjected to column chromatography (silica gel, hexane-EtOAc). Ethyl acetate (20%) in hexane eluted the (Z)-3-(2-hydroxyprop-1-enyl)-4-phenylcyclobutene-1,2-dione **148**.



Yield **:** 0.080 g (75%)

mp **:** 152-154 ^{o}C

IR (KBr) **:** 3449, 1753, 1712 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 11.45 (s, 1H), 8.03-8.01 (m, 2H), 7.57-7.52 (m, 3H), 5.84 (s, 1H), 2.23 (s, 3H) *ppm* **(Spectrum No. 41)**

^{13}C NMR **:** (100 MHz) δ = 202.9, 188.6, 182.4, 178.5, 176.9, 133.0, 129.4, 129.3, 128.3, 92.9, 23.3 *ppm* **(Spectrum No. 42)**

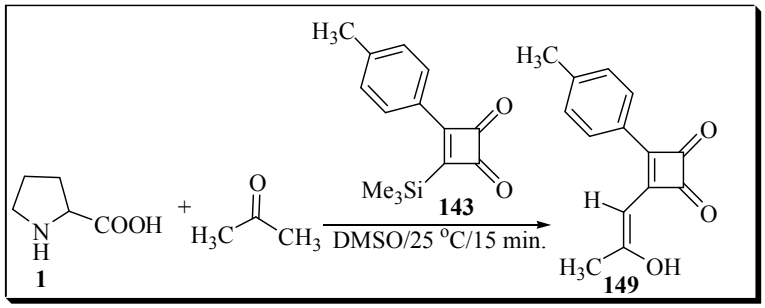
MS (EI) **:** *m/z* 213 (M-1)

Analysis **:** for $C_{13}H_{10}O_3$

Calculated: C, 72.89%; H, 4.71%

Found: C, 72.95%; H, 4.66 %

The above procedure was followed for the reaction of acetone with other cyclobutenediones.



Yield : 0.068 g (60%)

mp : 148-150 ^{o}C

IR (KBr) : 3437, 1761, 1707 cm^{-1}

^{1}H NMR : (400 MHz) δ = 11.46 (s, 1H), 7.93 (d, J = 7.2 Hz, 2H), 7.34 (d, J = 7.2 Hz, 2H), 5.81 (s, 1H), 2.45 (s, 3H), 2.22 (s, 3H) *ppm* **(Spectrum No. 43)**

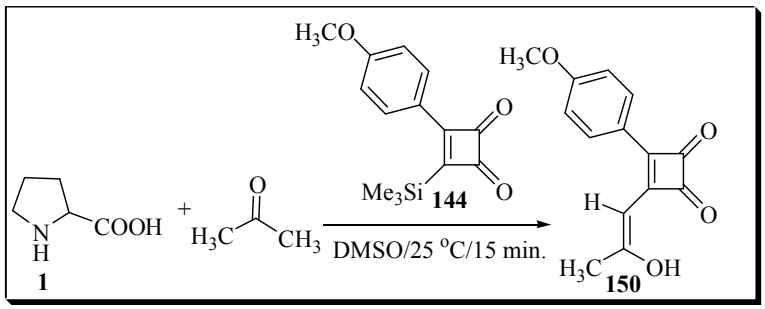
^{13}C NMR : (100 MHz) δ = 202.5, 188.8, 181.8, 178.6, 176.3, 144.3, 130.1, 128.3, 126.8, 92.9, 23.2, 22.0 *ppm* **(Spectrum No. 44)**

MS (EI) : *m/z* 229 (M+1)

Analysis : for $C_{14}H_{12}O_3$

Calculated: C, 73.67%; H, 5.30%

Found: C, 73.55%; H, 5.38 %



Yield **:** 0.079 g (65%)

mp **:** 150-152 ^{o}C

IR (KBr) **:** 3472, 1766, 1699 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 11.49 (s, 1H), 8.02 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 5.78 (s, 1H), 3.90 (s, 3H), 2.21 (s, 3H) *ppm*

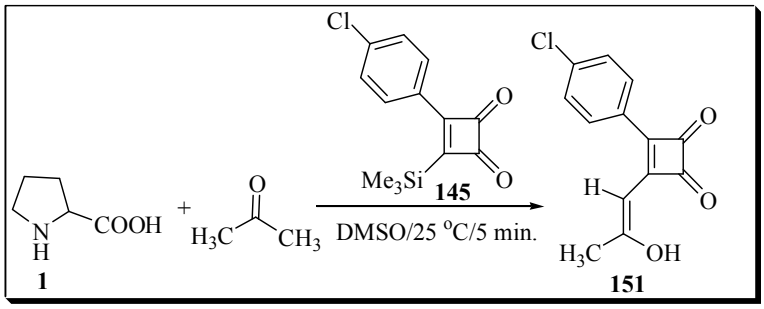
^{13}C NMR **:** (100 MHz) δ = 201.9, 188.9, 180.7, 178.0, 175.8, 163.5, 130.6, 122.4, 114.9, 92.8, 55.6, 23.2 *ppm*

MS (EI) **:** *m/z* 245 (M+1)

Analysis **:** for $C_{14}H_{12}O_4$

Calculated: C, 68.85%; H, 4.95%

Found: C, 68.71%; H, 4.86%



Yield **:** 0.064 g (52%)

mp **:** 134-136 ^{o}C

IR (KBr) **:** 3491, 1761, 1712 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 11.47 (s, 1H), 7.96 (d, *J*= 8.8 Hz, 2H), 7.52 (d, *J*= 8.8 Hz, 2H), 5.80 (s, 1H), 2.24 (s, 3H) *ppm*

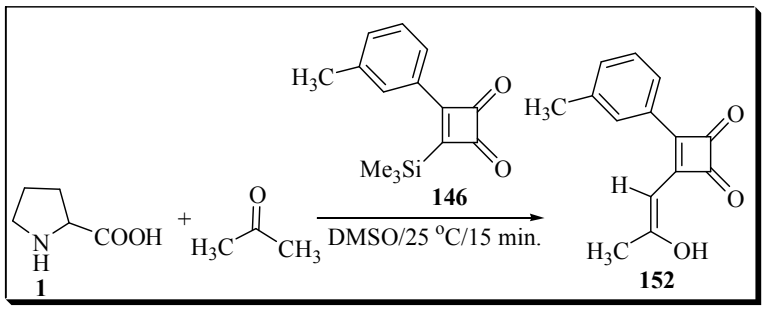
^{13}C NMR **:** (100 MHz) δ = 202.6, 188.2, 182.3, 177.5, 176.7, 139.2, 129.8, 129.4, 127.7, 92.9, 23.3 *ppm*

MS (EI) **:** *m/z* 249 (M+1)

Analysis **:** for $C_{13}H_9ClO_3$

Calculated: C, 62.79%; H, 3.65%

Found: C, 62.59%; H, 3.71%



Yield **:** 0.066 g (58%)

mp **:** 132-134 ^{o}C

IR (KBr) **:** 3540, 1747, 1712 cm^{-1}

^{1}H NMR **:** (400 MHz) δ= 11.46 (s, 1H), 7.81 (s, 1H), 7.80-7.78 (m, 1H), 7.45-7.37 (m, 2H), 5.84 (s, 1H), 2.44 (s, 3H), 2.23 (s, 3H) *ppm*

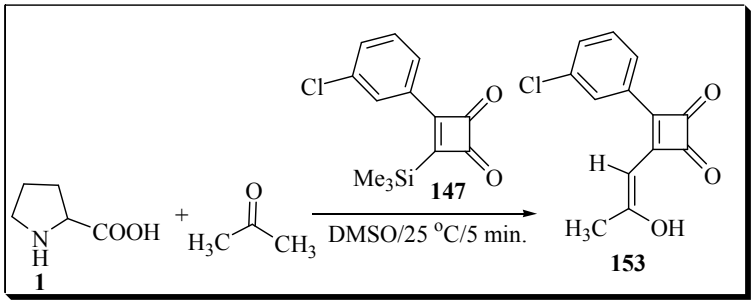
^{13}C NMR **:** (100 MHz) δ = 202.9, 188.7, 182.4, 178.8, 176.7, 139.2, 133.9, 129.3, 129.2, 128.8, 125.4, 92.9, 23.3, 21.4 *ppm*

MS (EI) **:** *m/z* 229 (M+1)

Analysis **:** for $C_{14}H_{12}O_3$

Calculated: C 73.67%; H, 5.30%

Found: C, 73.75%; H, 5.22%



Yield **:** 0.068 g (55%)

IR (KBr) **:** 3443, 1745, 1714 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 11.46 (s, 1H), 7.96 (s, 1H), 7.93-7.91 (m, 1H), 7.57-7.49 (m, 2H), 5.84 (s, 1H), 2.28 (s, 3H) *ppm*

^{13}C NMR **:** (100 MHz) δ = 202.9, 188.0, 182.7, 177.9, 176.4, 135.4, 132.6, 130.7, 130.6, 127.7, 126.2, 92.9, 23.4 *ppm*

MS (EI) **:** *m/z* 247 (M-1)

Analysis **:** for $C_{13}H_9ClO_3$

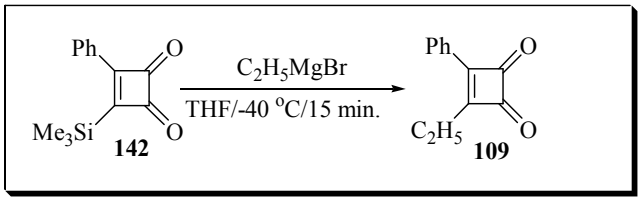
Calculated: C, 62.79%; H, 3.65%

Found: C, 62.85%; H, 3.61%

2.4.6 Preparation of 3-ethyl-4-phenylcyclobut-3-ene-1,2-dione 110

Magnesium turnings (1mmol, 0.024 g) were treated with bromoethane (1 mmol, 0.07 mL) in THF (5 mL) for 1 h at 25 °C. The ethyl magnesium bromide prepared in this way was added slowly to the solution of 3-phenyl-4-(trimethylsilyl)-cyclobutene-1,2-dione (0.230 g, 1 mmol) in THF (10 mL) at –40 °C. The contents were stirred for 15 min at the same temperature. The reaction mixture was brought to room temperature and quenched

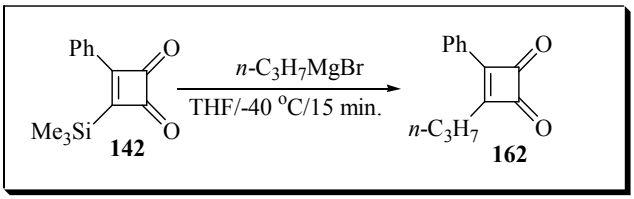
with saturated NH_4Cl solution (5 mL) and extracted with diethyl ether (3x10 mL). The combined organic extract was washed with brine solution and dried over anhydrous Na_2SO_4. The solvent was removed and the residue was subjected to column chromatography (silica gel, hexane-EtOAc). Ethyl acetate (3%) in hexane eluted the 3-ethyl-4-phenylcyclobutenedione **110.**



Yield **:** 0.083 g (45%)

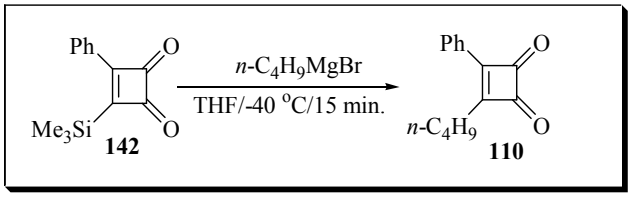
The IR, ^1H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound previously obtained in the reaction of ethyl phenyl acetylene with the $Fe(CO)_5$/NaH/MeI reagent system (Chapter **1**).

The above procedure was followed for the addition of other Grignard reagents to 3-phenyl-4-(trimethylsilyl) cyclobutenedione **142**.



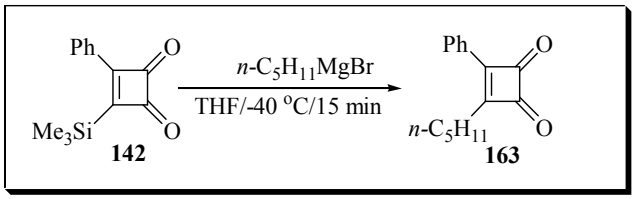
Yield **:** 0.092 g (46%)

The IR, ^1H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound previously obtained in the reaction of 1-phenyl-1-pentyn with the $Fe(CO)_5$/*t*-BuOK reagent system (Chapter **1**)



Yield **:** 0.109 g (51%)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound previously obtained in the reaction of 1-phenyl-1-hexyne with the $Fe(CO)_5$/*t*-BuOK reagent system (Chapter **1**)



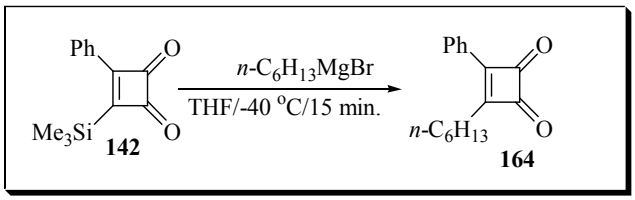
Yield **:** 0.091 g (40%)

IR (KBr) **:** 1751 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 8.02-8.00 (m, 2H), 7.59-7.56 (m, 3H), 3.05 (t, *J* = 7.6 Hz, 2H), 1.89-1.82 (m, 2H), 1.46-1.36 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H). *ppm*

^{13}C NMR **:** (100 MHz) δ = 198.5, 198.1, 197.4, 190.6, 133.5, 129.5, 128.5, 32.0, 27.7, 25.7, 22.3, 13.9. *ppm*

MS (EI) **:** *m/z* 227(M-1)



Yield : 0.101 g (42%)

IR (KBr) : 1766 cm^{-1}

^{1}H NMR : (400 MHz) δ = 8.03-8.01 (m, 2H), 7.59-7.57 (m, 3H), 3.05 (t, *J* = 7.6 Hz, 2H), 1.89-1.81 (m, 2H), 1.45-1.32 (m, 6H), 0.89 (t, *J* = 6.8 Hz, 3H). *ppm*

^{13}C NMR : (100 MHz) δ = 198.5, 198.1, 197.4, 190.5, 133.4, 129.4, 128.5, 31.4, 29.6, 27.8, 26.0, 22.4, 14.0. *ppm*

MS (EI) : *m/z* 243 (M+1)

Analysis : for $C_{16}H_{18}O_2$

Calculated: C, 79.31%; H, 7.49%

Found: C, 79.15%; H, 7.41%

2.5 References

1. Hegedus, L. S. *J. Am. Chem. Soc*. **2009**, *131*, 17995.

2. *(*a) Dalko, P. I.; Moisan, L. *Angew. Chem., Int. Ed.* **2001**, *40*, 3726. (b) List, B. *Tetrahedron* **2002**, *58*, 5573. (c) Notz, W.; Tanaka, F.; Barbas, C. F., III. *Acc. Chem. Res.* **2004**, *37*, 580. (d) Dalko, P. I.; Moisan, L. *Angew. Chem., Int. Ed.* **2004**, *43*, 5138. (e) Enders, D.; Grondal, C.; Huttl, M. R. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 1570. (f) Erkkila, A.; Majander, I.; Pihko, P. M. *Chem. Rev.* **2007**, *107*, 5416. (g) Bertelsen, S.; Jørgensen, K. A. *Chem. Soc. Rev*. **2009**, *38*, 2178.

3. (a) Bertelsen, S.; Marigo, M.; Brandes, S.; Diner, P.; Jørgensen, K. A. *J. Am. Chem. Soc.* **2006**, *128,* 12973. (b) Utsumi, N.; Zhang, H.; Tanaka, F.; Barbas, C. F., III. *Angew. Chem., Int. Ed.* **2007**, *46*, 1878. (c) Zhao, G. -L.; Rios, R.; Vesely, J.; Eriksson, L.; Cordova, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 8468. (d) Ramachary, D. B.; Ramakumar, K.; Narayana, V. V. *Chem. Eur. J*. **2008**, *14*, 9143. (e) Han. B.; Xiao, Y.-C.; He, Z.-Q; Chen. Y.-C. *Org. Lett.* **2009**, *11*, 4660. (f) Han, B.; He, Z. -Q; Li, J. -L.; Li, R.; Jiang, K.; Liu, T. -Y.; Chen, Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 5474. (g) Van Humbeck, J. F.; Simonovich, S. P.; Knowles, R. R.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2010**, *132*, 10012.

4. Heathcock, C. H. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Heathcock, C. H., Eds.; Pergamon: Oxford, **1991**; Vol. *2*, pp 133.

5. Hajos, Z. G.; Parrish, D. R. German Patent DE 2102623, **1971**.

6. Hajos, Z. G.; Parrish, D. R. *J. Org. Chem.* **1974**, *39*, 1615.

7. Agami, C.; Sevestre, H. *J. Chem. Soc., Chem. Commun.* **1984**, 1385.

8. Agami, C.; Platzer, N.; Sevestre, H. *Bull. Soc. Chim. Fr.* **1987**, *2*, 358.

9. Pidathala, C.; Hoang, L.; Vignola, N.; List, B. *Angew. Chem., Int. Ed.* **2003**, *42*, 2785.

10. List, B. In *Modern Aldol Reactions*; Mahrwald, R., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, **2004**; Vol. 1, pp 161.

11. Enders, D.; Niemeier, O.; Straver, L. *Synlett* **2006**, 3399.

12. (a) List, B. *Synlett* **2001**, 1675. (b) List, B.; Lerner, R. A.; Barbas, C. F., III. *J. Am. Chem. Soc.* **2000**, *122*, 2395. (c) Notz, W.; List, B. *J. Am. Chem. Soc.* **2000**, *122*, 7386. (d) List, B.; Pojarliev, P.; Castello, C. *Org. Lett.* **2001**, *3*, 573.

13. Tokuda, O.; Kano, T.; Gao, W. G.; Ikemoto, T.; Maruoka, K. *Org.Lett.* **2005**, *7*, 5103.

14. Samanta, S.; Liu, J.; Dodda, R.; Zhao, C. -G. *Org. Lett.* **2005**, *7*, 5321.

15. Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483.

16. Pan, Q.; Zou, B.; Wang, Y.; Ma, D. *Org. Lett.* **2004**, *6*, 1009.

17. Grondal, C.; Enders, D. *Tetrahedron* **2006**, *62*, 329.

18. Enders, D.; Grondal, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 1210.

19. Cordova, A.; Notz, W.; Barbas, C. F., III. *J. Org. Chem.* **2002**, *67*, 301.

20. Bøgevig, A.; Kumaragurubaran, N.; Jørgensen, K. A. *Chem. Commun.* **2002**, 620.

21. Northrup, A. B.; Mangion, I. K.; Hettche, F.; MacMillan, D. W. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 2152.

22. Alcaide, B.; Almendros, P.; Luna, A.; Torres, M. R. *J. Org. Chem.* **2006**, *71*, 4818.

23. (a) Komnenos, T. *Liebigs Ann. Chem.* **1883**, 145. (b) Michael, A. *J. Prakt. Chem.* **1887**, *36*, 349. (c) Rossiter, B. E.; Swingle, N. M. *Chem. Rev.* **1992**, *92*, 771. (d) Perlmutter, P. *Conjugate Addition Reactions in Organic Synthesis*; Pergamon Press: Oxford, 1992.

24. List, B.; Pojarliev, P.; Martin, H. J. *Org. Lett.* **2001**, *3*, 2423.

25. List, B.; Castello, C. *Synlett* **2001**, 1687.

26. Melchiorre, P.; Jørgensen, K. A. *J. Org. Chem.* **2003**, *68*, 4151.

27. Asato, A. E.; Watanabe, C.; Li, Xiao-Yuan.; Liu, R. S. H. *Tetrahedron Lett.* **1992**, *33*, 3105.

28. List, B.; Pojarliev, P.; Biller, W. T.; Martin, H. J. *J. Am. Chem. Soc.* **2002,** *124,* 827.

29. Notz, W.; Tanaka, F.; Watanabe, S.; Chowdari, N. S.; Turner, J. M.; Thayumanavan. T.; Barbas, C. F., III. *J. Org. Chem.* **2003**, *68*, 9624.

30. List, B. *J. Am. Chem. Soc.* **2002**, *124*, 5656.

31. Chowdari, N. S.; Ramachary, D. B.; Barbas, C. F., III. *Org. Lett.* **2003**, *5*, 1685.

32. (a) Hayashi, Y.; Yamaguchi, J.; Hibino, K.; Shoji, M. *Tetrahedron Lett.* **2003**, *44*, 8293. (b) Hayashi, Y.; Yamaguchi, J.; Sumiya, T.; Shoji, M. *Angew. Chem., Int. Ed.*

2004, *43*, 1112. (c) Hayashi, Y.; Yamaguchi, J.; Sumiya, T.; Hibino, K.; Shoji, M. *J. Org. Chem.* **2004**, *69*, 5966.

33. Mase, N.; Tanaka, F.; Barbas, C. F., III. *Org. Lett.* **2003**, *5*, 4369.

34. Ramachary, D. B.; Chowdari, N, S.; Barbas C. F., III. *Synlett* **2003**, 1910.

35. Fioravanti, S.; Pellacani, L.; Tardella, P. A.; Vergari, M. C. *Org. Lett.* **2008**, *10*, 1449.

36. Lu, L.-Q.; Xing, X.-N.; Wang, X.-F.; Ming, Z.-H.; Wang,H.-M.; Xiao, W.-J. *Tetrahedron Lett*. **2008**, *49*, 1631.

37. Fan, M. –J.; Qian, B.; Zhao, L. -B; Liang, Y. –M. *Tetrahedron* **2007**, *63*, 8987.

38. Kumar, A.; Maurya, R. A. *Tetrahedron* **2007**, *63*, 1946.

39. Chandrasekhar, S.; Vijeender, K.; Sridhar, Ch. *Tetrahedron Lett*. **2007**, *48*, 4935.

40. Varala, R.; Nasreen, A.; Enugala, R.; Adapa, S. R. *Tetrahedron Lett*. **2007**, *48*, 69.

41. Shi, C. –L.; Shi, D. –Q.; Kim, S. H.; Huang, Z. –B.; Ji, S. –J.; Ji, M. *Tetrahedron* **2008**, *64*, 2425.

42. Xie, H.; Zu, L.; Oueis, H. R.; Li, H.; Wang, J.; Wang, W. *Org. Lett.*, **2008**, *10*, 1923.

43. Kumar, A.; Kumar, M.; Gupta, M. K. *Tetrahedron Lett*. **2009**, 50, 7024.

44. Goswami, P.; Das, B. *Tetrahedron Lett*. **2009**, *50*, 897.

45. Wang, J.-F.; Lei, M.; Li, Q.; Ge, Z.-M.; Wang, X.; Li, R.-T. *Tetrahedron* **2009**, *65*, 4826.

46. Samai, S.; Nandi, G. C.; Singh, P.; Singh, M. S. *Tetrahedron* **2009**, *65*, 10155.

47. Mukhopadhyay, C.; Tapaswi, P. K.; Butcher, R. J. *Tetrahedron Lett*. **2010**, *51*, 1797.

48. (a) Gardner, S. H.; Freyschmidt-Paul, P.; Hoffman, R.; Sundberg, J. P.; Happle, R.; Nigel, J.; Tobin, D. J. *Eur. J. Dermatol.* **2000**, *10*, 443. (b) Freyschmidt-paul, P.; Sundberg, J. P.; Happle, R.; McElwee, K. J.; Metz, S.; Boggess, D; Hoffman, R. J. *Investigative Dermatol.* **1999**, *113*, 61.

49. (a) Kazumasa, M.; Motonobu, N.; Miyako, N.;Tatsuo, K.; Yoshiki, M. *J. Dermatol.* **2002**, *29*, 661. (b) Silverberg, N. B.; Lim, J. K.; Paller, A. S.; Mancini, A. J. *J. Am. Acad. Dermatol.* **2000**, *42*, 803.

50. (a) Douglas, K. T.; Nadvi, I. N. *FEBS Lett*. **1979**, *106*, 393. (b) Burka, L. T.; Doran, J.; Wilson, B. *J. Biochem. Pharmacol.* **1982**, *31*, 79. (c) Xie, J.; Comeau, A. B.; Seto, C. T. *Org. Lett.* **2004,** *6*, 83. (d) Sato, K.; Seio, K.; Sekine, M. *J. Am. Chem. Soc*. **2002**, *124*, 12715. (e) Beaulieu, P. L.; Cameron, D. R.; Ferland, J. -M.; Gauthier, J.; Ghiro, E.; Gillard, J.; Gorys, V.; Poirier, M.; Rancourt, J.; Wernic, D.; Llinas-Brunet, M.; Betageri, R.; Cardozo, M.; Hickey, E. R.; Ingraham, R.; Jakes, S.; Kabcenell, A.; Kirrane, T.; Lukas, S.; Patel, U.; Proudfoot, J.; Sharma, R.; Tong, L.; Moss, N. *J. Med. Chem*. **1999**, *42*, 1757.

51. (a) Kinney, W. A.; Abou-Gharbia, M.; Garrison, D. T.; Schmidt, J.; Kowal, D. M.; Bramlett, D. R.; Miller, T. L.; Tasse, R. P.; Zaleska, M. M.; Moyer, J. A. *J. Med. Chem*. **1998**, *41*, 236. (b) Chan, P. C. M.; Roon, R. J.; Koerner, J. F.; Taylor, N. J.; Honek, J. F. *J. Med. Chem*. **1995**, *38*, 4433.

52. Butera, J. A.; Jenkins, D. J.; Lennox, J. R.; Sheldon, J. H.; Norton, D. Warga, N. W.; Argentierib, T. M. *Bioorg. Med. Chem. Lett*. **2005**, *15*, 2495.

53. (a) Avirah, R. R.; Jyothish, K.; Ramaiah, D. *Org. Lett*. **2007**, *9,* 121. (b) Ajayaghosh, A.; Eldo, J. *Org. Lett*. **2001**, 3, 2595. (c) Jyothish, K.; Arun, K. T.; Ramaiah, D**.** *Org. Lett.* **2004**, *6,* 3965. (d) Jyothish, K.; Avirah, R. R.; Ramaiah, D.; *Org. Lett.* **2006**, *8,* 111. (e) Volkova, K. D.; Kovalska, V. B.; Tatarets, A. L.; Patsenker, L. D.; Kryvorotenko, D. V.; Yarmoluk, S. M. *Dyes Pigments* **2007**, *72*, 285.

54. Ried, W.; Vogl, M. *Chem Ber*. **1982**, *115*, 403.

55. Jung, M. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Semmelhack, M. F., Eds.; Pergamon: Oxford, **1991**; Vol. 4.

56. (a) Bergmann, E. D.; Ginsburg, D.; Pappo, R. *Org. React*. **1959**, *10*, 179. (b) Kobayashi, S. *Synlett* **1994**, 689.

57. (a) Christoffers, J. *Eur. J. Org. Chem*. **1998**, *63,* 1259. (b) Srivastava, N.; Banik, B. K. *J. Org. Chem*. **2003**, *68*, 2109. (c) Shimizu, K. I.; Miyagi, M.; Kan-No, T.; Kodama, T.; Kitayama, Y. *Tetrahedron Lett*. **2003**, *44*, 7421.

58. (a) Hambrecht, J.; Straub, H.; Muller, E. *Chem. Ber*. **1974**, *107*, 3962. (b) Hambrecht, J.; Straub, H. *Tetrahedron Lett.* **1976**, 17, 1079.

59. Beesu. M.; Periasamy, M. *J. Org. Chem.* **2011**, *76*, 543.

Chapter 3

Synthetic Methods Based on Reactions of Aromatic Diketones and Diols with the Amine/$TiCl_4$ Reagent System

3.1 Introduction

Titanium reagents have been used in a multitude of reactions in organic, inorganic and polymer chemistry. Several titanium reagents have become very much popular in organic synthesis due to their availability, inexpensiveness, the possibility of adjusting reactivity and selectivity by ligands.[1a] The widespread applications of titanium reagents are due to their unique ability in functional group transformations and also in attaining better chemo, regio and stereoselectivities.

In recent years, the deoxygenative-reductive coupling reactions of carbonyl compounds (eg.: McMurry reaction) have been widely employed in synthesis using the low valent titanium (LVT) species, produced by the reduction of $TiCl_4$ with metals and metal hydrides.[1b] The $Cp_2TiCl_2/(CH_3)_3Al$ (The Tebbe's reagent) and the $TiCl_4/CH_2Br_2/Zn$ reagent systems have been used for the Wittig-type olefination of carbonyl compounds.[2a,b] The Reetz reagent, Me_2TiCl_2, has been employed in *gem*-dimethylation of carbonyl compounds.[2c] Several reports show that the transmetalation of organolithium or organomagnesium reagents with titanium reagents leads to better chemo-, regio- and stereoselectivities.[1,3]

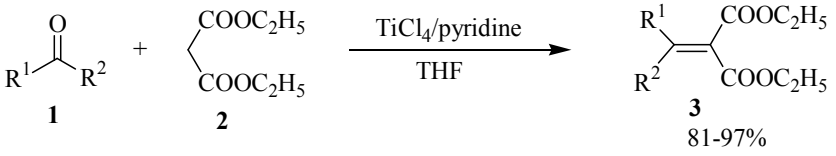
More recently, the $TiCl_4$/trialkylamine reagent system has been extensively employed in the preparation of titanium enolates for synthetic applications.[4] Also, the $TiCl_4$ has been used as Lewis acid for arylation as well as acylation of aromatic compounds.[5] We have undertaken research efforts on developing methods for the synthesis

of conjugated electron rich molecules by the arylation reaction of titanium reagents with cyclobutenediones and other diketones. Accordingly, it is of interest to briefly review the literature reports on these topics including previous reports from this laboratory.

3.1.1 Reactions of $TiCl_4/Et_3N$ reagent system via titanium enolates

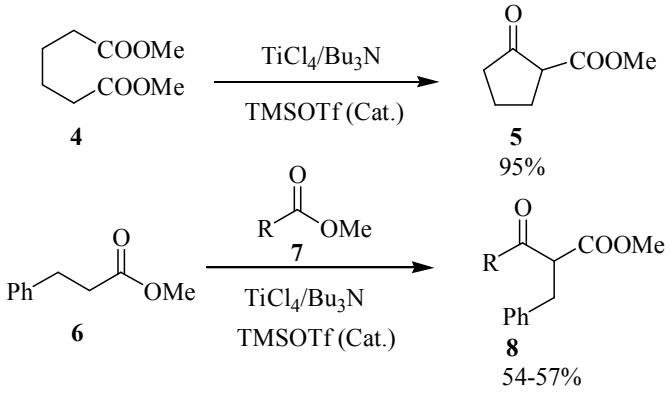
The $TiCl_4/R_3N$ reagent system has been widely used for the preparation of titanium enolates for applications in aldol and related reactions.[6] For example, it was reported that the ketones **1** and diester **2** react in the presence of $TiCl_4$/pyridine reagent to give the Knoevenagel condensation product **3** (**Scheme 1**).

Scheme 1



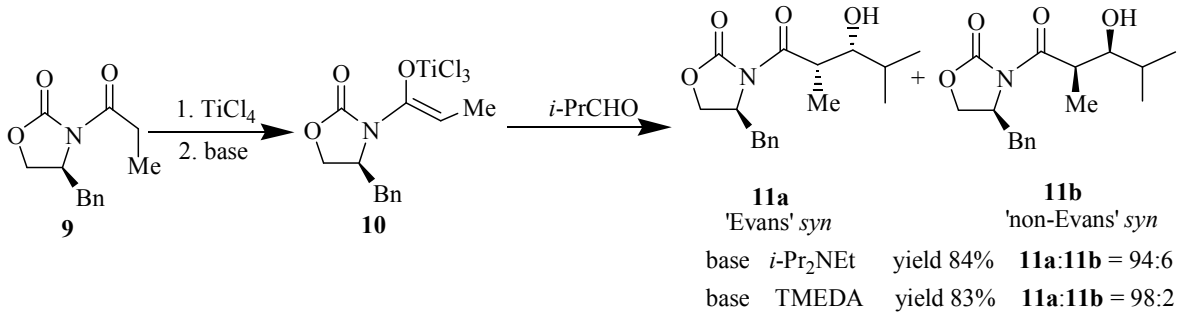
It has been also reported that the direct Claisen condensation products **5** and **8** were obtained intra and inter molecular reactions with esters (**Scheme 2**).[7]

Scheme 2



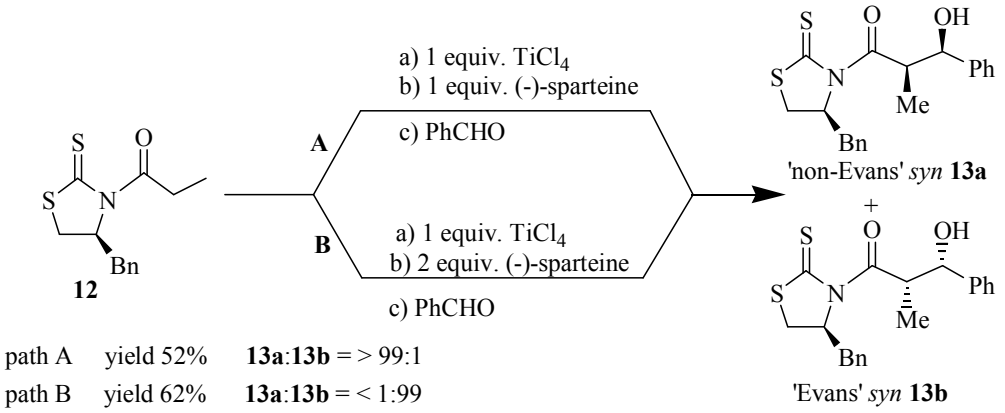
Evans *et al.*[4c] reported that the enantiomerically pure oxazolidinone **9** and isobutyraldehyde react in the presence of $TiCl_4$ and tertiary amine base to give the corresponding *syn* aldol product **11a** in good yield with excellent selectivity via the corresponding titanium enolate **10** (**Scheme 3).**

Scheme 3



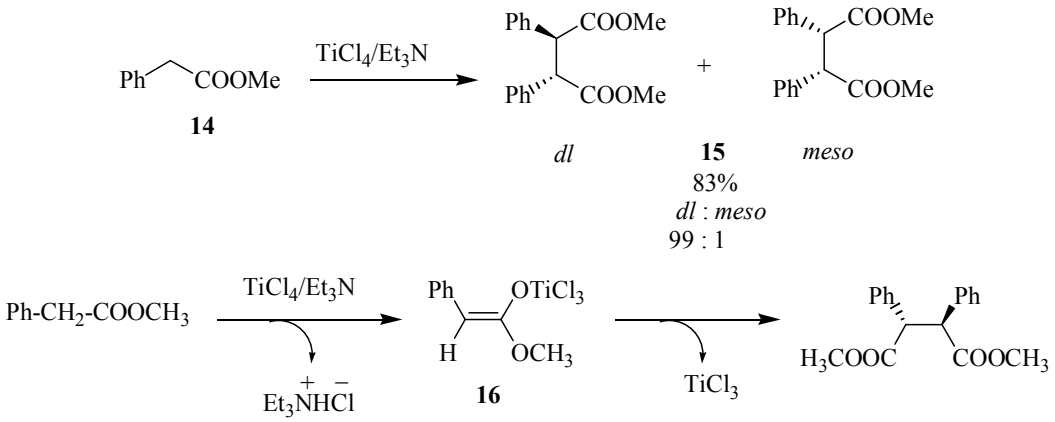
Interestingly, the amount of base has remarkable effect in the titanium-mediated asymmetric aldol reaction. For example, the reaction of *N*-propanoylthiazolidinethione **12** with benzaldehyde in the presence of 1 equiv. of (-)-sparteine afforded 'non-Evans' *syn* aldol product **13a**, whereas 2 equiv. of (-)-sparteine gave 'Evans' *syn* aldol product **13b** (**Scheme 4**).[8]

Scheme 4



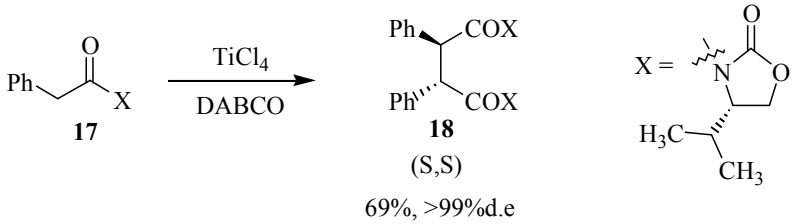
It has been reported that the $TiCl_4/NR_3$ reagent system is useful in the preparation of the *dl*-C_2 symmetric 2,3-diphenylsuccinic acid esters **15** from methyl phenylacetate **14**. The reaction is highly chemo and diastereoselective (**Scheme 5**).[9a] This reaction proceeds through the formation of the corresponding titanium enolates, followed by oxidative coupling with concomitant formation of the titanium (III) species.

Scheme 5



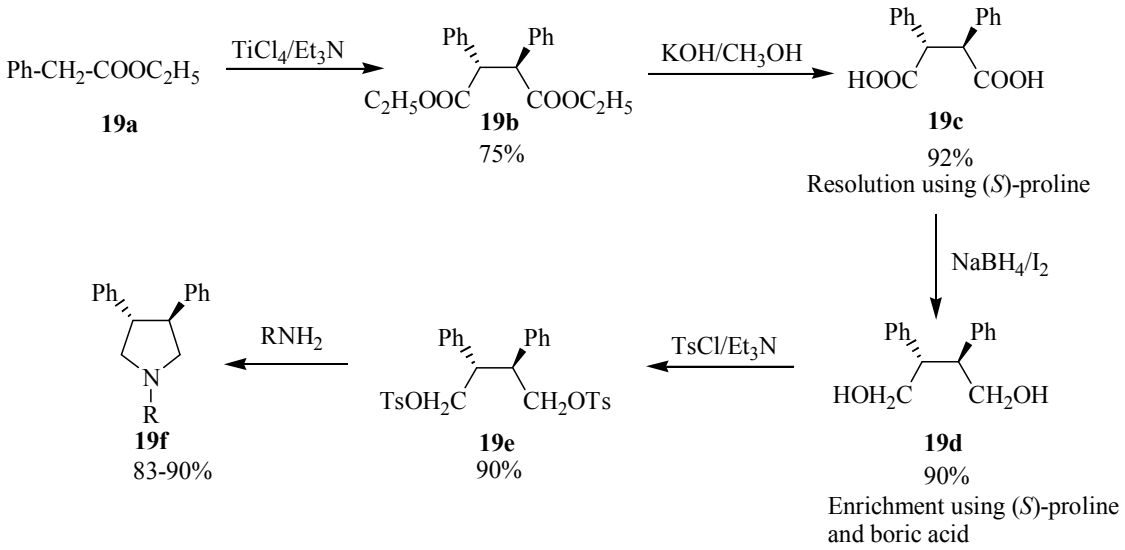
Also, the asymmetric version of the oxidative coupling of **17** using the $TiCl_4$/DABCO reagent system gives the product **18** with high selectivity (**Scheme 6**).[9b,c]

Scheme 6



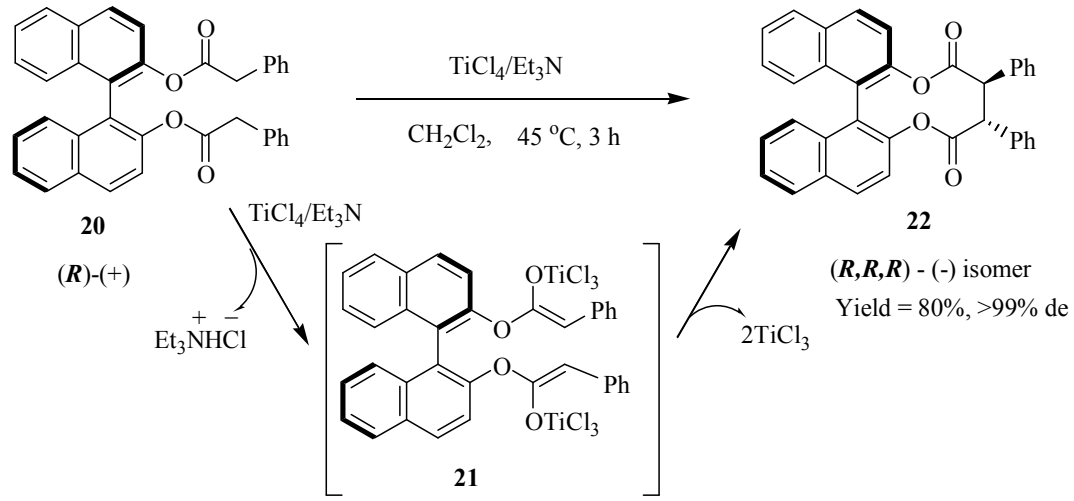
The dicarboxylic acid **19d**, formed in the oxidative coupling reaction of phenylacetate **19a** in the presence of $TiCl_4/Et_3N$ was used for the synthesis of chiral 3,4-diphenylpyrrolidine **19f** (**Scheme 7**).[10]

Scheme 7



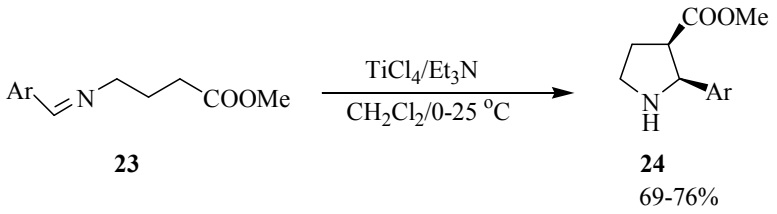
The chiral binaphthyl phenylacetate **20** on reaction with $TiCl_4/Et_3N$ reagent gives the corresponding diastereoselective cyclic compound **22** (**Scheme 8**).[11]

Scheme 8



Facile synthesis of the aryl-3-pyrrolidine carboxylates **24** from readily accessible γ-imino esters **23** via intramolecular cyclization mediated by the $TiCl_4/Et_3N$ reagent system has been reported (**Scheme 9**).[12]

Scheme 9

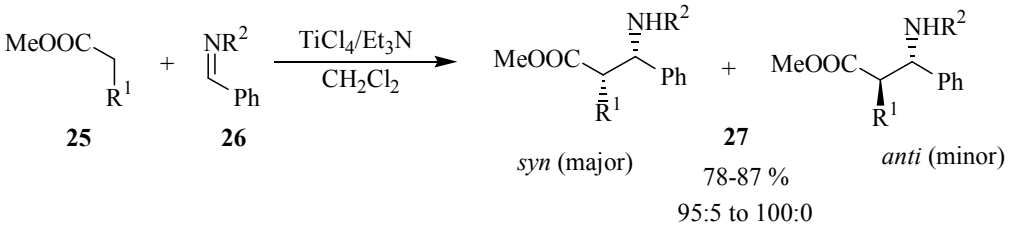


23 **24**

69-76%

Reaction of benzaldehyde imines **26** and esters **25** with the $TiCl_4/R_3N$ reagent system produced the *syn*-β-amino esters **27** stereoselectively (**Scheme 10**).[13]

Scheme 10

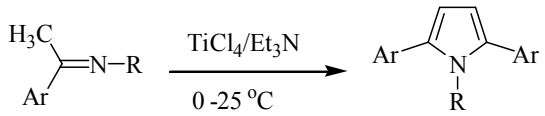


25 **26** *syn* (major) **27** 78-87 % 95:5 to 100:0 *anti* (minor)

3.1.2 Reactions of $TiCl_4/R_3N$ reagent system with imines and iminium ions

The reactivity of the $TiCl_4/Et_3N$ reagent system with other organic substrates containing acidic hydrogens have been reported. For example, the reaction of aromatic ketimines **28** with $TiCl_4/Et_3N$ produced the corresponding 2,5-disubstituted pyrroles **29** through oxidative coupling followed by aromatization reactions (**Scheme 11**).[14]

Scheme 11

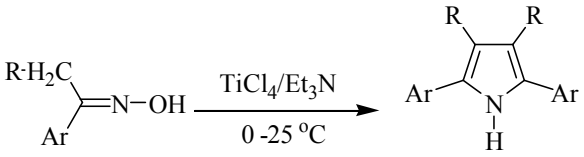


28 **29**

63-90%

Also, it was found that ketoximes **30** react with the $TiCl_4/NEt_3$ system to give the corresponding tetrasubstituted pyrroles **31** (**Scheme 12**).[15]

Scheme 12

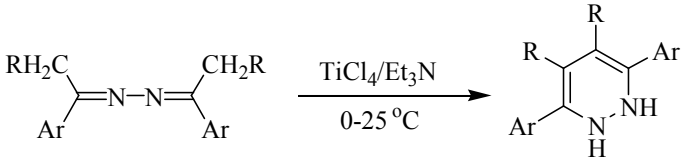


30 **31**

55-81%

The hydrazones **32** undergo intramolecular oxidative coupling in the presence of $TiCl_4/R_3N$ reagent system to give the corresponding 1,2-dihydropyridazines **33** (**Scheme 13**).[16]

Scheme 13



32 **33**

50-55%

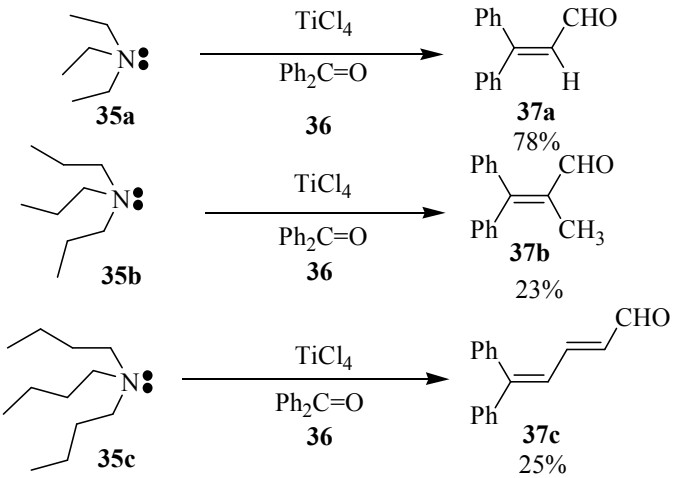
The $TiCl_4$ reacts with tertiary amines like $(CH_3)_3N$ to give the corresponding iminium salt **34** and $TiCl_3$.[17a]

$$2\,(CH_3)_3N + 2\,TiCl_4 \longrightarrow 2\,TiCl_3 + 2\,(CH_3)_2N^{+}{=}CH_2\;\bar{Cl} + 2\,(CH_3)_3N^{+}H\bar{Cl} \qquad \text{eq- (1)}$$

34

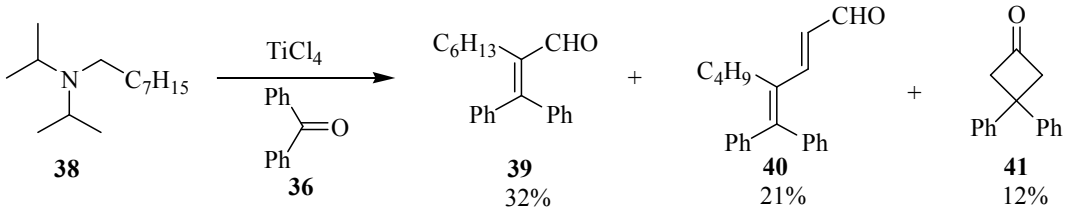
Such iminium ions that are expected to be formed using higher amines can be trapped with benzophenone to give the corresponding aldehydes. [17b, c]

Scheme 14



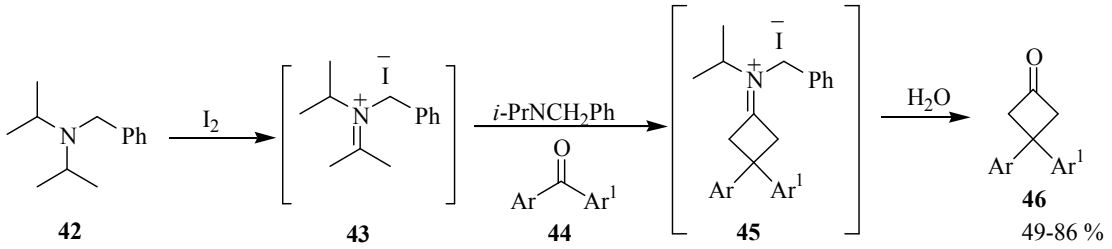
Also, it was found that the reaction of *N,N*-diisopropyloctylamine **38** with benzophenone in the presence of $TiCl_4$ leads to the formation of the corresponding cyclobutanone **41** in low yield (12%) in addition to the unsaturated aldehydes **39** and **40** (**Scheme 15**).[18]

Scheme 15



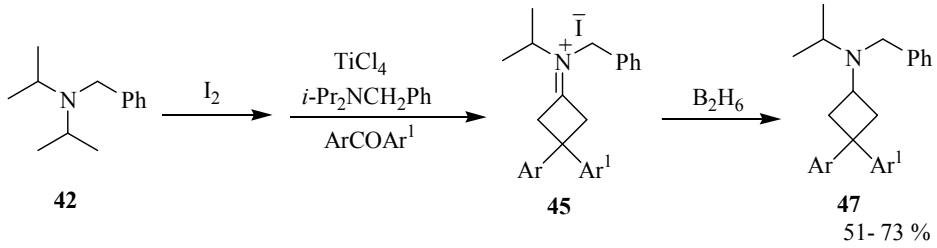
The iminium ions **43,** prepared *in situ* by the oxidation of *N,N*-diisopropyl-*N*-benzylamine **42** using iodine, react with diaryl ketones in the presence of $TiCl_4/R_3N$ to give the corresponding 3,3-diarylcyclobutanones **46** in 49-86% yields.(**Scheme 16**).[18]

Scheme 16



When the above reaction was carried out in the presence of B_2H_6, the 3,3-diarylcyclobutanone iminium ions **45** formed *in situ* is reduced to the corresponding 3,3-diarylcyclobutylamines **47** (**Scheme 17).**[18]

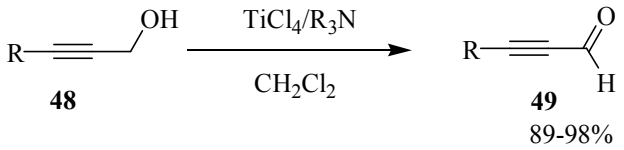
Scheme 17



3.1.3 Oxidation reactions using $TiCl_4/Et_3N$ reagent system

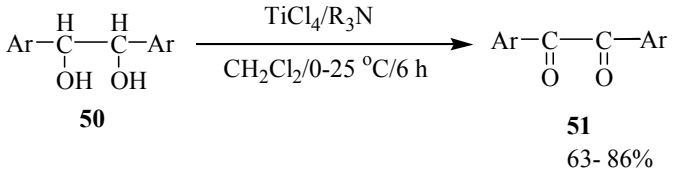
As discussed in the previous section, the $TiCl_4$ oxidizes trialkyl amines to the iminium ion and gets reduced to $TiCl_3$ species. The $TiCl_4/Et_3N$ reagent system also oxidizes the simple propargyl alcohols to the corresponding aldehydes **49** (**Scheme 18**).[19]

Scheme 18



1,2-Diphenylethane-1,2-diols **50** are oxidized by the $TiCl_4/Et_3N$ reagent in CH_2Cl_2 solvent to provide the corresponding 1,2-diketones in 63-86% yields (**Scheme 19).**[20]

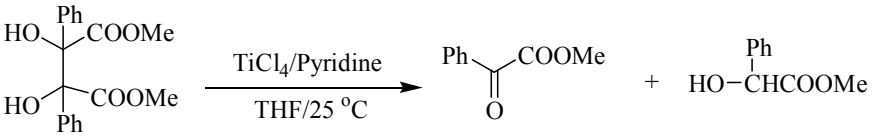
Scheme 19



50 **51** 63- 86%

The $TiCl_4$/amine reagent system has been also used in the oxidation of certain other alcohols. For example, the $TiCl_4$/pyridine reagent combination is useful for the oxidative cleavage of methyl diphenyltartrate **52** to methyl phenylglyoxalate **53** besides the hydroxy ester **54** (**Scheme 20**).[21]

Scheme 20

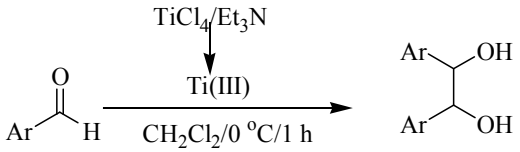


52 **53** 77% **54** 21%

3.1.4 Reductive coupling reactions using $TiCl_4/Et_3N$ reagent system

Lower valent titanium species generated *in situ* from the $TiCl_4/Et_3N$ reagent system reacts with aromatic aldehydes **55** to produce the corresponding 1,2-diarylethane-1,2-diols **56 (Scheme 21)**.[22]

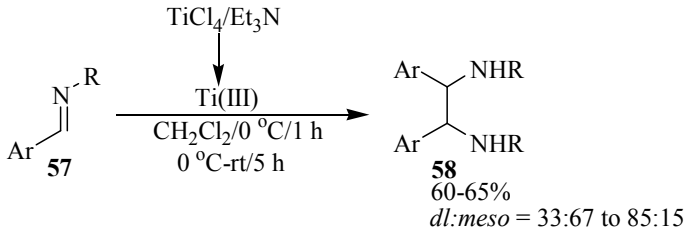
Scheme 21



55 **56** 58 -71%
dl:meso = 74:26 to100:0

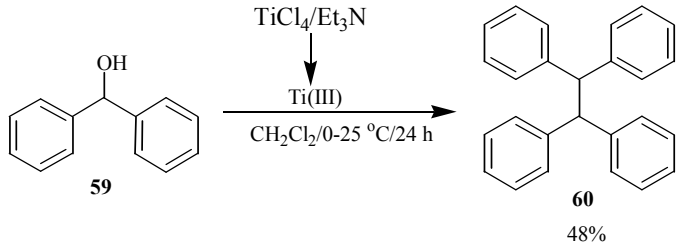
The Ti (III) species obtained from $TiCl_4/Et_3N$ reagent system has been utilized for imine **57** coupling to obtain the corresponding vicinal *dl*-diamines **58** (**Scheme 22**).[22]

Scheme 22



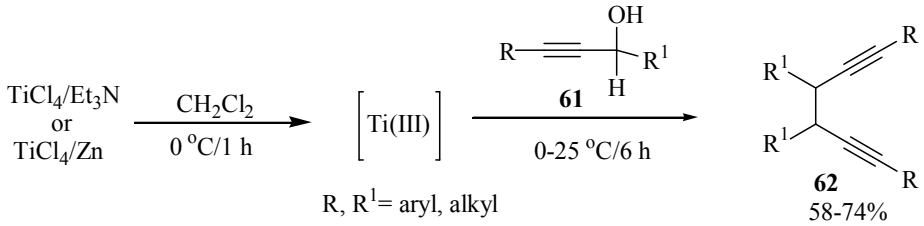
Also, the reaction of benzhydrol **59** with $TiCl_3$ species prepared using the $TiCl_4/Et_3N$ reagent system gives the tetraphenylethane **60** in 48% yield (**Scheme 23**).[23]

Scheme 23



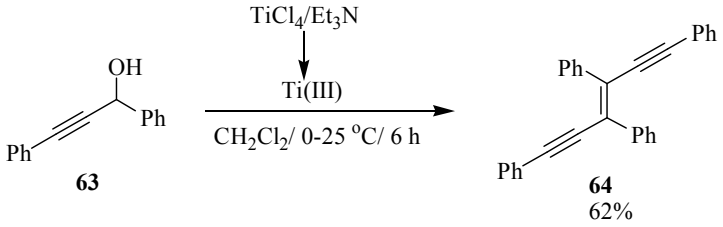
Low-valent titanium reagents prepared using $TiCl_4/Et_3N$ or $TiCl_4$/Zn reacts with propargyl alcohols **61** to give the corresponding 1,5-diynes **62** (**Scheme 24**).[24]

Scheme 24



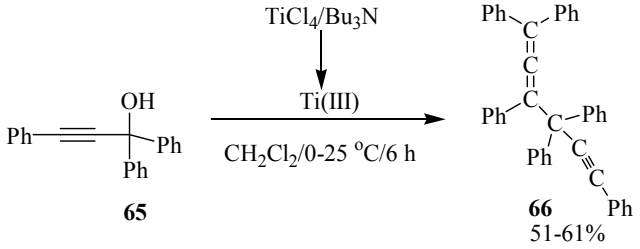
Interestingly, the reaction of propargyl alcohol **63** gives the enediyne product **64** in 62% yield (**Scheme 25**).[24]

Scheme 25



However, the propargyl alcohol **65** is converted to the corresponding allenynes **66** (**Scheme 26**).[24]

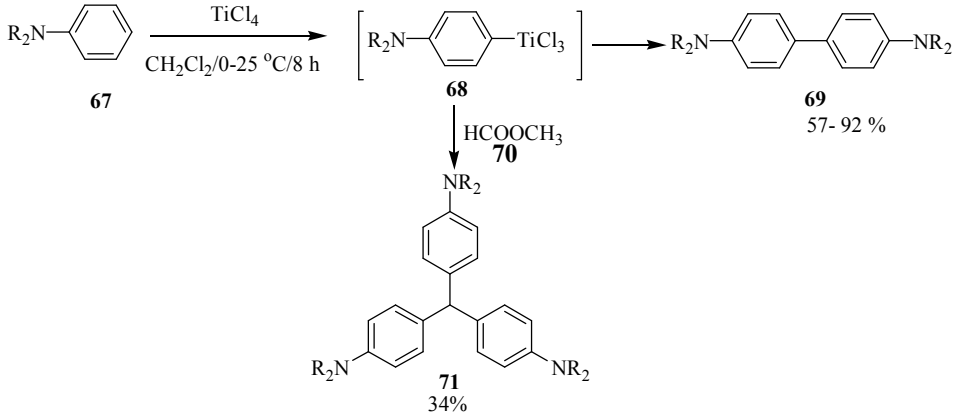
Scheme 26



3.1.5 Reaction of $TiCl_4/ArNR_2$ reagent system

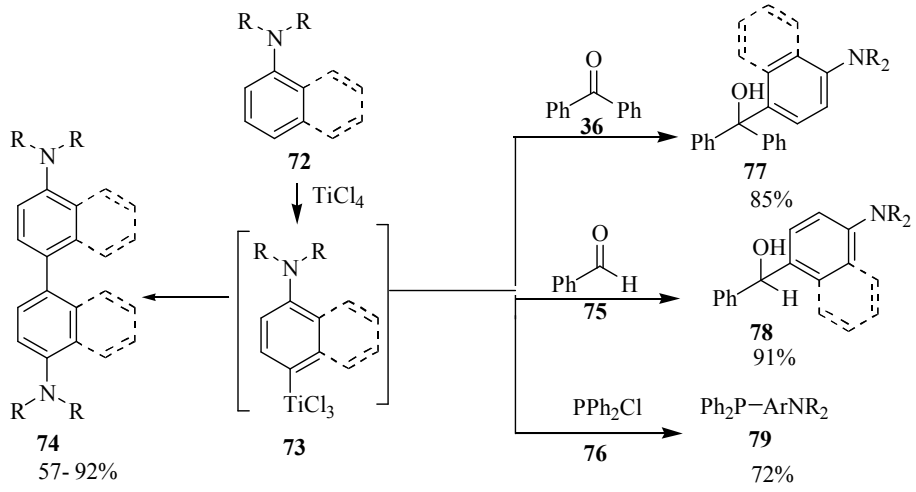
In the presence of $TiCl_4$, *N,N*-dialkylanilines **67** undergo oxidative coupling to provide the corresponding benzidine **69** products in good yields. This transformation can be rationalized considering the intermediacy of the corresponding aryl titanium species **68**. The aryl titanium species prepared *in situ* in this way react with $HCOOCH_3$ electrophile to give the coupled product **71** (**Scheme 27**).[25]

Scheme 27



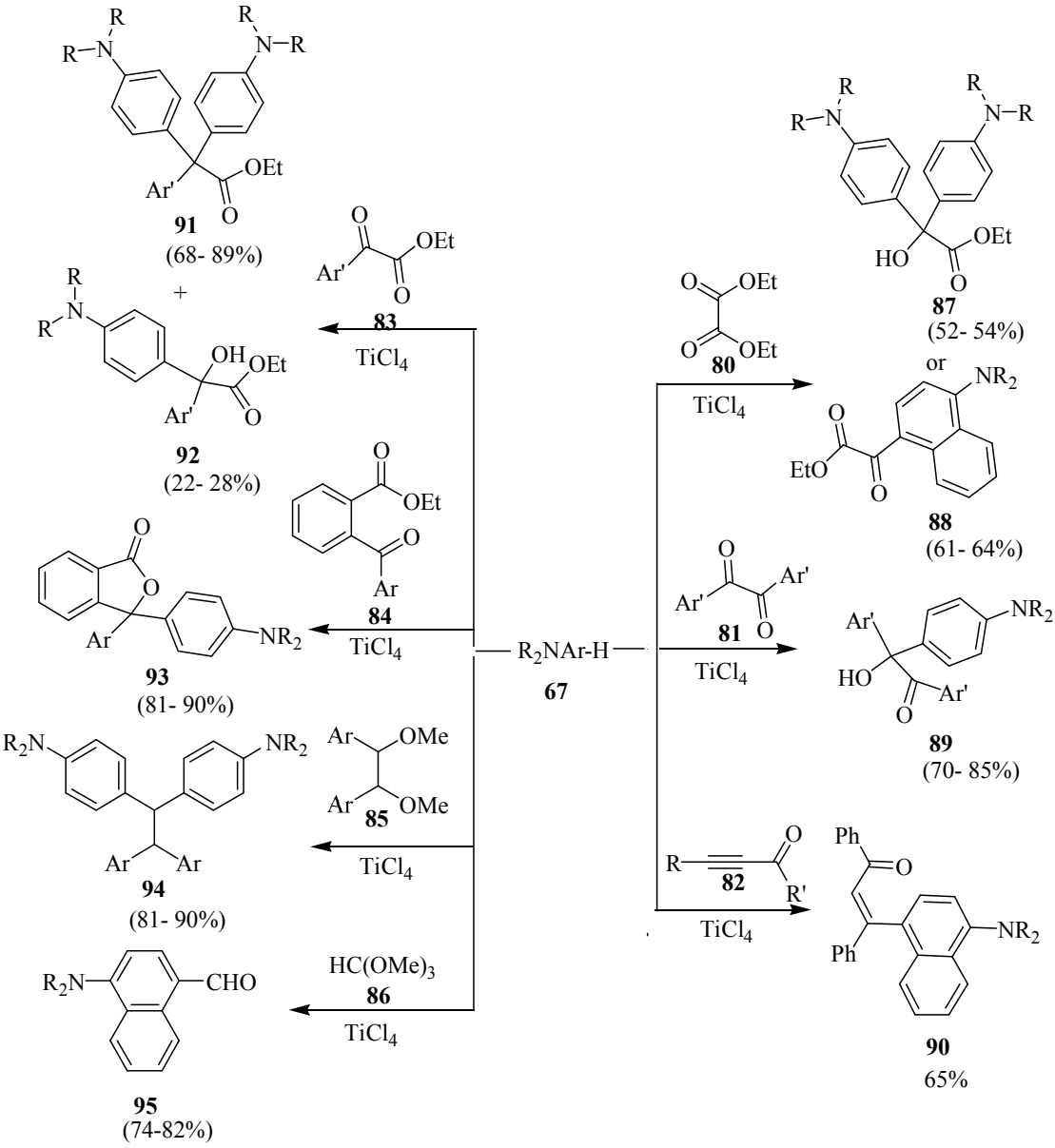
The reaction of the $TiCl_4/ArNR_2$ system was examined with various electrophiles (**Chart 1**). In the reaction with diaryl ketones and benzaldehyde the expected electrophilic addition products **77** and **78** were obtained. Reaction with chlorodiphenylphosphine gave the corresponding electrophilic substitution product **79** (**Chart 1**).[25]

Chart 1



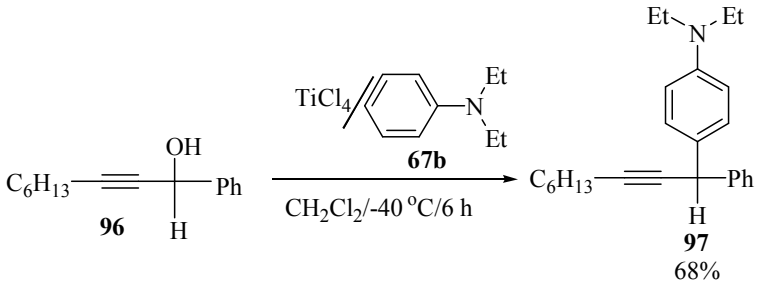
Interesting pattern of reactivity was observed in the reactions of $TiCl_4$/N,N-dialkylarylamine reagent system with several other organic substrates (**Chart 2**). [26]

Chart 2



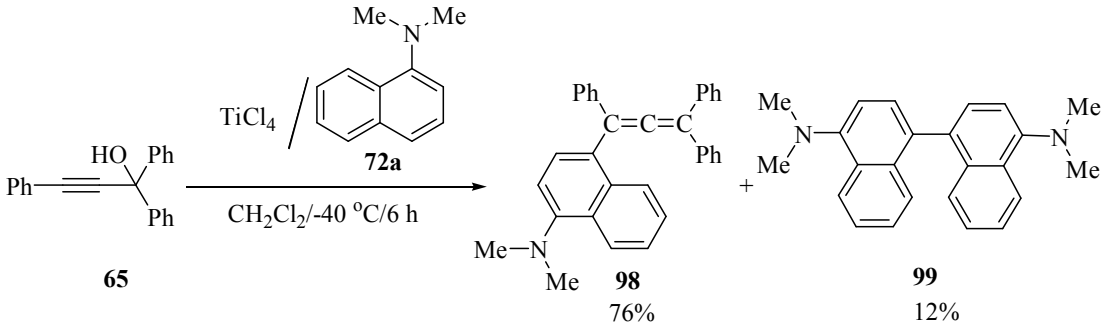
Cross coupling reaction takes place in the case of phenyl-2-octyn-1-ol **96**. The corresponding arylalkyne **97** was obtained in 68% yield (**Scheme 28**).[27]

Scheme 28



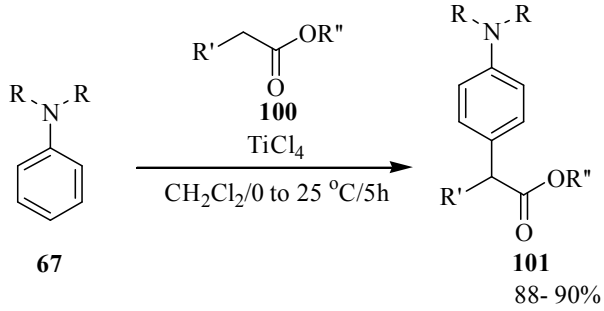
However, in the reaction using the propargyl alcohol and *N,N*-dimethylnapthylamine **72a** at –40 °C, the corresponding tetraarylallene **98** was obtained in 76% yield besides the diaryl compound **99 (Scheme 29)**.[27]

Scheme 29



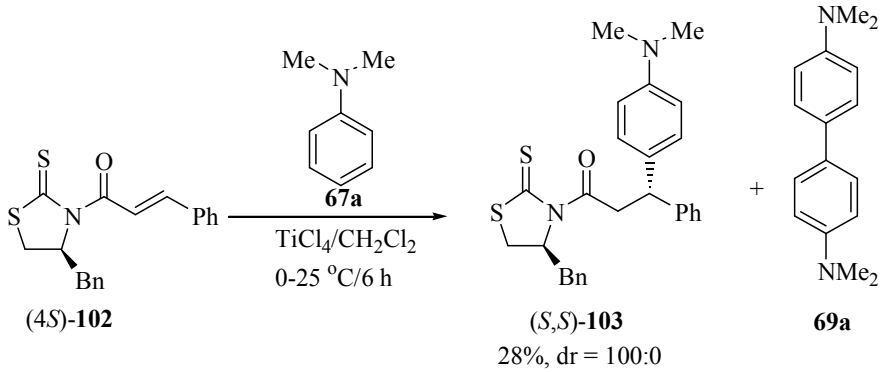
The *N*,*N*-dialkylarylamines also undergo cross coupling reaction with arylacetic acid esters **100** in the presence of $TiCl_4$ to produce the corresponding α-arylated products **101** in good yields (**Scheme 30).** [28]

Scheme 30



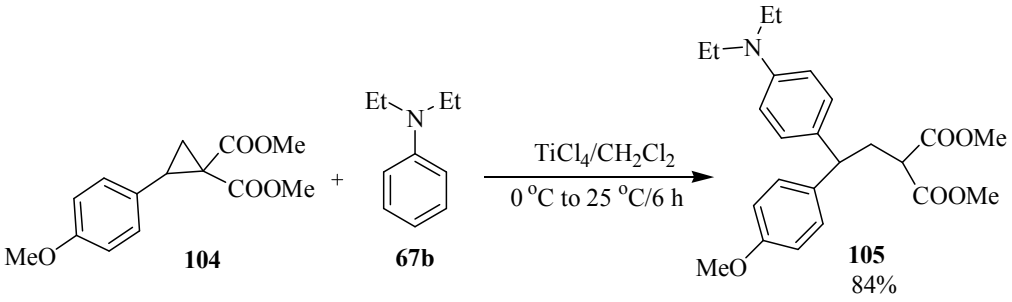
In the reaction of chiral enone (4*S*)- **102** with *N*,*N*-dimethylaniline the corresponding 1,4-addition product **103** is obtained in 28% yield along with the homocoupled benzidine product **69a**.[29a]

Scheme 31



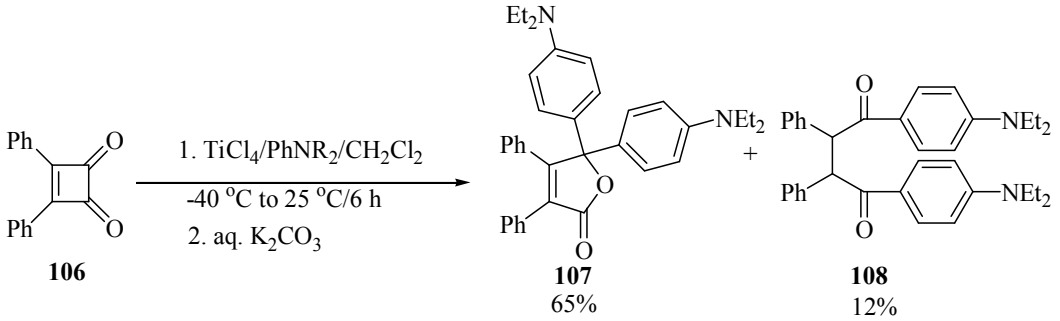
The cyclopropyl diester **104** reacts with *N,N*-diethylaniline **67b** in the presence of $TiCl_4$, to provide the corresponding addition product **105** in 84% yield (**Scheme 32**).[29b]

Scheme 32



It was observed that the diphenylcyclobutenedione **106** reacts with $TiCl_4$ and *N,N*-diethylaniline reagent system at -40 °C to provide the butenolide **107** in 65% yield along with the 1,4-diketone **108** (12%) (**Scheme 33**).[30a]

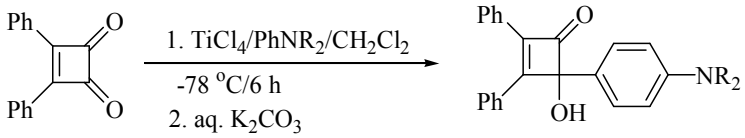
Scheme 33



106 **107** 65% **108** 12%

When the reaction was carried at –78 °C, the formation of the corresponding 1,2-addition **109** products (32-48%) were observed (**Scheme 34**).[30b]

Scheme 34



106 **109** 32-48%

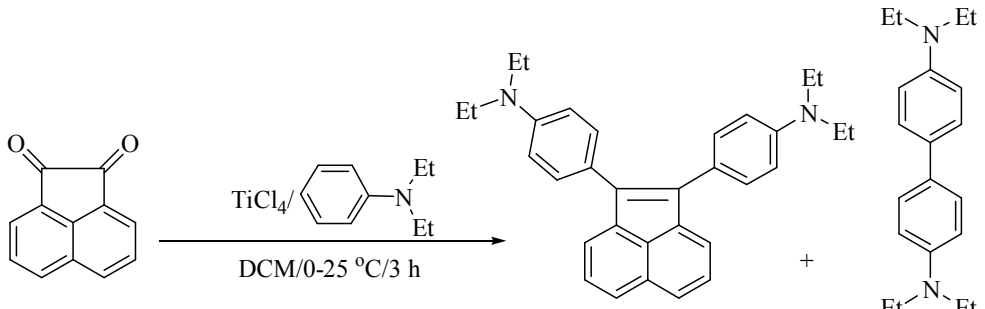
We have examined the reaction of the aryl titanium species prepared *in situ* using the $TiCl_4/ArNR_2$ reagent system with acenaphthenequinone, phenanthrenequinone and anthraquinone. The results are discussed in the next section.

3.2 Results and Discussion

3.2.1 Reaction of acenaphthenequinone with the $TiCl_4/Et_3N$/arylamine reagent system

As discussed in the introductory section **3.1.1**. *N,N*-dialkylaniline derivatives reacts with diphenylcyclobutenedione in the presence of $TiCl_4$ at -40 ^oC to give the corresponding butenolide along with the 1,4-diketone (**Scheme 33**).[30a] We have examined the reactivity of the $TiCl_4$/*N,N*-dialkylarylamine reagent system with 1,2-diones like acenaphthenequinone and phenanthrenequinone. Whereas the phenanthrenequinone did not react with the $TiCl_4$/*N,N*-dialkylaniline reagent system under ambient reaction conditions, the acenaphthenequinone (1 mmol) reacts with *N,N*-diethylaniline (3 mmol) and $TiCl_4$ (3 mmol) to give the corresponding 1,2-diarylacenaphthylene **114** in 45% yield along with *N,N,N,N*-tetraethylbenzidines besides some unidentifiable mixture of products.

Scheme 35

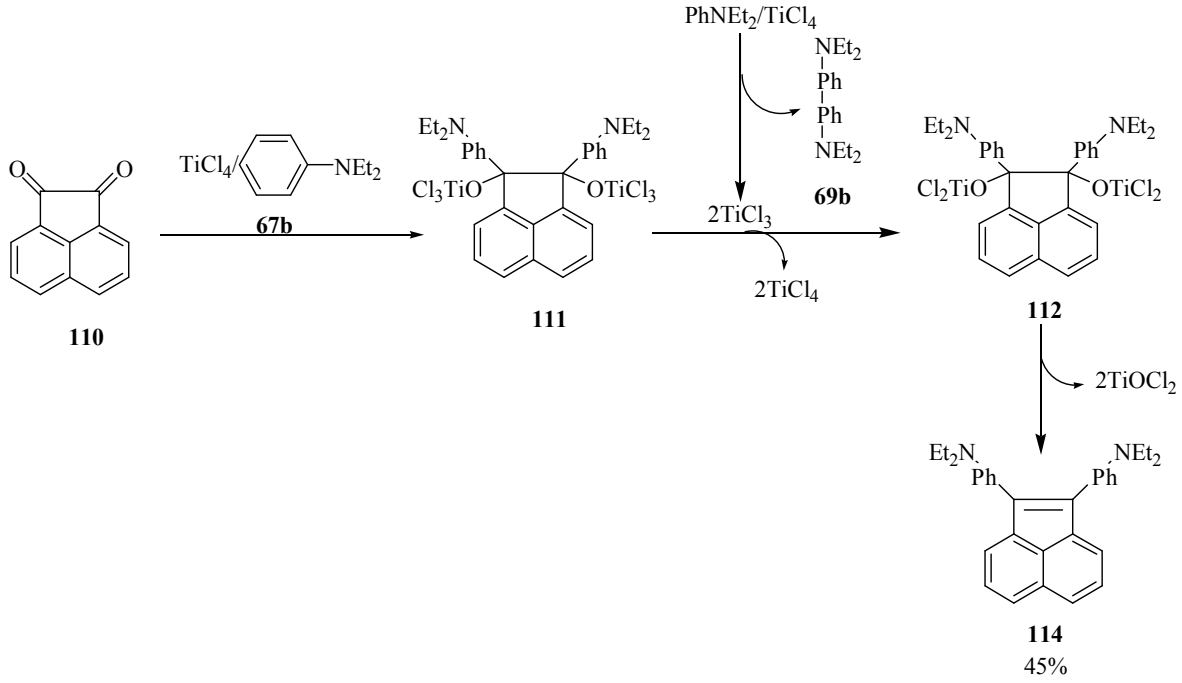


110 **114** 45% **69b** 12%

Initially, we have carried out this transformation using acenapthenequinone **110** (1 mmol), *N,N*-diethylaniline (3 mmol) and $TiCl_4$ (3 mmol) without using Et_3N. This

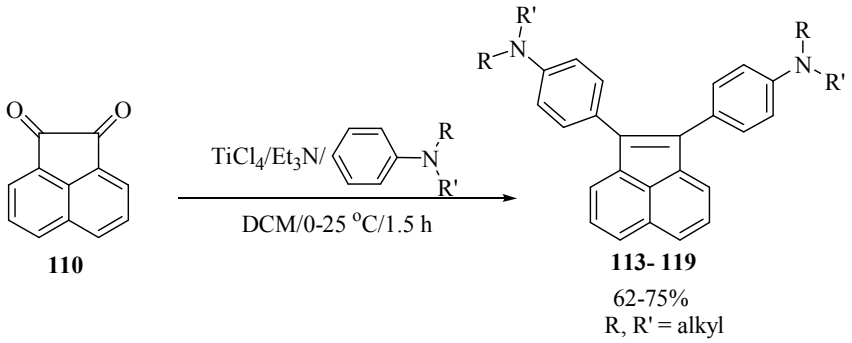
transformation may involve initial arylation of carbonyl groups followed by deoxygenation to give the diaryl product **114**.

Scheme 36



Surprisingly, the corresponding 1,2-diarylacenaphthylene derivative **114** is obtained in 75% yield when Et_3N was also used along with the arylamine in this transformation. Several other dialkylarylamines are converted to the corresponding 1,2-diarylacenaphthylenes in good yields (62-75%, **Table 2**) by reaction with acenaphthenequinone using $Et_3N/TiCl_4$. When the reaction of *N,N*-diethylaniline and acenaphthenequinone with Bu_3N or *i*-Pr_2NEt was carried out in the place of Et_3N, the product was obtained only in 60% and 55% yield, respectively.

Scheme 37



110 **113- 119**
62-75%
R, R' = alkyl

The structure of the 1,2-diarylacenaphthylene **113** was confirmed by single crystal X-ray data. Two independent molecules are present in the unit cell.

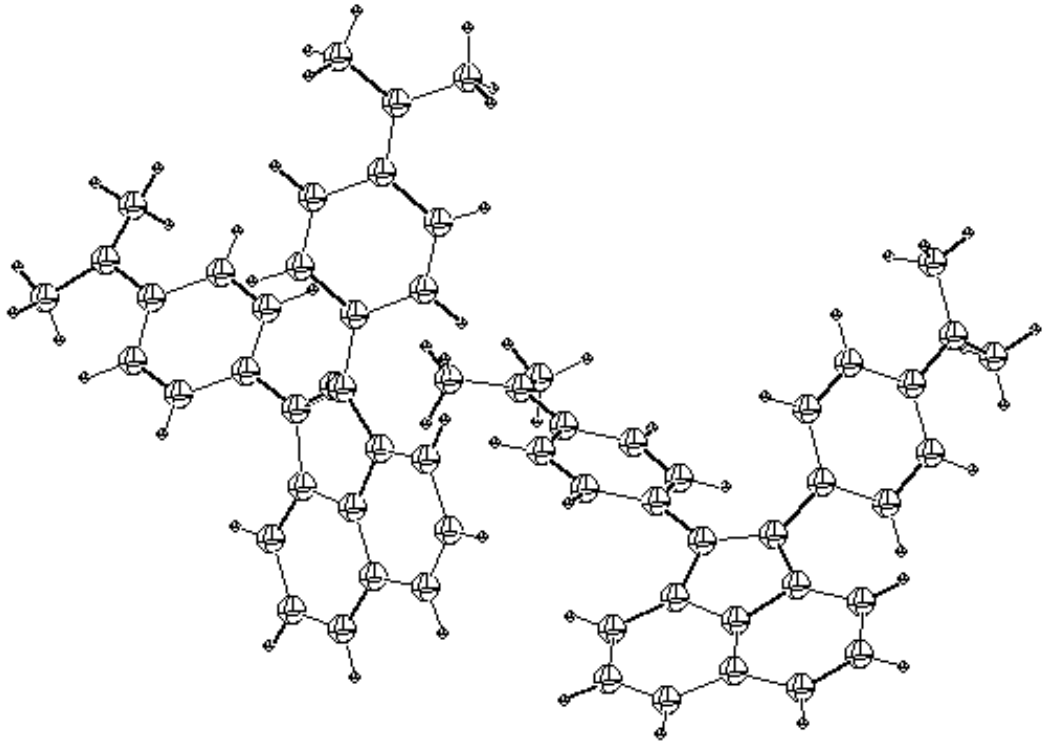
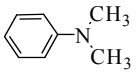
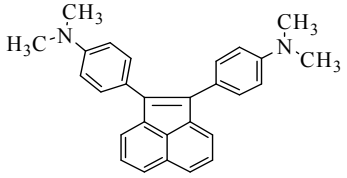
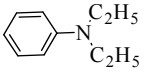
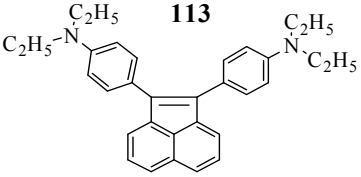
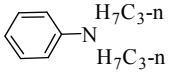
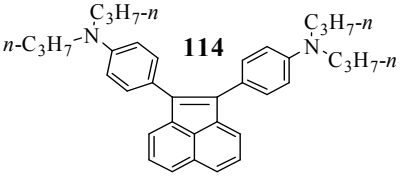
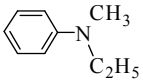
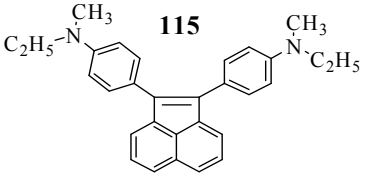
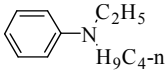
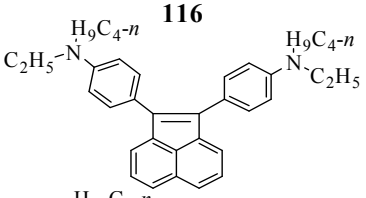
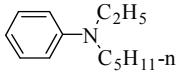
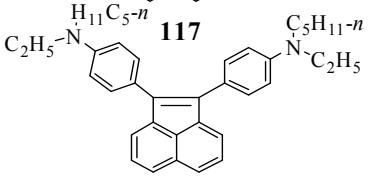
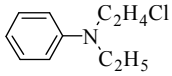
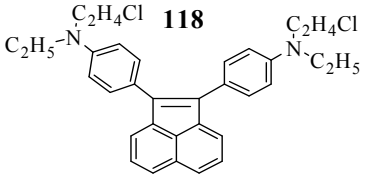


Figure 1. ORTEP diagram of compound **113**

Table 1. X-ray data collection and structure refinement for **113**

Empirical formula	$C_{56}\ H_{52}\ N_4$
Fw	781.02
Temp., wavelength	100(2), 0.71073 Å
Cryst. syst., space group	monoclinic, P2(1)/c
Unit cell dimensions	a= 16.397(2) Å, α=90˚
	b= 9.4410(13) Å, β= 94.170˚ (2)
	c= 26.943(4) Å, γ =90˚
Volume	4159.9(10) $Å^3$
Z, calcd. density	4, 1.247 mg/m^3
Abs. coeff.	0.073 mm^{-1}
F(000)	1664
Cryst. size	0.42×0.31×0.24 mm
θ range for data collection	1.52 to 25.00˚
Limiting indices	-19≤h≤19, -11≤k≤11, -32≤l≤32
Reflns. collected, unique	37434, 7323 [R(int)=0.0673]
Refinement method	full-matrix least-square on F^2
Data/restraints/params	7323/0/549
Goodness-of-fit on F^2	1.169
Final *R* indices[I> 2σ (I)]	R_1= 0.0748, wR_2= 0.1563
R indices (all data)	R_1= 0.0876, wR_2= 0.1620
Largest diff. peak and hole	0.332, -0.317 e. $Å^{-3}$

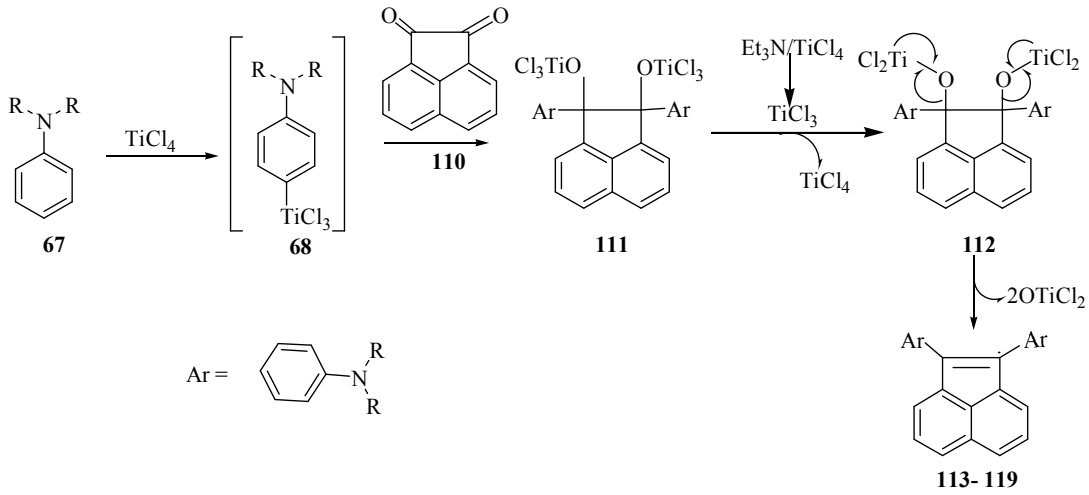
Table 2. Formation of 4,4'-(acenaphthylene-1,2-diyl)bis(*N,N*-dialkylaniline) in the reaction of acenaphthenequinone with the $TiCl_4/Et_3N$/arylamine reagent system.[a]

Entry	Aryl amine	Product[b]	Yield (%)[c]
1	 **67a**	 **113**	62
2	 **67b**	 **114**	75
3	 **67c**	 **115**	72
4	 **67d**	 **116**	68
5	 **67e**	 **117**	70
6	 **67f**	 **118**	67
7	 **67g**	 **119**	66

[a] All the reactions were carried out using acenaphthenequinone **110** (1 mmol), $TiCl_4$ (3 mmol), aryl amine (3 mmol) and Et_3N (3 mmol). [b] The products were identified by spectral data (IR, ^{1}H-NMR ^{13}C-NMR and Mass). [c] Yields reported are for the isolated products and based on the amount of acenaphthenequinone **110** used.

The formation of diarylacenaphthenes from acenaphthnequinone and N,N-dialkylaryl amine can be explained by considering the tentative mechanism outlined in **Scheme 38**. According to this, the aryl titanium species generated from the aryl amine and $TiCl_4$ undergoes reaction with acenaphthenequione to give the intermediate **111** which is converted to intermediate **112** by reaction with $TiCl_3$ species produced *in situ*. Homolysis of the carbon oxygen bond in **112** would give the 1,2-diarylacenaphthylene product with concomitant formation of oxygen containing titanium species.

Scheme 38

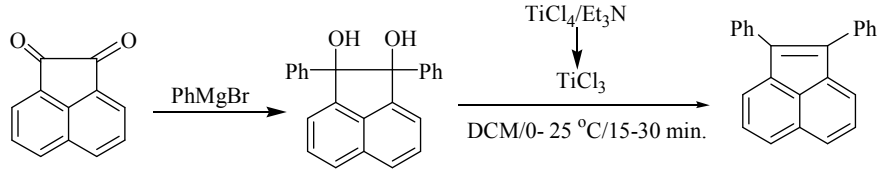


3.2.2 Conversion of 1,2-diarylacenaphthylene-1,2-diols to 1,2-diarylacenaphthylene derivatives using the $TiCl_4/Et_3N$ reagent system

As discussed in the previous section, the arylamine/Et_3N/$TiCl_4$ reagent system is useful for the synthesis of 4,4'-(acenaphthylene-1,2-diyl)bis(*N,N*-dialkylaniline) derivatives **113-119**. However, it is of interest to devise a general method of synthesis of various polycyclic aromatic hydrocarbons from the corresponding diols which are readily accessible via Grignard reaction.[46a,b]

Initially, we have examined this transformation using the 1,2-diphenyl-1,2-dihydro acenaphthylene-1,2-diol (1 mmol) **120,** $TiCl_4$ (2 mmol) and Et_3N (4 mmol) in dichloromethane solvent. In this experiment, the corresponding 1,2-diphenyl-acenaphthylene **127** was obtained in 90% yield (**Scheme 39**). We have carried out this experiment with different amines like Bu_3N and *i*-Pr_2NEt in place of Et_3N. It was found that the Et_3N gave better yields (**Table 3**). In reactions using Bu_3N and *i*-Pr_2NEt, the 1,2-diphenylacenaphthylene **127** was obtained in 78% and 70% yields, respectively.

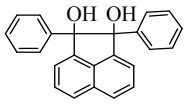
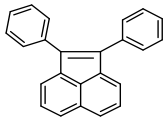
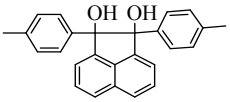
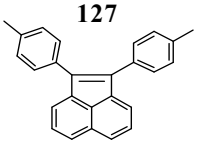
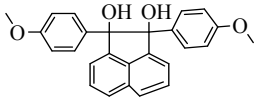
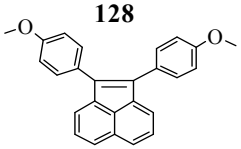
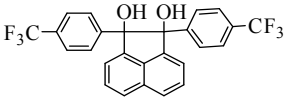
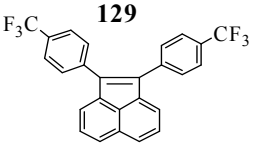
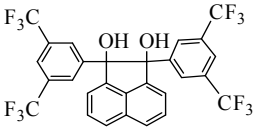
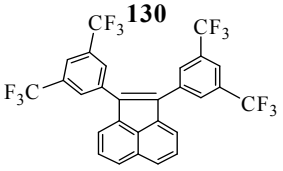
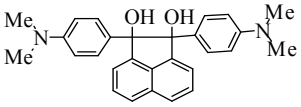
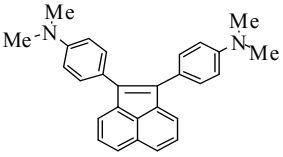
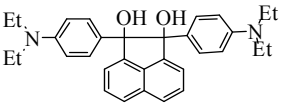
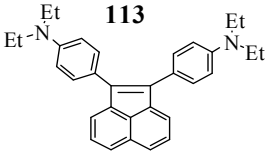
Scheme 39



110 **120** 78% **127** 90%

We have also studied the generality of this transformation and synthesized several 1,2-diarylacenaphthylene derivates. The results are summarized in **Table 3**.

Table 3. Synthesis of 1,2-diarylacenaphthenes from 1,2-diphenyl-1,2-dihydro-acenaphthylene-1,2-diol by using $TiCl_4/Et_3N$ reagent system[a]

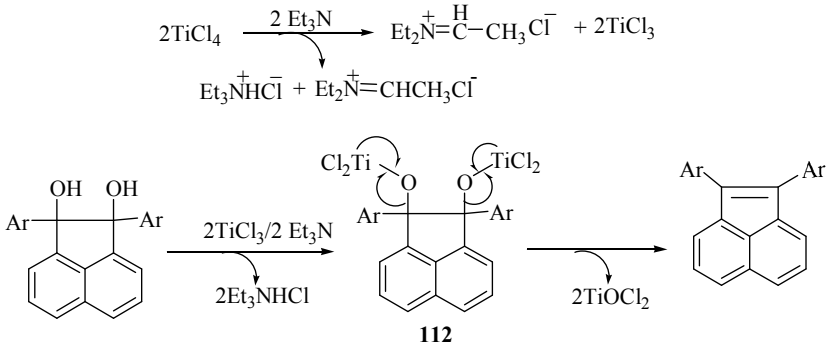
Entry	Diol	Product[b]	Time (min.)	Yield(%)[c]
1	 **120**	 **127**	30	90
2	 **121**	 **128**	30	92
3	 **122**	 **129**	30	88
4	 **123**		30	85
5	 **124**	 **130** **131**	30	83
6	 **125**	 **113**	15	80
7	 **126**	 **114**	15	88

[a] All the reactions were carried out using diaryldiol (1 mmol), $TiCl_4$ (2.0 mmol) and Et_3N (4.0 mmol) at 25 °C. [b] The products were identified by spectral data (IR, ^{1}H-NMR ^{13}C-NMR and Mass). [c] Yields reported are for the isolated products and based on the amount of diol used.

It appears that the electronic effect plays some role in the rate of this transformation. Whereas in the case of *N,N*-diaklylaniline derivatives, the products were obtained in good yields in a short reaction time (15 min.) (**Table 3, Entries 6** and **7**), in other cases the transformation required 30 min. for completion.

The formation of 1,2-diarylacenaphthylenes from the corresponding diols can be explained by the mechanism outlined in **Scheme 40**. The reactive lower valent titanium species Ti(III) generated *in situ* using the $TiCl_4/Et_3N$ reagent system would undergo reaction with the diol in the presence of Et_3N, to give the titanium species **112**, Which could then produce the hydrocarbon and $OTiCl_2$ species as envisaged in **Scheme 40**.

Scheme 40

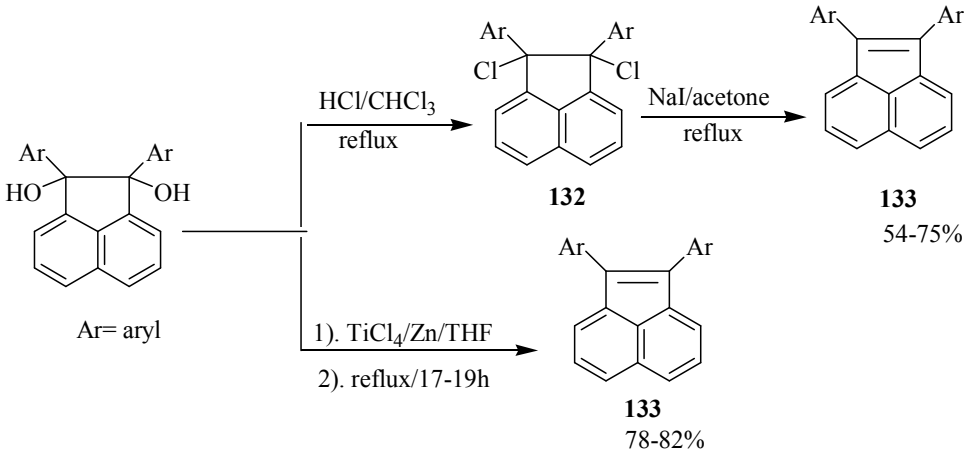


The derivates of acenaphthylenes are useful as synthetic intermediates for the synthesis of various polycyclic aromatic hydrocarbons with unusual properties.[31,32] The discovery of fullerenes has motivated attention to the synthesis and properties of polycyclic aromatic hydrocarbons with integrated five-membered rings, thus representing partial structure of these nanospheres.[33] Therefore, the method described here for the synthesis of

diaryl acenaphthylenes from readily accessible acenaphthenequinone by using $TiCl_4/Et_3N$/aryl amine reagent system has good synthetic potential.

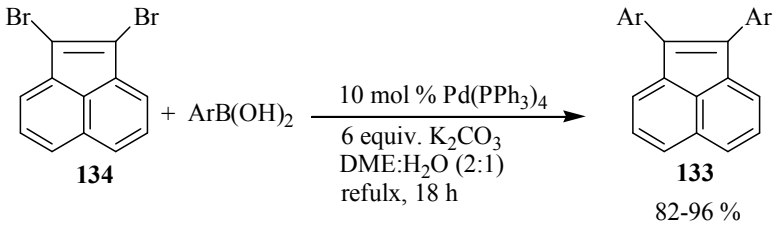
Previously, diarylacenaphthylene derivatives were synthesized from the corresponding diols in moderate yields after long reaction time under harsh reaction conditions (**Scheme 41**).[34,35]

Scheme 41



Recently, some 1,2-diarylacenaphthylenes were synthesized via Suzuki–Miyaura cross coupling reaction by using the expensive Pd reagents (**Scheme 42**).[36]

Scheme 42

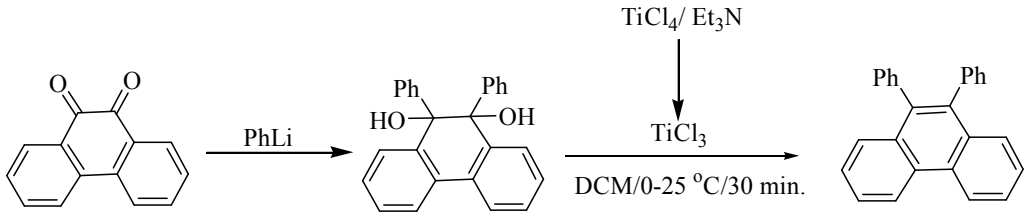


The procedure described here using the $TiCl_4/Et_3N$ reagent system compares favorably with these reported procedures.

3.2.3 Synthesis of 9,10-diarylphenanthrenes using the $TiCl_4/Et_3N$ reagent system

The 9,10-dihydro-9,10-diarylphenanthrene can be readily accessed by the reaction of 9,10-phenanthrenequinone with aryl lithium reagents and Grignard reagents.[46c,42] We have examined the reaction of the low valent titanium prepared *in situ* using the $TiCl_4/Et_3N$ reagent system with the 9,10–dihydroxy-9,10–diphenylphenathrene. In this case, the corresponding 9, 10-diphenyllphenanthrene **140** was obtained in 80% yield.

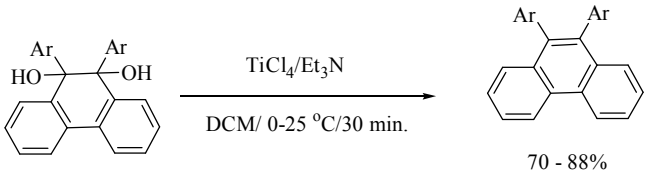
Scheme 43

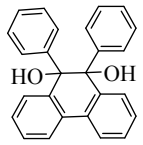
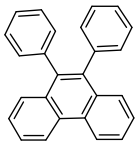
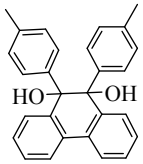
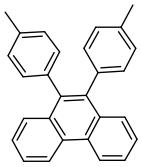
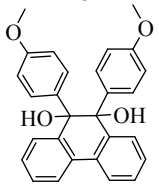
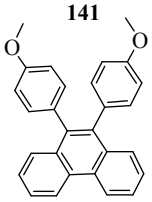
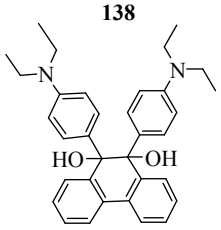
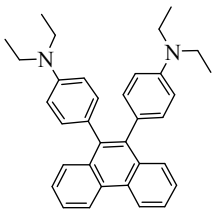


135 **136** 75% **140** 80 %

We synthesized several 9,10-diarylphenanthrene derivatives from the corresponding 9,10-dihydroxy,9,10-diarylphenanthrene derivatives by following this procedure using the $TiCl_4/Et_3N$ reagent system in 70-88% yields (**Table 4**). Here also, the amine substituted phenanthrene derivatives were obtained in shorter reaction time (10 min.) and other diaryl phenanthrenes were obtained in 30 min.

Table 4. Formation of 9,10-diarylphenanthrenes from 9,10-dihydroxy-9,10-diarylphenanthrene derivatives by using the $TiCl_4/Et_3N$ reagent system[a]

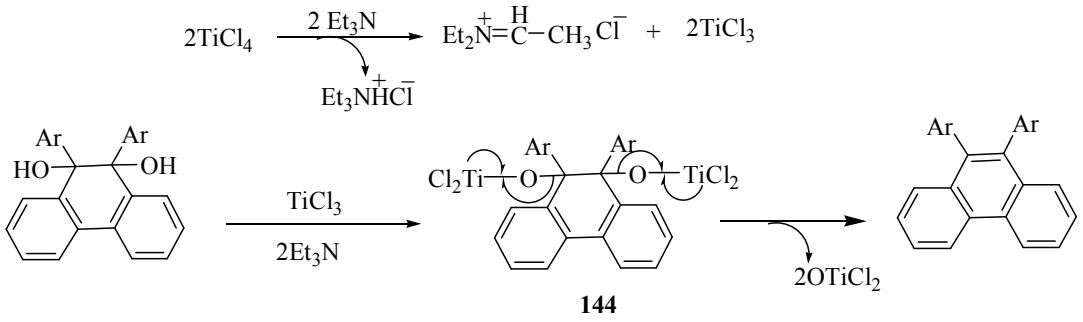


Entry	Diol	Product[b]	Time(min.)	Yield(%)[c]
1	 **136**	 **140**	30	80
2	 **137**	 **141**	30	85
3	 **138**	 **142**	30	88
4	 **139**	 **143**	10	70

[a] All the reactions were carried out using diaryl diol (0.5 mmol) $TiCl_4$ (1 mmol.) and Et_3N (2 mmol) at 25 °C. [b] The products were identified by spectral data (IR, ^{1}H-NMR, ^{13}C-NMR and Mass). [c] Yields reported are for the isolated products and based on the amount of diol used.

The formation of 9,10-diarylphenanthrene from the corresponding diols can be also explained by considering the mechanism outlined in **Scheme 44** similar to that considered earlier (**Scheme 40).**

Scheme 44

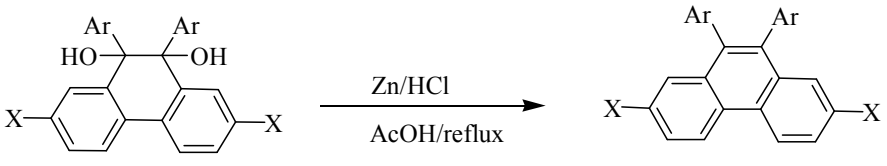


144

Phenanthrene belongs to an important skeleton of organic compounds due to its presence in core structure in natural products [37] with interesting biological activities such as anti malarial,[38] anti cancer[39] and emetic activity.[40] Some phenanthrene derivatives exhibit properties like photoconductivity and electroluminescence and hence are useful structural motifs in material science.[41]

Recently, some 9,10-diarylphenanthrene derivatives **146** were synthesized in 22-98% yields from 9,10-dihydroxy-9,10-diaryl-9,10-dihydrophenanthrene derivatives **145** using Zn/HCl in acetic acid solvent under reflux conditions (**Scheme 45**).[42]

Scheme 45



145 **146**

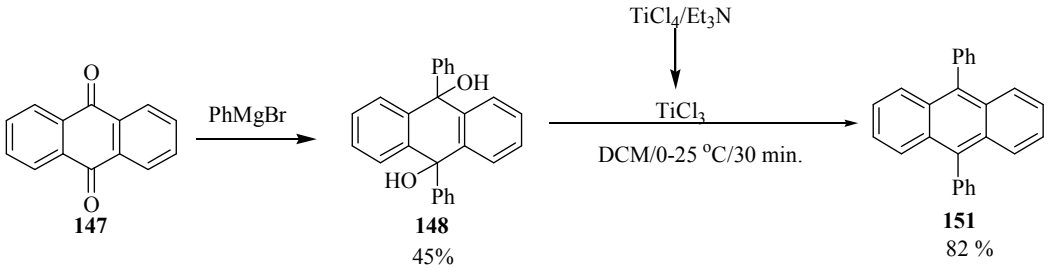
22- 98%

The present procedure described here using the $TiCl_4/Et_3N$ reagent system under ambient conditions compares favorably with this reported procedure.

3.2.4 Synthesis of 9,10-diarylanthracenes using the $TiCl_4/Et_3N$ reagent system

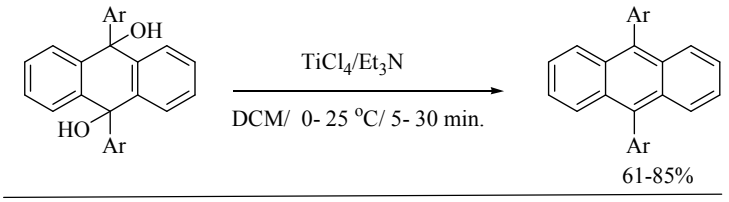
As anticipated, the low valent titanium reagent prepared *in situ* using the $TiCl_4/Et_3N$ reagent system is also useful for the synthesis of 9,10-diarylanthracene derivatives. Again, the 9,10-dihydroxy-9,10-diarylanthracene derivatives were readily accessed by Grignard reaction. The corresponding 9,10-diphenylanthracene was obtained in 82% yield in the conversion using low valent titanium species prepared *in situ* using the $TiCl_4/Et_3N$ reagent system (**Scheme 46**).

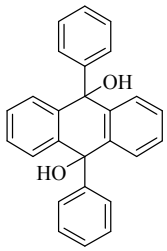
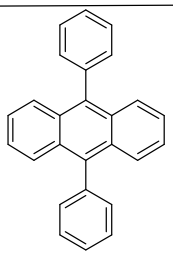
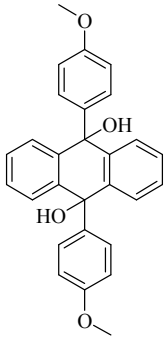
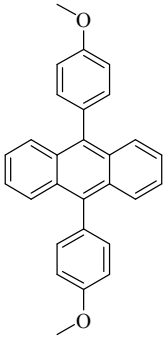
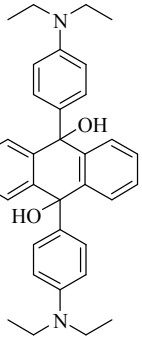
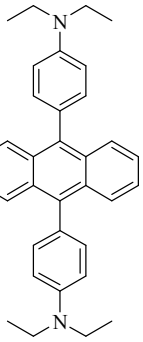
Scheme 46



Several other 9,10-diarylanthracene derivatives were prepared in 61-85% yields form the corresponding 9,10-dihydroxy-9,10-diarylanthracene derivatives following this procedure and the results are summarized in **Table 5**.

Table 5. Formation of 9,10-diarylanthracenes from 9,10-dihydroxy-9,10-diaryl-anthracenes by using $TiCl_4/Et_3N$ reagent system[a]



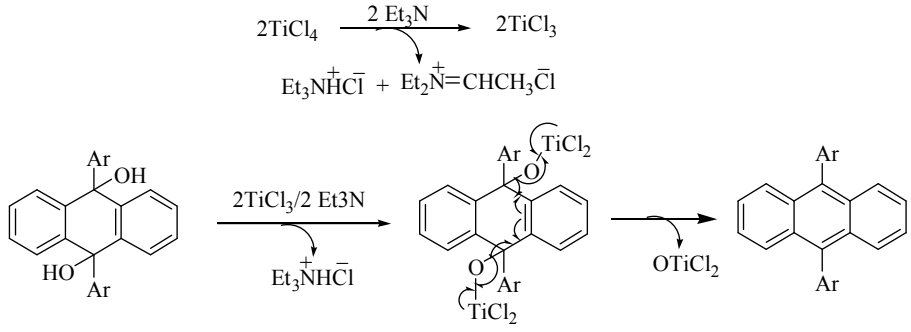
Entry	Diol	Product[b]	Time (min.)	Yield(%)[c]
1	 **148**	 **151**	30	82
2	 **149**	 **152**	30	85
3	 **150**	 **153**	5	61

[a] All the reactions were carried out using diaryldiol (0.5 mmol) $TiCl_4$(1 mmol) and Et_3N (2 mmol) at 25 ^oC. [b] The products were identified by spectral data (IR, ^1H-NMR ^{13}C-NMR and Mass). [c] Yields reported are for the isolated products and based on the amount of diol used.

Again, the deoxygenation reaction with the low valent titanium species is faster with the 9,10-diols synthesized with *N,N*-dialkylamine derivatives (5 min.).

Here, the formation of diarylanthracene from the corresponding diaryldiol can be explained by considering the reactive low valent titanium species and homolysis of the C-O single bond (**Scheme 47**).

Scheme 47

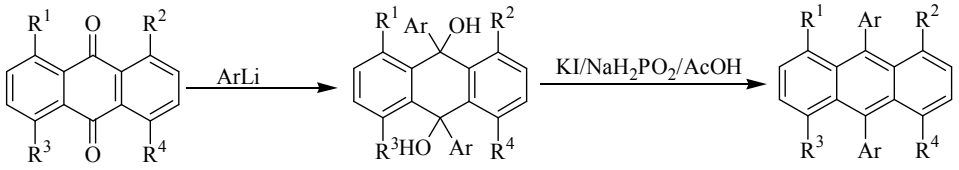


154

The derivatives of anthracenes act as donor-aceptor type compounds showing interesting properties in electron transfer and photosynthetic reactions. They are also useful basic materials in non-linear optics.[43]

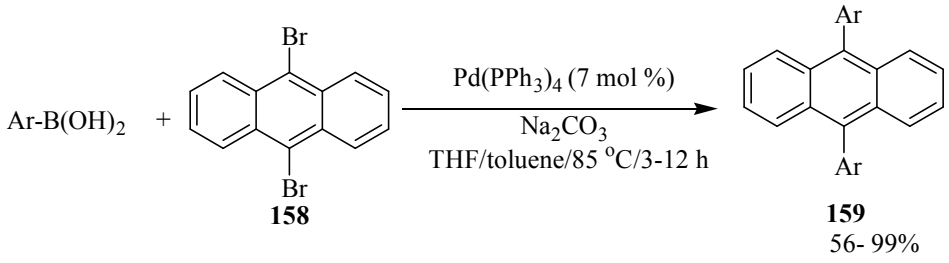
Previously, such anthraquinone derivatives were prepared using aryl lithium compounds followed by further reduction with KI/NaH_2PO_2 in acetic acid at 80 ^oC (**Scheme 48**).[44]

Scheme 48



Recently, some 9,10-diarylanthracenes were synthesized by using expensive Pd reagents via Suzuki–Miyaura cross crosscoupling reaction from 9,10-dibromoanthracene and arylboronic acids in THF/toluene solvent mixture at 85 ^{o}C (**Scheme 49**). [45]

Scheme 49



Again, the method described here using the $TiCl_4/Et_3N$ reagent system compares favorably with these reported procedures.

3.3 Conclusions

We have developed a method for synthesis of several new functionalized diaryl acenaphthylene derivatives via a single pot operation from easily accessible starting materials using the $TiCl_4$ and *N,N*-dialkylarylamine derivatives under ambient reaction conditions.

We have also developed a simple, general one pot method for the synthesis of 1,2-diarylacenaphthene, 9,10-diarylphenanthrene and 9,10-diarylanthracene derivatives from the corresponding dihydroxy derivatives using the low valent titanium species prepared *in situ* using the $TiCl_4/Et_3N$ reagent system under ambient reaction conditions. The procedures described for these conversions have good synthetic potential for further synthetic exploitations.

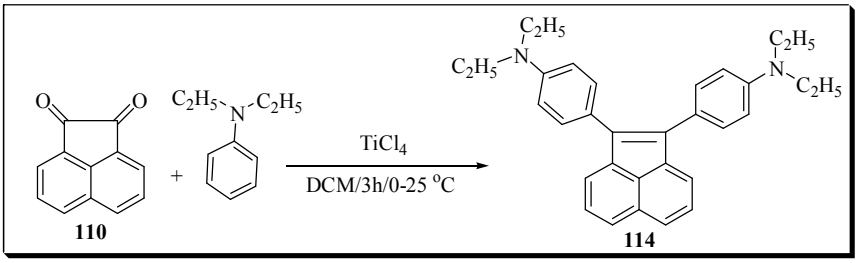
3.4 Experimental Section

3.4.1 General information:

The general information given in the section 1.4 is also applicable to the experiments outlined in this section. THF was distilled over sodium benzophenone ketyl system. $TiCl_4$ was supplied by LOBA chemicals India. Et_3N, *N,N*-diethylaniline and *N,N*-dimethylaniline supplied by Spectrochem (P) Ltd., India, were distilled and stored over anhydrous KOH. DCM was distilled over calcium hydride and stored over molecular sieves.

3.4.2 Reaction of $TiCl_4$/arylamine reagent system with acenaphthene-quinone 110

To a mixture of acenaphthenequinone (0.182 g, 1 mmol) and *N,N*-diethylaniline (0.48 mL, 3 mmol) in CH_2Cl_2 (10 mL), $TiCl_4$ (0.66 mL of 1:1 solution of $TiCl_4/CH_2Cl_2$, 3 mmol) in CH_2Cl_2 (10 mL) was added dropwise at 0 ºC under N_2 atmosphere. The contents were stirred for 3 h at 25 ^oC. A saturated aqueous K_2CO_3 solution (10 mL) was added and stirred for 0.5 h. The reaction mixture was filtered through a Buchner funnel. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2x25 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 **114** was eluted using hexane/ethyl acetate 97:3.



Yield : 0. 201 g (45%)

mp : gummy

IR (neat) : 3038, 2970, 1608 cm^{-1}

^{1}H NMR : (400 MHz) δ = 7.85-7.83 (m, 4H), 7.65-7.61 (m, 2H), 7.52-7.49 (m, 4H), 6.77 (d, J = 8.4 Hz, 4H), 3.45 (q, J = 6.8 Hz, 8H), 1.27 (t, J = 6.8 Hz, 12H) *ppm*

^{13}C NMR : (100 MHz) δ = 146.5, 141.0, 135.9, 131.0, 128.5, 128.1, 127.5, 126.2, 123.0, 122.7, 111.4, 44.2, 12.7 *ppm*

MS (EI) : *m/z* 447 (M+1)

Analysis : for $C_{32}H_{34}N_2$

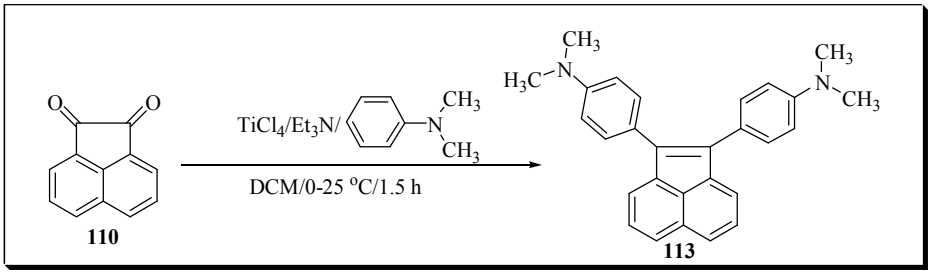
Calculated: C, 86.05%; H, 7.67%; N, 6.27%

Found: C, 86.15%; H, 7.72%; N, 6.37%

3.4.3 Reaction of $TiCl_4$/arylamine/Et_3N reagent system with acenaphth enequinone 110

To a solution of acenaphthenequinone (0.182 g, 1 mmol) in DCM (10 mL), $TiCl_4$ (0.66 mL of 1:1 solution of $TiCl_4/CH_2Cl_2$, 3 mmol) was added at 0 °C and stirred for 5 min. under N_2 atmosphere. A mixture of *N,N*-dimethylaniline (0.38 mL, 3 mmol) and Et_3N

(0.42 mL, 3 mmol) in DCM (10 mL) was added dropwise for 0.5 h at 0 °C and further stirred for 1.5 h at 0-25 °C. A saturated aqueous K_2CO_3 solution (10 mL) was added and the contents were stirred for 0.5 h. The reaction mixture was filtered through a Buchner funnel. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2x25 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 **113** was eluted using hexane/ethyl acetate 97:3.



110 **113**

Yield : 0.242 g (62%)

mp : 206-208 °C

IR (KBr) : 3040, 2922, 1606 cm^{-1}

^{1}H NMR : (400 MHz) δ = 7.81 (d, J = 8 Hz, 2H), 7.76 (d, J = 8 Hz, 2H), 7.60-7.56 (m, 2H), 7.46-7.43 (m, 4H), 6.79 (d, J = 8.4 Hz, 4H), 3.02 (s, 12H) *ppm* **(Spectrum No. 45)**

^{13}C NMR : (100 MHz) δ = 149.3, 141.0, 136.4, 130.9, 128.6, 128.3, 127.7, 126.5, 123.9, 123.2, 112.3, 40.5 *ppm* **(Spectrum No. 46)**

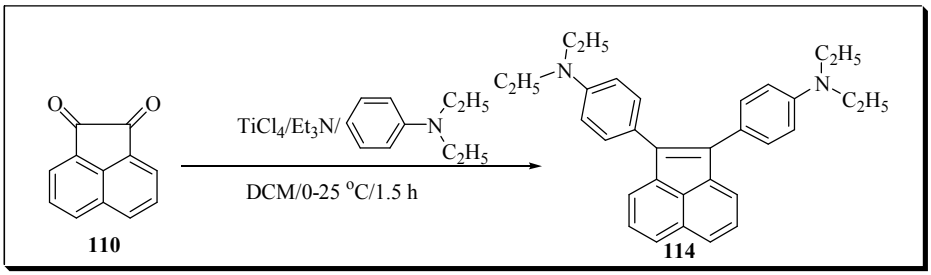
MS (EI) : *m/z* 391 (M+1)

Analysis : for $C_{28}H_{26}N_2$

Calculated: C, 86.12%; H, 6.71%; N, 7.17%

Found: C, 86.08%; H, 6.65%; N, 7.25%

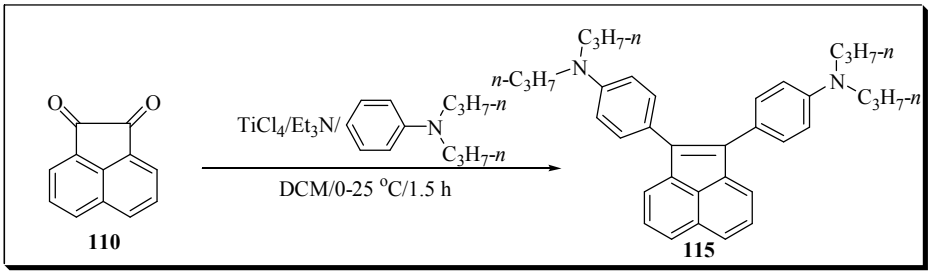
The above procedure was followed for the reaction of other arylamines with acenaphthenequinone.



110 **114**

Yield **:** 0. 334 g (75%)

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



110 **115**

Yield **:** 0.362 g (72%)

mp **:** gummy

IR (neat) **:** 3038, 2959, 1606 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 7.80-7.76 (m, 4H), 7.59-7.55 (m, 2H), 7.42 (d, J = 8.4 Hz, 4H), 6.68 (d, J = 8.4 Hz, 4H), 3.30 (t, J = 7.6 Hz, 8H), 1.73-1.64 (m, 8H), 0.98 (t, 7.4 Hz, 12H).*ppm*

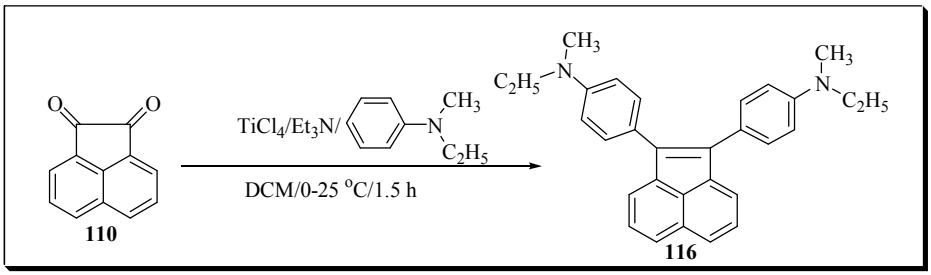
^{13}C NMR **:** (100 MHz) δ = 147.0, 141.2, 136.0, 131.0, 128.6, 128.2, 127.6, 126.2, 123.1, 122.6, 111.3, 52.9, 20.6, 11.5 *ppm*

MS (EI) **:** *m/z* 504 (M+1)

Analysis **:** for $C_{36}H_{42}N_2$

Calculated: C, 86.01%; H, 8.42%; N, 5.57%

Found: C, 85.91%; H, 8.51%; N, 5.48%



110 **116**

Yield **:** 0.284 g **(**68%)

mp **:** 118-120 ^{o}C

IR (KBr) **:** 3043, 2968, 1608 cm^{-1}

^{1}H NMR **:** (400 MHz) δ= 7.81-7.61 (m, 4H), 7.60-7.56 (m, 2H), 7.44 (d, *J* = 8.4 Hz, 4H), 6.76 (d, *J* = 8.4 Hz, 4H), 3.45 (q, *J* = 6.8 Hz, 4H), 2.98, (s, 6H), 1.19 (t, *J* = 6.8 Hz, 6H) *ppm* **(Spectrum No. 47)**

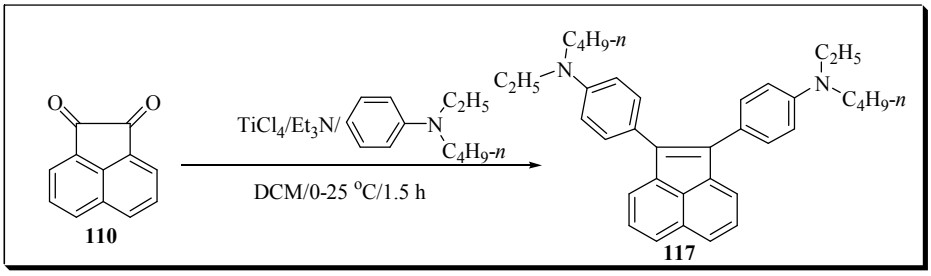
^{13}C NMR **:** (100 MHz) δ= 147.8, 141.0, 136.3, 131.0, 128.6, 128.3, 127.7, 126.4, 123.4, 123.2, 112.0, 46.8, 37.5, 11.6 *ppm* **(Spectrum No. 48)**

MS (EI) **:** *m/z* 419 (M+1)

Analysis **:** for $C_{30}H_{30}N_2$

Calculated: C, 86.08%; H, 7.22%; N, 6.69 %

Found: C, 85.91%; H, 7.32%; N, 6.60%



Yield **:** 0.352 g (70%)

IR (neat) **:** 3038, 2959, 1606 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 7.80-7.75 (m, 4H), 7.58-7.54 (m, 2H), 7.42 (d, *J* = 8.4 Hz, 4H), 6.70 (d, *J* = 8.4 Hz, 4H), 3.42 (q, *J* = 6.8 Hz, 4H), 3.31 (t, *J* = 7.6 Hz, 4H), 1.68-1.60 (m, 4H), 1.45-1.36 (m, 4H), 1.22 (t, *J* = 6.8 Hz, 6H), 1.00 (t, *J* = 7.2 Hz, 6H) *ppm* **(Spectrum No. 49)**

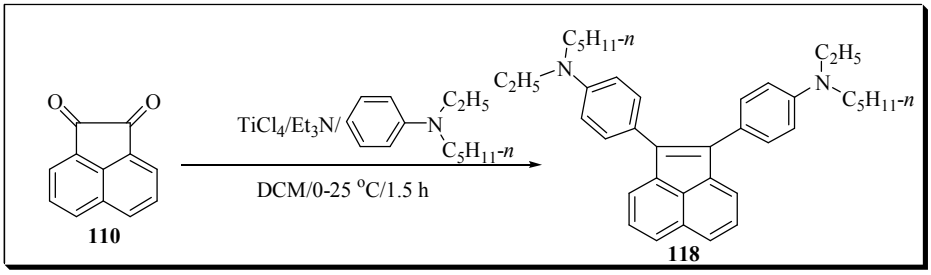
^{13}C NMR **:** (100 MHz) δ = 146.8, 141.0, 135.9, 131.0, 128.5, 128.2, 127.5, 126.1, 123.0, 122.6, 111.3, 50.1, 44.9, 29.8, 20.4, 14.0, 12.5 *ppm* **(Spectrum No. 50)**

MS (EI) **:** *m/z* 504 (M+1)

Analysis **:** for $C_{36}H_{42}N_2$

Calculated: C, 86.01%; H, 8.42%; N, 5.57%

Found: C, 86.22%; H, 8.35%; N, 5.49%



110 **118**

Yield : 0.356 g **(**67%)

IR (neat) : 3038, 2970, 1608 cm^{-1}

^{1}H NMR : (400 MHz) δ = 7.80-7.76 (m, 4H), 7.56-7.55 (m, 2H), 7.44-7.40 (m, 4H), 6.70 (d, *J* = 8.8 Hz, 4H), 3.42 (q, *J* = 6.8 Hz, 4H), 3.30 (t, *J* = 7.2 Hz, 4H), 1.68-1.64 (m, 4H), 1.44-1.28 (m, 8H), 1.22 (t, *J* = 6.8 Hz, 6H), 0.96 (t, *J* = 6.8 Hz, 6H) *ppm*

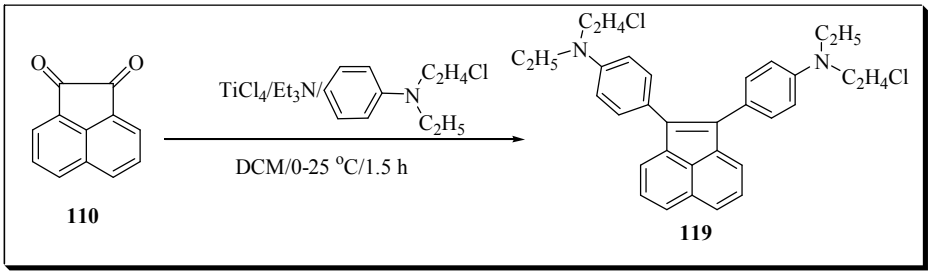
^{13}C NMR : (100 MHz) δ = 146.8, 141.2, 136.0, 131.1, 128.6, 128.2, 127.6, 126.2, 123.1, 122.7, 111.4, 50.5, 44.9, 29.5, 27.4, 22.7, 14.2, 12.5 *ppm*

MS (EI) : *m/z* 532 (M+1)

Analysis : for $C_{38}H_{46}N_2$

Calculated: C, 85.99%; H, 8.74%; N, 5.28%

Found: C, 85.91%; H, 8.82%; N, 5.15%



110 **119**

Yield **:** 0.340 g (66%)

IR (neat) **:** 3040, 2968, 1608 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 7.85-7.58 (m, 6H), 7.45 (d, *J* = 8.4 Hz, 4H), 6.73 (d, *J* = 8.4 Hz, 4H), 3.69 (s, 8H), 3.47 (q, *J* = 7.2 Hz, 4H), 1.25 (t, *J* = 7.2 Hz, 6H) *ppm* **(Spectrum No. 51)**

^{13}C NMR **:** (100 MHz) δ = 145.8, 140.8, 136.1, 131.2, 128.4, 128.2, 127.6, 126.4, 123.8, 123.2, 111.5, 52.3, 45.3, 40.5, 12.6 *ppm* **(Spectrum No. 52)**

MS (EI) **:** *m/z* 515 (M), 517 (M+2)

Analysis **:** for $C_{32}H_{32}N_2Cl_2$

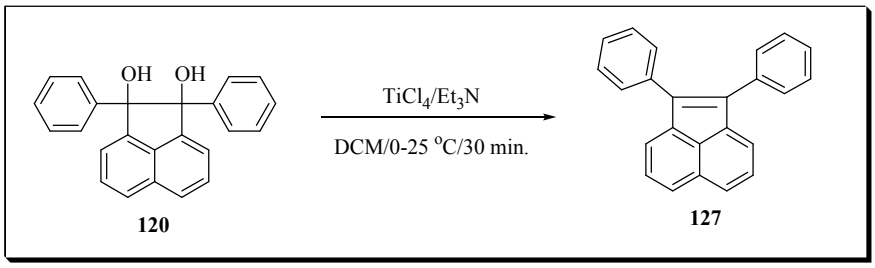
Calculated: C, 74.55%; H, 6.26%; N, 5.43 %

Found: C, 74.66%; H, 6.21%; N, 5.36 %

3.4.4 Reaction of $TiCl_4/Et_3N$ reagent system with 1,2-diaryl-1,2-dihydro-acenaphthylene-1,2-diols

The 1,2-diphenyl-1,2-dihydroacenaphthylene-1,2-diol **120** was synthesized via the reaction of Grignard reagent, prepared using bromobenzene (0.84 mL, 8 mmol) and Mg (0.192 g, 8 mmol) with acenaphthenequinone (0.364 g, 2 mmol) in THF (25 mL) following a slightly modified reported procedure.[46a,b] Yield : 0.527 g (78%); mp : 150-152 ^oC (Lit.[46a] mp : 154-155 ^oC); IR (KBr) = 3830, 3454 cm^{-1}; ^{1}H NMR : δ = 7.87 (d, *J* = 8 Hz, 2H), 7.63-7.59 (m, 2H), 7.32-7.30 (m, 8H), 7.21-7.19 (m, 4H), 2.15 (s, 2H) *ppm*; ^{13}C NMR : δ = 145.5, 140.7, 137.2, 130.9, 128.9, 128.0, 127.9, 127.7, 125.2, 121.7, 89.9 *ppm.*

To a solution of diol **120** (1 mmol, 0.338 g) and Et_3N (4 mmol, 0.56 mL) in DCM (15 mL), $TiCl_4$ (0.44 mL of 1:1 solution of $TiCl_4/CH_2Cl_2$, 2 mmol) DCM (5 mL) was added dropwise for 5 min. at 0 °C under N_2 atmosphere. The contents were stirred for 0.5 h at 0-25 ^oC. It was quenched with saturated NH_4Cl solution. The organic layer was separated and the aqueous layer was extracted with CH_2C1_2 (2x25 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 silica gel column. The product **127** was eluted using hexane/ethyl acetate 97:3.



Yield : 0.274 g (90%)

mp : 162-163 ^oC (Lit.[36] mp 162-163 ^oC)

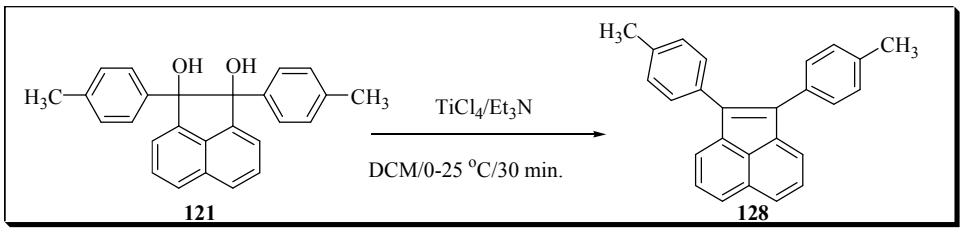
IR (KBr) : 3059, 1479, 1427 cm^{-1}

^{1}H NMR : (400 MHz) δ = 7.88 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 7.2 Hz, 2H), 7.63-7.59 (m, 2H), 7.47-7.44 (m, 4H), 7.39-7.29 (m, 6H) *ppm*

^{13}C NMR : (100 MHz) δ = 139.9, 138.0, 135.2, 130.8, 128.4, 128.2, 128.1, 127.8, 127.3, 127.1, 124.0 *ppm*

MS (EI) : *m/z* 305 (M+1).

The above procedure was followed for the conversion of other diaryl diols to corresponding diarylacenaphthylenes.



121 **128**

Yield **:** 0.305 g (92%)

mp **:** 120-122 ^{o}C

IR (KBr) **:** 3036, 2914, 1481, 1431 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 7.87 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 6.8 Hz, 2H), 7.63-7.59 (m, 2H), 7.40-7.39 (m, 4H), 7.23-7.20 (m, 4H), 2.43 (s, 6H) *ppm*

^{13}C NMR **:** (100 MHz) δ = 140.2, 137.7, 136.8, 132.4, 129.9, 129.2, 128.4, 128.3, 127.8, 127.1, 123.8, 21.4 *ppm*

MS (EI) **:** *m/z* 333 (M+1)

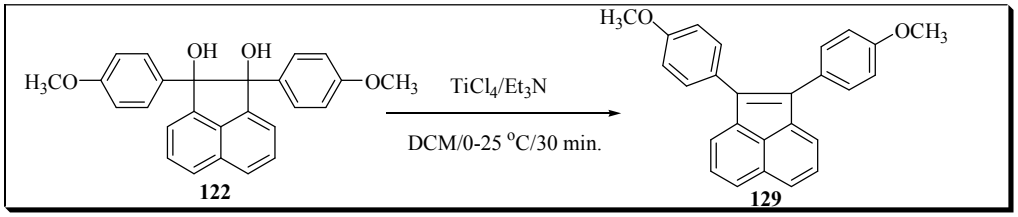
Analysis **:** for $C_{26}H_{20}$

Calculated: C, 93.94%; H, 6.06%

Found: C, 93.76%; H, 6.12%

(The starting diol **121** was prepared by following a similar procedure used earlier for the preparation of the diol **120.** Yield : 0.549 g (75%); mp : 182-184 ^{o}C (Lit.[46a] mp : 184-186 ^{o}C); IR (KBr) = 3513, 3418 cm^{-1}; ^{1}H NMR : δ = 7.93 (d, *J* = 8 Hz, 2H), 7.70-7.64

(m, 2H), 7.40-7.35 (m, 2H), 7.18-7.16 (m, 8H), 2.43 (s, 6H), 2.27 (s, 2H) *ppm*; ^{13}C NMR : δ = 145.6, 137.7, 137.6, 137.1, 130.9, 128.7, 128.6, 127.6, 125.1, 121.6, 89.7, 21.1 *ppm*)



122 **129**

Yield **:** 0.320 g **(**88%)

mp **:** 106-108 °C (Lit.[36] mp 106-107 °C)

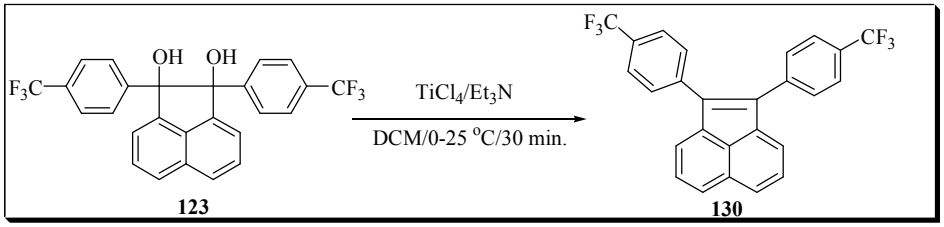
IR (KBr) **:** 3040, 2955, 1541, 1491 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 7.84 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 6.8 Hz, 2H), 7.60-7.56 (m, 2H), 7.39 (d, *J* = 8.8 Hz, 4H), 6.92 (d, *J* = 8.8 Hz, 4H), 3.85 (s, 6H) *ppm* **(Spectrum No. 53)**

^{13}C NMR **:** (100 MHz) δ = 158.7, 140.3, 136.9, 131.2, 128.3, 128.2, 127.8, 127.7, 127.0, 123.6, 113.9, 55.2 *ppm* **(Spectrum No. 54)**

MS (EI) **:** *m/z* 365 (M+1).

(The starting diol **122** was prepared by following a similar procedure used earlier for the preparation diol of the **120.** Yield : 0.557 g (70%); mp : 154-156 °C (Lit.[46b] mp : 159-160 °C); IR (KBr) = 3551, 3489 cm^{-1}; ^{1}H NMR : δ = 7.89 (d, *J* = 8 Hz, 2H), 7.65-7.61 (m, 2H), 7.35-7.34 (m, 2H), 7.18-7.16 (m, 4H), 6.87 (d, *J* = 8.8 Hz, 4H), 3.85 (s, 6H), 2.22 (s, 2H) *ppm*; ^{13}C NMR : δ = 159.4, 145.7, 137.1, 132.7, 131.1, 129.1, 128.9, 125.2, 121.7, 113.4, 89.6, 55.3 *ppm*)



123 **130**

Yield **:** 0.374 g (85%)

mp **:** 166-168 ^{o}C

IR (KBr) **:** 3057, 1614, 1433, 1323 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 7.95 (d, *J* = 8 Hz, 2H), 7.76 (d, *J* = 6.8 Hz, 2H), 7.67- 7.65 (m, 6H), 7.54 (d, *J* = 8 Hz, 4H) *ppm* **(Spectrum No. 55)**

^{13}C NMR **:** (100 MHz) δ = 138.9, 138.5, 137.8, 130.2, 129.4 (q, *J* = 32 Hz), 128.6, 128.1, 128.0, 125.6, 125.5, 124.4, 124.3 (q, *J* = 271 Hz) *ppm* **(Spectrum No. 56)**

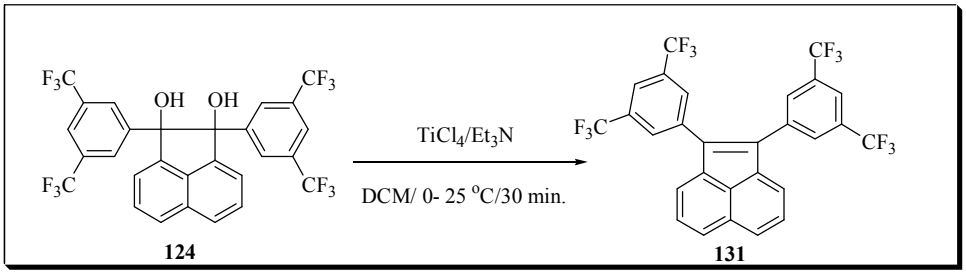
MS (EI) **:** *m/z* 441 (M+1)

Analysis **:** for $C_{26}H_{14}F_6$

Calculated: C, 70.91%; H, 3.20%

Found: C, 70.85%; H, 3.28%

(The starting diol **123** was prepared by following a similar procedure used earlier for the preparation of the diol **120.** Yield : 0.739 g (78%); mp : 164-166 ^{o}C; IR (KBr) = 3539, 3468 cm^{-1}; ^{1}H NMR : δ = 7.95 (d, *J* = 8.4 Hz, 2H), 7.69-7.59 (m, 6H), 7.39-7.26 (m, 6H), 2.14 (s, 2H) *ppm*; ^{13}C NMR : δ = 144.9, 144.4, 137.2, 131.4, 130.2 (q, *J* = 32 Hz), 129.1, 128.4, 125.5, 124.7 (*J* = 40 Hz), 124.1 (q, *J* = 270 Hz), 121.8, 89 *ppm*)



124 131

Yield : 0.478 g (83%)

mp : 160-162 °C

IR (KBr) : 3057, 1618, 1539 cm^{-1}

^{1}H NMR : (400 MHz) δ = 8.02 (d, *J* = 8.4 Hz, 2H), 7.90-7.70 (m, 10H) *ppm*

^{13}C NMR : (100 MHz) δ = 137.7, 136.9, 136.4, 132.3 (q, *J* = 33 Hz), 129.9, 129.0, 128.8, 128.3, 127.8, 124.8, 123.0 (q, *J* = 271 Hz), 121.4 *ppm*

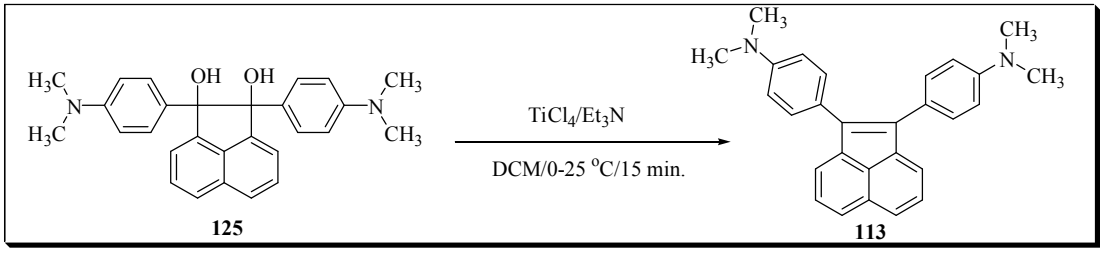
MS (EI) : *m/z* 578 (M+2)

Analysis : for $C_{28}H_{12}F_{12}$

Calculated: C, 58.36%; H, 2.10 %

Found: C, 58.45%; H, 2.16 %

(The starting diol **124** was prepared by following a similar procedure used earlier for the preparation of the diol **120.** Yield : 0.878 g (72%); mp : 172-174 °C; IR (KBr) = 3557, 3433 cm^{-1}; ^{1}H NMR : δ = 8.03 (d, *J* = 8.4 Hz, 2H), 7.95 (s, 2H), 7.80-7.73 (m, 6H), 7.39 (d, *J* = 6.8 Hz, 2H), 2.29 (s, 2H) *ppm*; ^{13}C NMR : δ = 143.9, 142.0, 137.5, 132.2, 130.9 (q, *J* = 33 Hz), 129.4, 128.7, 126.8, 123.4 (q, *J* = 271 Hz), 122.2, 121.7, 88.3*ppm*)

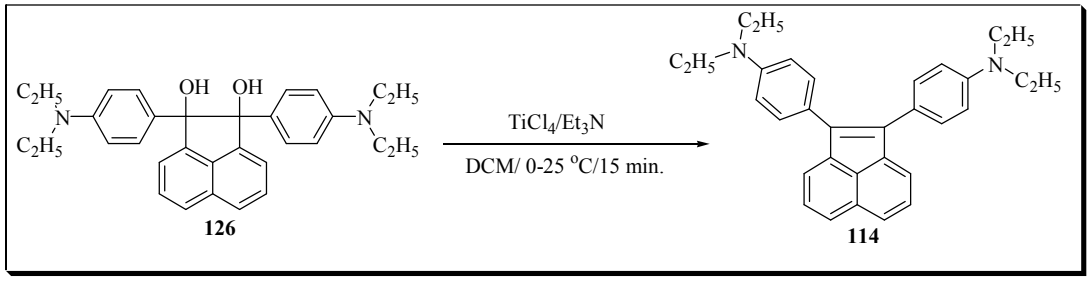


125 **113**

Yield **:** 0.312 g **(**80%)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound obtained using the $TiCl_4$/arylamine/Et_3N reagent System

(The starting diol **125** was prepared by following a similar procedure used earlier for the preparation of the diol **120.** Yield 0.636 g (75%); mp : 208-210 ^{o}C; IR (KBr) = 3528, 1520 cm^{-1}; ^{1}H NMR: δ = 7.88 (d, *J* = 8 Hz, 2H), 7.66-7.62 (m, 2H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.15-7.13 (d, *J* = 8.4 Hz, 4H), 6.71 (d, *J* = 8.4 Hz, 4H), 2.98 (s, 12H), 2.29 (s, 2H) *ppm*; ^{13}C NMR: δ = 150.2, 146.2, 137.2, 131.0, 128.7, 128.6, 128.0, 124.9, 121.7, 111.9, 89.9, 40.5 *ppm*)



126 **114**

Yield **:** 0.392 g (88%)

The IR, ^{1}H NMR and ^{13}C NMR data show 1:1 correspondence with the data of the compound obtained using the $TiCl_4$/arylamine/Et_3N reagent system.

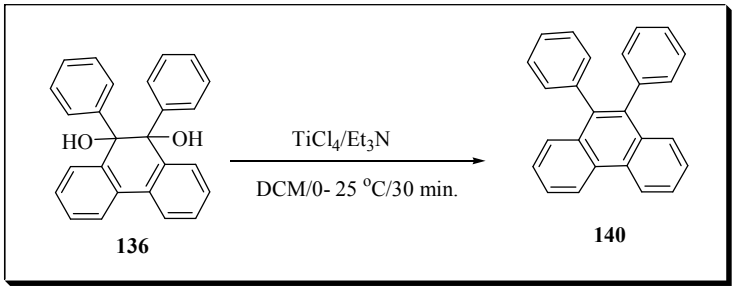
(The starting diol **126** was prepared by following a similar procedure used earlier for the preparation of the diol **120.** Yield : 0.672 g (70%); mp : 168-170 ^{o}C; IR (KBr) = 3528, 2966, 1520 cm^{-1}; ^{1}H NMR : δ = 7.89 (d, *J* = 8.4 Hz, 2H), 7.66-7.62 (m, 2H), 7.40 (d, *J* = 6.8 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 4H), 6.65 (d, *J* = 8.4 Hz, 4H), 3.40 (q, *J* = 6.8 Hz, 8H), 2.44 (s, 2H), 1.22 (q, *J* = 6.8 Hz, 12H) *ppm*; ^{13}C NMR : δ = 147.3, 146.1, 137.0, 128.7, 128.5, 126.9, 124.5, 121.5, 110.8, 89.8, 44.1, 12.5 *ppm*)

3.4.5 Reaction of $TiCl_4/Et_3N$ reagent system with 9,10-diaryl-9,10-dihydrophenanthrene-9,10-diol

The 9,10-diphenyl-9,10-dihydrophenanthrene-9,10-diol **136** was synthesized via the reaction of phenyllithium reagent prepared using bromobenzene (0.48 mL, 2.3 equiv., 4.6 mmol) and *n*-BuLi (1.76 mL, 2.2 equiv., 2.5 M in hexane, 4.4 mmol) with phenanthrenequinone (0.416 g, 2 mmol) in 25 mL THF following a reported procedure.[42] Yield : 0.546 g (75%); mp : 180-182 ^{o}C (Lit.[46c] mp : 181-182 ^{o}C); ^{1}H NMR : δ = 7.94 (d, *J* = 7.6 Hz, 2H), 7.51- 7.18 (m, 16H), 2.23 (s, 2H) *ppm*; ^{13}C NMR : δ = 141.3, 140.0, 133.7, 129.1, 128.7, 128.2, 127.9, 127.7, 126.6, 123.2, 80.8 *ppm.*

To a solution of the diol **136** (0.5 mmol, 0.182 g) and Et_3N (2 mmol, 0.28 mL) in DCM (10 mL), $TiCl_4$ (0.22 mL of 1:1 solution of $TiCl_4/CH_2Cl_2$, 1 mmol) in DCM (2.5 mL) was added dropwise for 5 min. at 0 °C under N_2 atmosphere. The contents were stirred for 0.5 h at 0-25 ^{o}C. It was quenched with saturated NH_4C1 solution. The organic layer was separated, and the aqueous layer was extracted with CH_2C1_2 (2x15 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 **140** was eluted using hexane/ethyl acetate 98:2.



136 **140**

Yield **:** 0.132 g (80%)

mp **:** 242-244 °C (Lit.[46d] mp 238-239 °C)

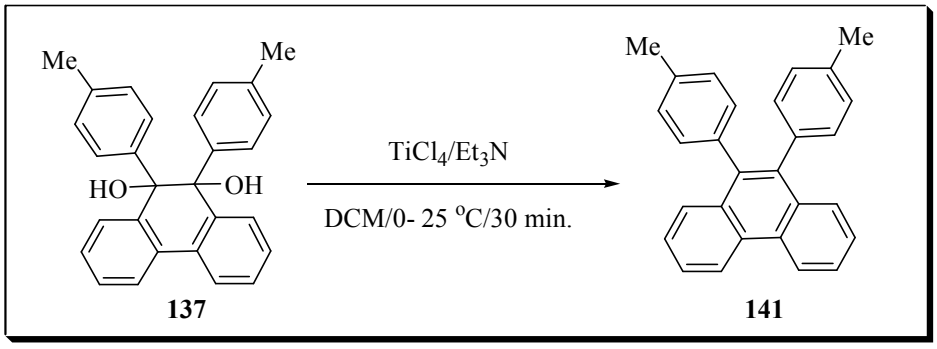
IR (KBr) **:** 3047, 1485, 1439 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 8.84 (d, J = 8 Hz, 2H), 7.71-7.50 (m, 6H), 7.26-7.18 (m, 10H) *ppm*

^{13}C NMR **:** (100 MHz) δ = 139.6, 137.2, 131.9, 131.1, 130.0, 127.9, 127.6, 126.6, 126.5, 126.4, 122.5 *ppm*

MS (EI) **:** *m/z* 331 (M+1)

The above procedure was followed for the conversion of other diaryl diols to the corresponding diarylphenanthrene derivatives.



137 **141**

Yield **:** 0.152 g **(**85%)

mp **:** 256-58 ^{o}C (Lit.[42] mp 261-263 ^{o}C)

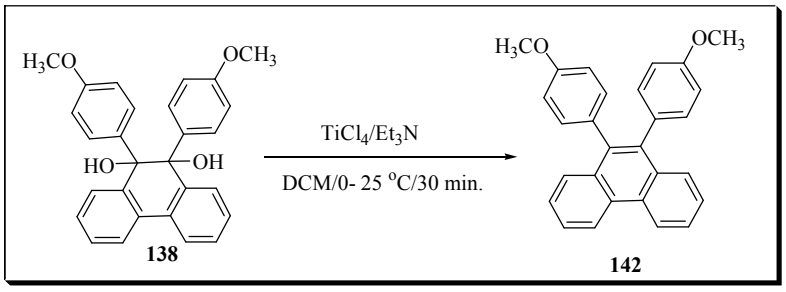
IR (KBr) **:** 3026, 2922, 1682, 1504 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 8.82 (d, *J* = 8.4 Hz, 2H), 7.67- 7.47 (m, 6H), 7.08 (m, 8H), 2.35 (s, 6H) *ppm*

^{13}C NMR **:** (100 MHz) δ = 137.2, 136.6, 135.8, 132.2, 130.9, 129.9, 128.4, 127.9, 126.5, 126.2, 122.5, 21.3 *ppm*

MS (EI) **:** *m/z* 359 (M+1)

(The starting diol **137** was prepared by following a similar procedure used earlier to prepare the diol **136.** Yield : 0.486 g (62%); mp : 150-152 ^{o}C (Lit.[42] mp : 149-151 ^{o}C); ^{1}H NMR : δ = 7.96 (d, *J* = 8 Hz, 2H), 7.55-7.25 (m, 10H), 7.30 (d, *J* = 8 Hz, 4H), 2.30 (s, 2H), 2.26 (s, 6H) *ppm*; ^{13}C NMR : δ = 141.5, 137.3, 137.0, 133.6, 128.9, 128.8, 128.4, 127.7, 126.4, 123.0, 80.7, 20.8 *ppm*)



138 **142**

Yield **:** 0.172 g (88%)

mp **:** 264-268 ^{o}C (Lit.[42] mp 274-275 ^{o}C)

IR (KBr) **:** 3059, 2951, 1608, 1506 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 8.80 (d, J = 8.4 Hz, 2H), 7.68-7.47 (m, 6H), 7.06 (d, J = 8.8 Hz, 4H), 6.80 (d, J = 8.8 Hz, 4H), 3.80 (s, 6H) *ppm* **(Spectrum No. 57)**

^{13}C NMR **:** (100 MHz) δ = 157.9, 137.1, 132.3, 132.1, 132.0, 129.9, 127.8, 126.5, 126.3, 122.5, 113.1, 55.1 *ppm* **(Spectrum No. 58)**

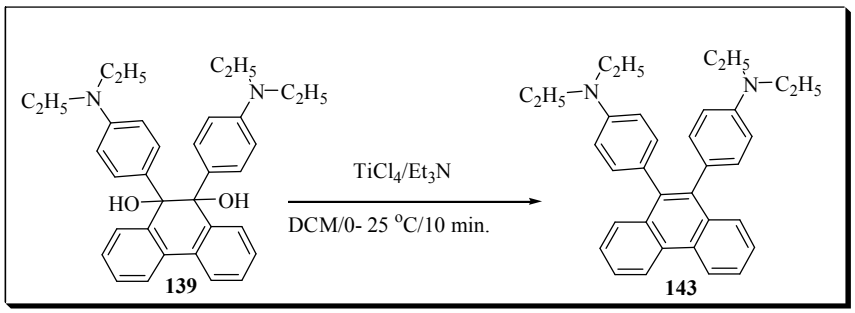
MS (EI) **:** *m/z* 391 (M+1)

Analysis **:** for $C_{28}H_{22}O_2$

Calculated: C, 86.13%; H, 5.68 %

Found: C, 86.32 %; H, 5.61 %

(The starting diol **138** was prepared by following a similar procedure used earlier to prepare the diol **136.** Yield : 0.509 g (60%); mp : 161-163 ^{o}C (Lit.[42] mp 163-164 ^{o}C); ^{1}H NMR : δ = 7.95 (d, J = 8 Hz, 2H), 7.55-7.26 (m, 10H), 6.73 (d, J = 8.4 Hz, 4H), 3.72 (s, 6H), 2.27 (s, 2H) *ppm*; ^{13}C NMR : δ = 158.9, 141.7, 133.6, 132.0, 129.2, 129.0, 128.6, 126.5, 123.1, 113.5, 80.6, 55.0 *ppm*)



Yield **:** 0.165 g **(**70%)

mp **:** 214-216^{o}C

IR (KBr) **:** 2964, 1612, 1514 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 8.79 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 8 Hz, 2H), 7.65- 7.46 (m, 4H), 6.98 (d, *J* = 8 Hz, 4H), 6.61(d, *J* = 8 Hz, 4H), 3.33 (q, *J* = 6.8 Hz, 8H), 1.14 (t, *J* = 6.8 Hz, 12H) *ppm* **(Spectrum No. 59)**

^{13}C NMR **:** (100 MHz) δ = 146.2, 137.7, 132.8, 132.0, 129.9, 128.1, 127.3, 126.3, 125.8, 122.3, 111.7, 44.4, 12.5 *ppm* **(Spectrum No. 60)**

MS (EI) **:** *m/z* 473 (M+1) *ppm*

Analysis **:** for $C_{34}H_{36}N_2$

Calculated: C, 86.40 %; H, 7.68 %; N, 5.93%

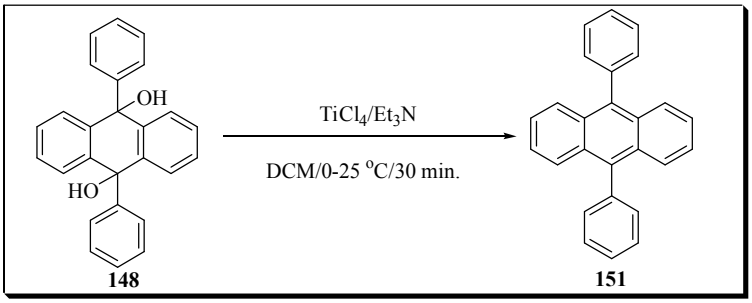
Found: C, 86.25%; H, 7.76 %; N 5.85%

(The starting 9,10-bis (4-(diethylamino) phenyl)-9,10-dihydrophenanthrene-9,10-diol **139** was synthesized via reaction of Grignard reagent prepared using 4-bromo-N,N-diethylaniline (8 mmol, 1.82 g) and magnesium turnings (8 mmol, 0.192 g) with phenanthrenequinone (2 mmol, 0.416 g) in 30 mL THF. Yield : 0.556 g (55%); mp 170-172 ^{o}C; IR (KBr) = 3528 cm^{-1}; ^{1}H NMR : δ = 7.91 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.42-7.38 (m, 2H), 7.28-7.25 (m, 6H), 6.48 (d, *J* = 8.4 Hz, 4H), 3.26 (q, *J* = 7.2 Hz, 8H), 2.37 (s, 2H), 1.20 (t, *J* = 7.2 Hz, 12H) *ppm*; ^{13}C NMR : δ = 147.0, 142.5, 133.7, 128.9, 128.7, 128.0, 126.8, 126.1, 122.7, 111.1, 80.7, 44.1, 12.6 *ppm*)

3.4.6 Reaction of $TiCl_4/Et_3N$ reagent system with 9,10-diaryl-9,10-dihydroanthracene-9,10-diol

The 9,10-diphenyl-9,10-dihydroanthracene-9,10-diol **148** was synthesized via reaction of Grignard reagent prepared using bromobenzene (0.84 mL, 8 mmol) and magnesium turnings (8 mmol, 0.192 g) in 30 mL THF with anthraquinone (2 mmol, 0.416 g) in 60 mL 1,4-dioxane. Yield: 0.328 g (45%); mp 242-244 ^oC; IR (KBr) = 3576 cm^{-1}; ^1H NMR : δ = 7.51-7.23 (m, 18H), 2.69 (s, 2H) *ppm*; ^{13}C NMR : δ = 148.1, 140.6, 128.5, 128.4, 128.1, 126.8, 126.6, 74.4 *ppm*

To a solution of the diol **148** (0.5 mmol, 0.182 g) and Et_3N (2 mmol, 0.28 mL) in DCM (10 mL), $TiCl_4$ (0.22 mL of 1:1 solution of $TiCl_4/CH_2Cl_2$, 1 mmol) in DCM (2.5 mL) was added dropwise for 5 min. at 0 °C under N_2 atmosphere. The contents were stirred for 0.5 h at 0-25 ^oC. It was quenched with saturated NH_4Cl solution. The organic layer was separated and the aqueous layer was extracted with CH_2C1_2 (2x15 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 **151** was eluted using hexane/ethyl acetate 98:2.



Yield **:** 0.135 g (82%)

mp **:** 242-244 ^{o}C (Lit.[45] mp 248-250 ^{o}C)

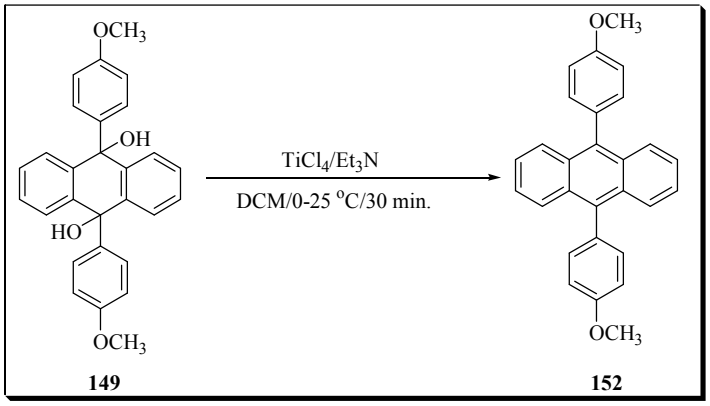
IR (KBr) **:** 3024, 1489, 1386 cm^{-1}

^{1}H NMR **:** (400 MHz) δ= 7.74-7.71 (m, 4H), 7.65-7.50 (m, 10H), 7.37-7.34 (m, 4H) *ppm*

^{13}C NMR **:** (100 MHz) δ = 139.1, 137.1, 131.4, 129.9, 128.4, 127.5, 126.9, 125.0 *ppm*

MS (EI) **:** *m/z* 331 (M+1)

The above procedure was followed for the conversion of other diaryl diols to the corresponding diarylanthracene derivatives.



149 **152**

Yield **:** 0.166 g **(**85%)

mp **:** 270-272 ^{o}C (Lit.[45] mp 274 ^{o}C)

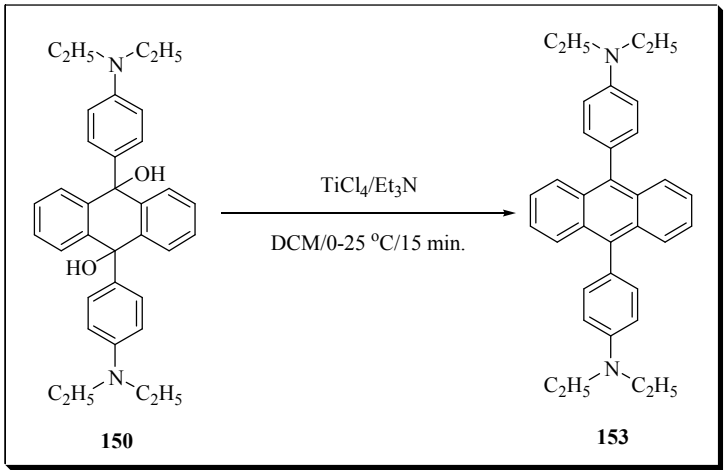
IR (KBr) **:** 1604, 1512, 1390 cm^{-1}

^{1}H NMR **:** (400 MHz) δ= 7.75-7.73 (m, 4H), 7.40-7.32 (m, 8H), 7.14 (d, *J* = 8.8 Hz, 4H), 3.97 (s, 6H) *ppm* **(Spectrum No. 61)**

^{13}C NMR **:** (100 MHz) δ = 159.0, 136.7, 132.4, 131.1, 130.3, 127.0, 124.9, 113.9, 55.4 *ppm* **(Spectrum No. 62)**

MS (EI) **:** *m/z* 391 (M+1) *ppm*

(The starting diol **149** was prepared by following a similar procedure used earlier to prepare the diol **148.** Yield 0.432 g (51%); mp : 248-250 ^{o}C; IR (KBr) =3562, 3468 cm^{-1}; ^{1}H NMR: δ = 7.42-7.36 (m, 8H), 7.28-7.26 (m, 4H), 6.84 (d, *J* = 9.2 Hz, 4H), 3.80 (s, 6H), 2.62 (s, 2H) *ppm*; ^{13}C NMR: δ = 158.3, 140.9, 140.2, 128.24, 128.21, 127.8, 113.3, 74.3, 55.2 *ppm*)



150 **153**

Yield **:** 0.144 g (61%)

mp **:** > 250 ^{o}C

IR (KBr) **:** 2972, 1606, 1518 cm^{-1}

^{1}H NMR **:** (400 MHz) δ = 7.89-7.87 (m, 4H), 7.33-7.30 (m, 8H), 6.90 (d, *J* = 8.8 Hz, 4H), 3.50 (q, *J* = 7.2 Hz, 8H), 1.30 (t, *J* = 7.2 Hz, 12H) *ppm* **(Spectrum No. 63)**

^{13}C NMR **:** (100 MHz) δ = 147.0, 137.2, 132.3, 130.5, 127.4, 125.6, 124.5, 111.4, 44.4, 12.8. *ppm* **(Spectrum No. 64)**

MS (EI) **:** *m/z* 473 (M+1)

Analysis **:** for $C_{34}H_{36}N_2$

Calculated: C, 86.40 %; H, 7.68 %; N 5.93

Found: C, 86.22 %; H, 7.61 %; N 6.03

(The starting diol **150** was prepared by following a similar procedure used earlier to prepare the diol **148.** Yield 0.556 g (55%) ; mp : 222-224 ^{o}C; IR (KBr) =3553, 3427 cm^{-1}; ^{1}H NMR : δ = 7.52-7.49 (m, 4H), 7.29-7.27 (m, 4H), 7.21 (d, *J* = 8 Hz, 4H), 6.61 (d, *J* = 8 Hz, 4H), 3.34 (q, *J* = 7.2 Hz, 8H), 2.59 (s, 2H), 1.22 (t, *J* = 7.2 Hz, 12H) *ppm*; ^{13}C NMR : δ = 146.6, 141.7, 134.1, 127.9, 127.8, 127.7, 110.9, 74.5, 44.2, 12.6 *ppm*)

3.5 References

1. (a) Reetz, M. T. *Organotitanium reagents in organic synthesis*, Springer-Verlag, Berlin, **1986**. (b) *Organometallics in Synthesis A Manual*, M. Schlosser (Ed), John Wiley & Sons, **2002**, p 817. (c) McMurry, J. E. *Chem. Rev.* **1989**, *89*, 1513.
2. (a) *Titanium and Zirconium derivatives in organic synthesis: A review with procedures* by Seebach, D.; Weidmann, B.; Wider, L. in *Modern Synthetic Methods 1983*, Ed. Scheffold, R. Wiley, New York, **1983**, p 217. (b) Takai, K.; Hotta, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1978**, *19*, 2417. (c) Reetz, M. T.; Westermann, J.; Steinbach, R. *J. Chem. Soc., Chem. Commun.* **1981**, 237.
3. Pastor, I. M.; Yus, M. *Tetrahedron* **2001**, 57, 2365 and references cited there in.
4. (a) Periasamy, M. *ARKIVOC* **2002** (*VII*), 151. (b) Harrison, C. R. *Tetrahedron Lett*. **1987**, *28*, 4135. (c) Evans, D. A.; Clark, J. S.; Metternich, R.; Novack, V. J.; Sheppard, G. S. *J. Am. Chem. Soc*. **1990**, *112*, 866. (d) Evans, D. A.; Rieger, D. L.; Bilodeau, M. T.; Urpi, F. *J. Am. Chem. Soc*. **1991**, *113*, 1047. (e) Crimmins, M. T.; King, B. W.; Tabet, E. A. *J. Am. Chem. Soc*. **1997**, *119*, 7883. (f) Yoshida, Y.; Hayashi, R.; Sumihara, H.; Tanabe, Y. *Tetrahedron Lett.* **1997**, *38*, 8727 and references cited therein.
5. Reddy, M. N. Ph.D Thesis, **2005**, University of Hyderabad, Hyderabad, India.
6. (a) Lehnert, W. *Tetrahedron Lett*. **1970**, *11*, 4723. (b) Lehnert, W. *Tetrahedron.* **1974**, *30*, 301.

7. Yoshida, Y.; Matsumoto, N.; Hamasaki, R.; Tanabe, Y. *Tetrahedron Lett.* **1999**, *40*, 4227.

8. Crimmins, M. T.; Chaudhary, K. *Org. Lett.* **2000**, *2*, 775.

9. (a) Matsumura, Y.; Nishimura, M.; Hiu, H.; Watanabe, M.; Kise, N. *J. Org. Chem.* **1996**, *61*, 2809. (b) Kise, N.; Tokioka, K.; Aoyama, Y.; Matsumura, Y. *J. Org. Chem.* **1995**, *60*, 1100. (c) Kise, N.; Kumada, K.; Terao, Y.; Ueda, N. *Tetrahedron* **1998**, *54*, 2697.

10. Rao, V. D.; Periasamy, M. *Synthesis* **2000**, 703.

11. Rao, V. D.; Periasamy, M. *Tetrahedron: Asymmetry* **2000**, *11*, 1151.

12. Suresh, S.; Periasamy, M. *Tetrahedron Lett.* **2004**, *45*, 6291.

13. Periasamy, M.; Suresh, S.; Ganesan, S. S. *Tetrahedron Lett.* **2005**, *46*, 5521.

14. Periasamy, M.; Srinivas, G.; Bharathi. P. *J. Org. Chem.* **1999**, *64*, 4204.

15. Periasamy, M.; Srinivas, G.; Seenivasaperumal, M. *J. Chem. Res.* **2004**, 270.

16. Srinivas, G. Ph. D. Thesis, **2002,** University of Hyderabad, Hyderabad, India.

17 (a) Antler, W.; Laubengayer, A. W. *J. Am Chem. Soc*. **1955,** *77***,** 5250. (b) Bharathi, P.; Periasamy, M. *Org. Lett*. **1999**, *1*, 857. (c). Periasamy, M.; Jayakumar, K. N.; Bharathi, P. *Chem. Commun.* **2001**, 1728.

18. Periasamy, M.; Jayakumar, K. N.; Bharathi, P. *J. Org. Chem.* **2005**, *70*, 5420.

19. Han, Z.; Shinokubo, H; Oshima, K. *Synlett* **2001**, 1421.

20. Bharathi, P. Ph. D. Thesis, **2000**, University of Hyderabad, Hyderabad, India.

21. Clerici, A.; Clerici, L.; Porta, O. *J. Org. Chem.* **1995**, *60*, 480.

22. Periasamy, M.; Srinivas, G.; Bharathi, P.; Karunakar, G. V. *Tetrahedron Lett*. **1999**, *40*, 7577.

23. Karunakar, G. V. Ph. D. Thesis, **2005**, University of Hyderabad, Hyderabad, India

24. (a) Karunakar, G. V.; Periasamy, M. *Tetrahedron Lett*. **2006,** *47*, 3549.

25. Periasamy, M.; Jayakumar, K. N.; Bharathi, P. *J. Org. Chem.* **2000,** *65,* 3548.

26. (a) Kishorebabu, N. Ph. D. Thesis, **2006**, University of Hyderabad, Hyderabad, India. (b) Periasamy, M.; Kishorebabu, N.; Jayakumar, K. N. *Tetrahedron Lett.* **2007**, *48*, 1955**.**

27. Karunakar, G. V.; Periasamy, M. *J. Org. Chem.* **2006**, *71*, 7463.

28. Periasamy, M.; KishoreBabu, N.; Jayakumar, K. N. *Tetrahedron Lett.* **2003**, *44*, 8939.

29. (a) Suresh. S. Ph. D. Thesis, **2005**, University of Hyderabad, Hyderabad, India.

(b**)** Selva Ganesan, S. Ph. D. Thesis, **2009**, University of Hyderabad, Hyderabad, India

30. (a) Mukkanti A. Ph. D. Thesis, **2004**, University of Hyderabad, Hyderabad, India

(b) Shyam Raj, D. Ph. D. thesis, **2009,** University of Hyderabad, Hyderabad, India

31. (a) Wu, Y.-T.; Siegel, J. S. *Chem. Rev.* **2006**, *106*, 4843. (b) Tsefrikas, V. M.; Scott, L. T. *Chem. Rev.* **2006**, *106*, 4868. (c) Echavarren, A. M.; Gomez-Lor, B.; Gonzalez, J. J.; de Frutos, O. *Synlett* **2003**, 585.

32. (a) Neudorff, W. D.; Schulte, N.; Lentz, D.; Schlüter, A. D. *Org. Lett.* **2001**, *3*, 3115. (b) Gourdon, A. *Eur. J. Org. Chem.* **1998**, 2797.

33. (a) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996,** *29,* 235. (b). Mehta. G.; Rao, H. S. P. *Tetrahedron* **1998**, *54*, 13325.

34. Bachmann, W. E.; Chu, E. -J. *J. Am. Chem. Soc*., **1936,** *58***,** 1118.

35. Schank, K.; Beck, H.; Buschlinger, M.; Eder, J.; Heisel, T.; Pistorius, P.; Wagner, C. *Helv. Chim. Acta* **2000,** *83***,** 801.

36. Kurata, H; Takehara, Y; Kim, S; Sakai, K; Matsumoto, K; Kawase, T; Oda, M. *Synlett* **2007**, 2053.

37. (a) Floyd, A. J.; Dyke, S. F.; Ward, S. E. *Chem. Re*v. **1976**, *76*, 509. (b) Cragg, G. M.; Newman, D. J. *J. Nat. Prod*. **2004**, *67*, 232. (c) Li, Z.; Jin, Z.; Huang, R. *Synthesis* **2001**, 2365.

38. Colwell, W. T.; Brown, V.; Christie, P.; Lange, J.; Reece, C.; Yamamoto, K.; Henry, D. W. *J. Med. Chem*. **1972**, *15*, 771.

39. (a) Banwell, M. G.; Bezos, A.; Burns, C.; Kruszelnicki, I.; Parish, C. R.; Su, S.; Sydnes, M. O. *Bioorg. Med. Chem. Lett*. **2006**, *16*, 181. (b) Wei, L.; Brossi, A; Kendall, R.; Bastow, K. F.; Morris-Natschke, S. L.; Shi, Q.; Lee, K.-H. *Bioorg. Med. Chem*. **2006**, *14*, 6560.

40. Cannon, J. G.; Khonje, P. R.; Long, J. P. *J. Med. Chem*. **1975**, *18*, 110.

41. (a) Lewis, F. D.; Burch, E. L. *J. Phys. Chem*. **1996**, *100*, 4055. (b) Lewis, F. D.; Barancyk, S. V.; Burch, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 3866. (c) Machado, A. M.; Munaro, M.; Martins, T. D.; Da´vila, L. Y. A.; Giro, R.; Caldas, M. J.; Atvars,

T. D. Z.; Akcelrud, L. C. *Macromolecules* **2006**, *39*, 3398. (d) Liu, R.; Farinha, J. P. S.; Winnik, M. A. *Macromolecules* **1999**, *32*, 3957.

42. He, B.; Tian, H.; Geng, Y.; Wang, F.; Mullen. K. *Org. Lett*. **2008,** *10*, 773.

43. (a) Marcus, R. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1111. (b) Paddon-Row, M. N. *Acc. Chem. Res.* **1994**, *27*, 18. (c) Huber, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 848. (d) Deisenhofer, J.; Michel, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 829. (e) Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 690. (f) Kanis, D. R.; Ratner, M. A.; Mark, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 10338. (g) Kaino, T.; Tomaru, S. *Adv. Mater.* **1993**, *5*, 172. (h) Grätzel, M.; Kalyanasundaram, K. *Curr. Sci.* **1994**, *66*, 706. (i) Babu, K. S. C.; Srivasta, O. N.; Rao, G. V. S. *Curr. Sci.* **1994**, *66*, 715. (j) Nalwa, H. S.; Kakuta, A. *Appl. Organomet. Chem.* **1992**, *6*, 645.

44. (a) Smet, M.; Dijk, J. V.; Dehaen, W. *Tetrahedron* **1999**, *55,* 7859. (b) Kim, Y.-H; Bark, K.-M; Kwon, S-K. *Bull. Korean Chem. Soc.* **2001**, *22*, 975

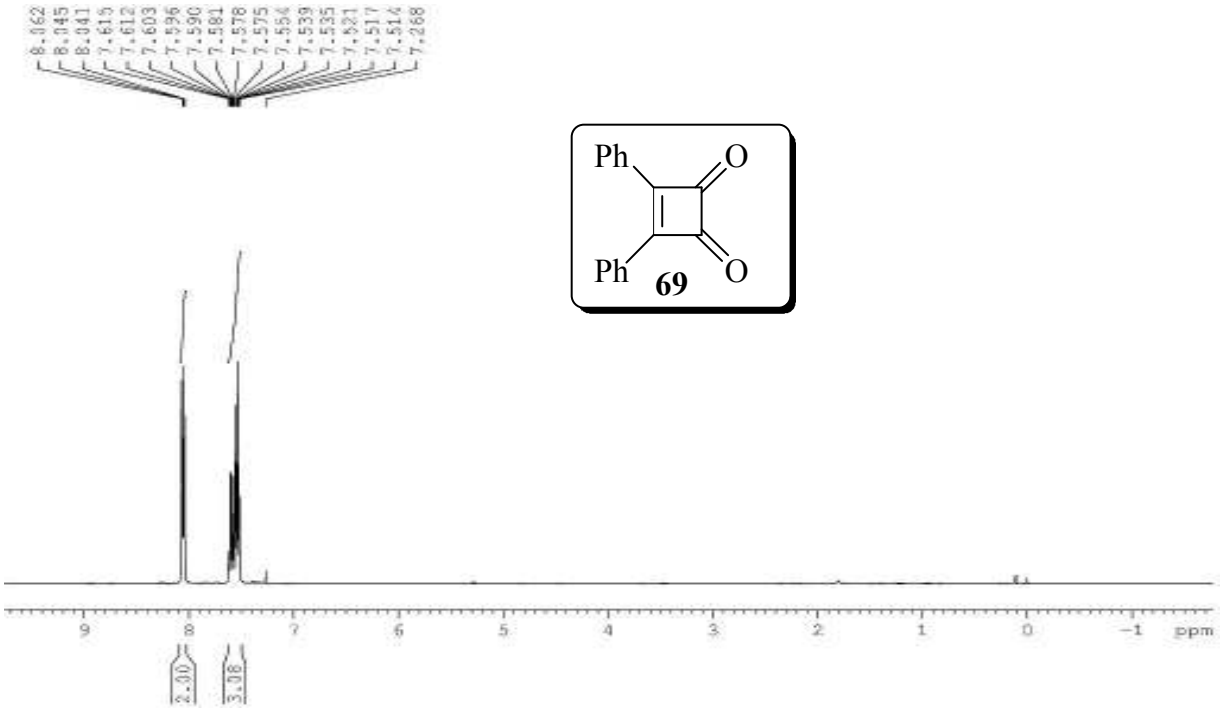
45. Kotha, S.; Ghosh, A. K.; Deodhar, K. D. *Synthesis* **2004**, 549.

46. (a) Moricnoni, E. J.; Connor, W. F. O.; Kuhn, L. P.; Keneally, E. A.; Wallenberger, F. T. *J. Am. Chem. Soc.* **1959**, 81, 6472. (b) Hussaini, S. S.; Raj, A. R. N.; Huq, C. A. M. A. *Tetrahedron Lett.* **2007**, *48*, 775. (c) Varea, T.; Medio, M.; Ballesteros. R.; Oniga, O.; Asensio, G. *Terrahedron* **1995**, *51*, 10093. **(**d). Kanno, K.; Liu, Y.; Lesato, A.; Nakajima, K.; Takahashi, T. *Org. Lett*. **2005**, 7, 5453.

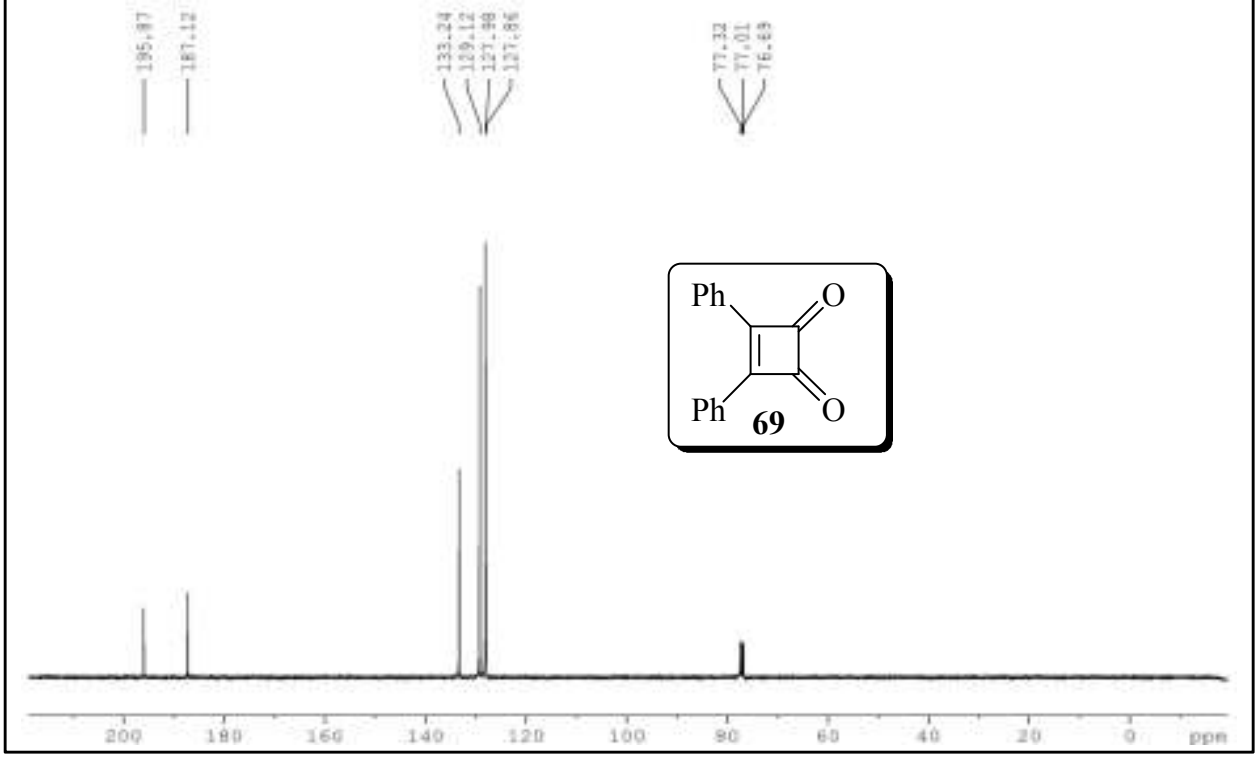
Appendix I

(Representative Spectra)

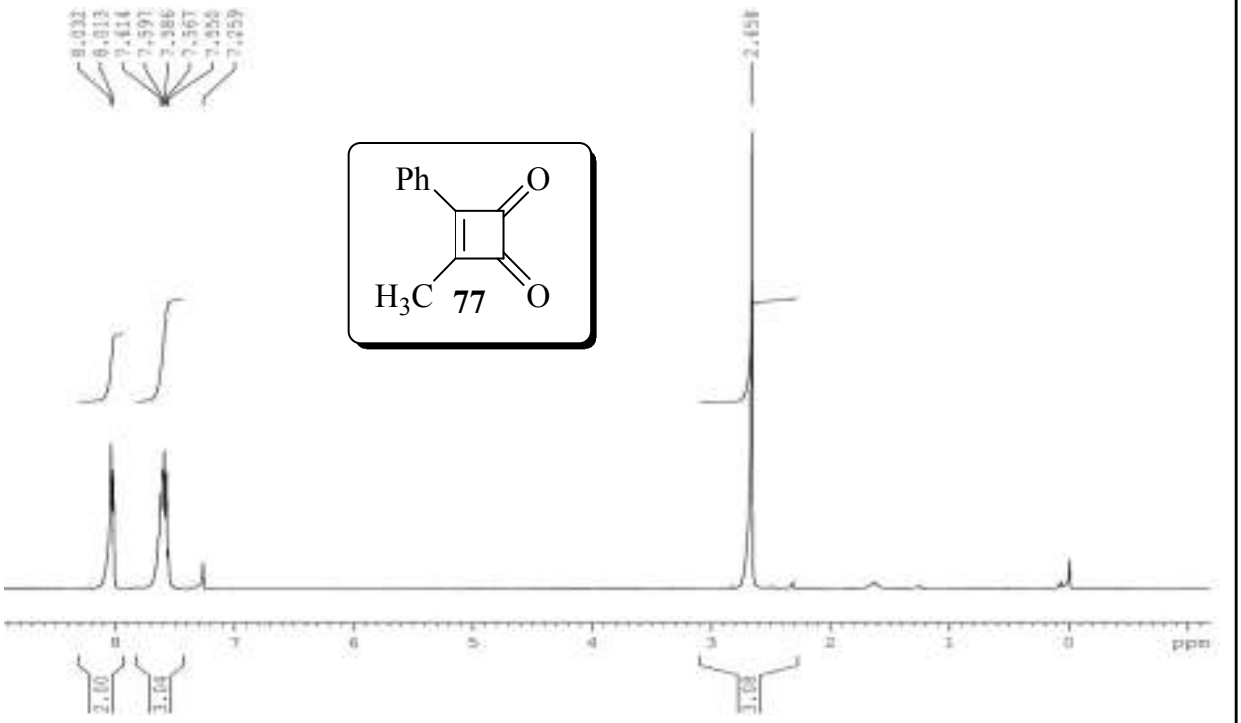
Spectrum No 1 (chapter 1) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



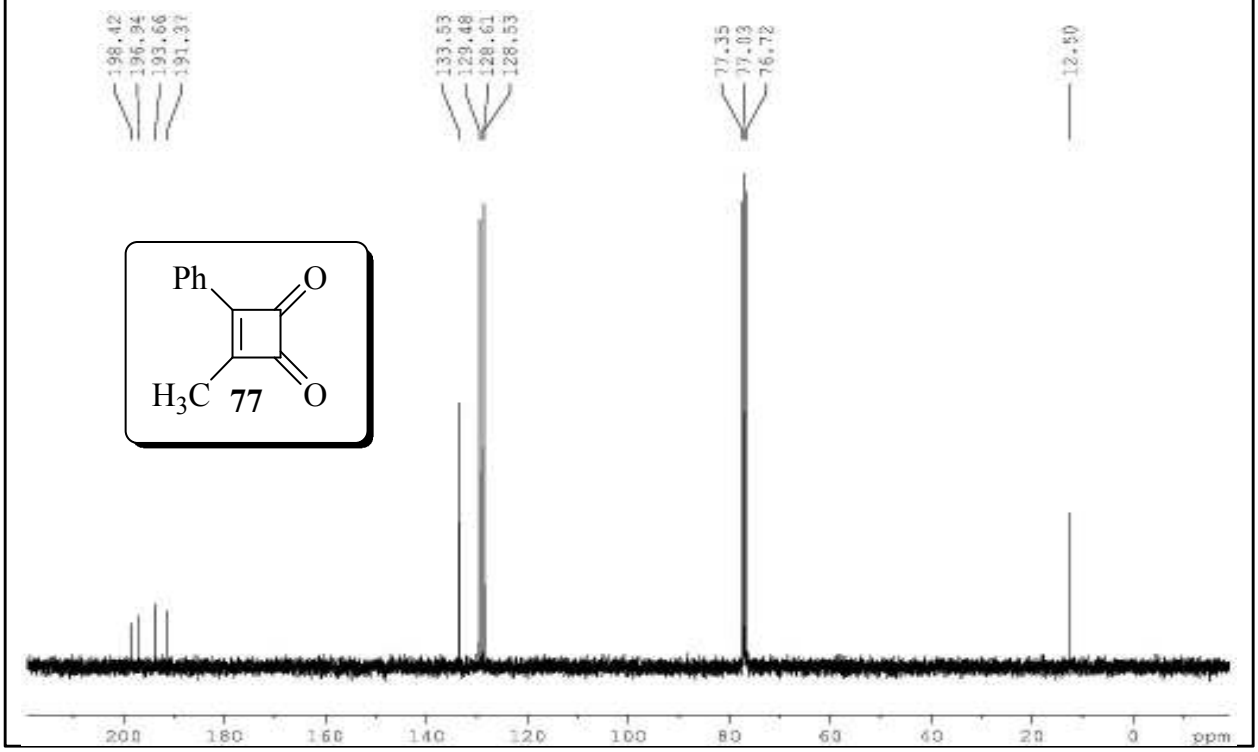
Spectrum No 2 (chapter 1) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



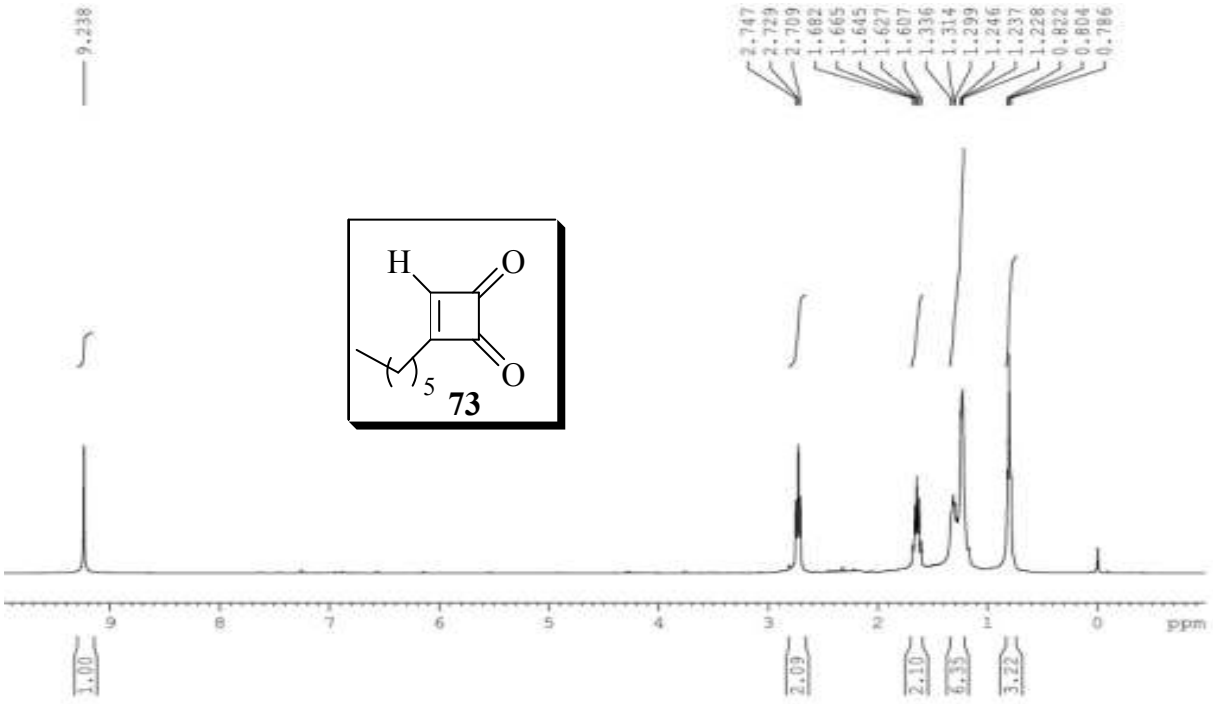
Spectrum No 3 (chapter 1) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



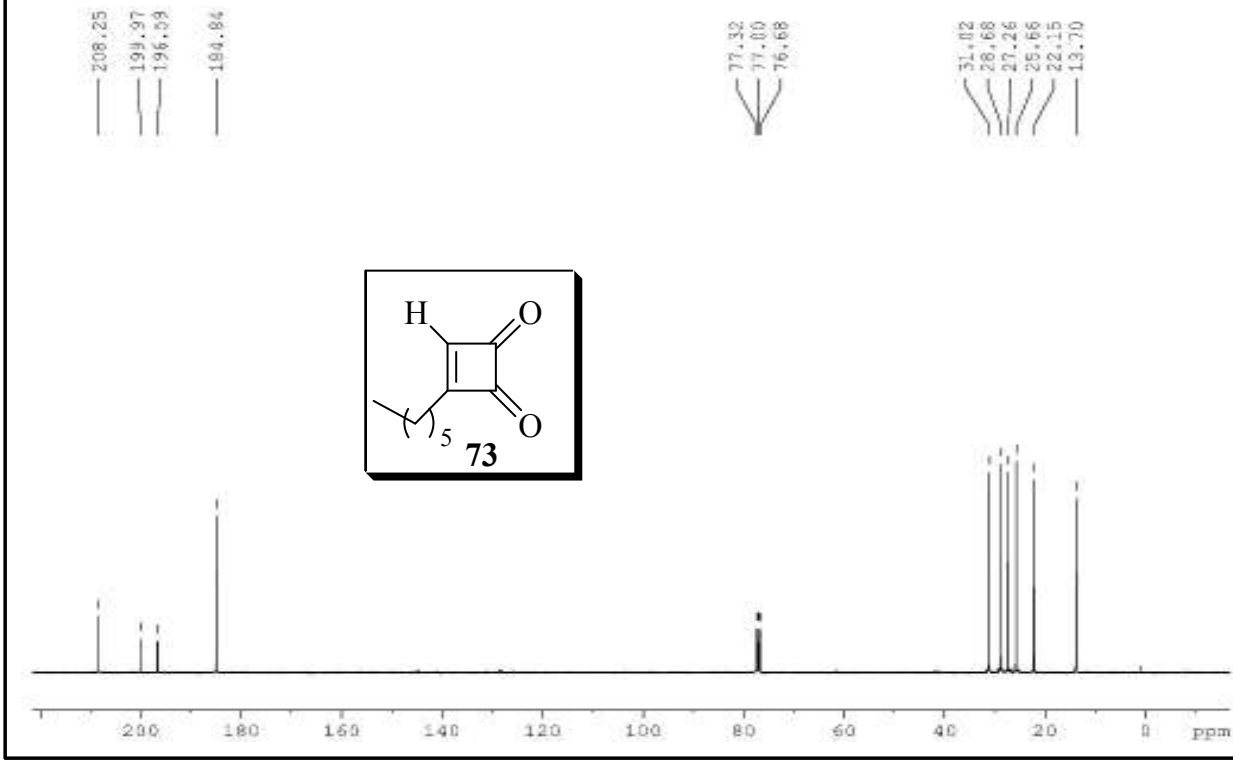
Spectrum No 4 (chapter 1) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



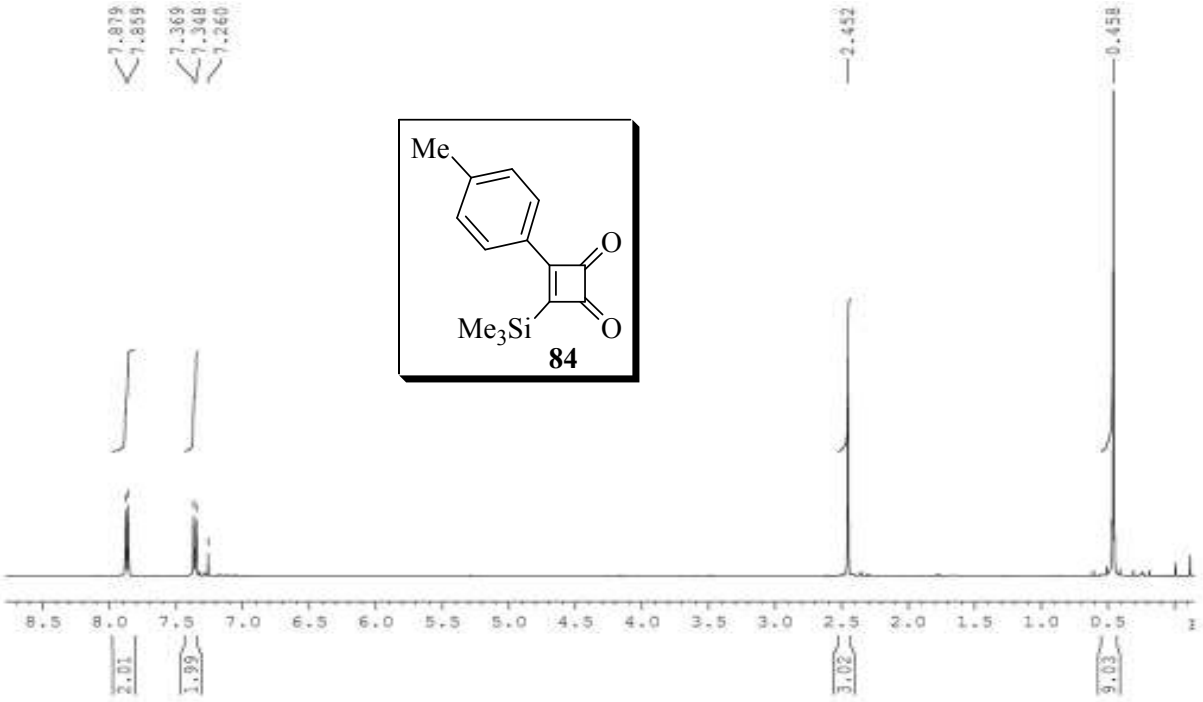
Spectrum No 5 (chapter 1) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



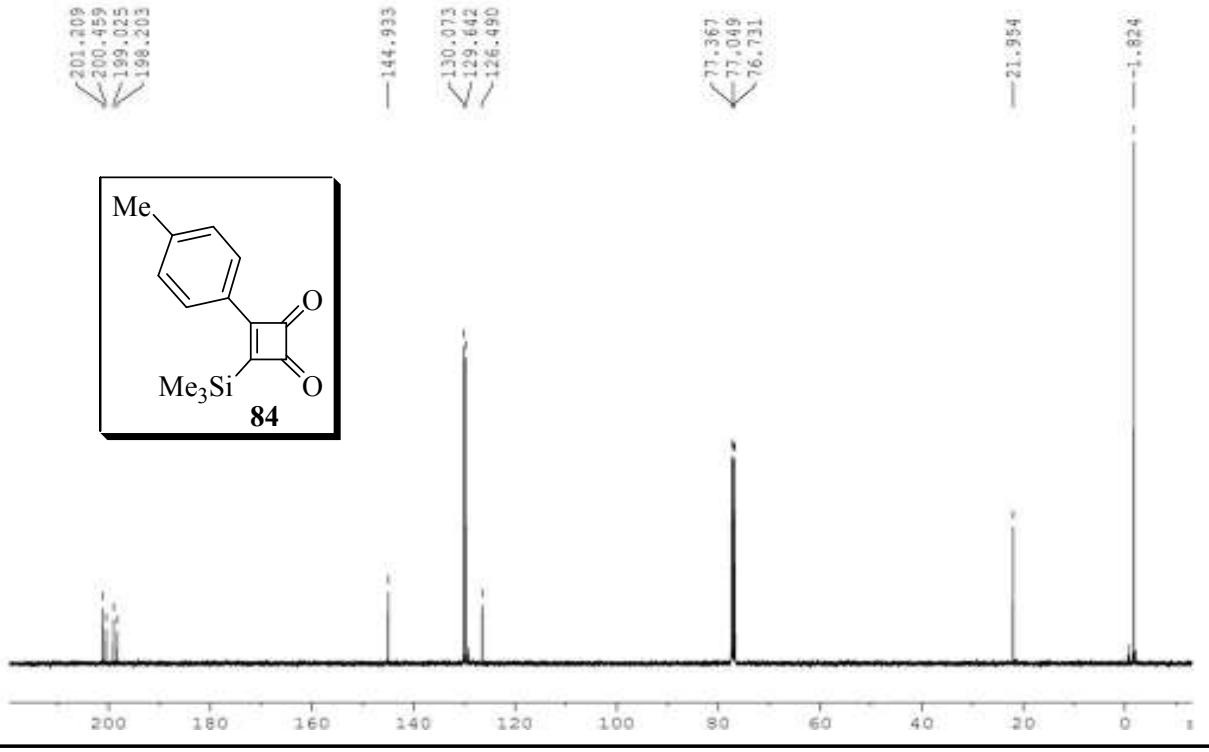
Spectrum No 6 (chapter 1) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



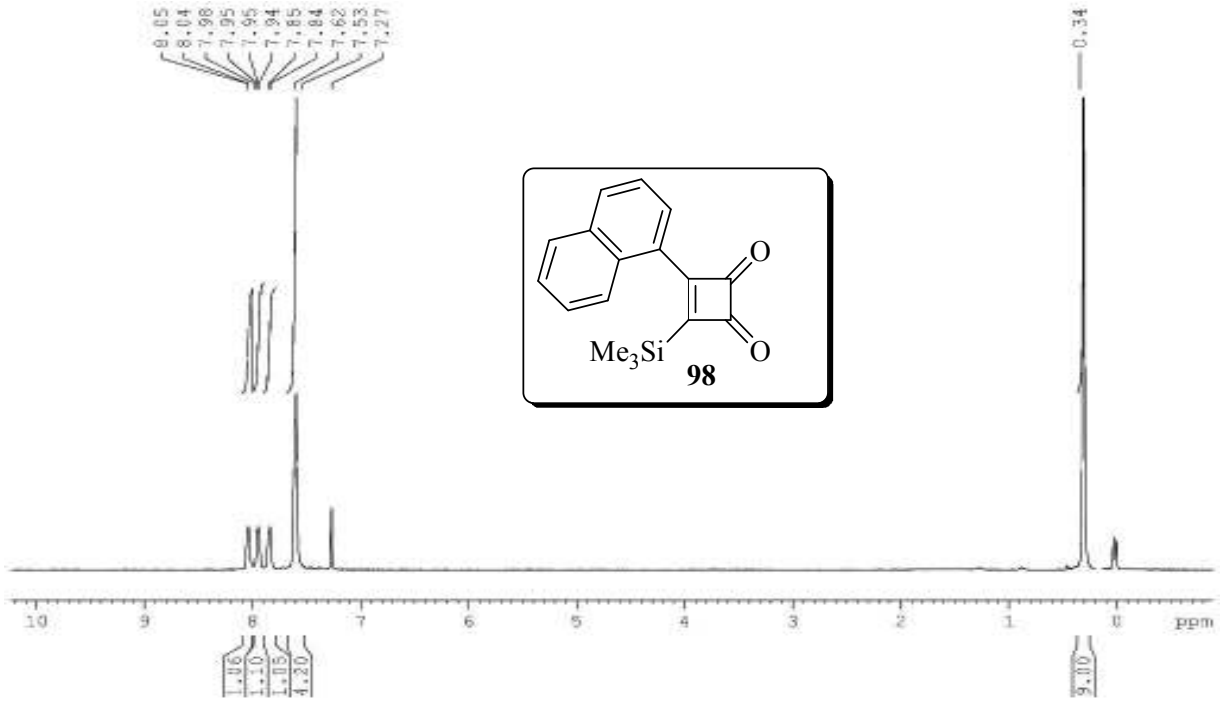
Spectrum No 7 (chapter 1) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



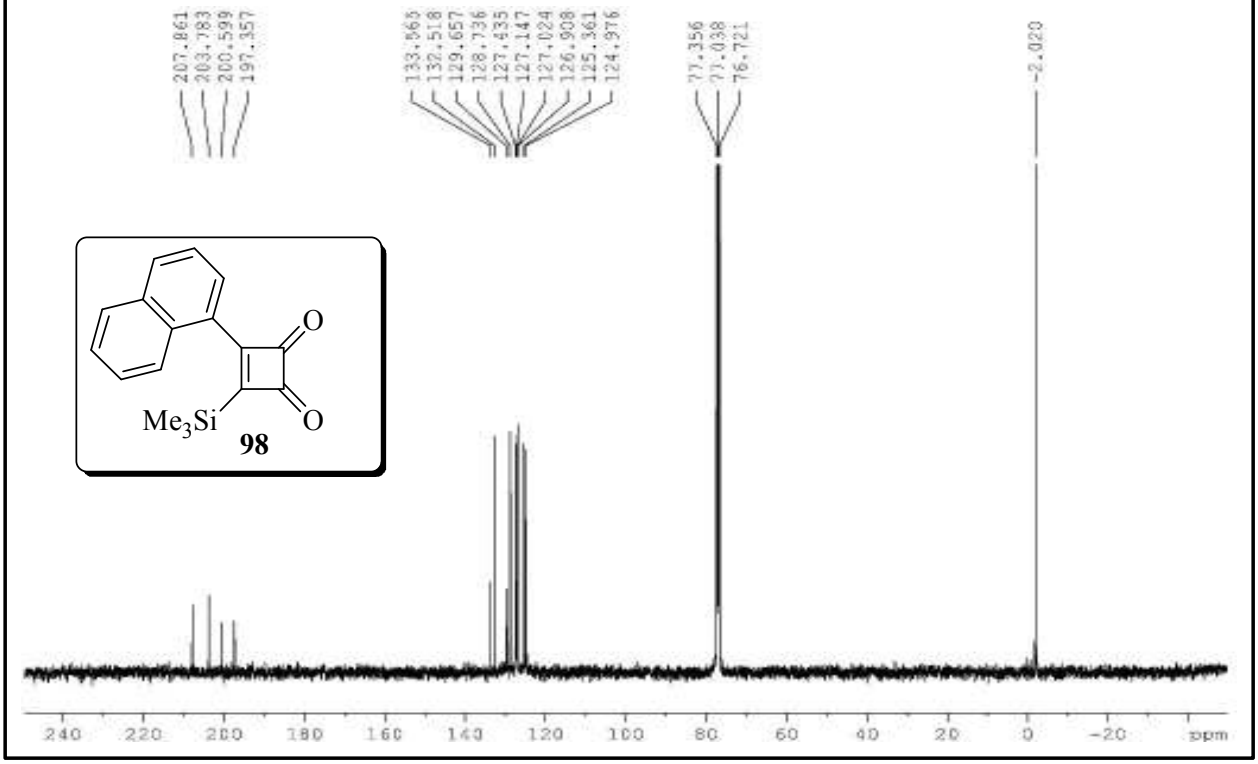
Spectrum No 8 (chapter 1) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



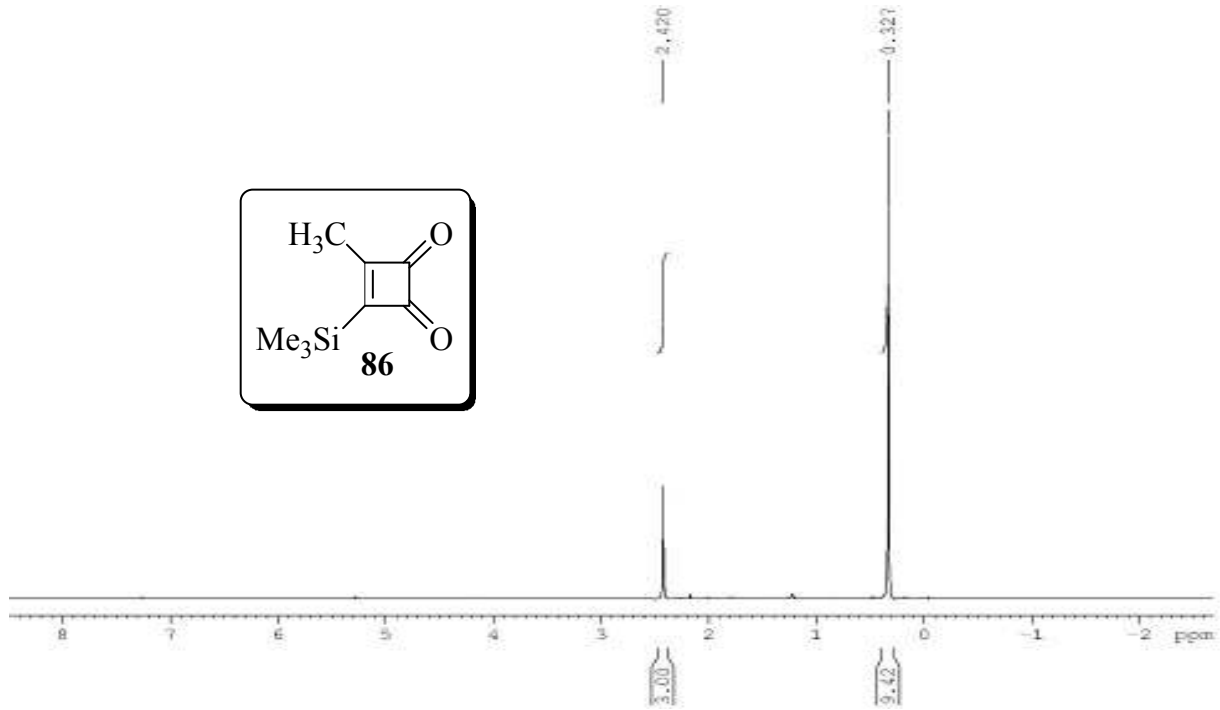
Spectrum No 9 (chapter 1) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



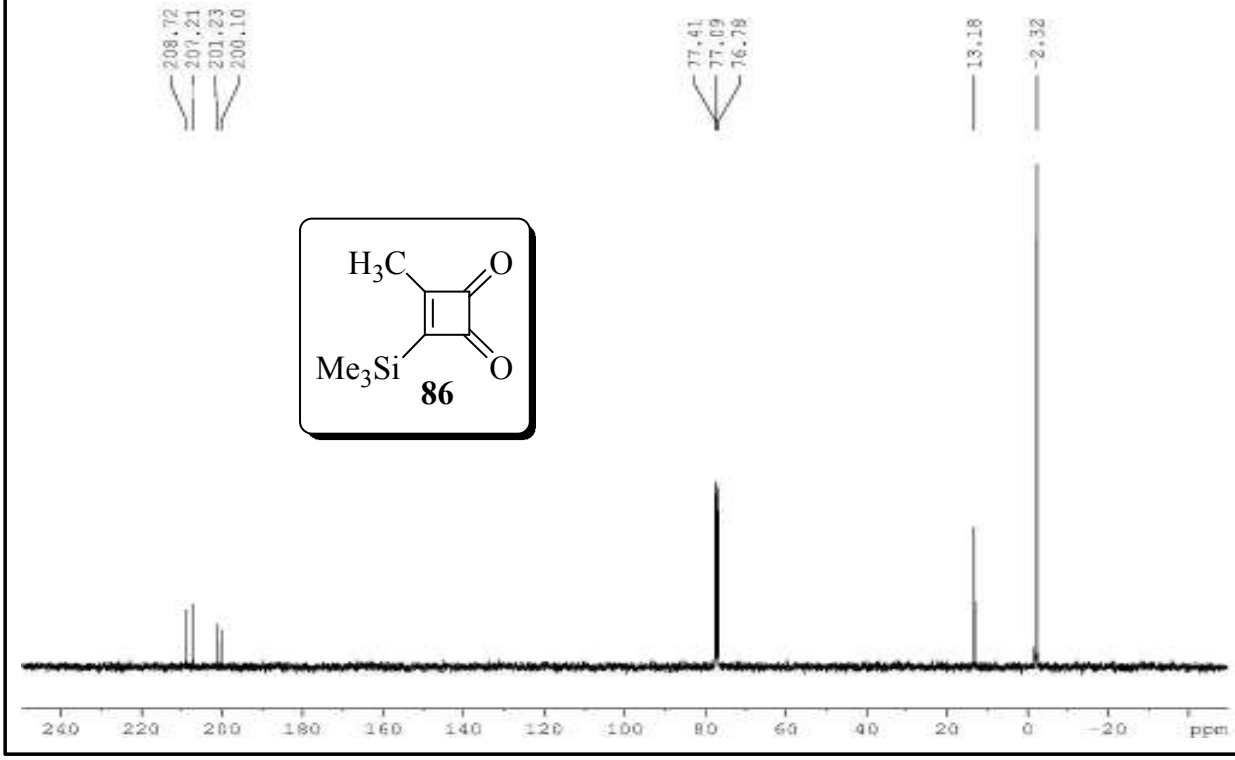
Spectrum No 10 (chapter 1) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



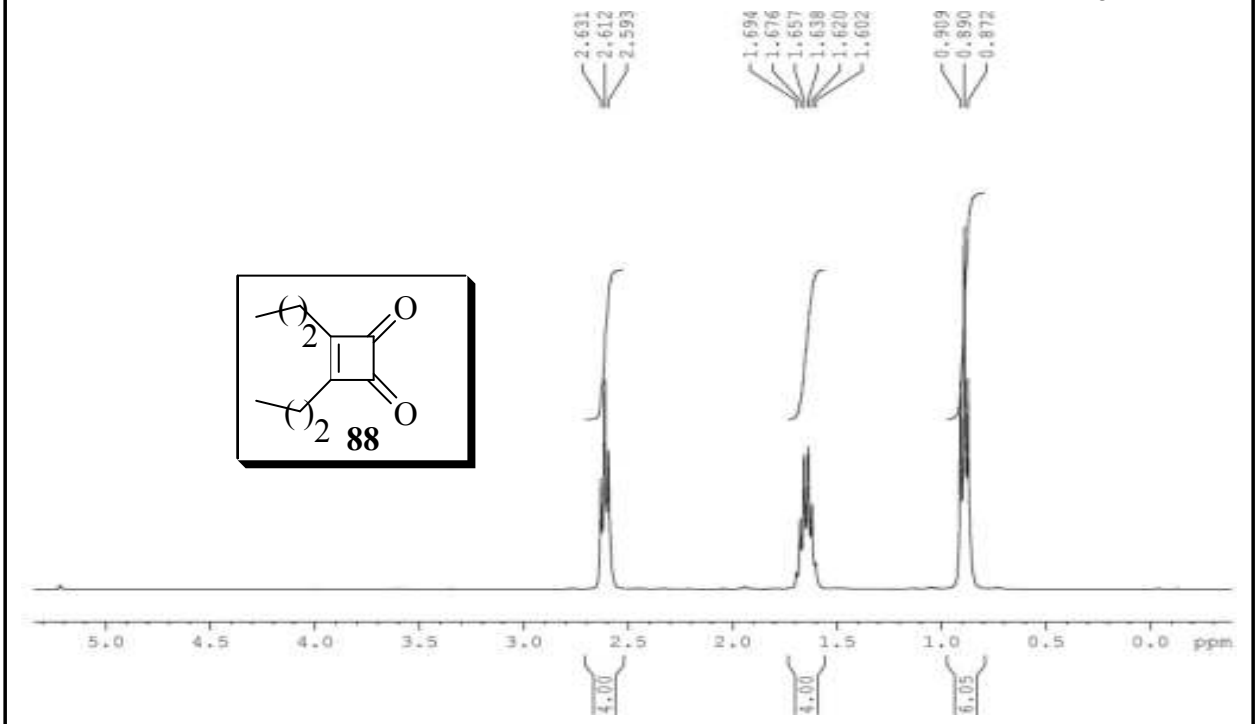
Spectrum No 11 (chapter 1) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



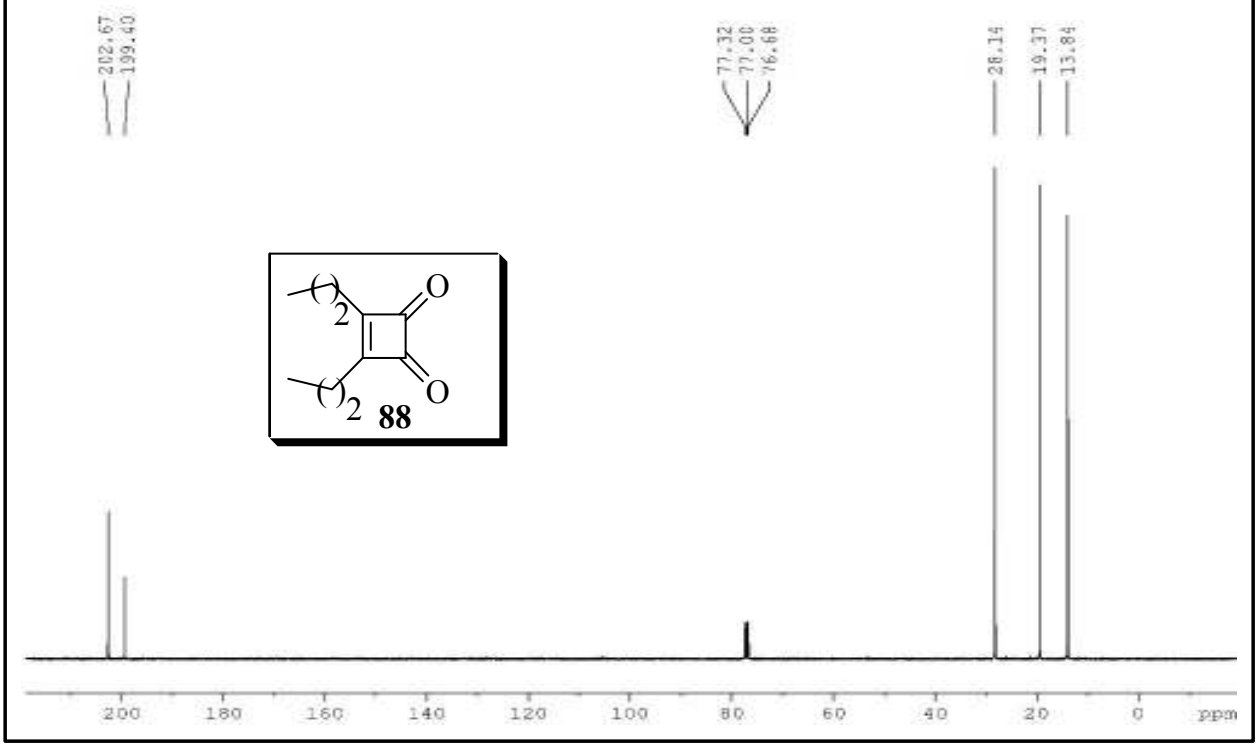
Spectrum No 12 (chapter 1) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



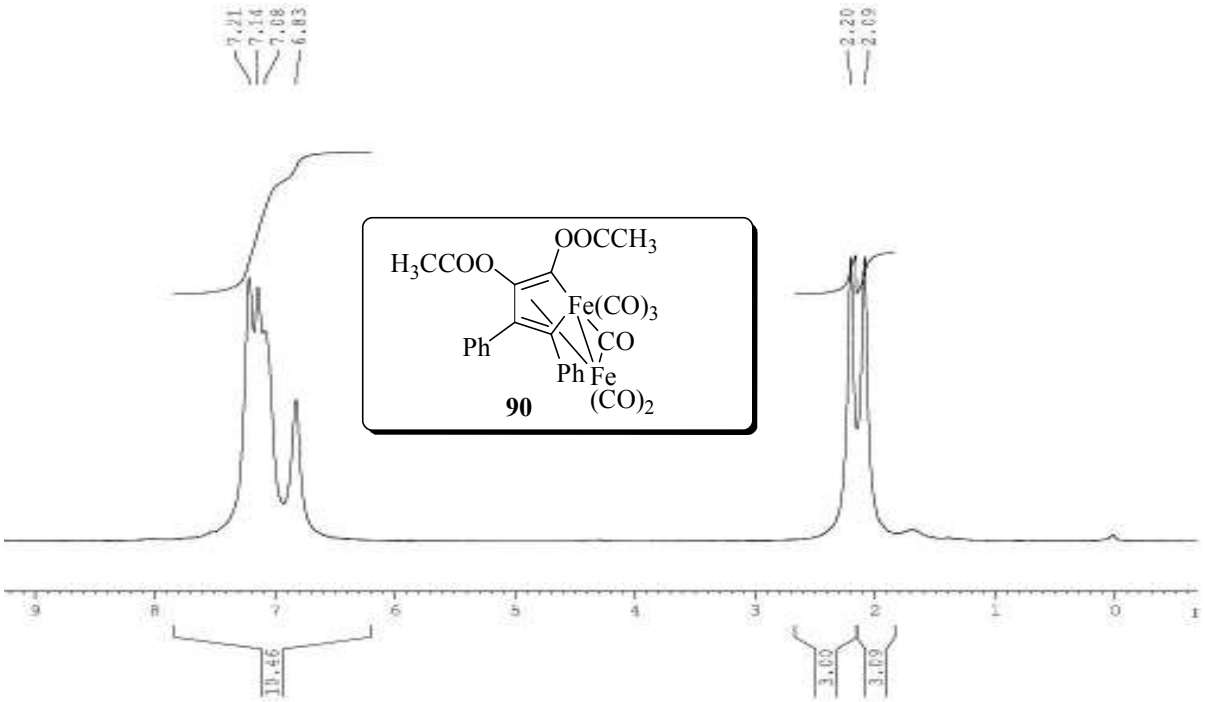
Spectrum No 13 (chapter 1) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



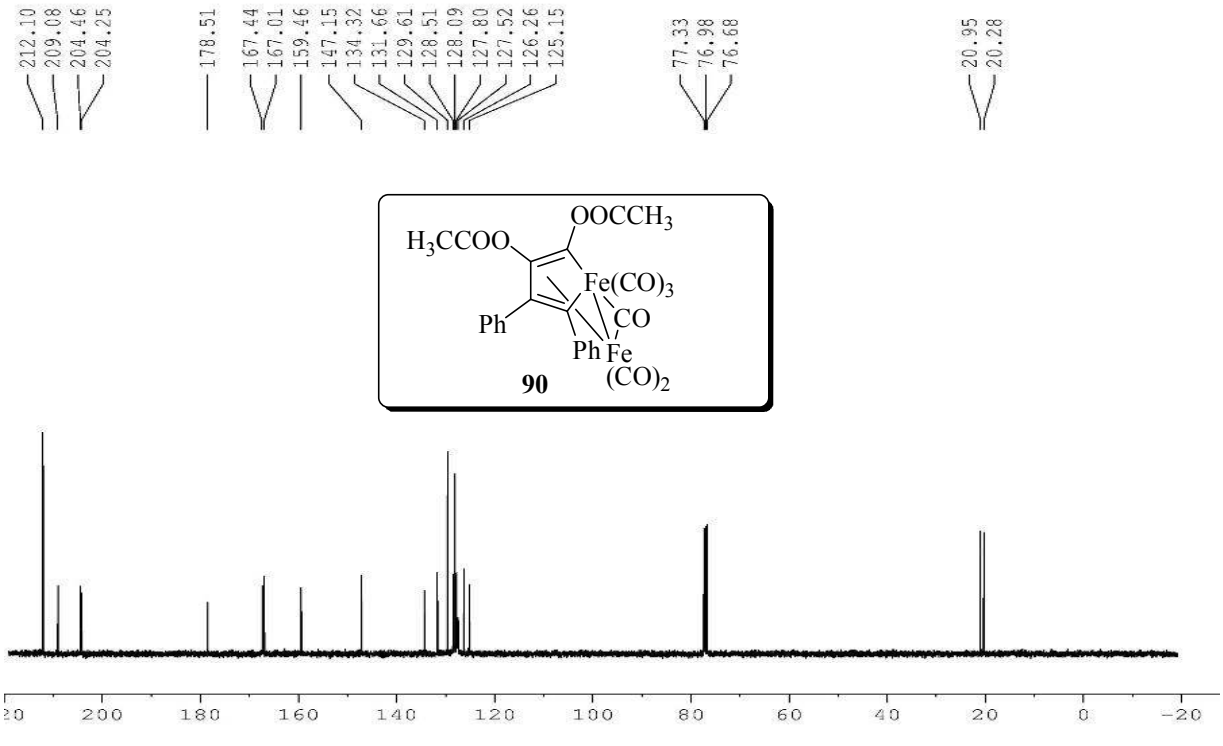
Spectrum No 14 (chapter 1) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



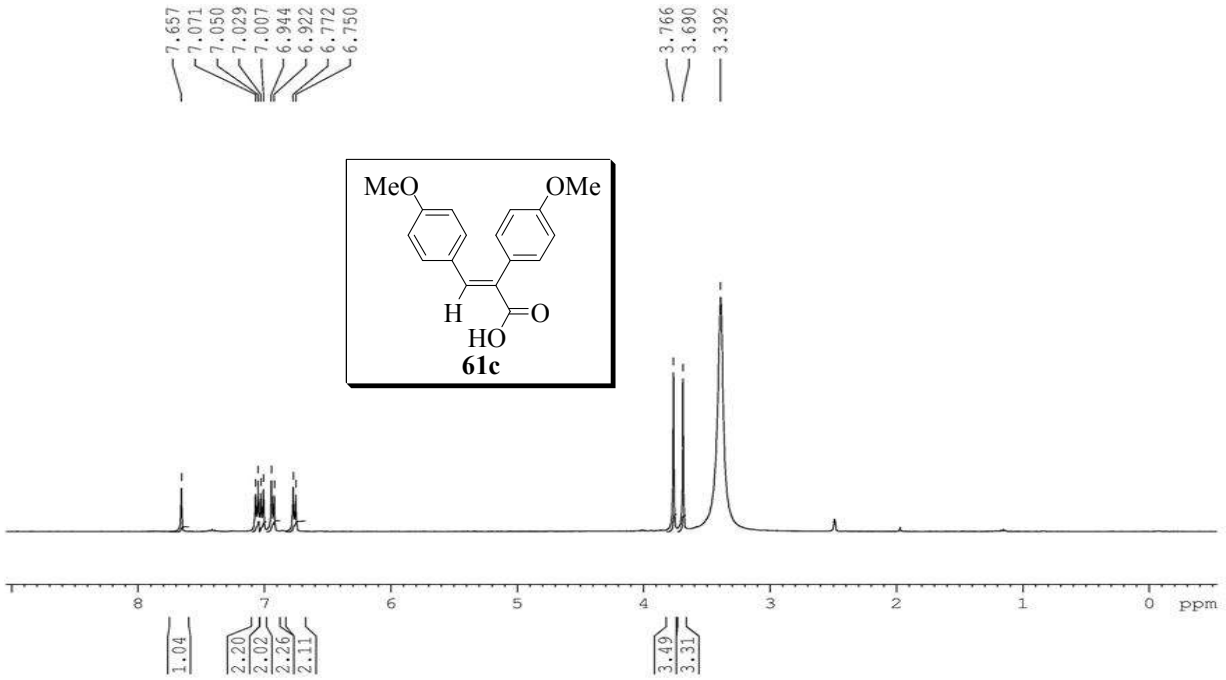
Spectrum No 15 (chapter 1) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



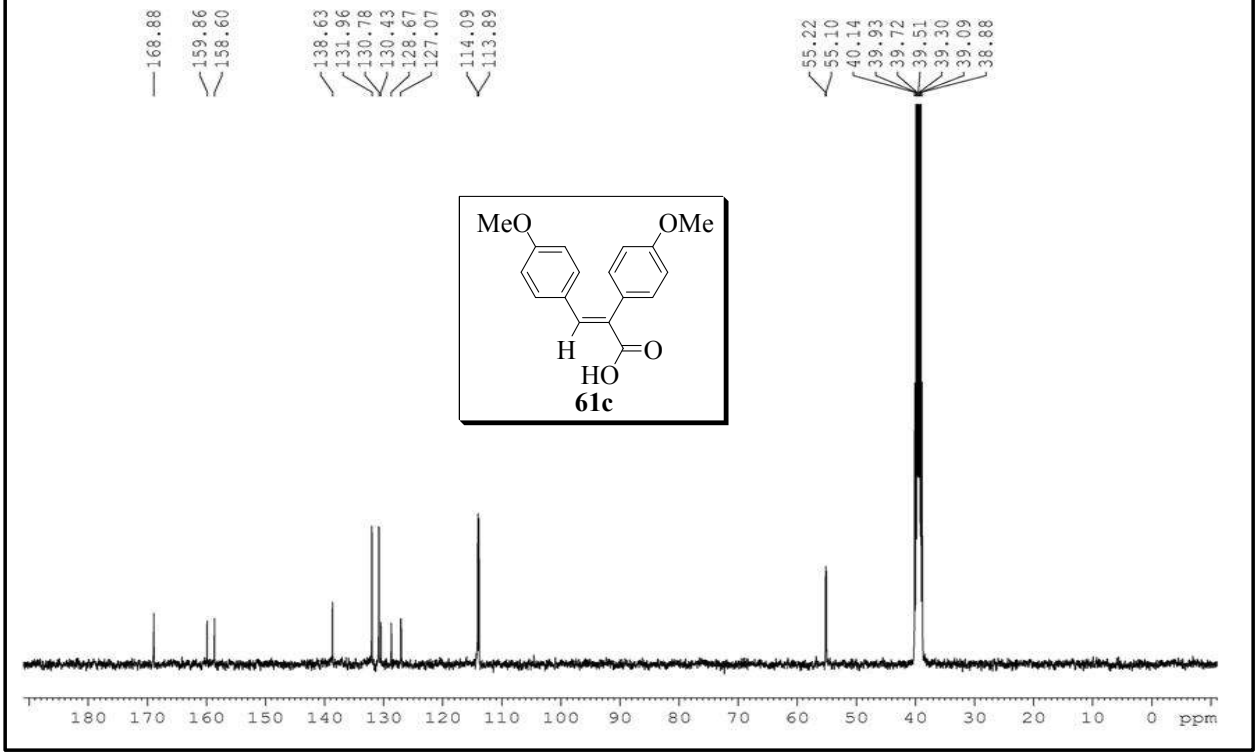
Spectrum No 16 (chapter 1) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



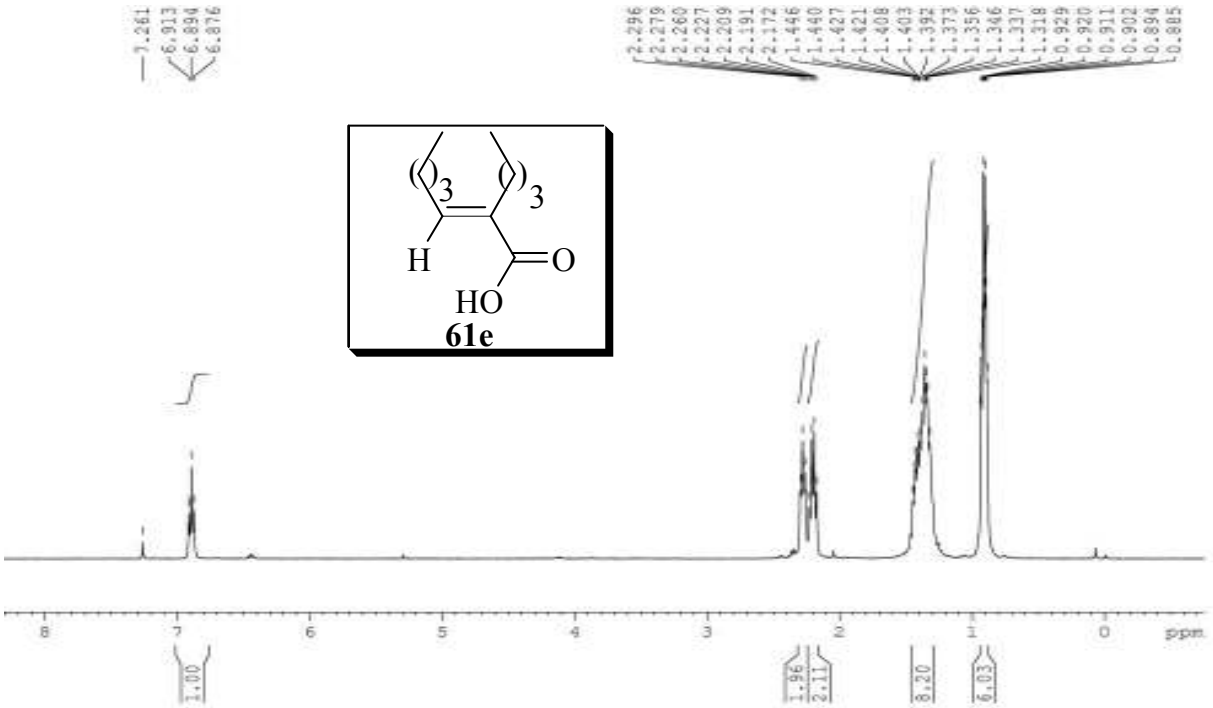
Spectrum No 17 (chapter 1) ^{1}H NMR Spectrum (400 MHz, DMSO-d_6)



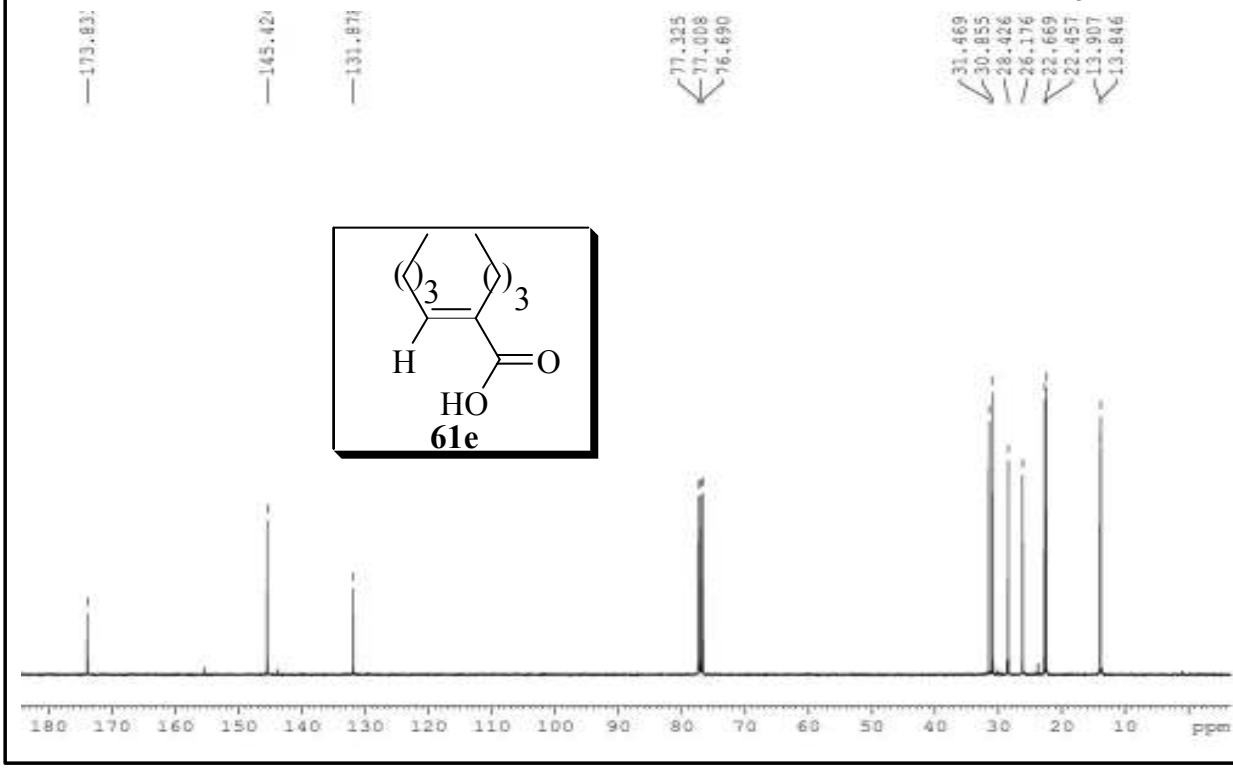
Spectrum No 18 (chapter 1) ^{13}C NMR Spectrum (100 MHz , DMSO-d_6)



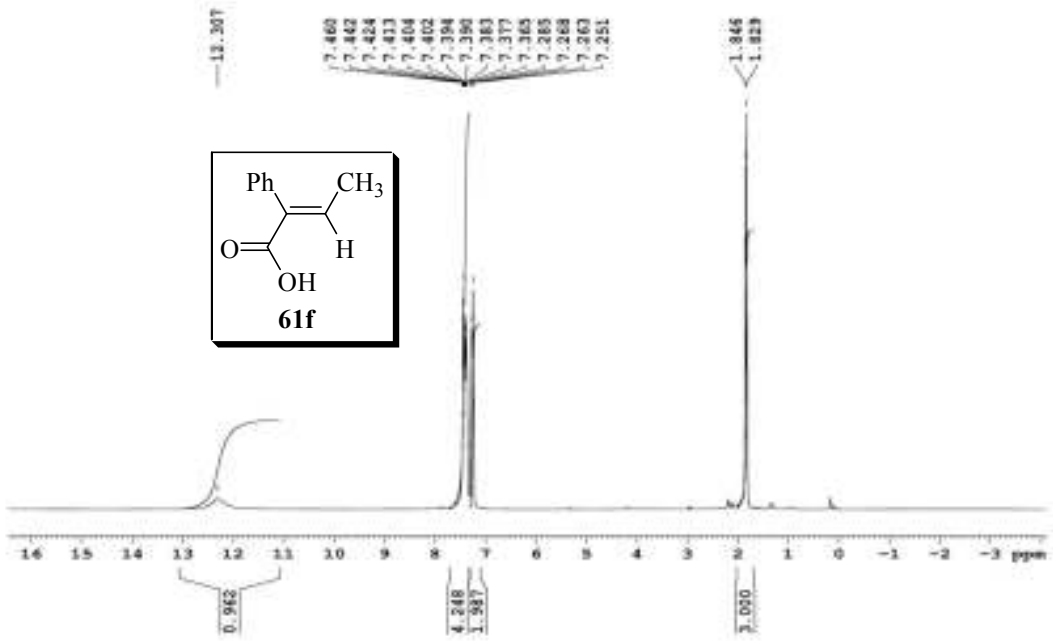
Spectrum No 19 (chapter 1) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



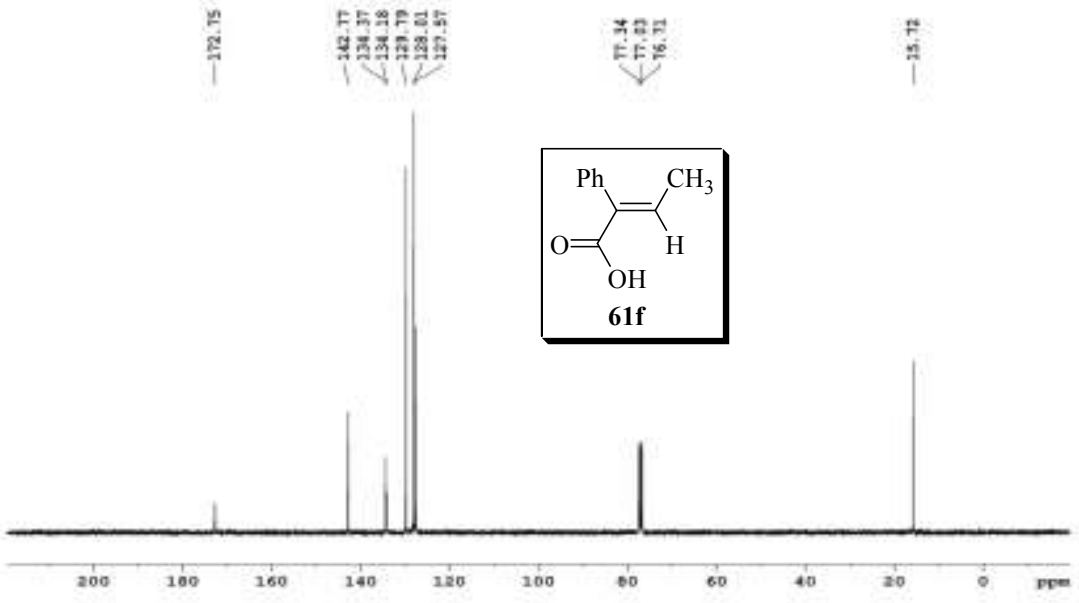
Spectrum No 20 (chapter 1) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



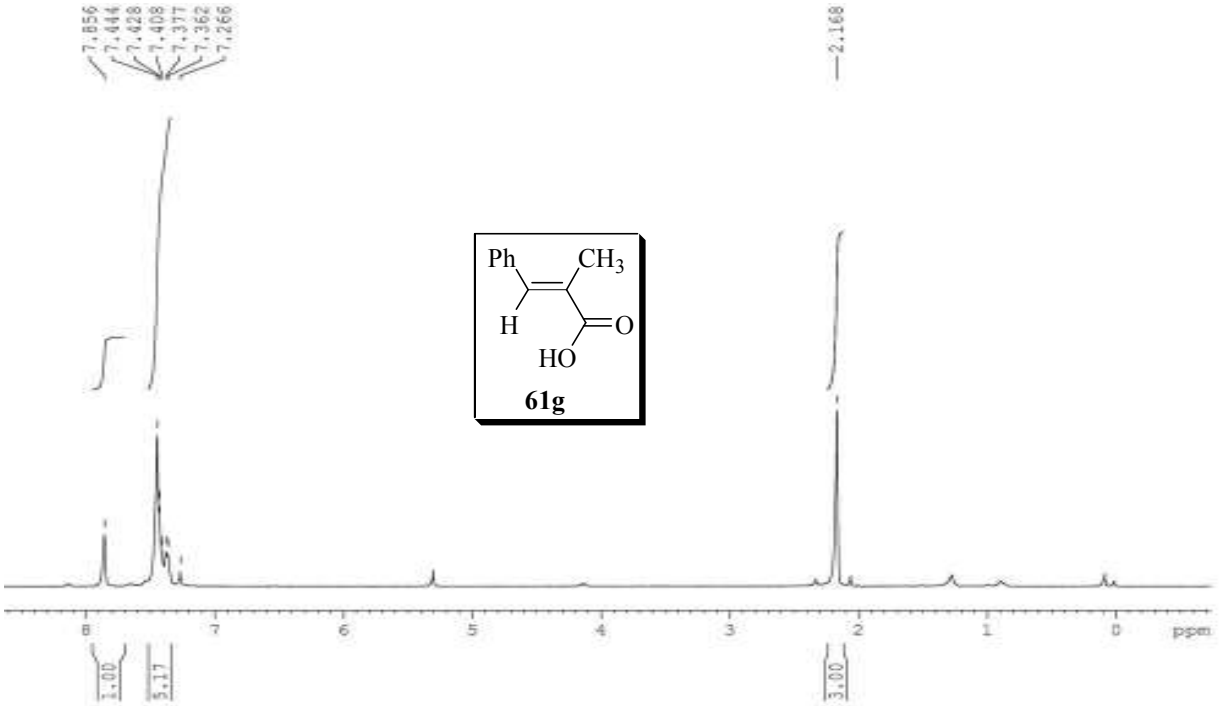
Spectrum No 21 (chapter 1) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



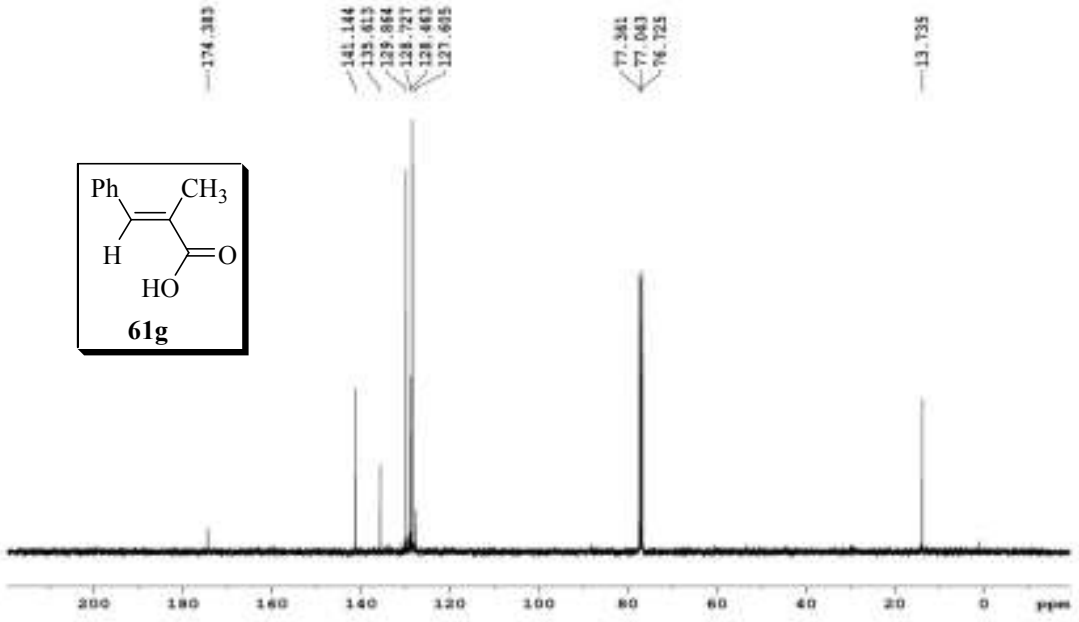
Spectrum No 22 (chapter 1) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



Spectrum No 23 (chapter 1) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)

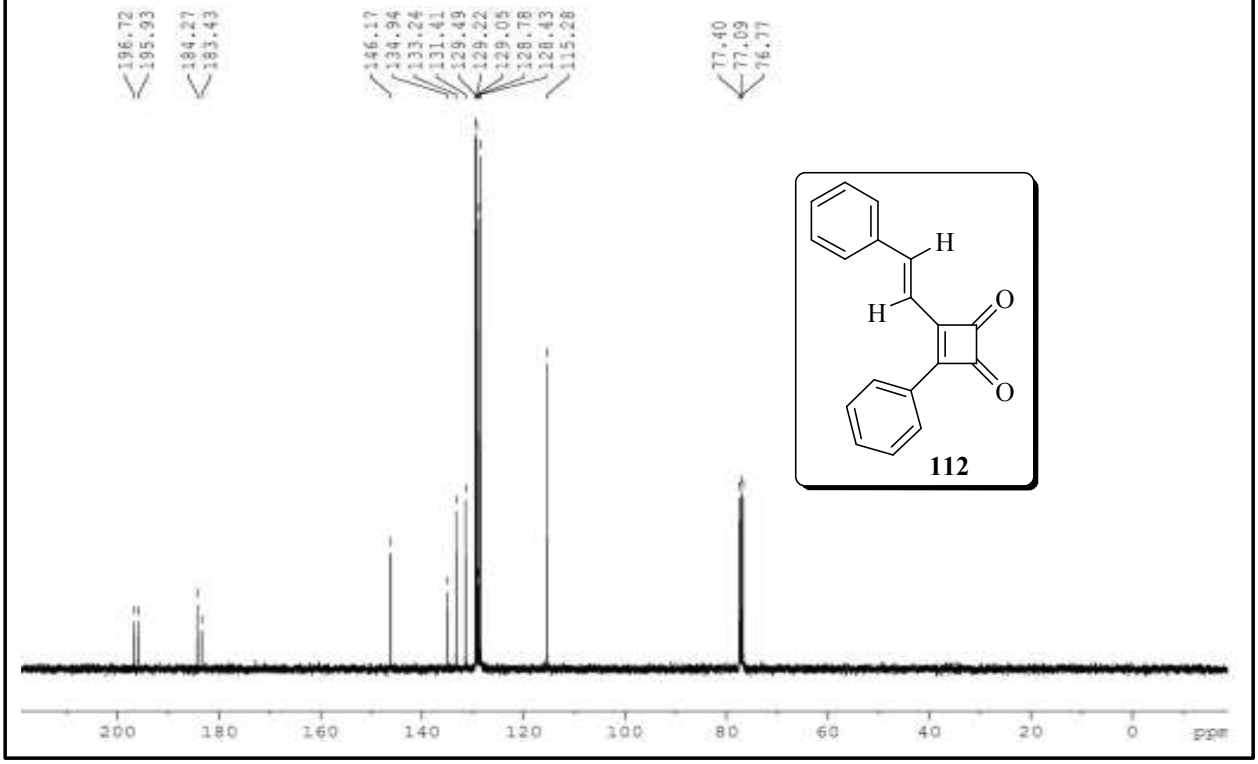


Spectrum No 24 (chapter 1) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)

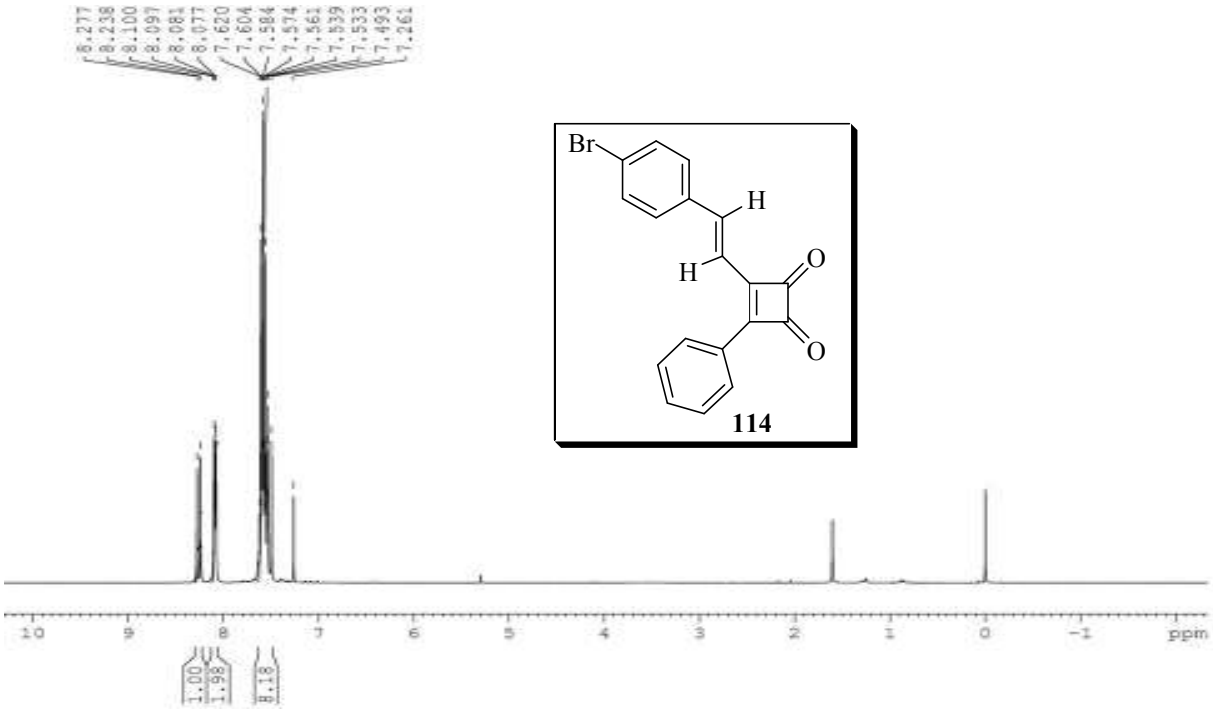


Spectrum No 25(chapter 2) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)

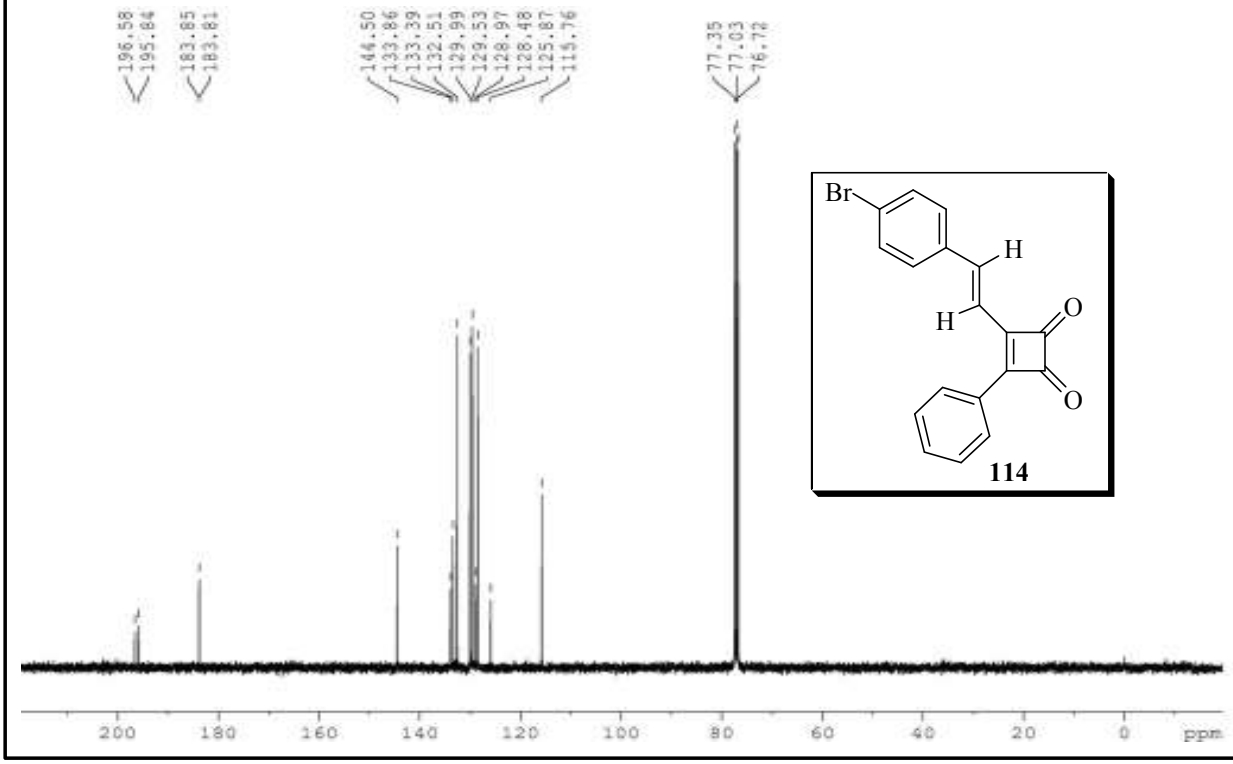
Spectrum No 26 (chapter 2) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



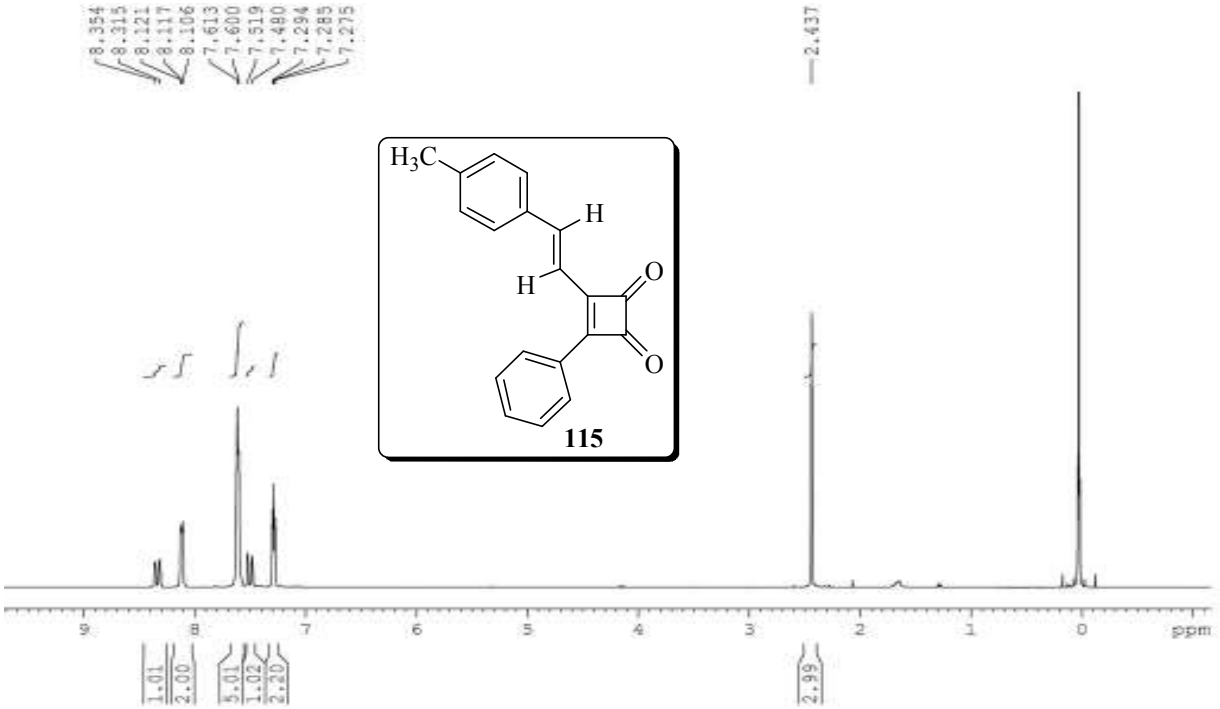
Spectrum No 27 (chapter 2) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



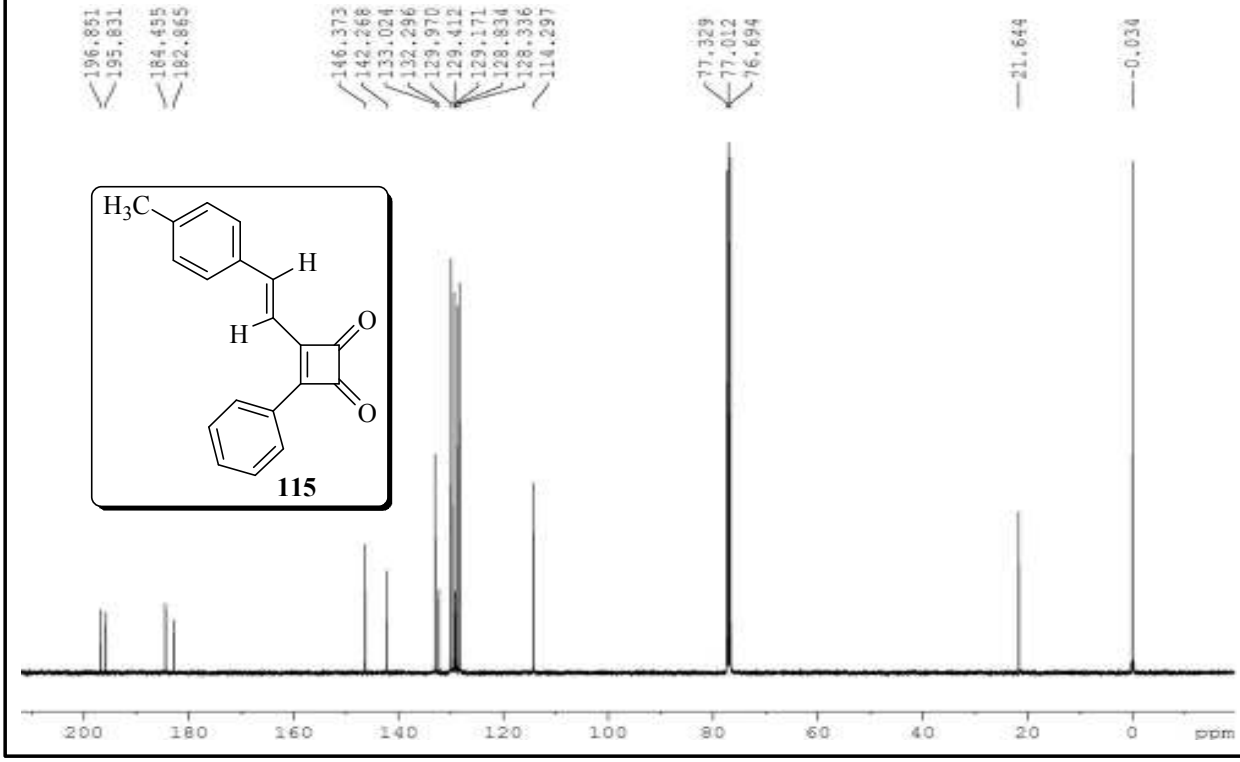
Spectrum No 28 (chapter 2) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



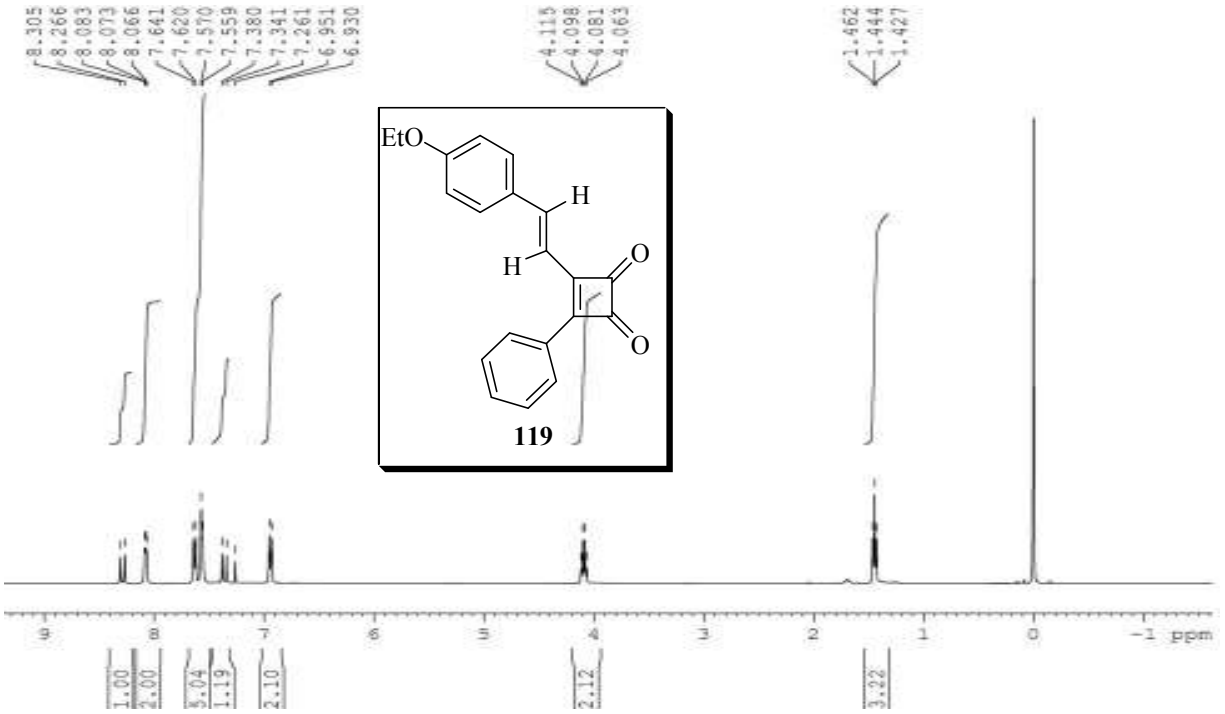
Spectrum No 29 (chapter 2) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



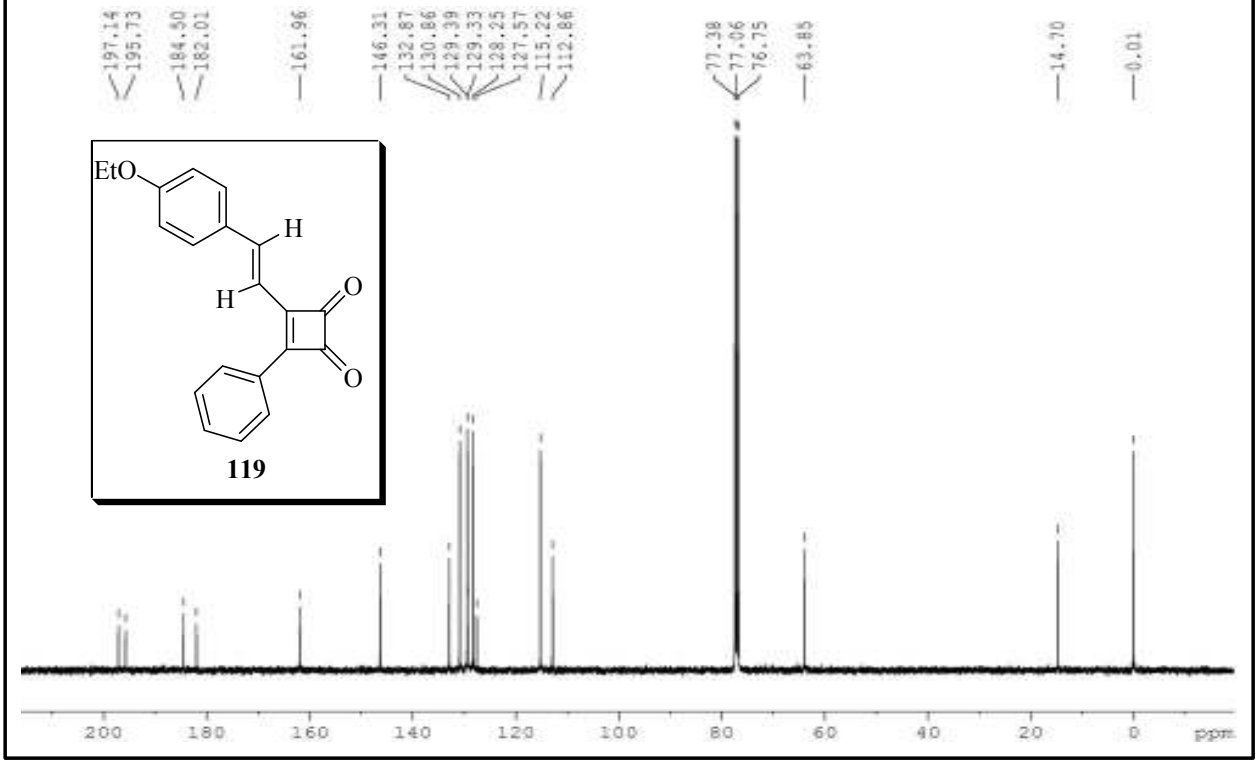
Spectrum No 30 (chapter 2) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



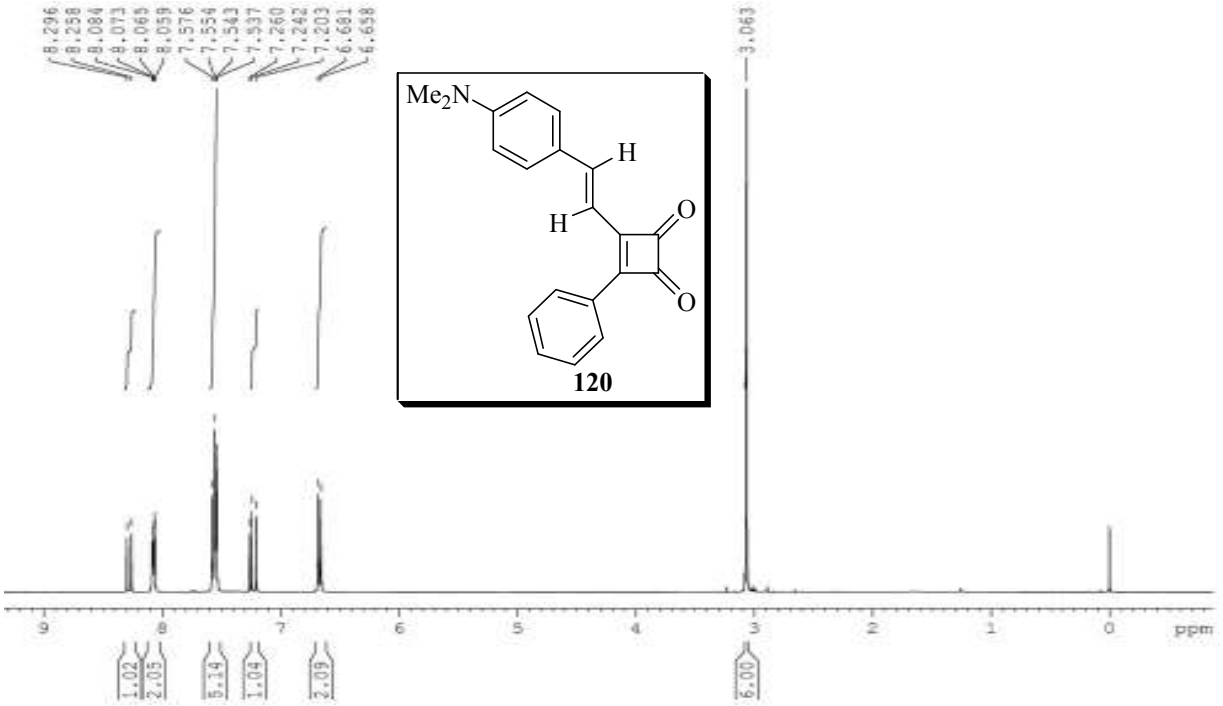
Spectrum No 31 (chapter 2) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



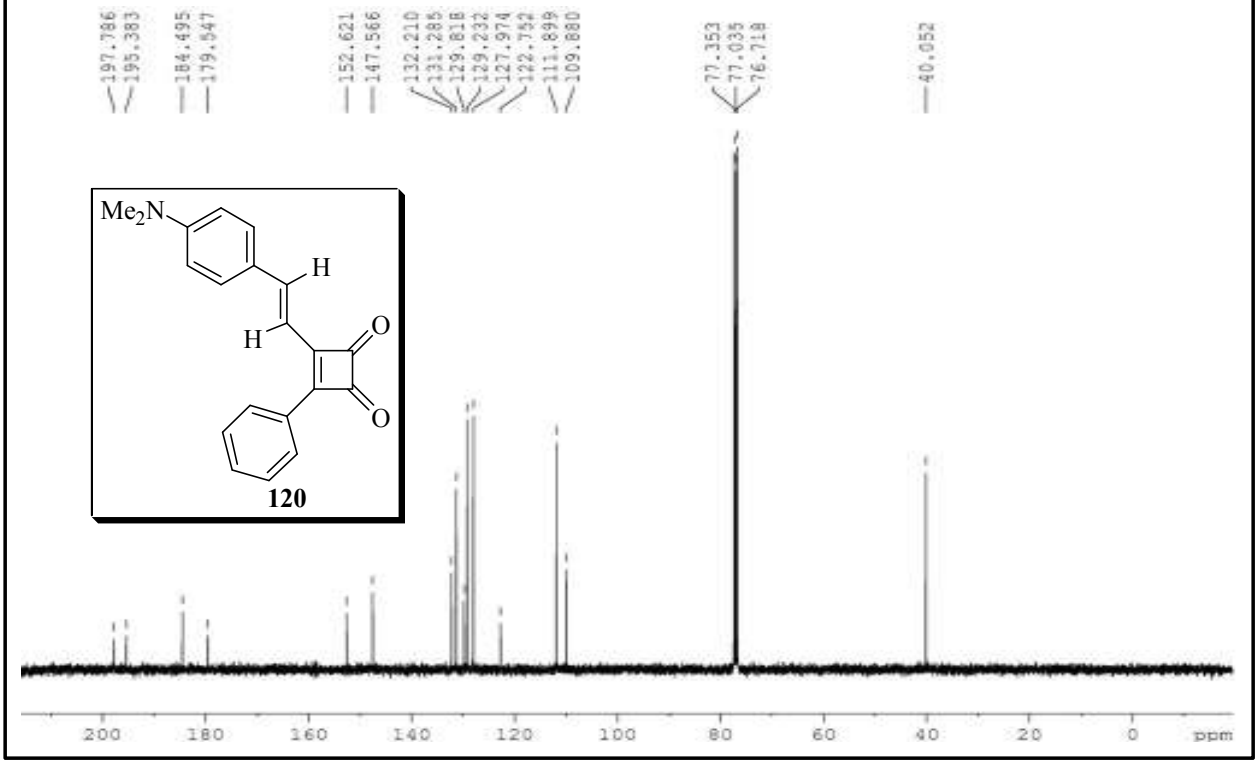
Spectrum No 32 (chapter 2) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



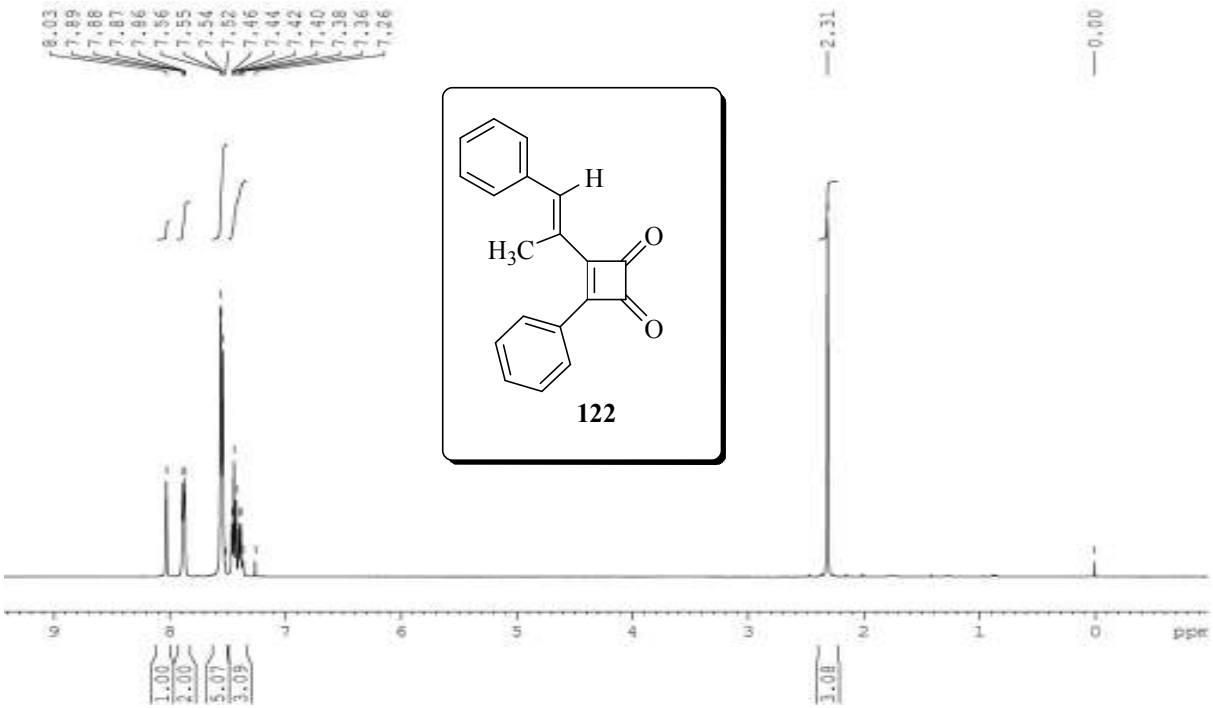
Spectrum No 33 (chapter 2) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



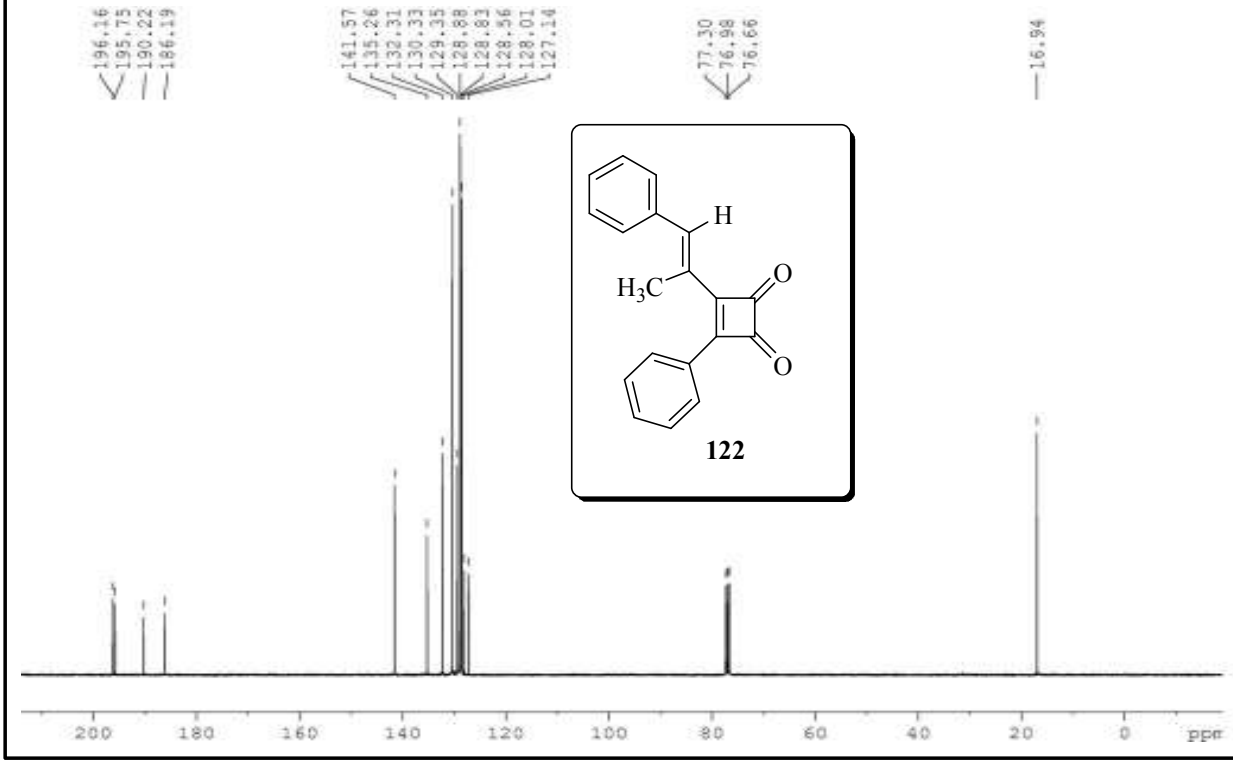
Spectrum No 34 (chapter 2) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



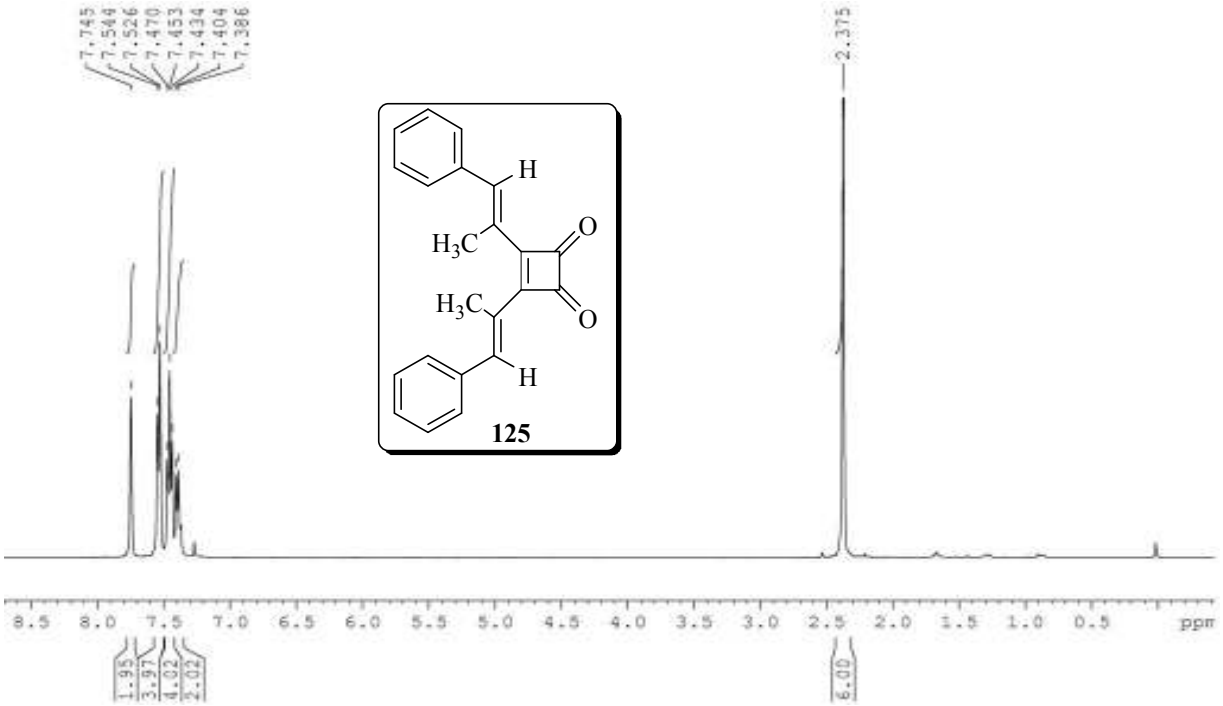
Spectrum No 35 (chapter 2) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



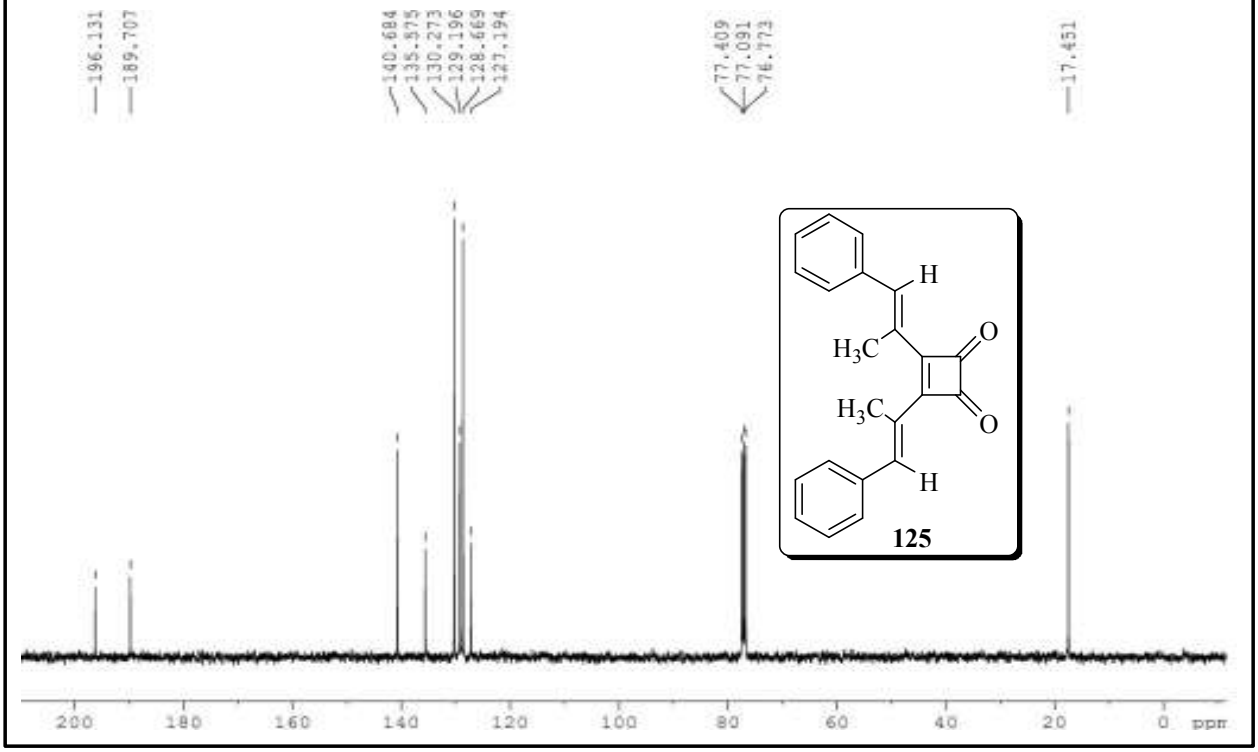
Spectrum No 36 (chapter 2) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



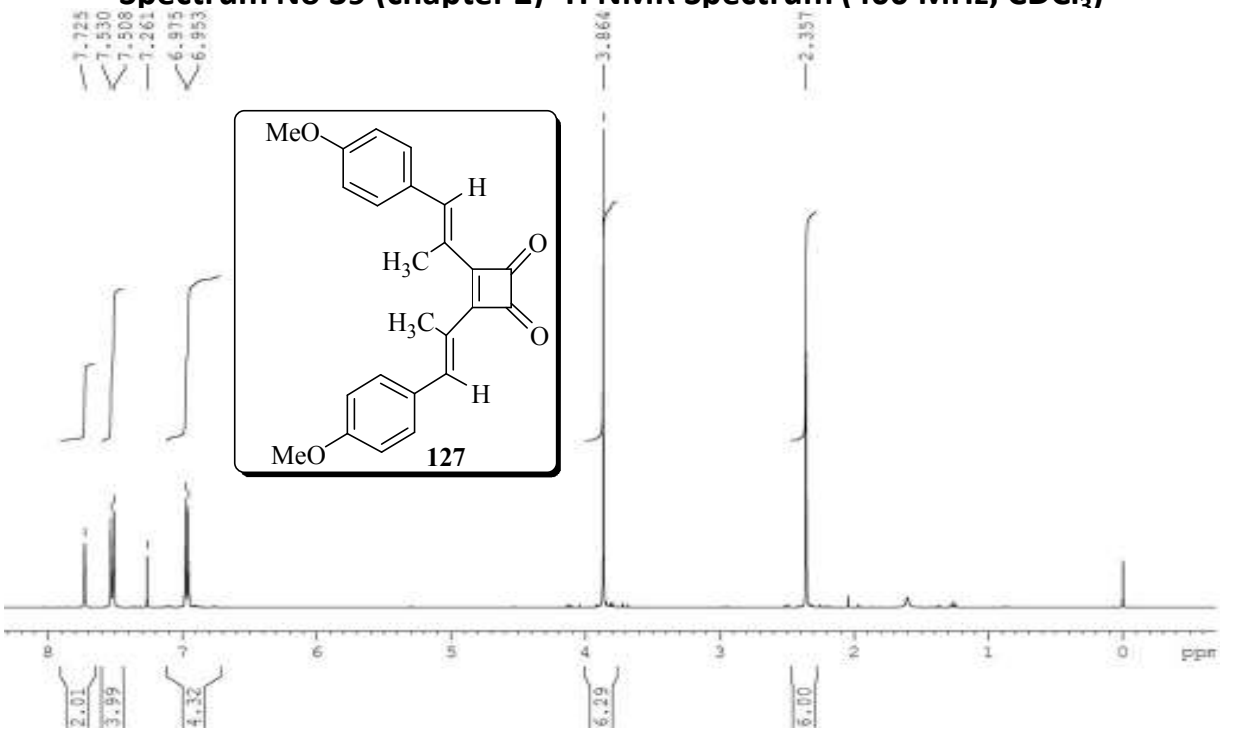
Spectrum No 37 (chapter 2) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



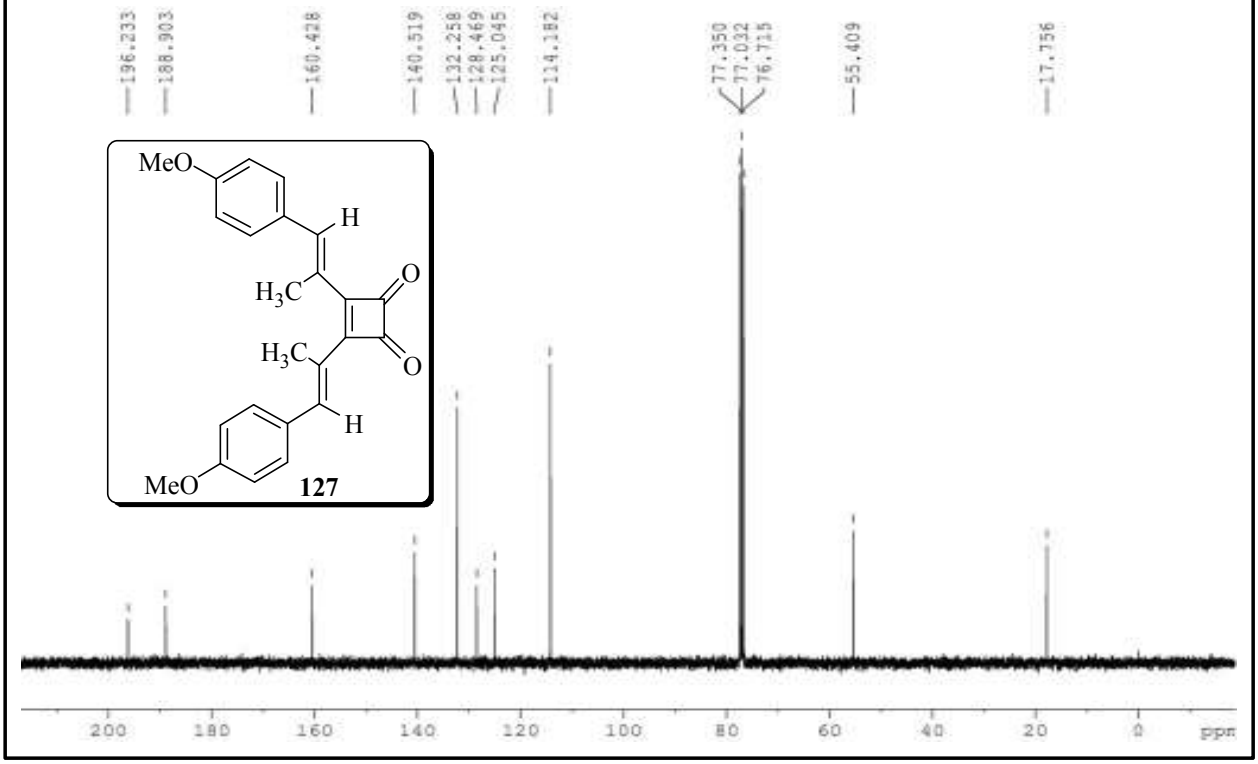
Spectrum No 38 (chapter 2) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



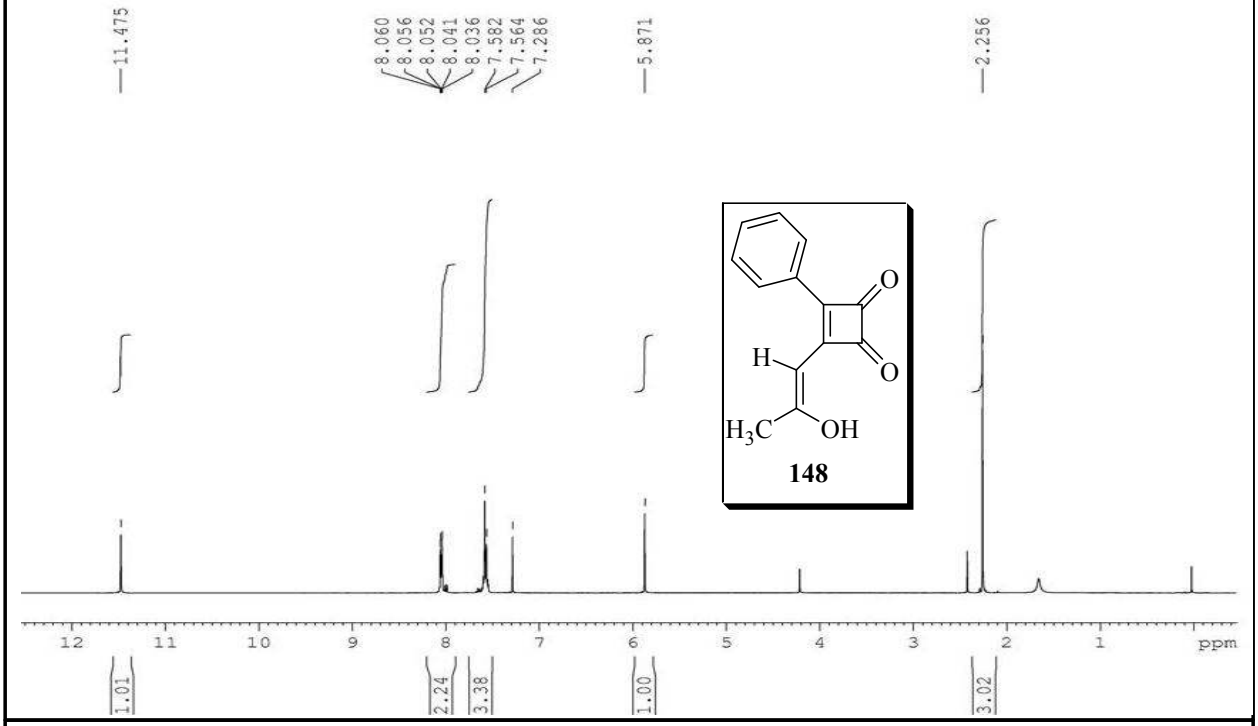
Spectrum No 39 (chapter 2) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



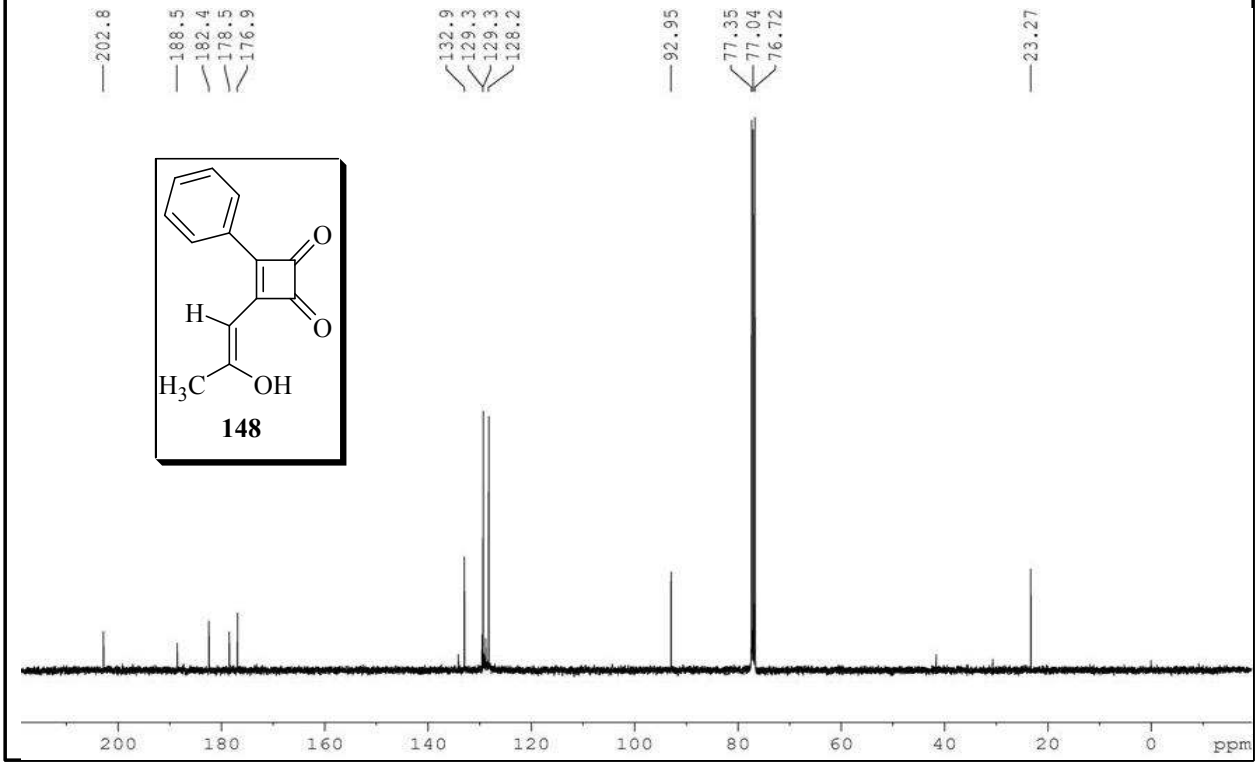
Spectrum No 40 (chapter 2) ^{13}C NMR Spectrum (400 MHz, $CDCl_3$)



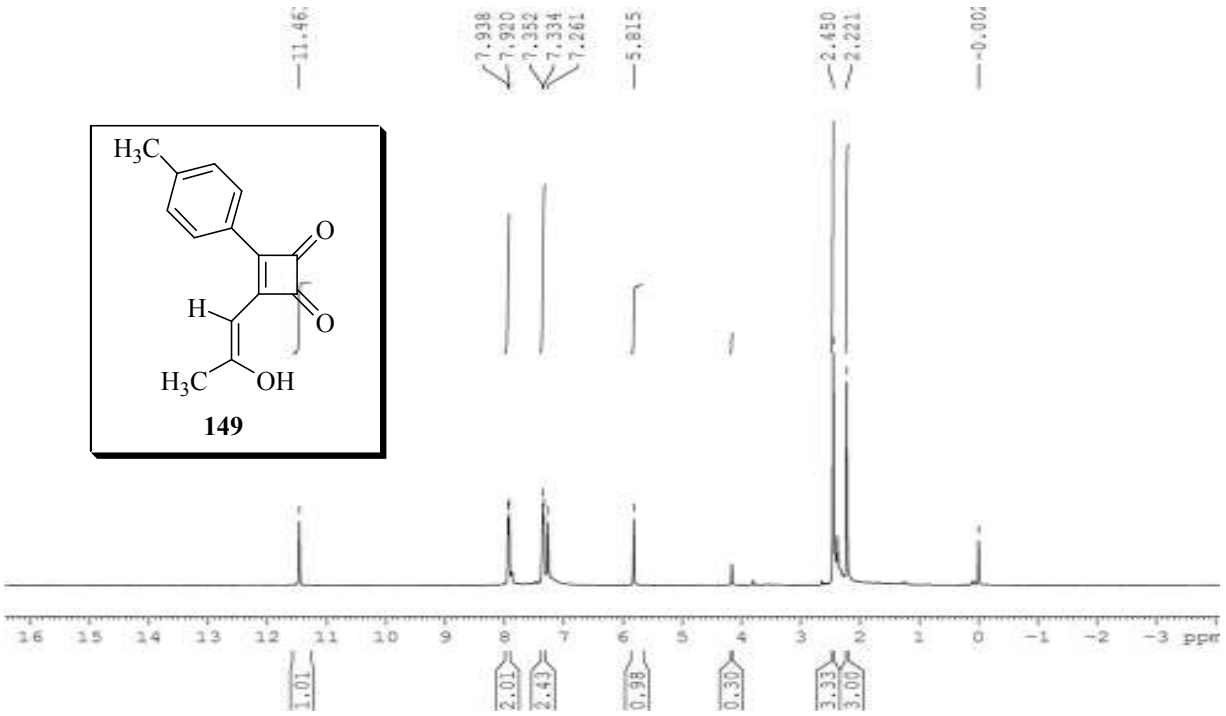
Spectrum No 41 (chapter 2) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



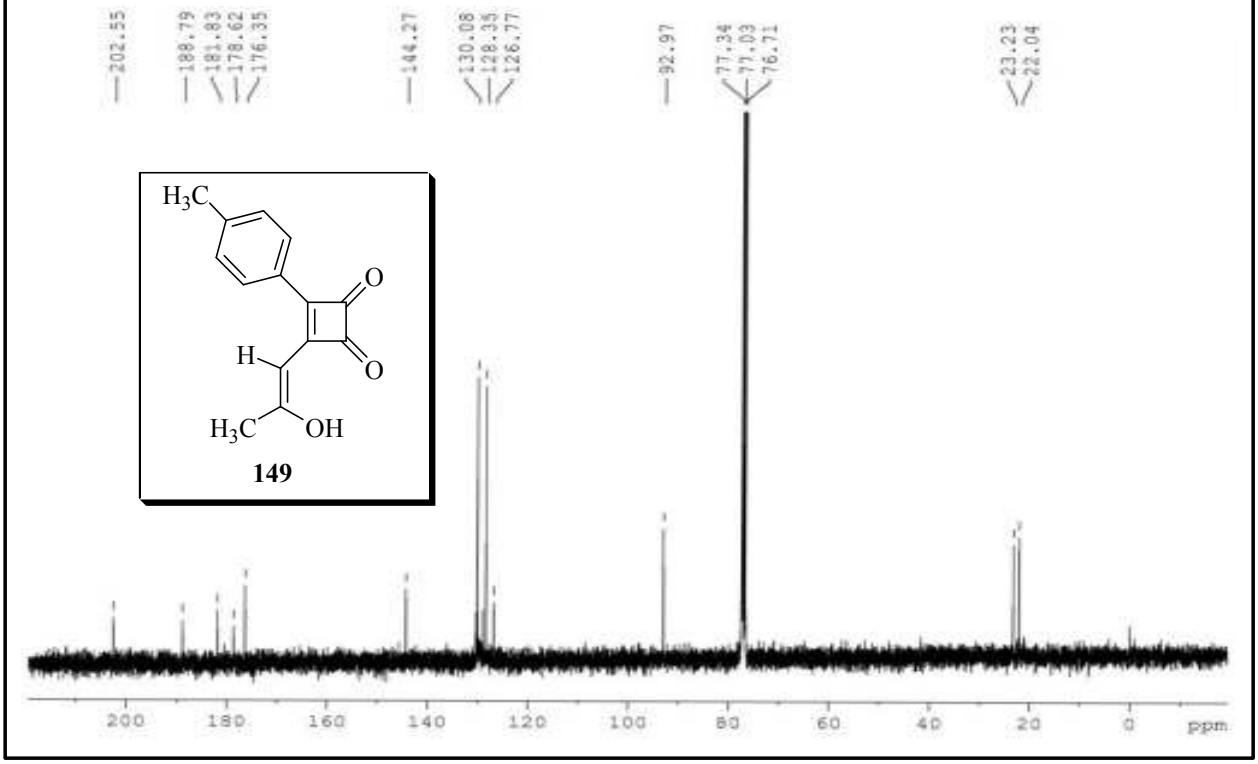
Spectrum No 42 (chapter 2) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



Spectrum No 43 (chapter 2) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)

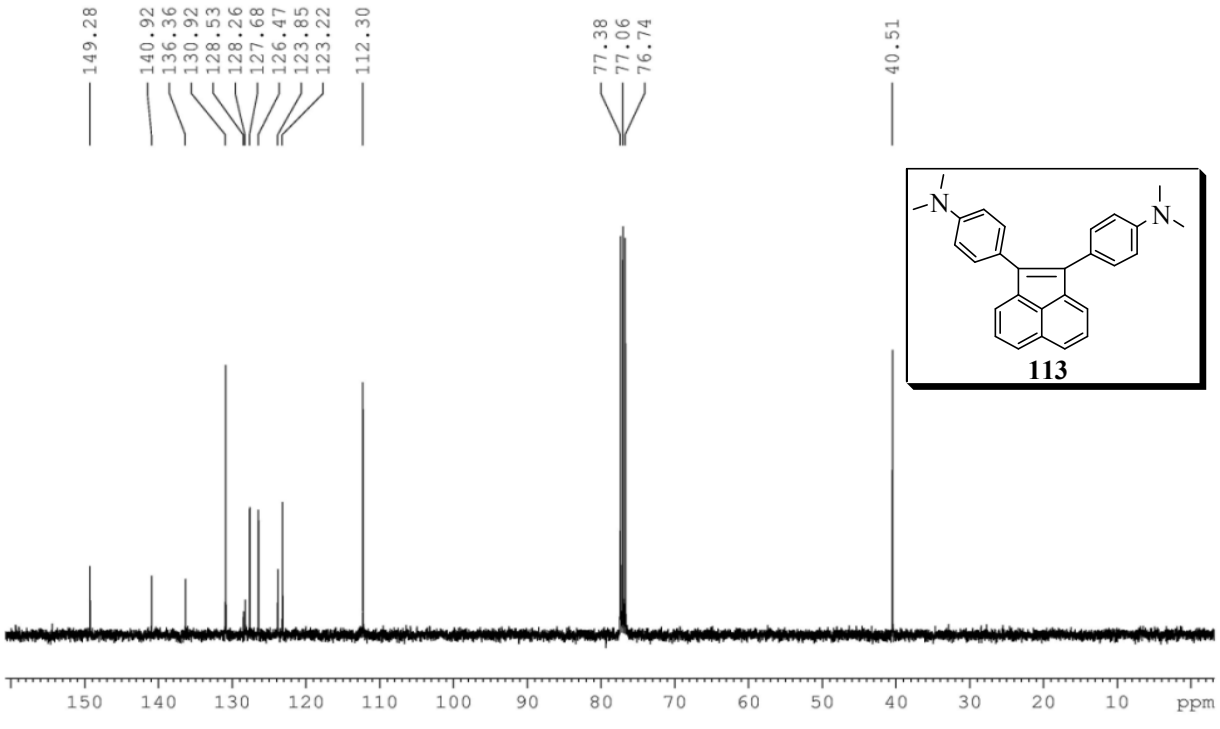


Spectrum No 44 (chapter 2) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)

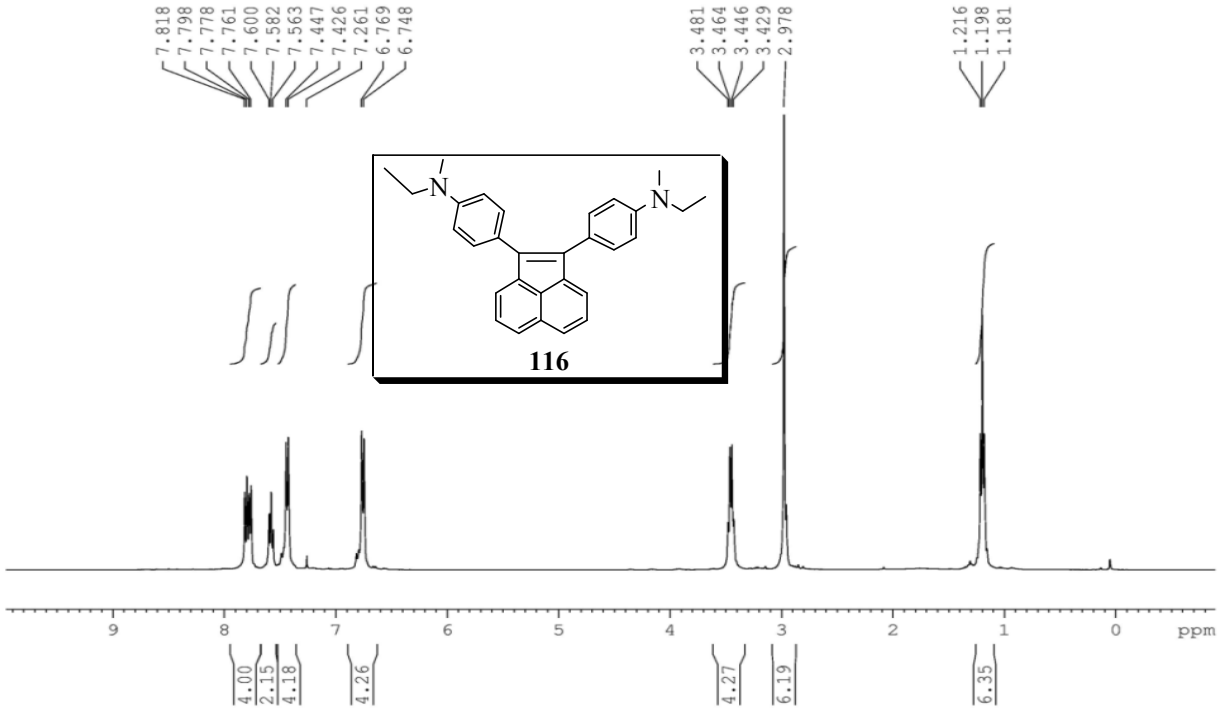


Spectrum No 45 (chapter 3) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)

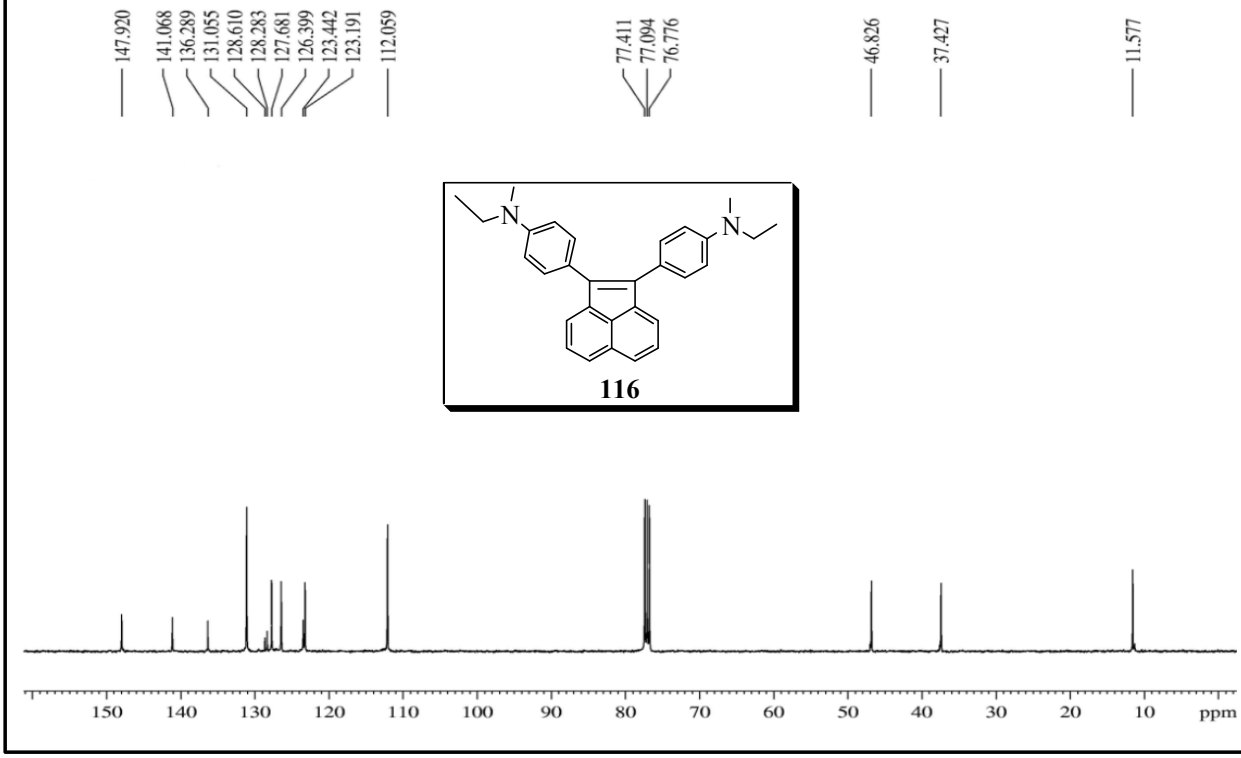
Spectrum No 46 (chapter 3) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



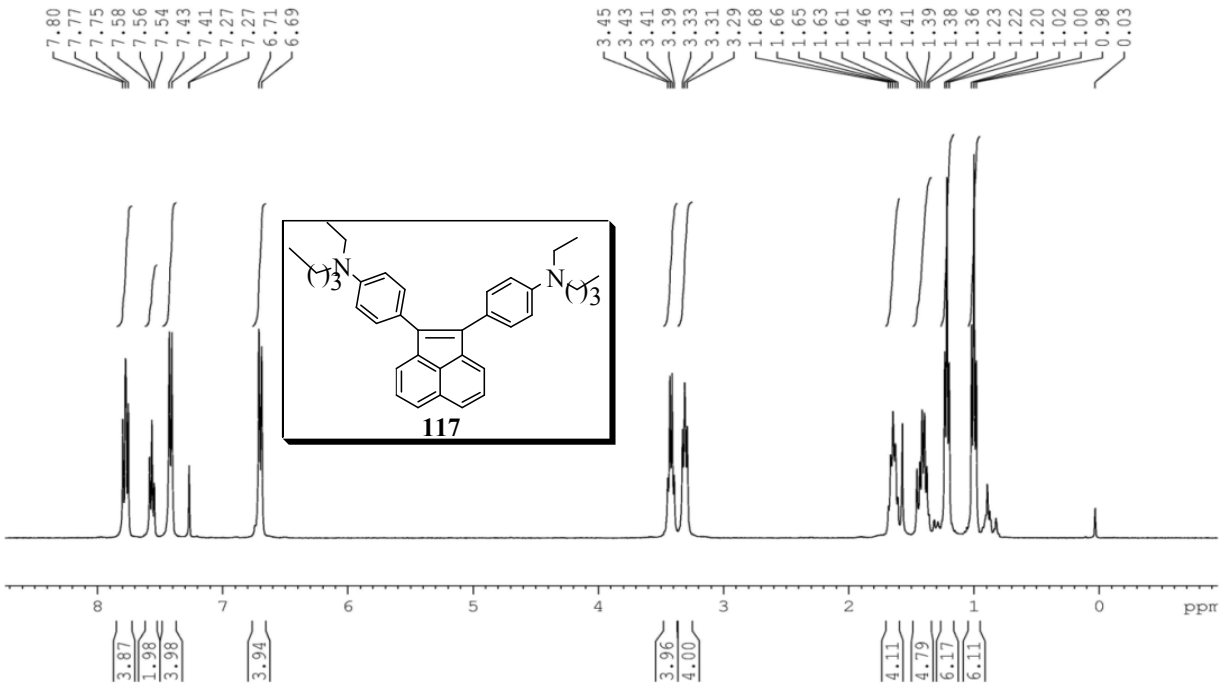
Spectrum No 47 (chapter 3) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



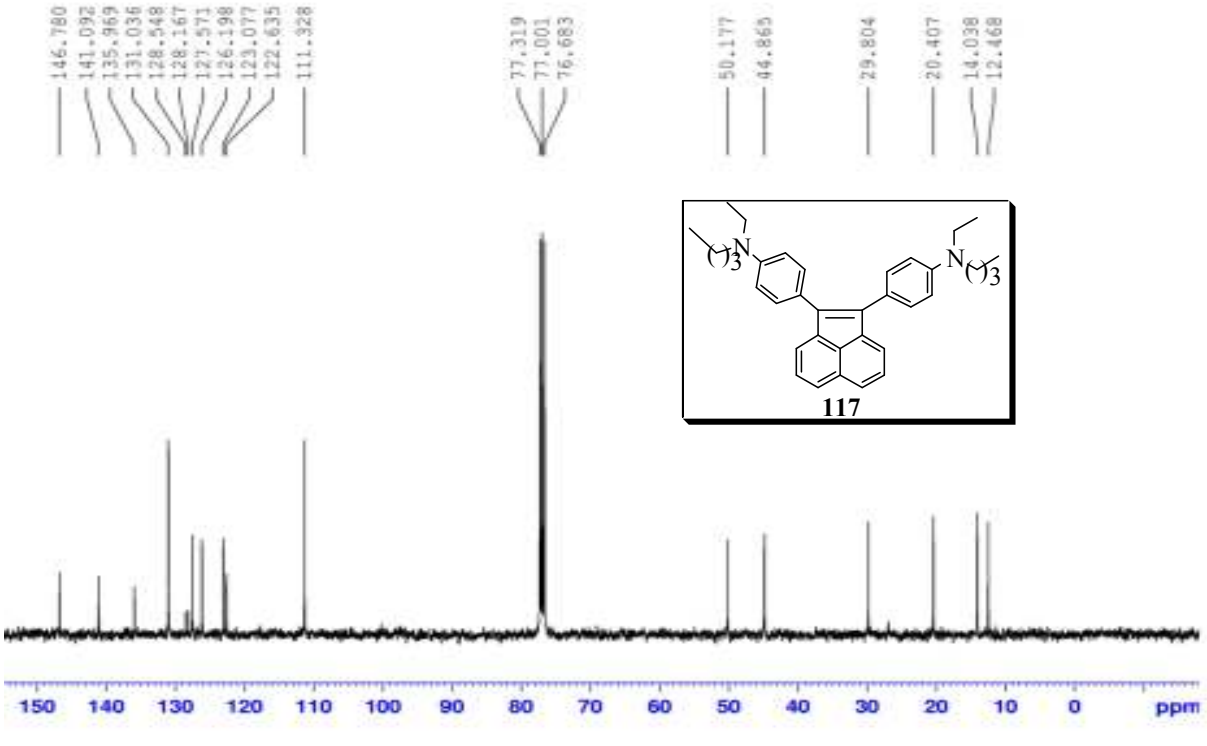
Spectrum No 48 (chapter 3) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



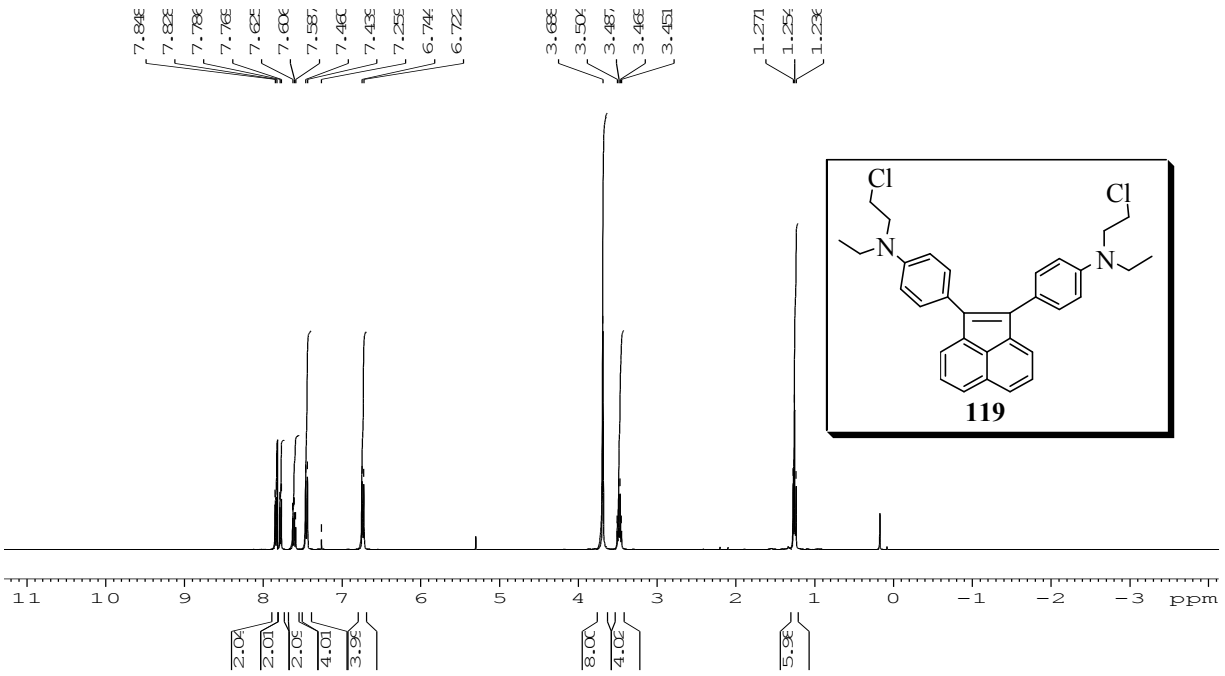
Spectrum No 49 (chapter 3) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



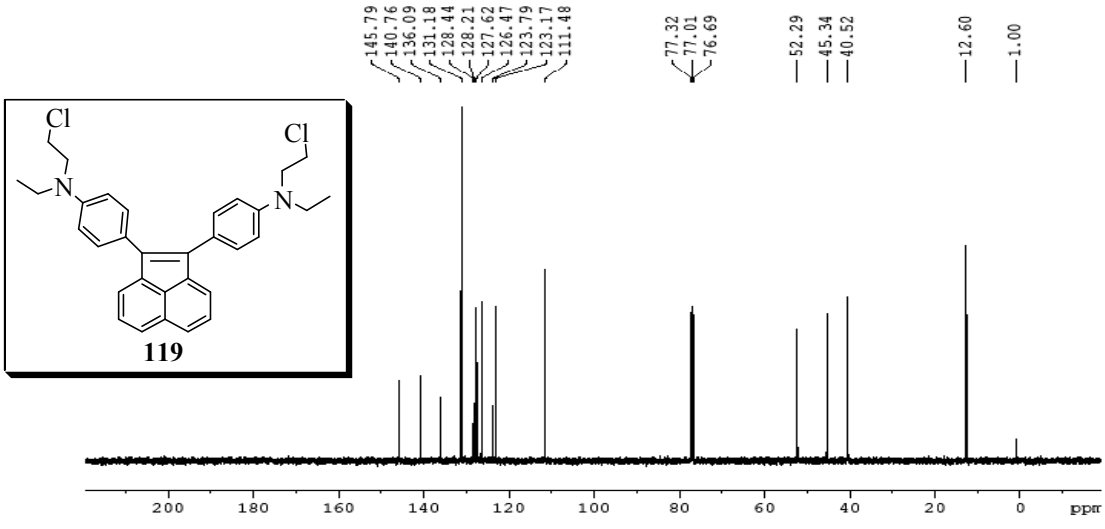
Spectrum No 50 (chapter 3) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



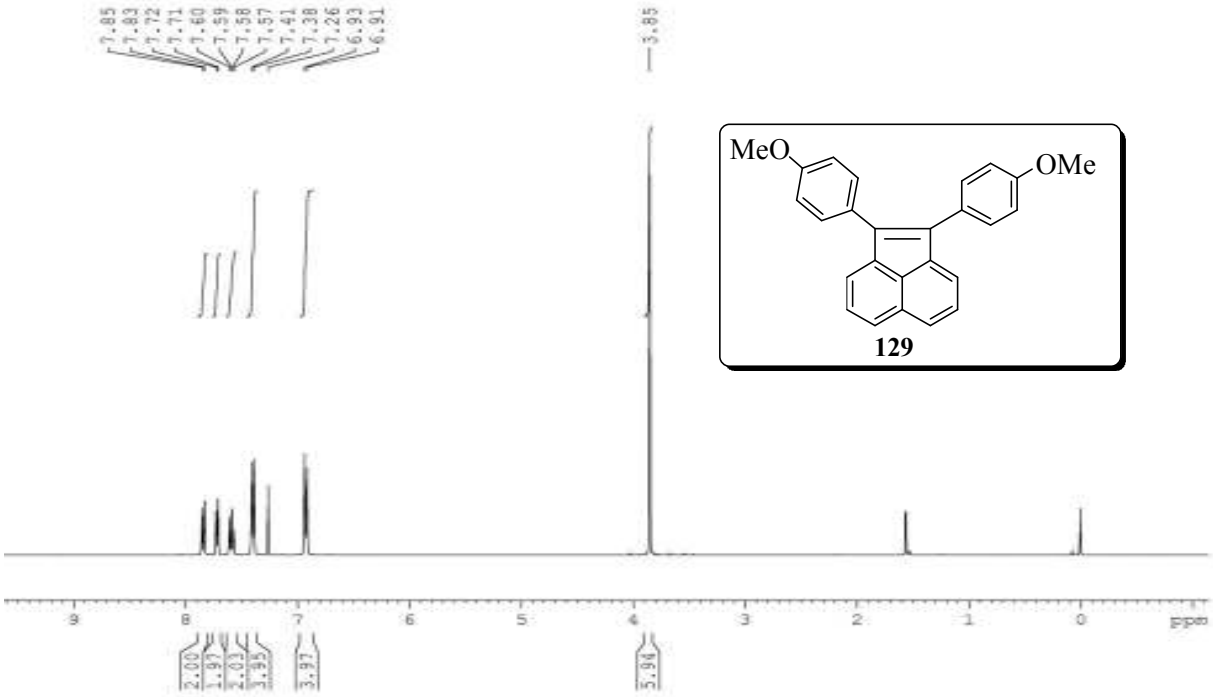
Spectrum No 51 (chapter 3) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



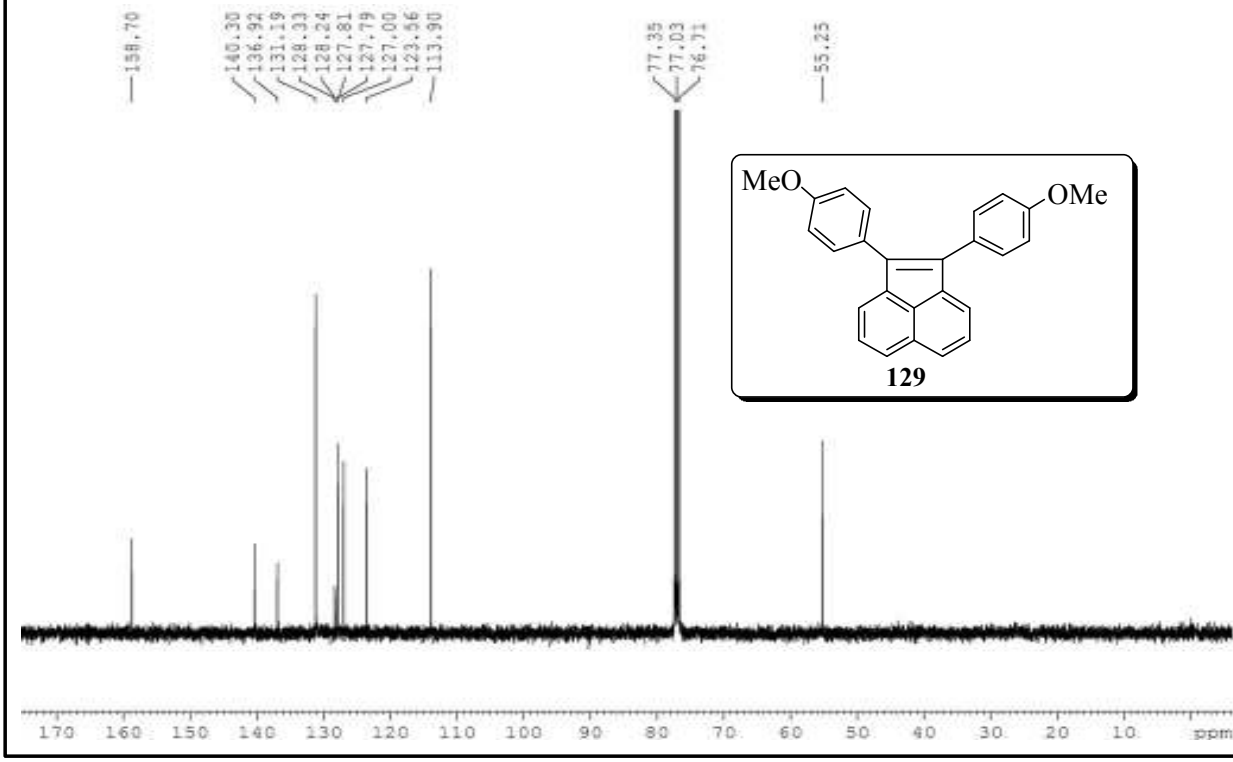
Spectrum No 52 (chapter 3) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



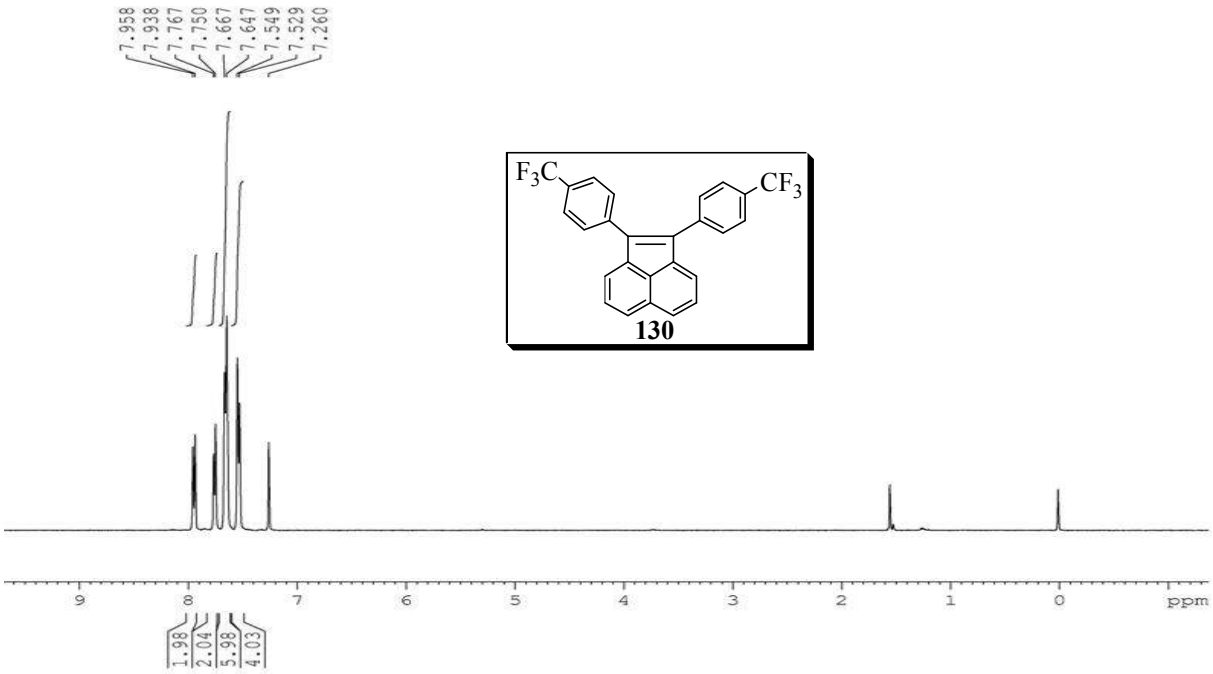
Spectrum No 53 (chapter 3) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



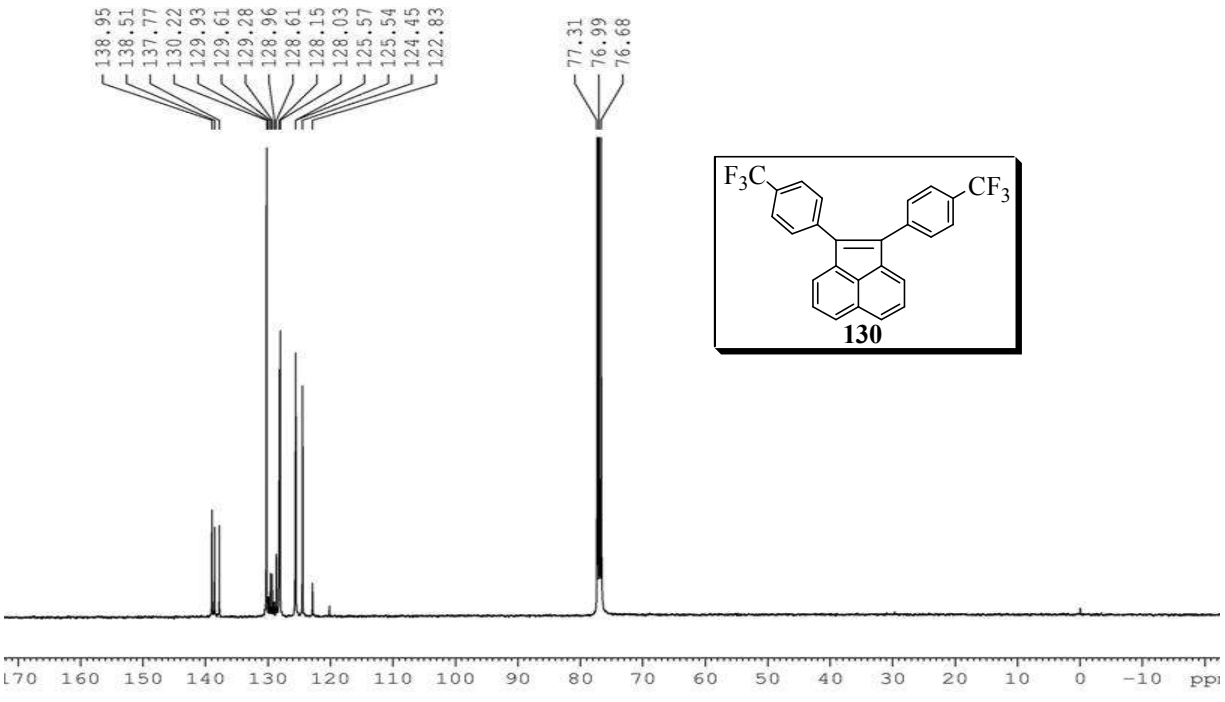
Spectrum No 54 (chapter 3) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



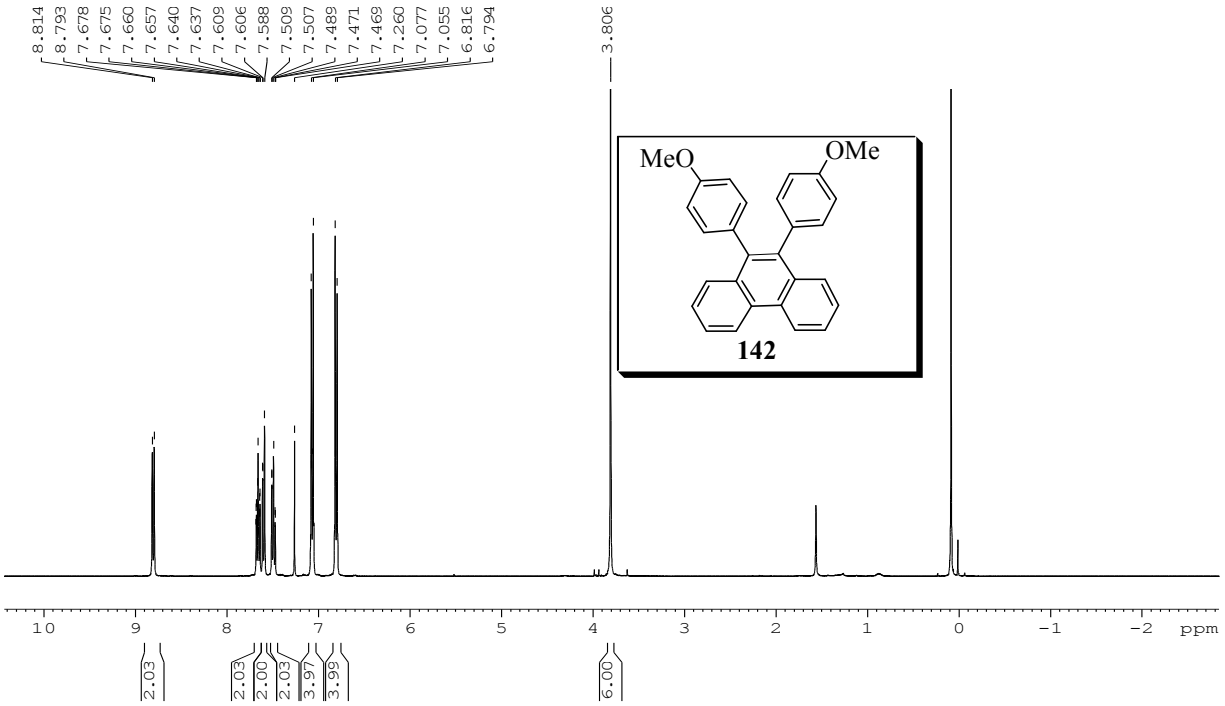
Spectrum No 55 (chapter 3) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



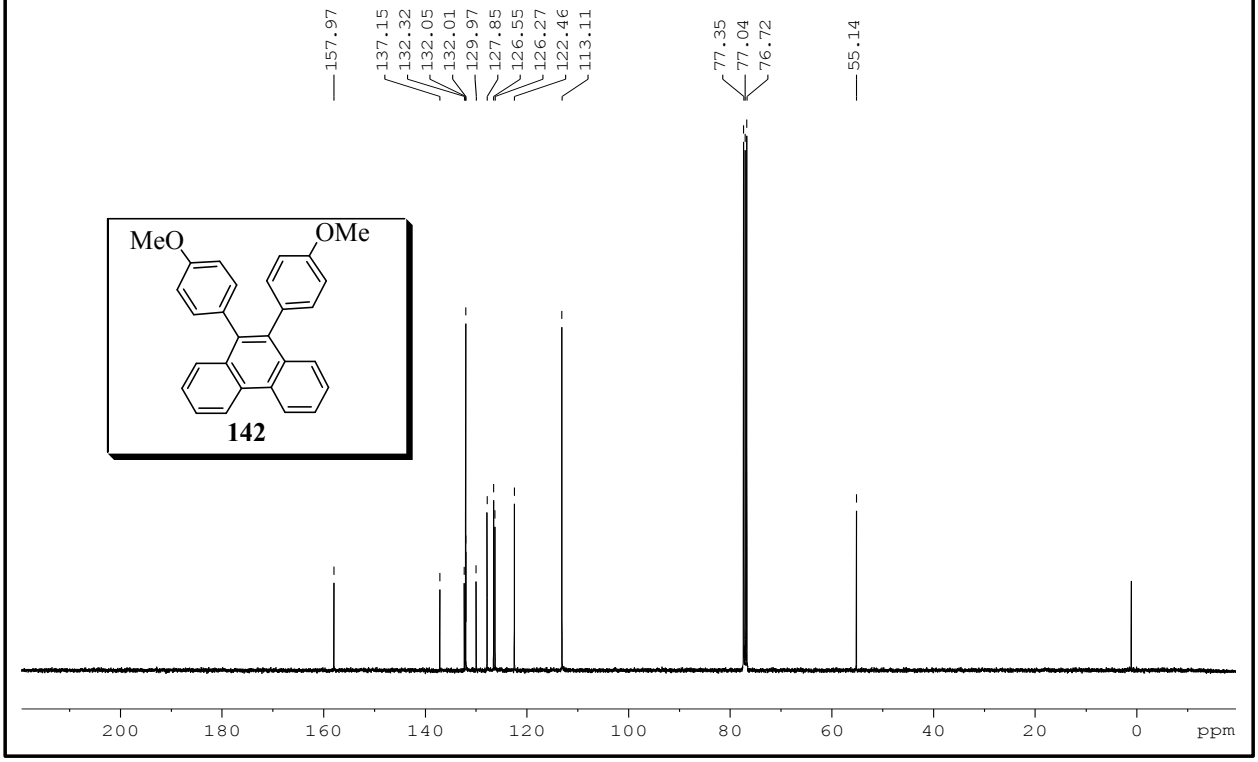
Spectrum No 56 (chapter 3) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



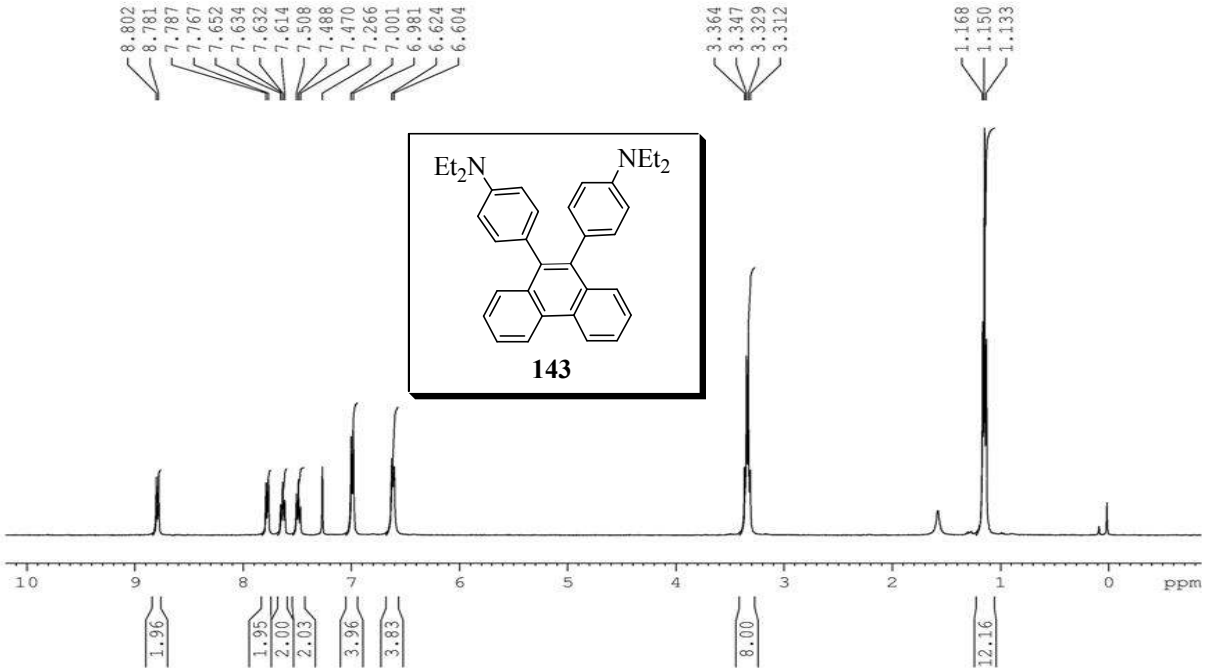
Spectrum No 57 (chapter 3) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



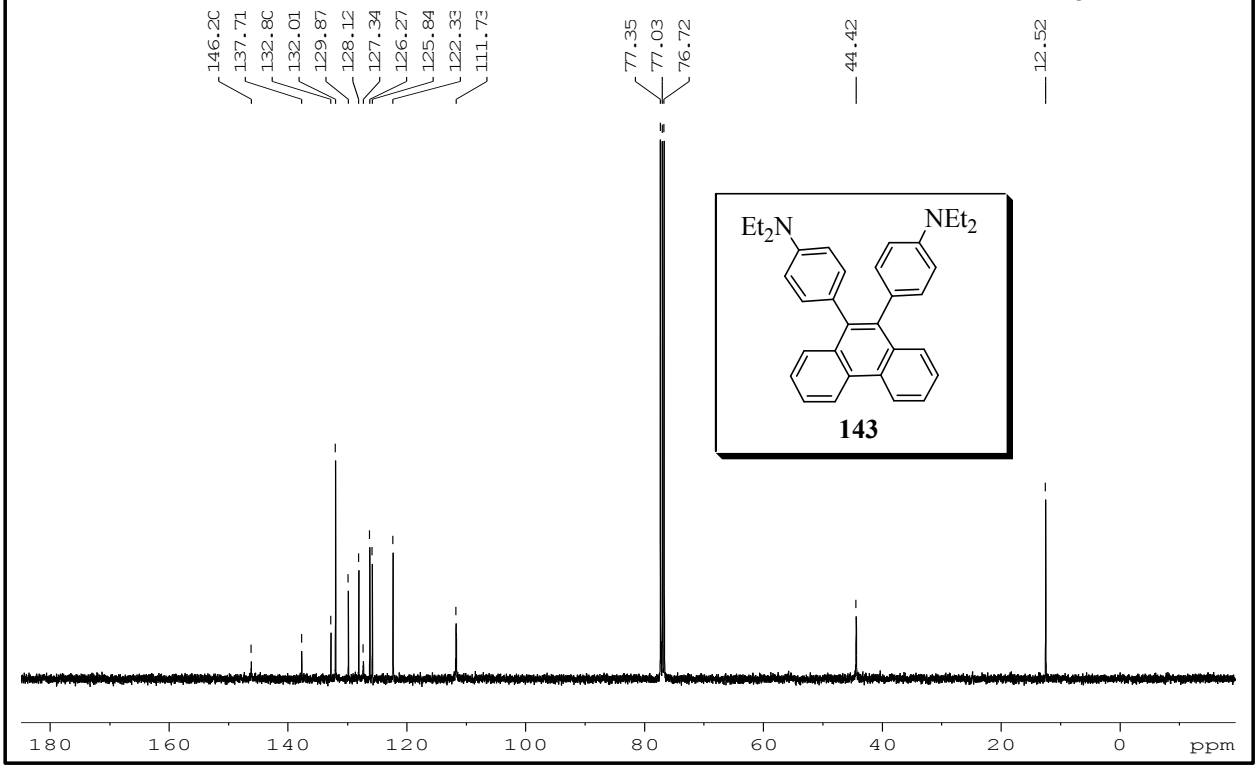
Spectrum No 58 (chapter 3) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



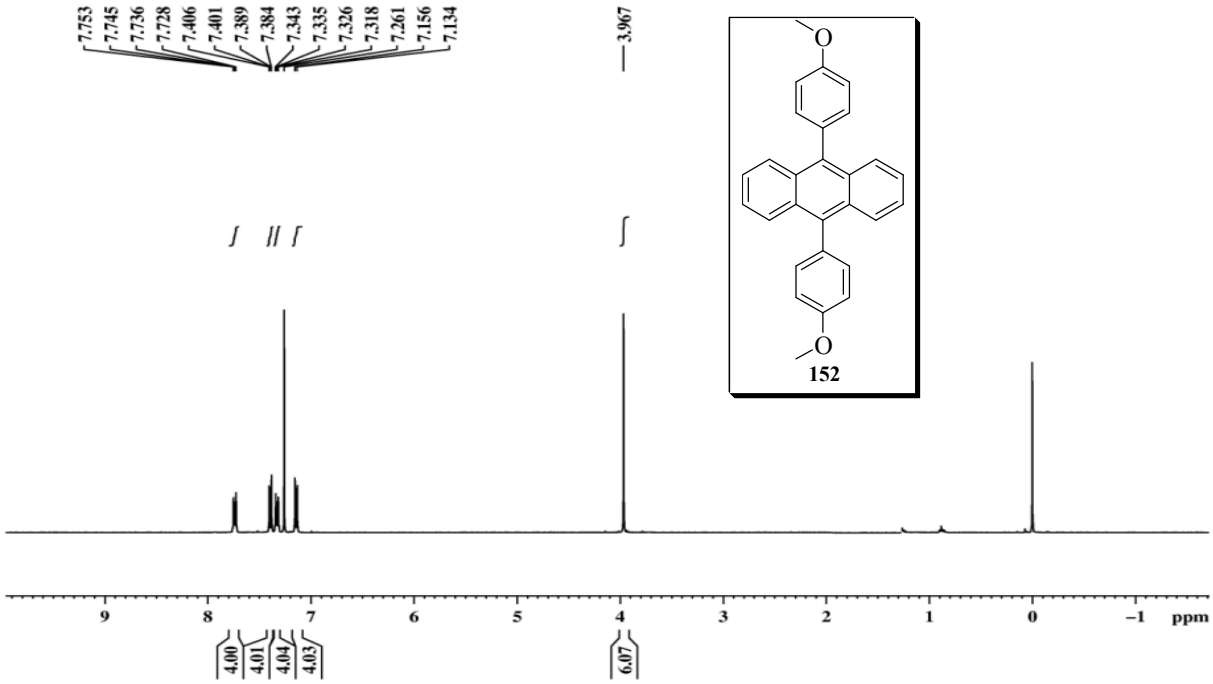
Spectrum No 59 (chapter 3) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



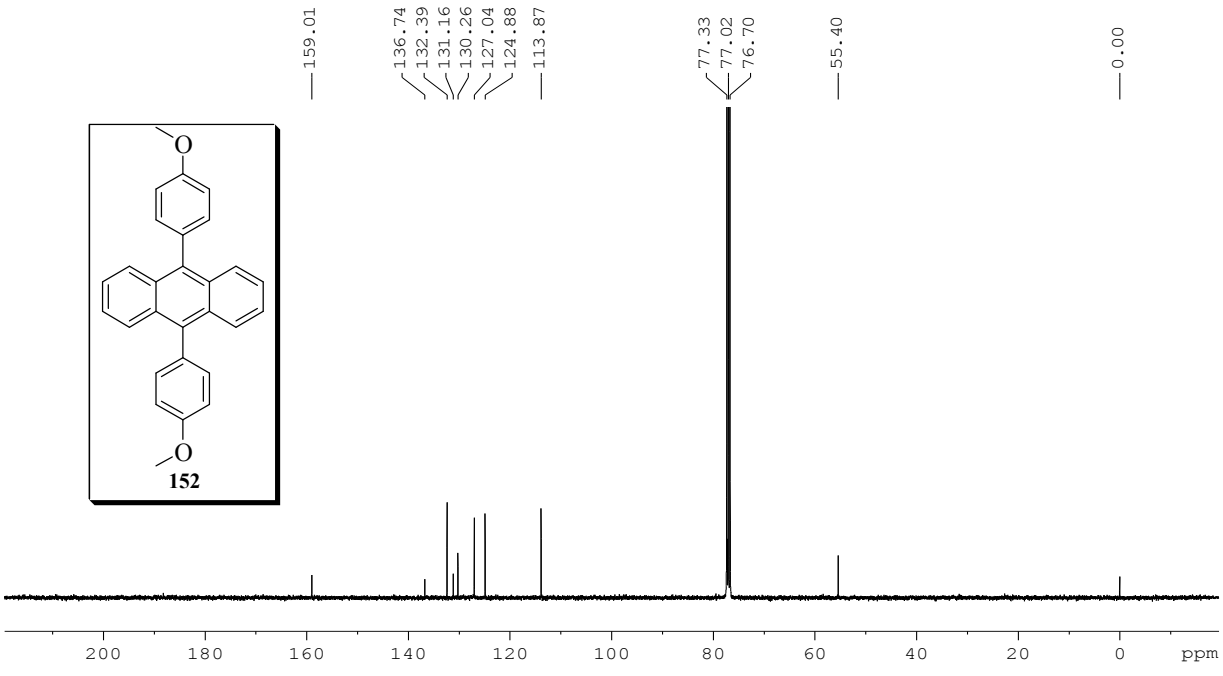
Spectrum No 60 (chapter 3) ^{13}C NMR Spectrum (100 MHz, $CDCl_3$)



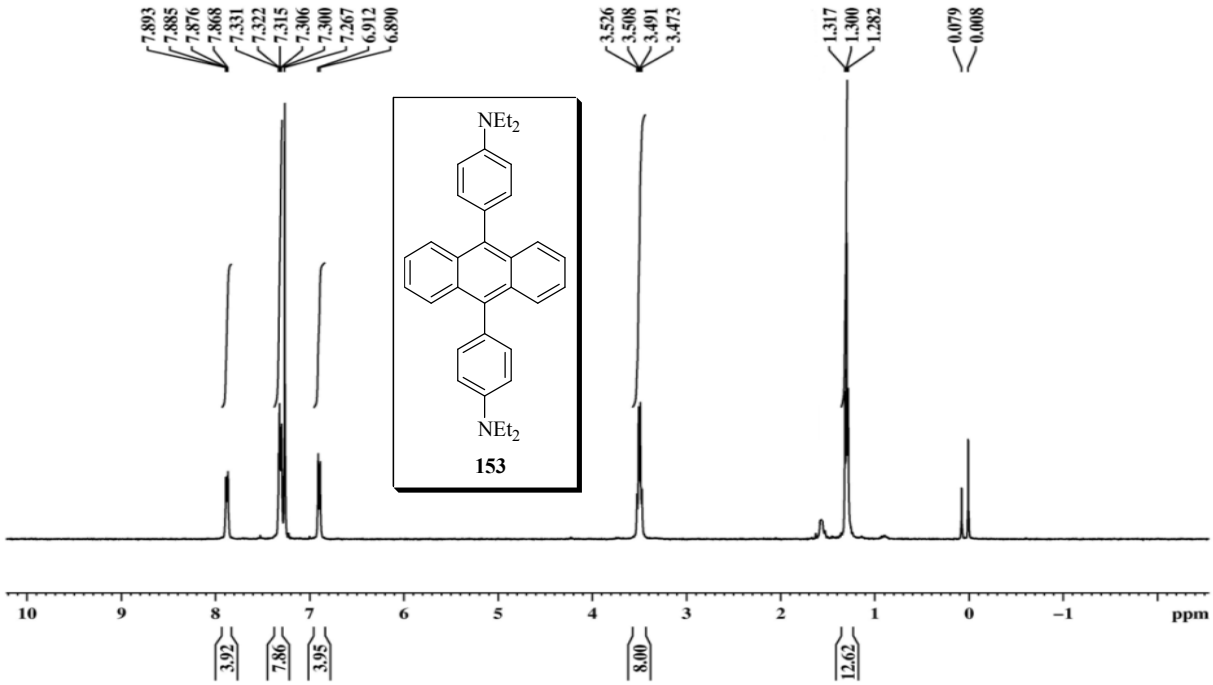
Spectrum No 61 (chapter 3) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



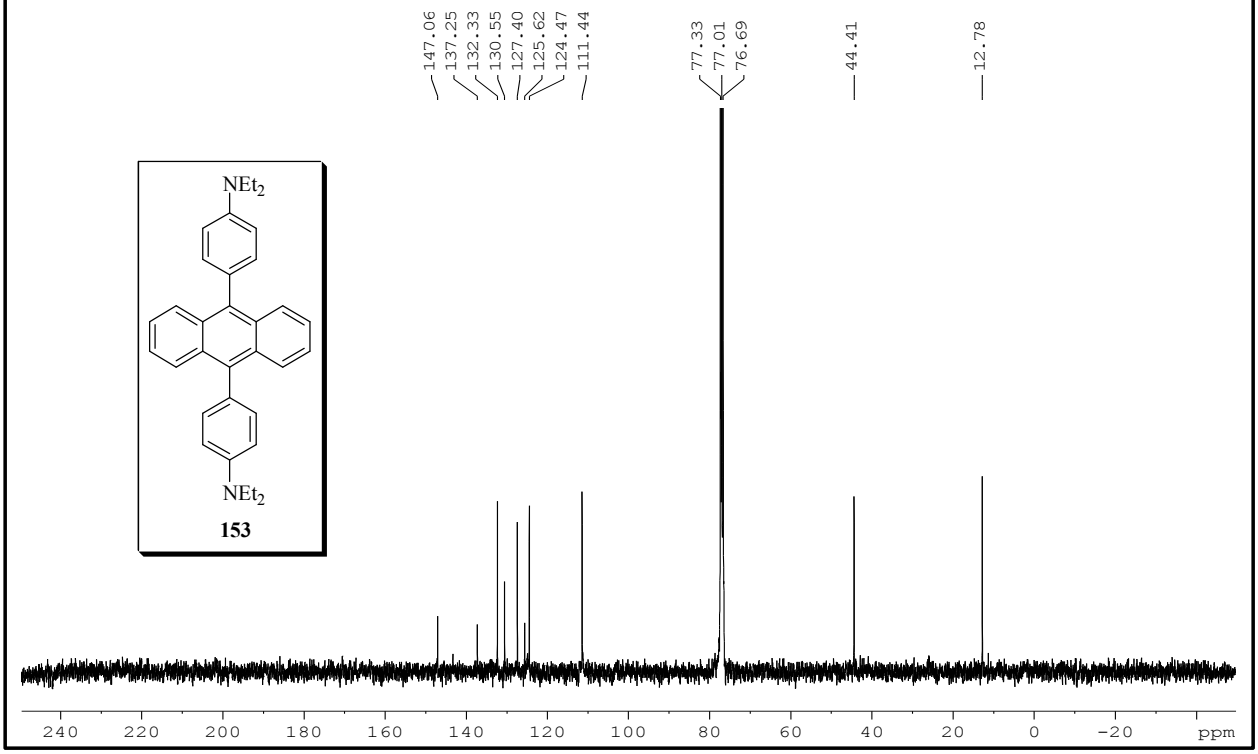
Spectrum No 62 (chapter 3) ^{1}H NMR Spectrum (100 MHz, $CDCl_3$)



Spectrum No 63 (chapter 3) ^{1}H NMR Spectrum (400 MHz, $CDCl_3$)



Spectrum No 64 (chapter 3) ^{1}H 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 **82** (**Chapter 1**, **Section 1.2.2**). U (eq) is defined as one third of the trace of the orthogonalized Uij tensor.

atom	x	y	z	U(eq)
O(1)	5565(2)	9328(1)	1645(2)	94(1)
O(2)	7953(2)	8449(1)	512(2)	94(1)
C(1)	5608(2)	7675(1)	1791(2)	58(1)
C(2)	6984(2)	6420(1)	1031(2)	61(1)
C(3)	6581(2)	7310(1)	1286(2)	56(1)
C(4)	4598(2)	7343(1)	2325(2)	61(1)
C(5)	2636(2)	6824(1)	3233(2)	55(1)
C(6)	5966(2)	8610(2)	1524(3)	67(1)
C(7)	7086(2)	8199(2)	980(3)	67(1)
C(8)	3713(2)	7107(1)	2767(3)	60(1)
C(9)	2530(2)	6010(1)	4053(3)	70(1)
C(10)	1684(2)	7354(2)	2812(3)	66(1)
C(11)	6374(2)	5672(2)	1438(3)	77(1)
C(12)	8001(2)	6310(2)	311(3)	75(1)
C(13)	537(2)	6269(2)	3992(4)	86(1)
C(14)	638(2)	7072(2)	3188(3)	80(1)
C(15)	1476(2)	5742(2)	4432(4)	84(1)
C(16)	6780(3)	4840(2)	1127(4)	97(1)
C(17)	7778(3)	4739(2)	398(4)	102(1)
C(18)	8381(3)	5470(2)	-9(4)	96(1)

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å x 10^3) for **90** (**Chapter 1**, **Section 1.2.2**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

atom	x	y	z	U(eq)
Fe(1)	1556(1)	5716(1)	2154(1)	38(1)
Fe(2)	2318(1)	5159(1)	4592(1)	39(1)
O(1)	- 200(1)	5322(1)	1677(3)	77(1)
O(2)	1859(2)	5701(2)	-1136(3)	95(1)
O(3)	1087(2)	7214(1)	2288(4)	98(1)
O(4)	1996(2)	3895(1)	6397(3)	112(1)
O(5)	3422(1)	5712(1)	7258(3)	82(1)
O(6)	851(1)	5833(2)	5554(3)	84(1)
O(7)	3076(1)	6569(1)	3297(2)	43(1)
O(8)	2341(2)	6937(1)	5224(3)	80(1)
O(9)	4058(1)	5419(1)	3592(2)	40(1)
O(10)	4280(1)	5915(1)	1275(2)	66(1)
C(1)	1506(1)	4098(1)	1784(3)	41(1)
C(2)	1995(1)	4730(1)	2343(2)	37(1)
C(3)	2676(1)	5920(1)	2992(3)	36(1)
C(4)	3224(1)	5349(1)	3040(2)	34(1)
C(5)	479(2)	5448(2)	1851(3)	51(1)
C(6)	2867(1)	4677(1)	2663(2)	35(1)
C(7)	1394(2)	5604(2)	4995(3)	55(1)
C(8)	5377(2)	5853(2)	3414(5)	77(1)
C(9)	3382(1)	4027(1)	2622(3)	42(1)
C(10)	4534(2)	5752(1)	2593(3)	47(1)
C(11)	2846(2)	7050(1)	4365(3)	52(1)

C(12)	836(2)	3873(1)	2503(3)	54(1)
C(13)	4060(2)	4044(2)	1781(3)	55(1)
C(14)	1256(2)	6635(2)	2283(4)	59(1)
C(15)	3206(2)	3403(1)	3360(3)	54(1)
C(16)	1728(2)	5719(2)	136(3)	55(1)
C(17)	2119(2)	4381(2)	5672(3)	66(1)
C(18)	1243(2)	3153(2)	-110(4)	70(1)
C(19)	1700(2)	3734(1)	448(3)	52(1)
C(20)	4404(2)	2859(2)	2534(5)	82(1)
C(21)	3715(2)	2822(2)	3320(4)	73(1)
C(22)	2979(2)	5503(2)	6246(3)	51(1)
C(23)	585(2)	2935(2)	639(4)	76(1)
C(24)	4569(2)	3461(2)	1749(5)	77(1)
C(25)	385(2)	3297(2)	1933(4)	70(1)
C(26)	3323(2)	7710(2)	4296(4)	82(1)

Table 3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å x 10^3) for **112** (**Chapter 2**, **Section 2.2.1**). U (eq) is defined as one third of the trace of the orthogonalized Uij tensor.

atom	**x**	**y**	**z**	**U(eq)**
O(2)	5834(1)	1886(2)	5135(1)	77(1)
O(1)	5110(1)	557(2)	3906(1)	79(1)
C(1)	4200(1)	2825(2)	4911(1)	53(1)
C(2)	5135(2)	2017(3)	4855(1)	59(1)
C(3)	2966(2)	1666(3)	3570(1)	60(1)
C(4)	4794(2)	1373(3)	4283(1)	60(1)
C(5)	3823(1)	3843(2)	5357(1)	51(1)

C(6)	3886(1)	2231(2)	4401(1)	56(1)
C(7)	2150(2)	1680(3)	3200(1)	56(1)
C(8)	2889(2)	4360(3)	5369(1)	62(1)
C(9)	4409(2)	4304(3)	5797(1)	66(1)
C(10)	3037(2)	2325(3)	4080(1)	64(1)
C(11)	2200(2)	919(3)	2677(1)	72(1)
C(12)	1309(2)	2434(3)	3348(1)	64(1)
C(13)	1439(2)	938(3)	2321(1)	84(1)
C(14)	621(2)	1701(3)	2469(1)	81(1)
C(15)	4068(2)	5267(3)	6229(1)	78(1)
C(16)	2557(2)	5309(3)	5804(1)	70(1)
C(17)	557(2)	2457(3)	2987(1)	75(1)
C(18)	3150(2)	5762(3)	6231(1)	75(1)

Table 4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å x 10^3) for **122** (**Chapter 2**, **Section 2.2.1**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

atom	**x**	**y**	**z**	**U(eq)**
O(1)	589(2)	-1639(1)	1506(3)	26(1)
O(2)	3052(2)	-1323(1)	724(3)	26(1)
C(1)	-1897(2)	1246(2)	3754(4)	19(1)
C(2)	-2860(2)	1438(2)	4371(4)	23(1)
C(3)	-3587(2)	766(2)	4571(4)	24(1)
C(4)	-3344(2)	-104(2)	4125(4)	21(1)
C(5)	-2385(2)	-300(2)	3515(4)	18(1)
C(6)	-1621(2)	356(2)	3330(4)	16(1)

C(7)	-628(2)	68(2)	2693(4)	16(1)
C(8)	296(2)	488(2)	2630(4)	15(1)
C(9)	1130(2)	-33(2)	1921(4)	16(1)
C(10)	1189(2)	-1021(2)	1552(4)	18(1)
C(11)	2326(2)	-871(2)	1126(4)	18(1)
C(12)	2134(2)	104(2)	1416(4)	15(1)
C(13)	2832(2)	845(2)	1058(4)	15(1)
C(14)	3899(2)	690(2)	1207(4)	19(1)
C(16)	4210(2)	2163(2)	105(4)	22(1)
C(17)	3164(2)	2323(2)	-62(4)	20(1)
C(15)	4591(2)	1347(2)	740(4)	21(1)
C(18)	2460(2)	1675(2)	413(4)	16(1)
C(19)	526(2)	1421(2)	3321(4)	18(1)

Table 5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å x 10^3) for **125** (**Chapter 2**, **Section 2.2.1**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

atom	**x**	**y**	**z**	**U(eq)**
O(1)	71(1)	2262(1)	6613(1)	52(1)
O(2)	66(1)	133(1)	5861(1)	58(1)
C(1)	3778(2)	-1730(1)	5074(1)	40(1)
C(2)	4187(2)	-2519(2)	4713(1)	46(1)
C(3)	3575(2)	-3074(2)	4271(1)	50(1)
C(4)	2540(2)	-2836(2)	4180(1)	47(1)
C(5)	2123(2)	-2051(1)	4542(1)	38(1)
C(6)	2730(1)	-1479(1)	4995(1)	33(1)

C(7)	2214(1)	-684(1)	5378(1)	35(1)
C(8)	2607(1)	170(1)	5618(1)	33(1)
C(9)	1881(1)	797(1)	5991(1)	33(1)
C(10)	721(1)	715(1)	6028(1)	40(1)
C(11)	727(1)	1700(1)	6411(1)	38(1)
C(12)	1887(1)	1656(1)	6391(1)	31(1)
C(13)	2624(1)	2299(1)	6736(1)	32(1)
C(14)	2226(1)	3147(1)	6985(1)	35(1)
C(15)	2706(2)	3947(1)	7380(1)	34(1)
C(16)	2036(2)	4555(1)	7758(1)	43(1)
C(17)	2400(2)	5330(2)	8156(1)	53(1)
C(18)	3443(2)	5524(2)	8181(1)	55(1)
C(19)	4118(2)	4944(2)	7804(1)	60(1)
C(20)	3762(2)	4161(2)	7409(1)	49(1)
C(21)	3691(2)	525(2)	5461(1)	47(1)
C(22)	3723(2)	1968(2)	6851(1)	48(1)

Table 6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å x 10^3) for **148** (**Chapter 2**, **Section 2.2.2**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

atom	**x**	**y**	**z**	**U(eq)**
C(1)	6880(2)	8239(1)	9962(4)	48(1)
C(2)	6024(3)	8346(1)	8000(5)	55(1)
C(3)	5596(3)	8954(1)	7391(5)	64(1)
C(4)	6011(3)	9461(1)	8720(6)	66(1)
C(5)	6850(3)	9362(1)	10682(6)	69(1)

C(6)	7282(3)	8755(1)	11299(5)	61(1)
C(7)	7349(2)	7612(1)	10707(4)	49(1)
C(8)	8317(3)	7411(1)	12635(6)	60(1)
C(9)	7968(3)	6728(1)	11933(4)	56(1)
C(10)	7050(2)	6986(1)	10014(4)	49(1)
C(11)	6205(3)	6685(1)	8285(4)	52(1)
C(12)	6065(3)	6053(1)	7997(5)	54(1)
C(13)	5148(3)	5766(1)	6137(6)	76(1)
O(1)	9071(2)	7663(1)	14107(4)	89(1)
O(2)	6729(2)	5611(1)	9285(4)	70(1)
O(3)	8257(2)	6198(1)	12613(4)	72(1)

Table 7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å x 10^3) for **113** (**Chapter 3**, **Section 3.2.1**). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

atom	**x**	**y**	**z**	**U(eq)**
C(1)	846(2)	3345(3)	3831(1)	17(1)
C(2)	2224(2)	3211(3)	680(1)	18(1)
C(3)	2605(2)	3279(3)	1170(1)	17(1)
C(4)	1400(2)	3190(3)	582(1)	17(1)
C(5)	482(2)	2390(3)	3480(1)	19(1)
C(6)	871(2)	3195(3)	977(1)	17(1)
C(7)	856(2)	3212(3)	1896(1)	15(1)
C(8)	1504(2)	3282(3)	2309(1)	16(1)
C(9)	1268(2)	3253(3)	1455(1)	14(1)

C(10)	1302(2)	3288(3)	2833(1)	16(1)
C(11)	12(2)	3118(3)	951(1)	21(1)
C(12)	2111(2)	3331(3)	1562(1)	14(1)
C(13)	3068(2)	3457(3)	2370(1)	16(1)
C(14)	4055(2)	2766(3)	3040(1)	22(1)
C(15)	710(2)	2375(3)	2997(1)	18(1)
C(16)	3295(2)	2656(3)	2794(1)	18(1)
C(17)	29(2)	3134(3)	1860(1)	19(1)
C(18)	1663(2)	4224(3)	3184(1)	18(1)
C(19)	-394(2)	3082(3)	1382(1)	23(1)
C(20)	-127(2)	2680(3)	4432(1)	24(1)
C(21)	1440(2)	4258(3)	3669(1)	18(1)
C(22)	908(2)	4511(3)	4639(1)	24(1)
C(23)	4425(2)	4492(3)	2444(1)	21(1)
C(24)	2249(2)	3366(3)	2114(1)	14(1)
C(25)	3663(2)	4354(3)	2204(1)	19(1)
C(26)	4643(2)	3712(3)	2879(1)	24(1)
C(27)	5950(2)	4950(4)	2992(1)	37(1)
C(28)	5620(2)	2980(3)	3553(1)	29(1)
C(29)	2346(2)	6990(3)	741(1)	16(1)
C(30)	2141(2)	7030(3)	1230(1)	17(1)
C(31)	2053(2)	9552(3)	1178(1)	18(1)
C(32)	3420(2)	11675(3)	-381(1)	18(1)
C(33)	2002(2)	8320(3)	1466(1)	17(1)
C(34)	4382(2)	11590(3)	504(1)	20(1)
C(35)	2427(2)	8204(3)	457(1)	16(1)
C(36)	2764(2)	7221(3)	-856(1)	18(1)
C(37)	2662(2)	8128(3)	-61(1)	16(1)

C(38)	2425(2)	6924(3)	-398(1)	17(1)
C(39)	3776(2)	12904(3)	-188(1)	18(1)
C(40)	1711(2)	7065(3)	2224(1)	21(1)
C(41)	2270(2)	9490(3)	692(1)	17(1)
C(42)	3106(2)	9079(3)	-319(1)	18(1)
C(43)	4025(2)	10374(3)	307(1)	21(1)
C(44)	3478(2)	8117(3)	-1676(1)	27(1)
C(45)	3170(2)	8526(3)	-828(1)	18(1)
C(46)	1981(2)	5704(3)	-368(1)	18(1)
C(47)	4253(2)	12898(3)	266(1)	19(1)
C(48)	2269(2)	5055(3)	-1214(1)	23(1)
C(49)	3081(2)	6846(3)	-1694(1)	24(1)
C(50)	1920(2)	4765(3)	-778(1)	22(1)
C(51)	2704(2)	6332(3)	-1269(1)	21(1)
C(52)	1500(2)	9643(3)	2159(1)	30(1)
C(53)	5092(2)	14059(3)	934(1)	28(1)
C(54)	3516(2)	10381(3)	-133(1)	18(1)
C(55)	3533(2)	8995(3)	-1246(1)	21(1)
C(56)	4169(2)	15476(3)	395(1)	28(1)
N(1)	5387(2)	3885(4)	3139(1)	44(1)
N(2)	640(1)	3327(3)	4325(1)	19(1)
N(3)	1840(2)	8371(2)	1961(1)	22(1)
N(4)	4598(2)	14136(2)	467(1)	23(1)

LIST OF PUBLICATIONS

1 A Simple and Convenient Method for the Synthesis of Cyclobutenediones from Alkynes using new $Fe(CO)_5$/NaH/MeI Reagent System, Periasamy, M.; **Beesu, M**.; Shyam Raj, D. *J. Organomet. Chem*. **2008,** *693*, 2843.

2 Reactive Iron Carbonyl Reagents via Reaction of Metal Alkoxides with $Fe(CO)_5$ or $Fe_2(CO)_9$: Synthesis of Cyclobutenediones via Double Carbonylation of Alkynes; **Beesu, M.**; Periasamy, M. *J. Org. Chem.* **2011**, *76*, 543.

3 Stereoselective Synthesis of Alkenyl Cyclobutenediones by Organocatalysis; **Beesu, M.**; Periasamy, M. *Communicated*.

4 Stereoselective Synthesis of α,β-Unsaturated Carboxylic Acids from Alkynes by using $Fe(CO)_5$/*t*-BuOK/AcOH/CH_2Cl_2 Reagent System; Periasamy, M.; **Beesu, M.**; *To be communicated*.

5 Synthesis of New 1,2-Diarylacenaphthylenes from Acenaphthenequinone by using the $TiCl_4$/Arylamine/Et_3N Reagent System; Periasamy, M.; **Beesu, M**. *To be communicated*.

6 A Convenient Method to Access of 1,2-Diarylacenaphthylene, 9,10-Diaryl phenanthrene and 9,10-Diarylanthracene Derivatives using $TiCl_4$/Et_3N reagent System; Periasamy, M.; **Beesu, M**.; Shanmugaraja, M. *To be communicated*.

7 L-Proline Catalyzed Michael Addition Reaction on Cyclobutenedione Derivatives; Periasamy, M., **Beesu, M**., Shyam Raj, D. *To be communicated.*

POSTERS/PAPERS PRESENTED IN SYMPOSIA

1. Synthesis and applications of Cyclobutenedione derivates; **Mallesh, B**.; Periasamy, M. Oral presentation in the *"7th Chemfest"* in house symposium held at University of Hyderabad, Hyderabad, January **2010**.
2. Synthesis and applications of Cyclobutenedione derivates; **Mallesh, B**.; Periasamy, M. Poster presentation in the *"7th Chemfest"* in house symposium held at University of Hyderabad, Hyderabad, January **2010**.