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DEVELOPMENT OF THE ACENAPHTHENEQUINONE REACTIONS

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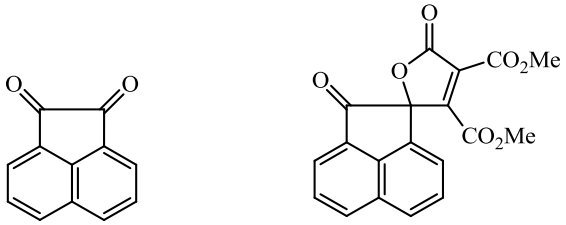
Abstract – Acenaphthenequinone and its derivatives have a broad spectrum of applications as biologically active compounds, dyes, pharmaceuticals, drugs, therapeutic agents and pesticides. This brief review represents various reactions such as pericyclic, multicomponent, ring opening and substitutions of acenaphthenequinone reactions.

CONTENTS

1. INTRODUCTION

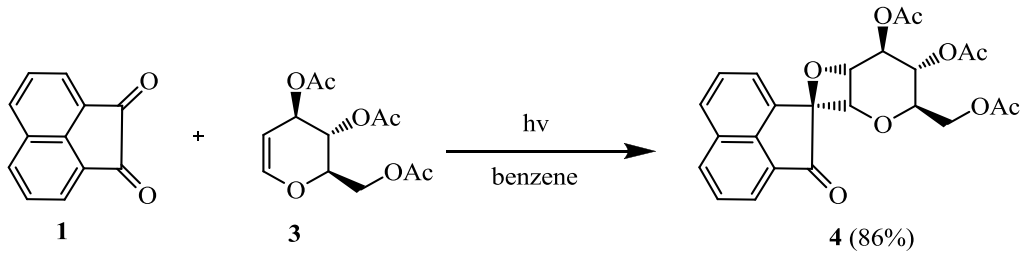
In the last decade, great attention has been paid to acenaphthenequinone in various reactions such as pericyclic, multicomponent and substitution reactions to attain useful products. Pericyclic reaction of acenaphthenequinone **1** can construct spirolactones **2** which are novel spiroheterocycles.[1] Consequently acenaphthenequinone **1** and its derivatives are used as biologically active compounds, dyes, pharmaceuticals, drugs, therapeutic agents and pesticides.[2-4] So, it has a broad spectrum of applications[5] which impelled us to review their new reactions.



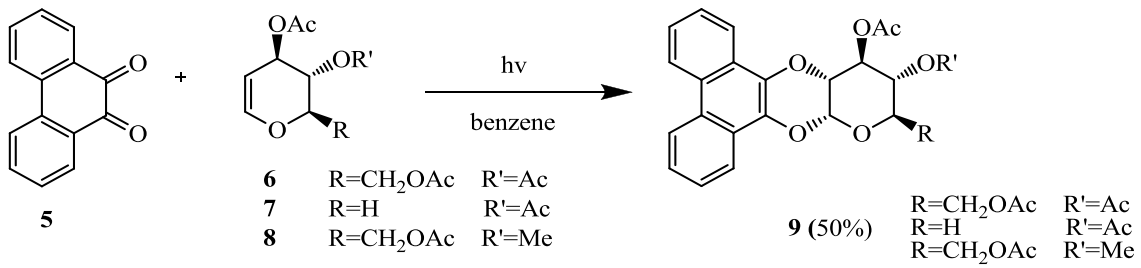
2. PERICYCLIC REACTIONS OF ACENAPHTHENEQUINONE

2.1 [4+2] AND [2+2] CYCLOADDITION OF ACENAPHTHENEQUINONE

Lichtenthaler et al. achieved distinctly different regioselectivities of photocycloadditions of phenanthrenequinone **5** and acenaphthenequinone **1** to 3,4,6-tri-*O*-acetyl-D-glucal **3**. The [2+2] cycloadduct (**4**, 86%) was attained by photocycloadditions of acenaphthenequinone **1** to 3,4,6-tri-*O*-acetyl-D-glucal **3** (**Scheme 1**). In addition, [4+2] cycloadduct (**9**, 50%) was accomplish by photocycloadditions of phenanthrenequinone **5** to the analogous of 3,4,6-tri-*O*-acetyl-D-glucal **3** such as **6**, **7** and **8** (**Scheme 2**).[6]

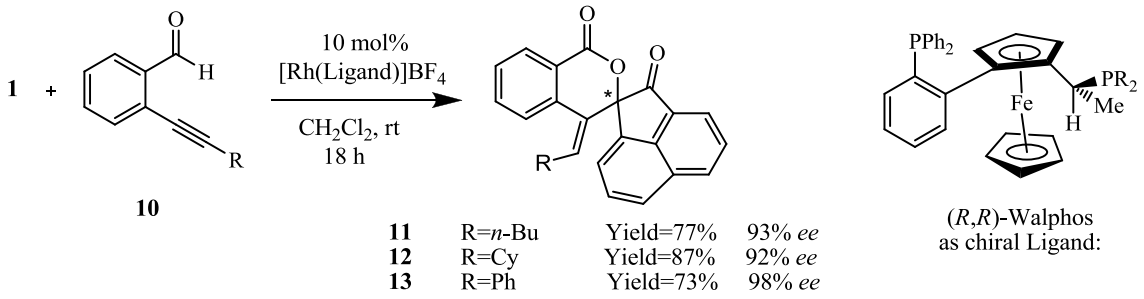


Scheme 1



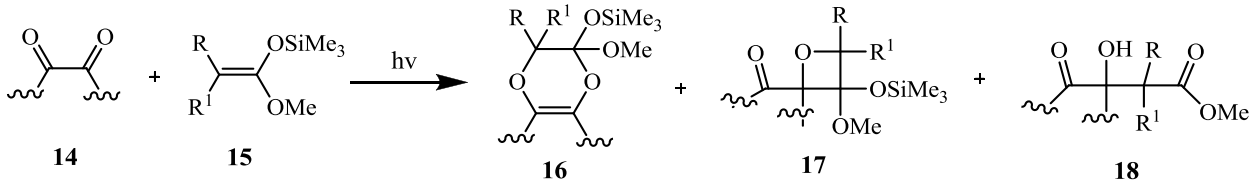
Scheme 2

Enantioselective [4+2] annulations of 2-alkynylbenzaldehydes **10** and acenaphthenequinone **1** was proceeded using cationic rhodium (I)/ (*R*,*R*)-Walphos complexes to compose spirocyclic benzopyranones **11-13** (**Scheme 3**). A number of cationic rhodium(I)/chiral bisphosphine complexes were screened due to their chemo- and enantioselectivity ability for cross [4+2] annulation. Ultimately, products were prepared with high yield and good enantioselectivity using (*R*,*R*)-Walphos as a chiral ligand.[7]



Scheme 3

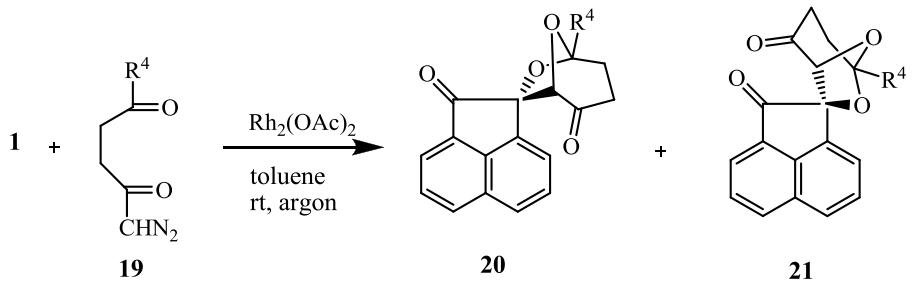
Photoreactions of 1,2-diketones **14** and silylketene acetals **15** are projected to follow three major competitive pathways leading from the excited states involving: (1) Direct [4+2]-cycloaddition to produce dioxenes **16**, (2) Classical Paterno-Büchi [2+2]-cycloaddition to construct oxetanes **17**, and (3) Desilylation to generate β-hydroxy-γ-ketoesters **18** or oxetanes **17** (**Scheme 4**). These competitive routes leading to these products are influenced by solvent polarity and the character of the silylketene acetal **15** and 1,2-diketone **14**.[8]



Scheme 4

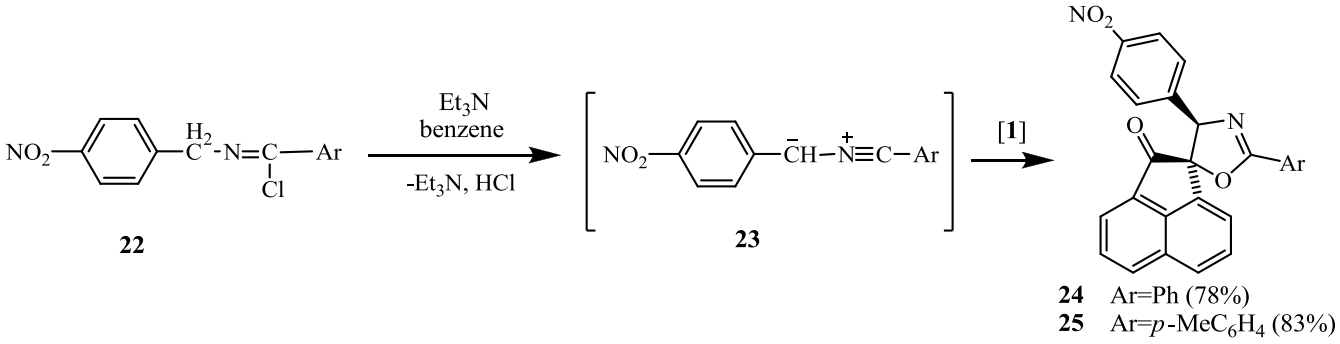
2.2 1, 3-DIPOLAR CYCLOADDITION OF ACENAPHTHENEQUINONE

Carbonyl ylides underwent 1,3-dipolar cycloaddition reaction with acenaphthenequinone **1** to synthesize novel spirooxabicycles **20**, **21** (**Scheme 5**). These reactions afforded a mixture of stereoisomers.[9]



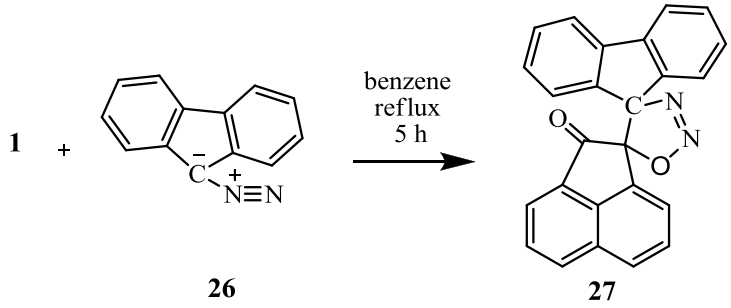
Scheme 5

Treatment of imidoyl chlorides **22** with triethylamine gave nitrile ylides **23** which undergo dipolar cycloaddition with acenaphthenequinone **1** to form novel spirooxazoline derivatives **24**, **25** in high yield (**Scheme 6**).[10]



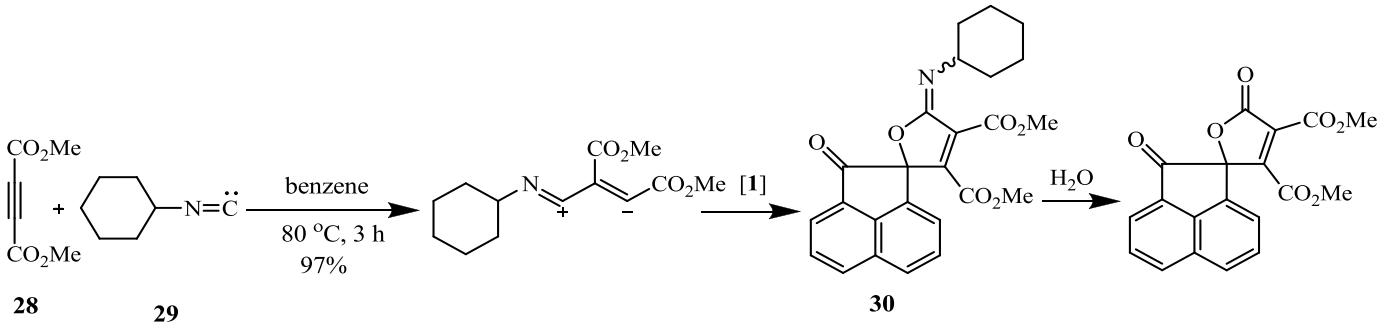
Scheme 6

Acenaphthenequinone **1** reacted via 1,3-dipolar cycloaddition with diazofluorene **26** to give new oxadiazole derivatives **27** which reacted with triphenylphosphine and triethyl phosphite to afford new organophosphorus compounds (**Scheme 7**).[11]



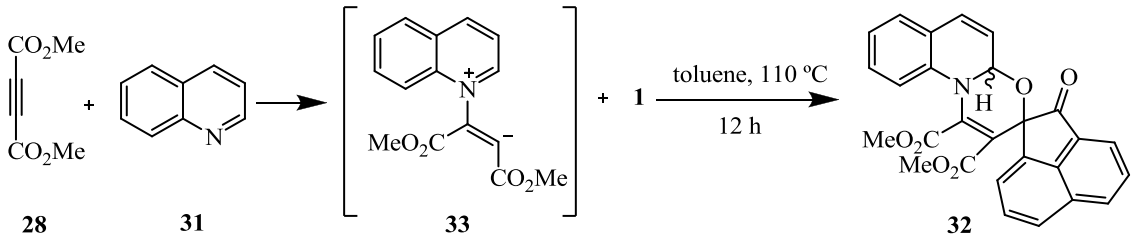
Scheme 7

1,3-Dipolar cycloaddition of zwitterionic intermediate generated in situ from dimethyl acetylenedicarboxylate (DMAD) **28** and cyclohexyl isocyanide **29** to acenaphthenequinone **1** gave iminolactone **30** which easily hydrolysed to spirolactones (**Scheme 8**).[12]



Scheme 8

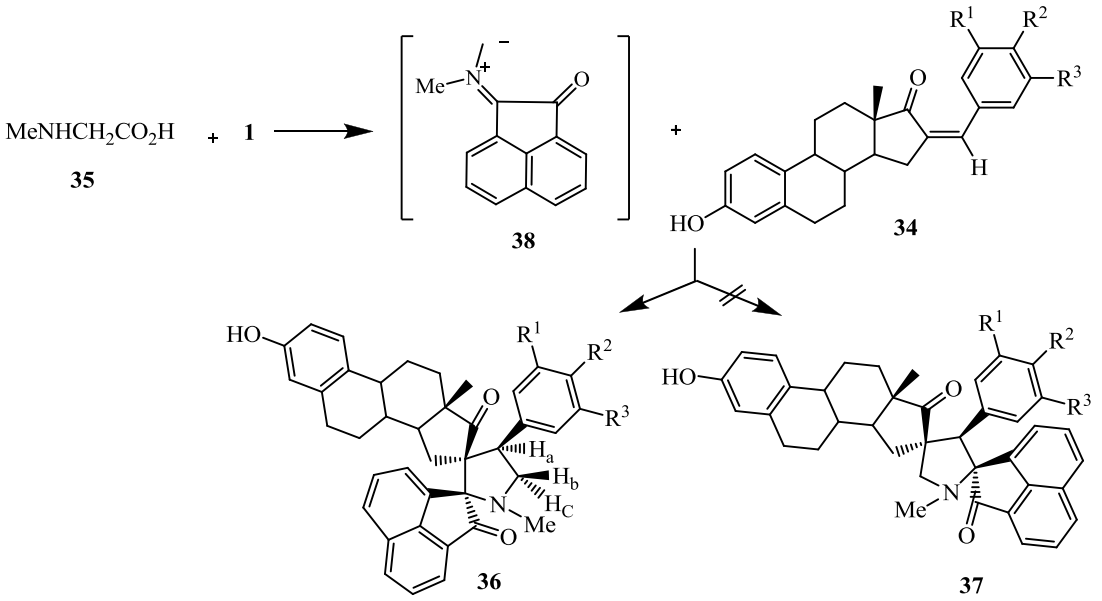
Pyridoquinoline and particularly oxazinoquinoline derivative **32** could be achieved via 1,4-dipolar cycloaddition reaction of acenaphthenequinone **1** and intermediate **33**. Dipolarophile **33** are attained via quinoline **31** and DMAD **28** (**Scheme 9**).[13] These novel functionalized heterocyclic compounds are the central core of biologically active molecules. For example pyridoquinoline derivatives are used as potential inhibitors of the fluoroquinolone efflux pump.[14]



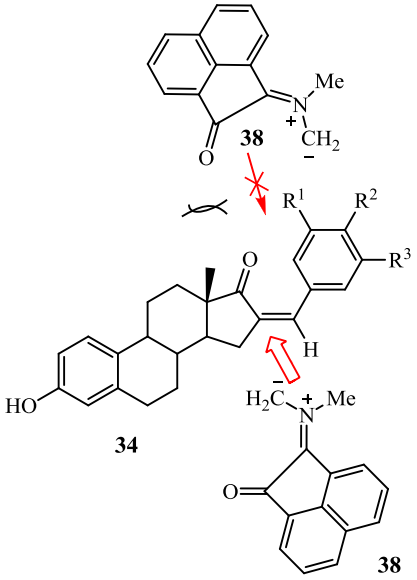
Scheme 9

2.2.1 1, 3-DIPOLAR CYCLOADDITION OF ACENAPHTHENEQUINONE VIA AZOMETHINE YLIDES

A facile 1,3-dipolar cycloaddition one-pot synthesis of novel steroidal dispiropyrrolidines **36** had performed by the reaction of steroidal dipolarophiles **34** and azomethine ylides **38** which derived from the reaction of acenaphthenequinone **1** and sarcosine **35,** under reflux in methanol for 6 h (**Scheme 10**). However, this reaction was carried out in different solvents such as toluene, MeCN and MeOH. The results were confirmed that in polar solvents, the reaction rate and the cycloadducts yield were good (60–72%).[15] The azomethine ylide **38** approaches to the prochiral carbon from the β-face that is the least hindered side of the steroidal dipolarophile to afford compound **36** with high selectivity (**Scheme 11**).

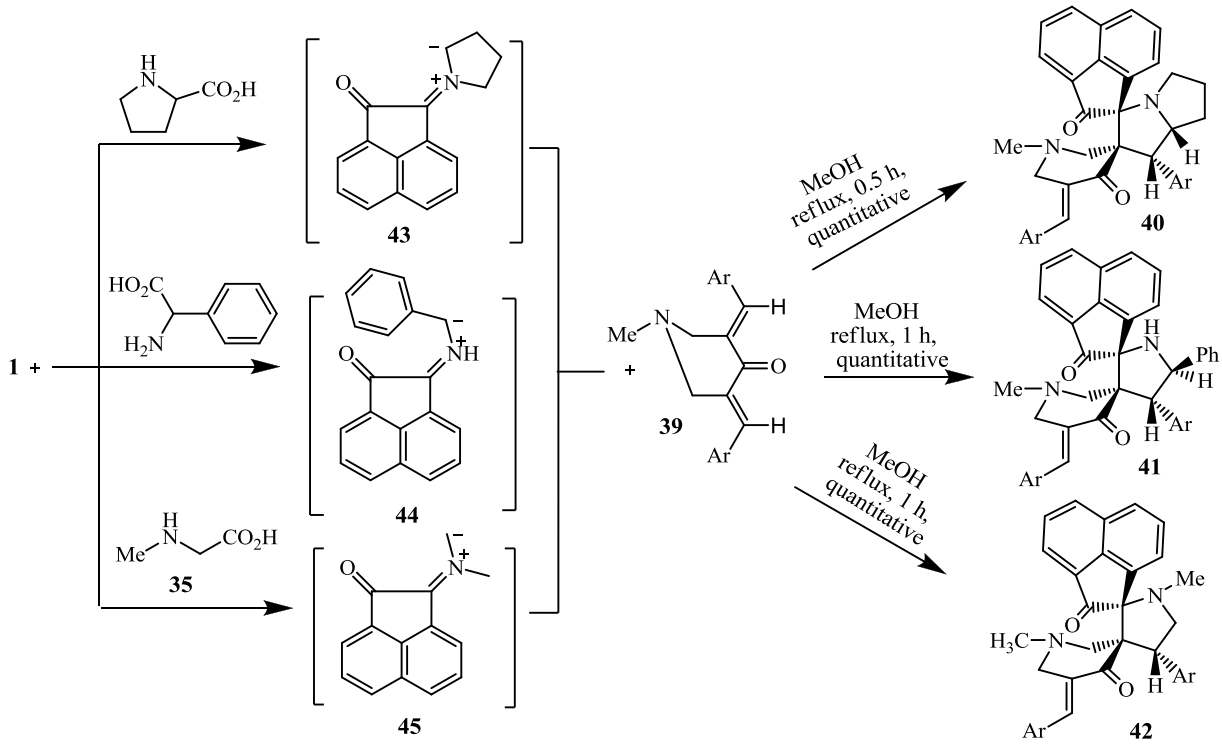


Scheme 10



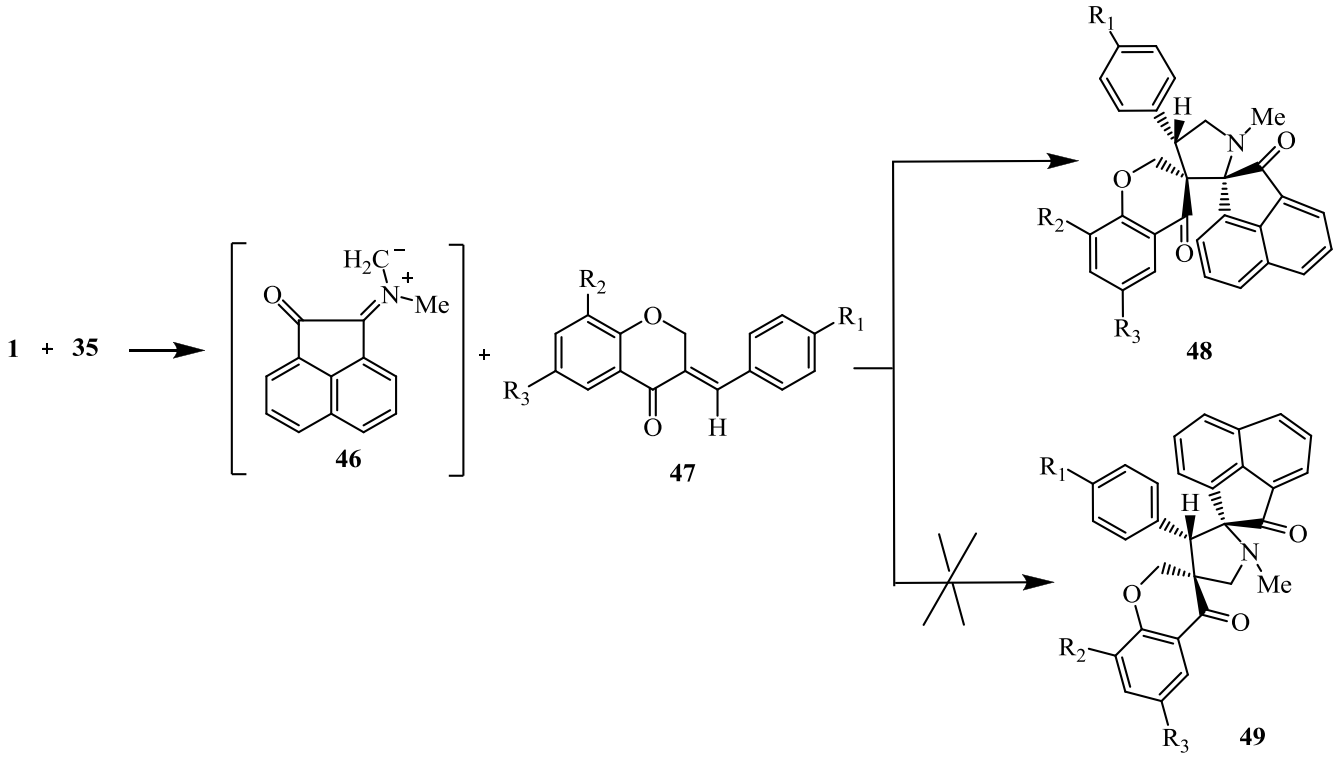
Scheme 11

A chemo-, regio- and stereoselective synthesis of the novel spiropyridopyrrolizines and -pyrrolidines **40**-**42** was achieved via 1,3-dipolar cycloaddition of azomethine ylides **43**-**45** derived from acenaphthenequinone **1** and amino acids such as proline, phenylglycine, and sarcosine **35** to a series of 1-methyl-3,5-bis[(*E*)-arylmethylidene]tetrahydro-4(1*H*)-pyridinones **39** (**Scheme 12**). These novel compounds **40**-**42**, achieved in methanol by refluxing for 30 min, were exhibited significant antimycobacterial activities.[16]



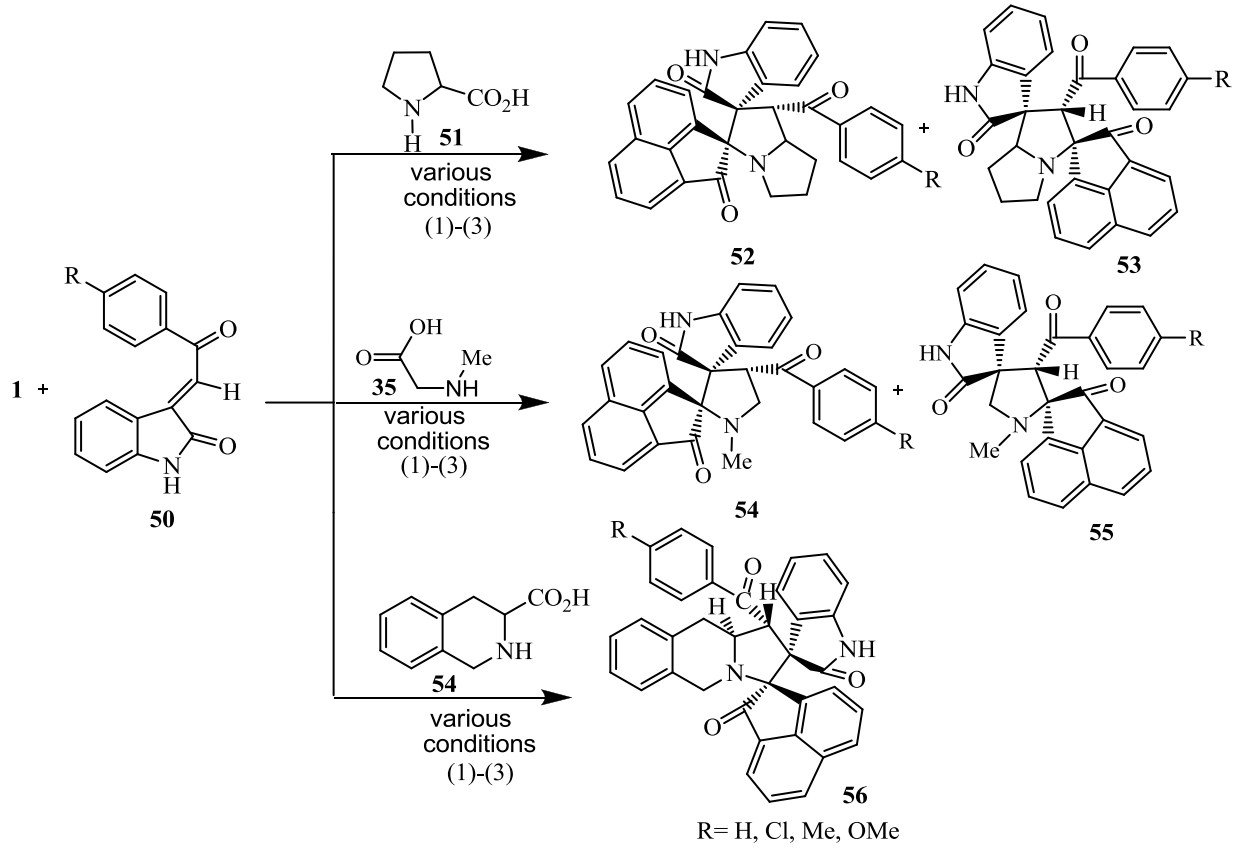
Scheme 12

Another regioselective synthesis of the spiropyrrolidines and spiropyrrolizines (dispiroheterocyclic compounds) was achieved via 1,3-dipolar cycloaddition of azomethine ylides **46,** derived from decarboxylated sarcosine **35** and acenaphthenequinone **1**, into the (*E*)-3-arylidene-4-chromanones **47** as dipolarophiles to afford dispiroheterocycles **48** in good yields (**Scheme 13**).[17]



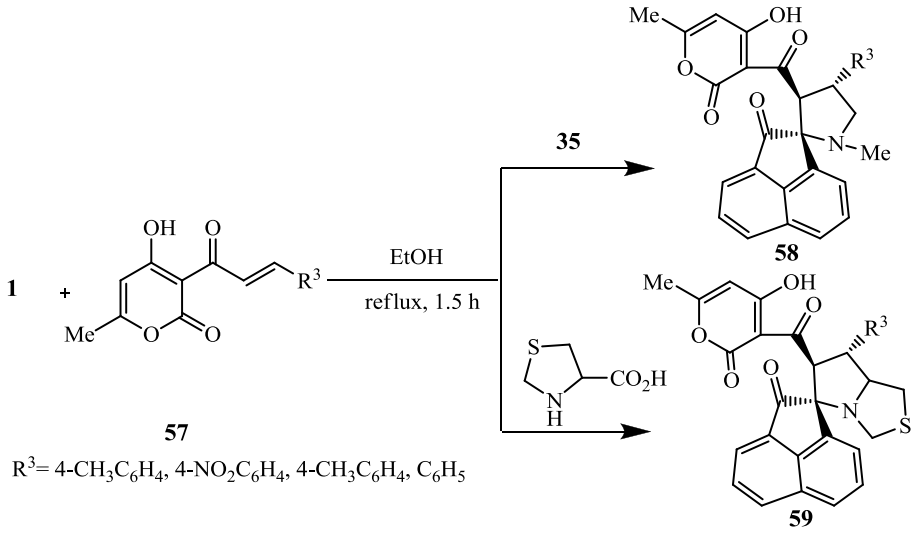
Scheme 13

A facile one-pot synthesis of novel dispiroheterocycles, dispirooxindolopyrrolidines and -pyrrolizidines **52-53**, was performed via [3+2] cycloaddition reaction of azomethine ylides **43** generated by acenaphthenequinone **1** and L-proline **51** or sarcosine **35** with (*E*)-2-oxoindolino-3-ylidene-acetophenones **50** in good yields through three process: (1) Ground in a pestle with Ball clay and subjected to microwave irradiation (2) Reaction mixture and $ZrOCl_2 \bullet 8H_2O$ in methanol was refluxed (3) Reaction mixture and $ZrOCl_2 \bullet 8H_2O$ was ground in a pestle and subjected to microwave irradiation (**Scheme 14**).[18] Also, novel bioactive dispiroheterocycles **56** have been achieved in another regio- and stereoselective reaction by solid-supported catalyst in good yields (80-95%).[19] Azomethine ylide **55** derived from the decarboxylative route of tetrahydroisoquinoline-3-carboxylic acid **54** and acenaphthenequinone **1** to various unusual dipolarophiles such as (*E*)-2-oxoindolino-3-ylidene-acetophenones **50** have been accomplished under various conditions: (1) silica/MW; (2) $BiCl_3$–silica/MW; (3) TiO_2–silica/MW (**Scheme 14**).



Scheme 14

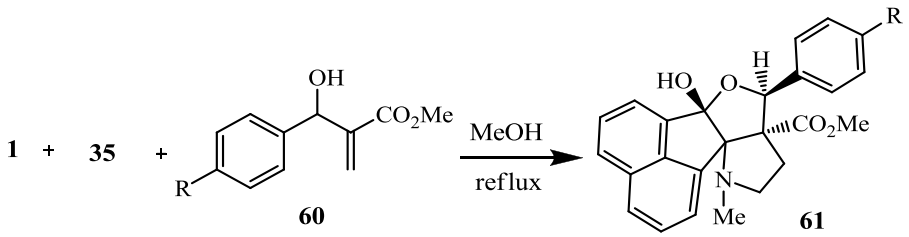
An efficient and regioselective three-component 1,3-dipolar cycloaddition reaction for the synthesis of spiropyrrolidines **58** and spirothiapyrrolizidines **59** in refluxing ethanol was reported by Liu and co-workers (**Scheme 15**).[20]



Scheme 15

As demonstrated in **Scheme 16**, a high regio and stereoselective synthesis of novel spiropyrrolidines and polycyclic heterocycles **61** was performed via [3+2] cycloaddition reaction of azomethine ylides

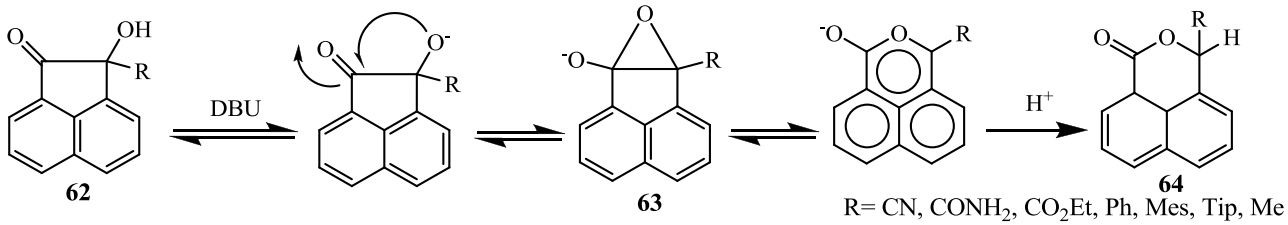
generated by the decarboxylative condensation of diketone **1** and sarcosine **35** with Baylis–Hillman adducts **60** as dipolarophiles. Various solvents were utilized such as DMF, xylene and methanol. When the reaction was carried out in methanol, there was a remarkable enhancing in the yield and reducing in the reaction time.[21]



Scheme 16

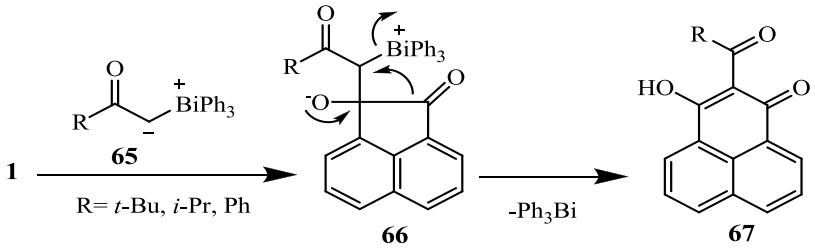
3. RING OPENING OF ACENAPHTHENEQUINONE

A facile rearrangement of 2-hydroxyacenaphthenone derivatives **62** occurred by the attack of nonnucleophilic bases such as the bicyclic tertiary amidine, DBU, as catalyst to yield the anlargement of ring **64**. The plausible mechanism was demonstrated in **Scheme 17**.[22]



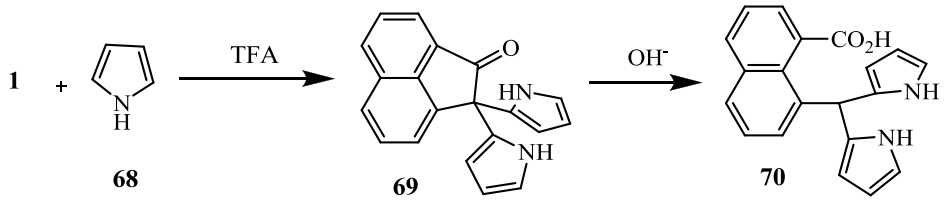
Scheme 17

A novel methodology was achieved by C-insertion of triphenylbismuthonium 2-oxoalkylides **65** between two carbonyl functions of acenaphthenequinone **1** to form 2-acyl-3-hydroxyphenalenones **67** in good yield (**Scheme 18**). In this protocol *t*-BuOK was added to a stirred suspension salt of **65** in THF at -78 ºC. Then, acenaphthenequinone **1** was added after 10 min and the resulting mixture was allowed slowly to warm to room temperature. The earlier route involved the ozonolytic cleavage of the olefinic bond in 1,2-disubstituted acenaphthene, followed by intramolecular Claisen condensation of the consequential carbonyl compound.[23]



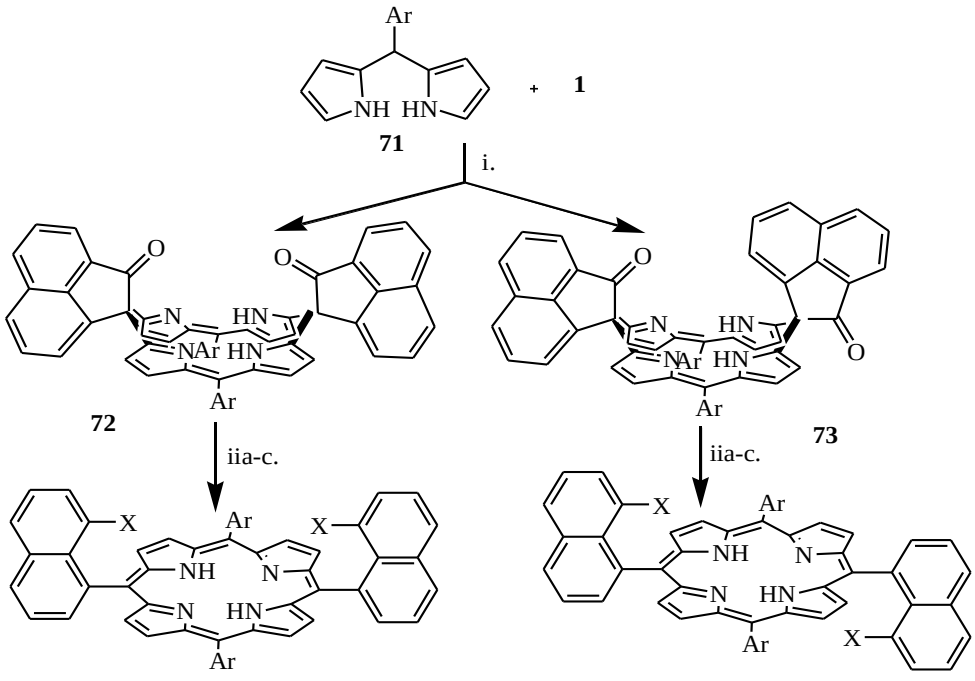
Scheme 18

Acenaphthenequinone **1** reacted with an excess of pyrrole **68** to produce the β-unsubstituted dipyrromethane moiety in compound **69** (**Scheme 19**). Ultimately, the compound **70** was obtained by ring opening and oxidation of compound **69**.[24]



Scheme 19

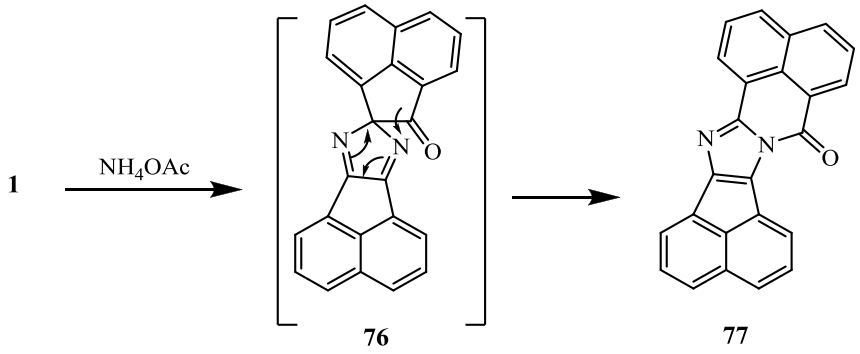
Some years later, Harmjanz et al. afforded a new methodology for the preparation of porphodimethenes **72, 73** (**Scheme 20**). 5-Substituted, β-unsubstituted dipyrromethanes **71** reacted with acenaphthenequinone **1** in the presence of catalytic amounts of either BF_3•OEt_2 or TFA to form porphodimethenes **72, 73**.[25] Aromatic porphyrin macrocycle **74, 75** was generated by broking a carbon-carbon bond in each of the spiro-linked acenaphthenone moieties **72**, **73**. Ring opening of respective porphodimethenes **72, 73** (syn and anti) was performed by refluxing in THF in the presence of 30% KOH.



Reagents and conditions: (i) 1. TFA or BF_3·OEt_2, CH_2Cl_2; 2. DDQ. (iia) 30% KOH(aq), THF, reflux, air. (iib) 1. NaOMe (THF/MeOH) rt; 2.O_2 . (iic) $NaBH_4$, THF/MeOH, rt, air.

Scheme 20

Reactions of acenaphthenequinone **1** and ammonium acetate led to the ring opening of acenaphthenequinone (**Scheme 21**).[26] Acenaphthenequinone, ammonium acetate, and acetic acid were heated at reflux for 2.5 h to produce 2*H*-isoimidazole **76**. Rearrangement of intermediate **76** occurred to produce product **77**.

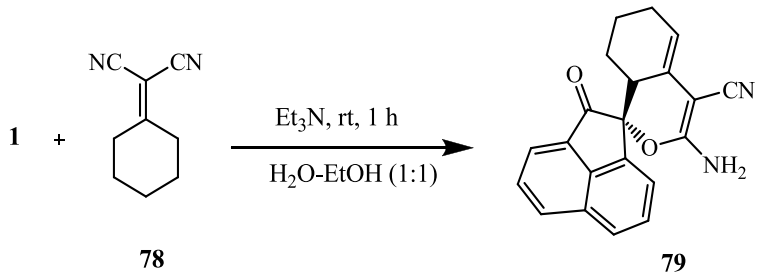


Scheme 21

4. MULTICOMPONENT REACTIONS OF ACENAPHTHENEQUINONE

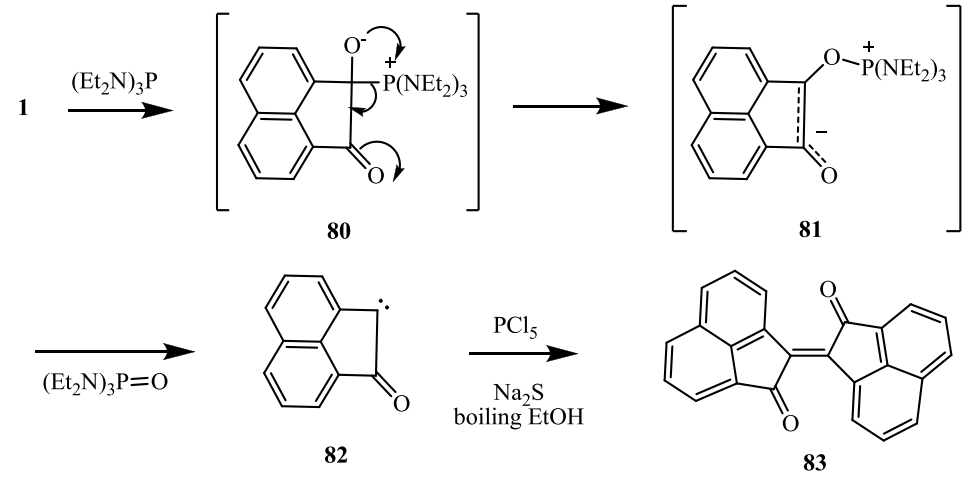
4.1 TWO-COMPONENT REACTION OF ACENAPHTHENEQUINONE

A novel, one-pot, green method catalyzed by triethylamine was reported in aqueous media for the synthesis of functionalized spirooxindoles **79** by the aldol reaction of vinyl malononitriles **78** as vinylogous nucleophiles and dione (**Scheme 22**).[27]



Scheme 22

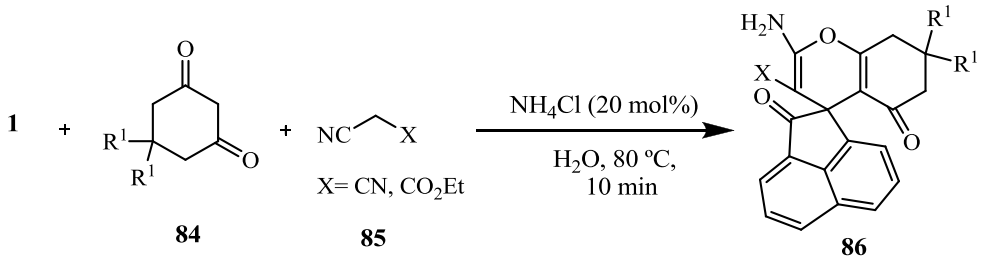
The known dye biacenaphthylidenedione **83** was achieved by deoxygenation of acenaphthenequinone **1** with hexaethylphosphorous triamide. First, dipolar intermediate **80** attained via nucleophilic attack of $P(NEt_2)_3$ on the carbonyl carbon atom of acenaphthenequinone to transform into structure **81** possessing a P-O-C bond. Then elimination of hexaethylphosphoric triamide from compound **81** offered carbene species **82** which underwent dimerization to yield the known dye biacenaphthylidenedione **83** (**Scheme 23**).[28] These compounds **83** were synthesized previously by treatment of acenaphthenequinone **1** with PCl_5 in the presence of Na_2S in boiling ethanol.[29]



Scheme 23

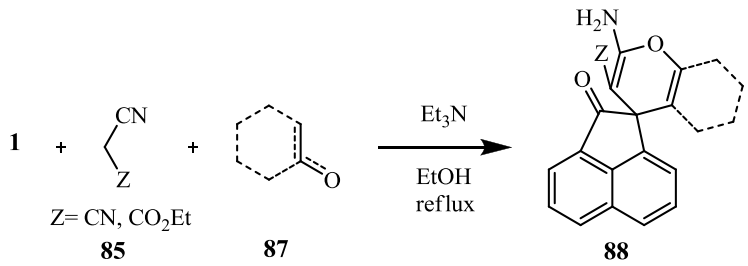
4.2 THREE-COMPONENT REACTION OF ACENAPHTHENEQUINONE

A facile one-pot three-component reaction of acenaphthoquinone **1**, an activated methylene reagent **85**, and 1,3-dicarbonyl compounds **84** for the synthesis of a series of spirochromene derivatives **86** catalyzed by ammonium chloride in water was reported by Dabiri and co-workers (**Scheme 24**).[30]



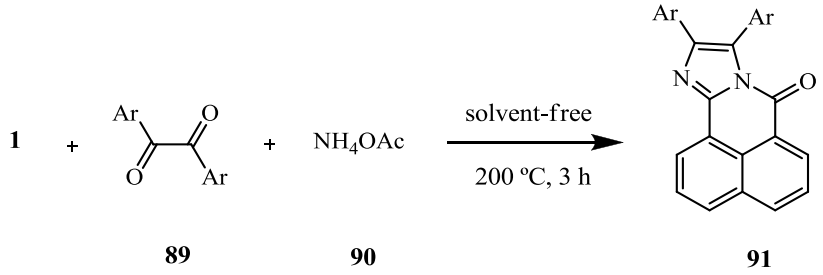
Scheme 24

Acenaphthequinone **1**, malononitrile/ethyl cyanoacetate **85** and various reagents including cyclic CH-acids **87** react to form new spiroacenaphthylene derivatives **88** via a facile and efficient one-pot three component synthesis (**Scheme 25**).[31] Also, the similar multicomponent cascade-reaction was performed by heating acenaphthenequinone **1**, cyclic CH-acids **87**, and malononitrile **85** at 80 ºC in water without any catalyst to form spiroacenaphthylene heterocycles in 90-95% yields. The former reaction was completed in 4-8 hour but the latter was performed in 15 min.[32]



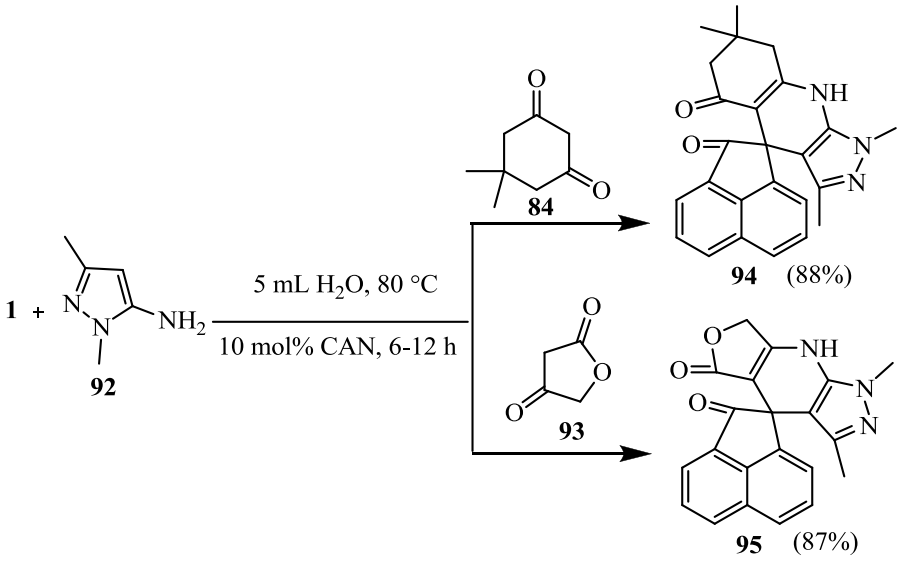
Scheme 25

Acenaphthoquinone **1**, various benzyls **89** and ammonium acetate **90** reacted under solvent-free conditions by heating. Thus, 9,10-diaryl-7*H*-benzo[*d*,*e*]imidazo[2,1-*a*]isoquinolin-7-ones **91** was synthesized in good to excellent yields (**Scheme 26**).[33]



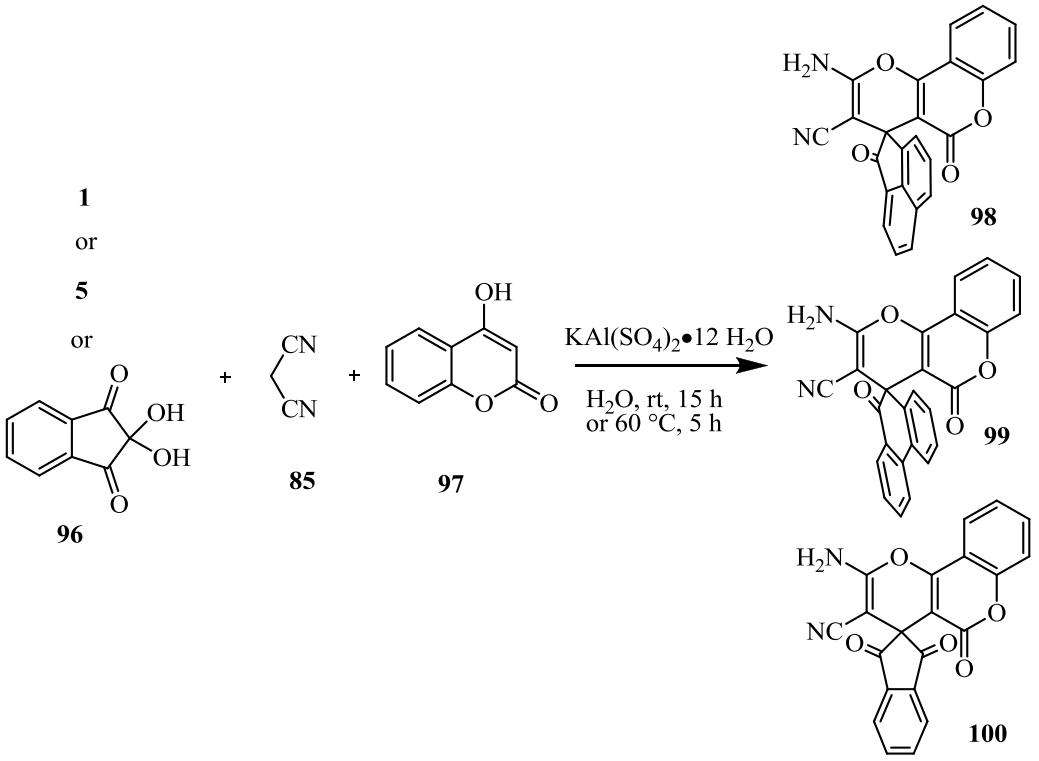
Scheme 26

Three-component synthesis of spiro[indoline-3,4′-pyrazolo[3,4-*b*]quinoline]dione **94**, **95** was reported by Chen and co-workers via a one-pot reaction of acenaphthenequinone **1**, 5-amino-3-methylpyrazole **92**, and 1,3-dicarbonyl compounds **84**, **93** in aqueous medium using ceric ammonium nitrate (CAN) as catalyst (**Scheme 27**).[34] Reaction mixture was stirred at 80 ºC for 6-12 h to produce desired product in good yield.



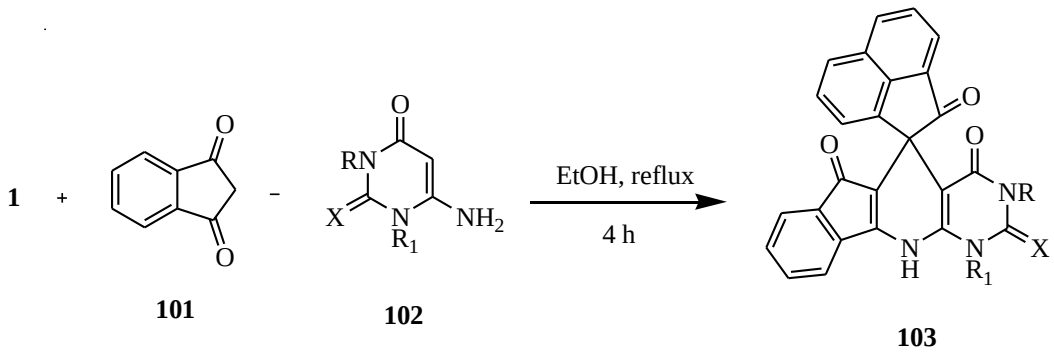
Scheme 27

Multicomponent condensation reaction of 4-hydroxycoumarin **97** and malononitrile **85** with acenaphthenequinone **1** catalyzed by alum ($KAl(SO_4)_2$•12 H_2O) afforded novel mono- and bis(spiro-2-amino-4*H*-pyrans) (**Scheme 28**).[35]



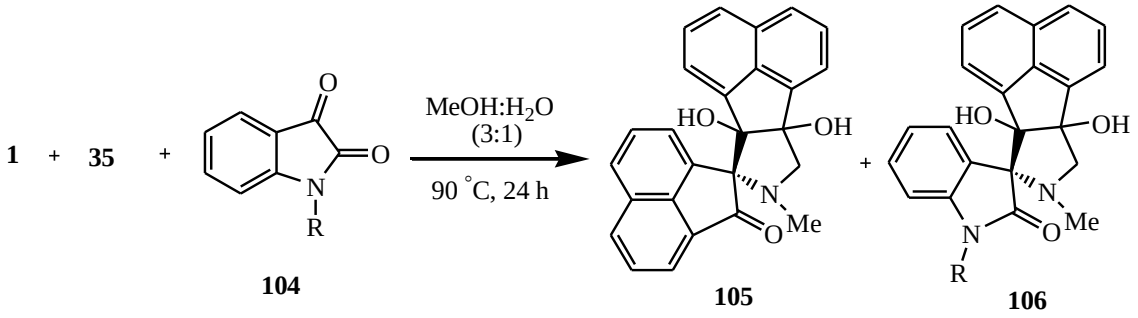
Scheme 28

An efficient, simple, and catalyst-free three-component reaction of 1,3-indandione **101**, amino uracils **102** and isatins or acenaphthylene-1,2-dione **1** is reported by Imani Shakibaei and co-workers in refluxing ethanol (**Scheme 29**). Spiroacenaphthylene-1,4′-indeno-1,5′-pyrido[2,3-*d*]pyrimidines **103** was prepared in good yields (78-89%).[36]

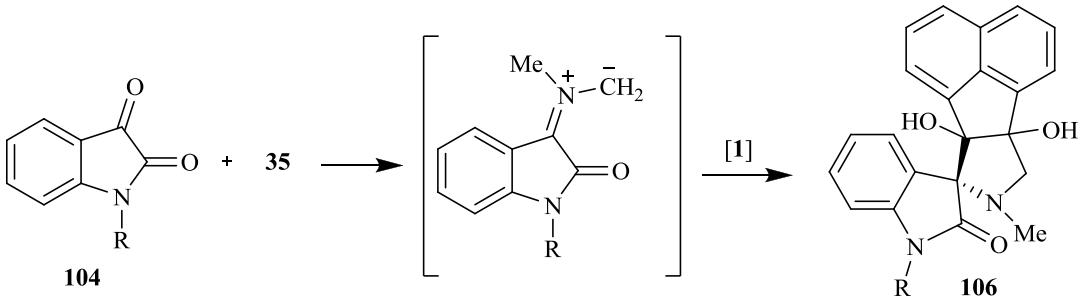


Scheme 29

A multicomponent reactions involving sarcosine **35**, isatin **104** and acenaphthenequinone **1** acquiescent novel spsiropyrrolidine derivatives **105**, **106** are reported by Nair and co-workers (**Scheme 30**). A reaction of sarcosine **35** and excess acenaphthenequinone **1** in aqueous MeOH at 90 ºC proceeded to afford a mixture of two products **105** and **106**. The mechanism of reaction was demonstrated in **Scheme 31**.[37]



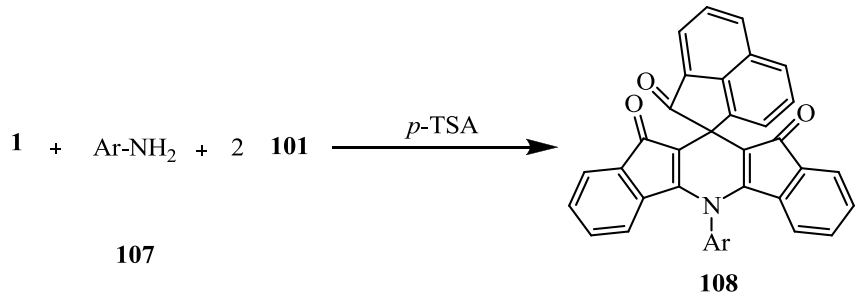
Scheme 30



Scheme 31

4.3 FOUR-COMPONENT REACTION OF ACENAPHTHENEQUINONE

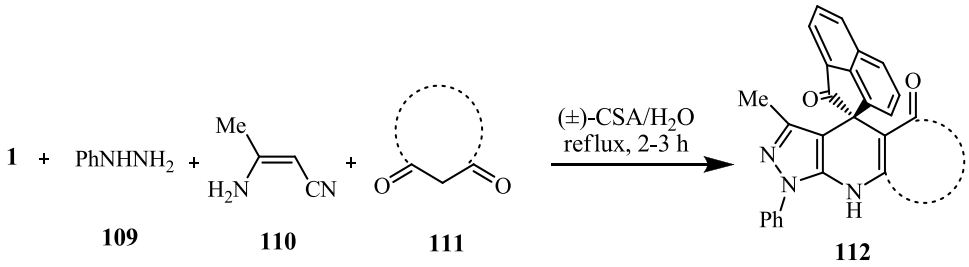
Spiro[acenaphthylene-diindenopyridine]triones **108** was obtained via a one-pot, pseudo four-component synthesis of 1,3-indandione **10**1, aromatic amines **107**, acenaphthylene-1,2-dione **1** and *p*-TSA by using a 'Grindstone Chemistry' in 3–4 min (**Scheme 32**).[38] Also, another procedure was reported to produce spiro[acenaphthylene-diindenopyridine]-triones with higher yields from 1,3-indandione **10**1, aromatic amines **107**, acenaphthylene-1,2-dione **1** and *p*-TSA by Ghahremanzadeh and co-workers. This protocol offered higher yield of products by refluxing in acetonitrile for 1 h.[39]



Scheme 32

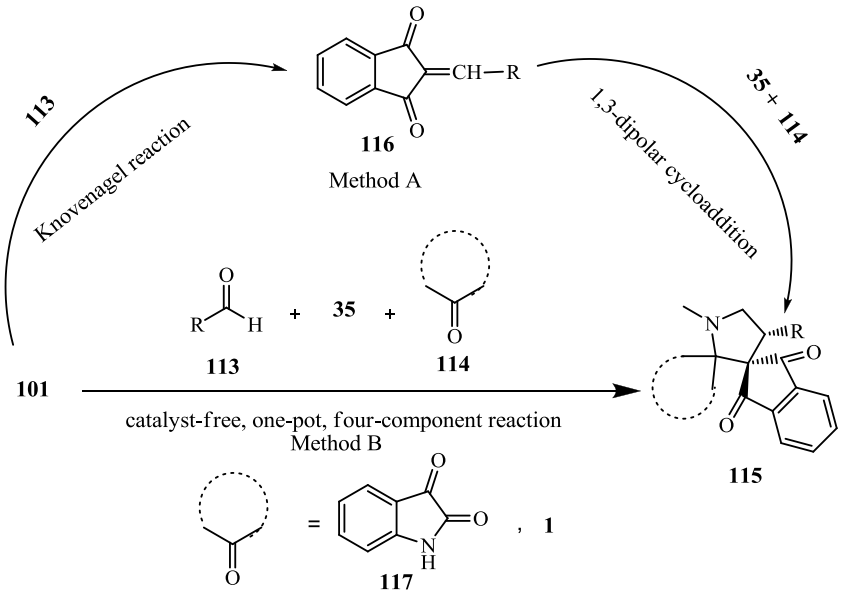
The one-pot synthesis of spiro[indoline/acenaphthylene-3,4′-pyrazolo[3,4-*b*]pyridine derivatives **112** were achieved by the four-component domino reactions of phenylhydrazine **109**, 3-aminocrotononitrile **110**, acenaphthylene-1,2-dione **1**, and cyclic 1,3-dicarbonyl compounds **111**, including cyclohexane-1,3-diones, barbituric acid, and 2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione, in the presence of (±)-

camphor-sulfonic acid (CSA) in aqueous medium by heating under reflux at 100 ºC for 2-3 h (**Scheme 33**).[40]



Scheme 33

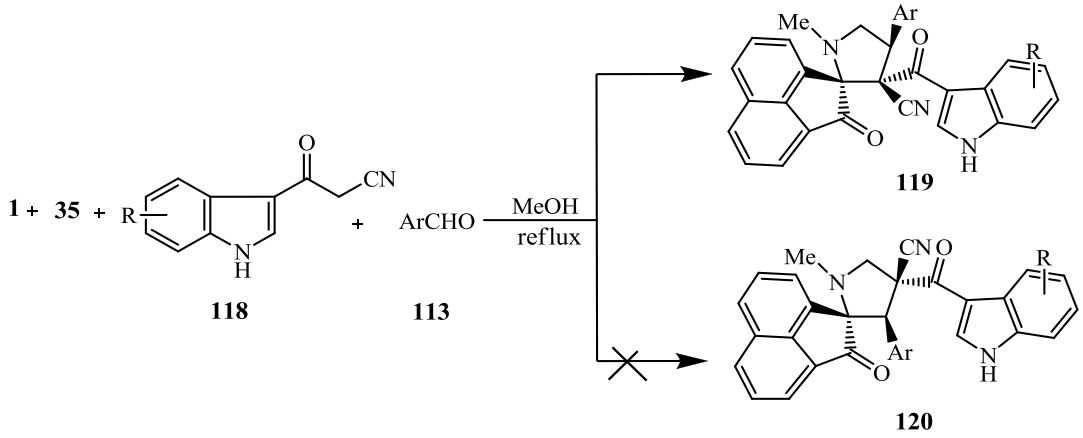
Although dispiropyrrolidines **115** was synthesized by a tandem Knoevenagel–1,3-dipolar cycloaddition reaction sequence (Method A), a highly flexible, rapid, mild, but effective extension procedure for a catalyst-free, four-component, one-pot reaction sequence of isatin **117** or acenaphthylene-1,2-dione **1**, sarcosine **35**, 1,3-indanedione **10**1, and aldehyde **113**, without the isolation of dipolarophiles was reported by Ming Li and co-workers (Method B). In this reaction 1,3-dipole azomethine ylide and dipolarophile was generated in situ (**Scheme 34**).[41] Such a strategy would afford access to a fast, one-pot synthesis of dispiroheterocycles **115**, which are otherwise accessible merely through multistep synthesis (Method A).



Scheme 34

Functionalized 3-spiropyrrolidine oxindoles and 3-spiropyrrolizidine oxindoles particularly 3-spiropyrrolidine acenaphthenones **119** was afforded by a regioselective one-pot four-component [3+2] cycloaddition reaction of 3-(cyanoacetyl)indoles **118**, aldehydes **113**, isatin/acenaphthylene-1,2-dione **1** and amino acid **35**. The reaction of azomethine ylides (produced by the reaction of **1** and **35**) with a novel dipolarophiles produced in situ through the rapid and convenient Knoevenagel condensation between 3-

(cyanoacetyl)indoles **118** and aldehydes **113** was performed in this protocol in MeOH at reflux for several hours (**Scheme 35**).[42]

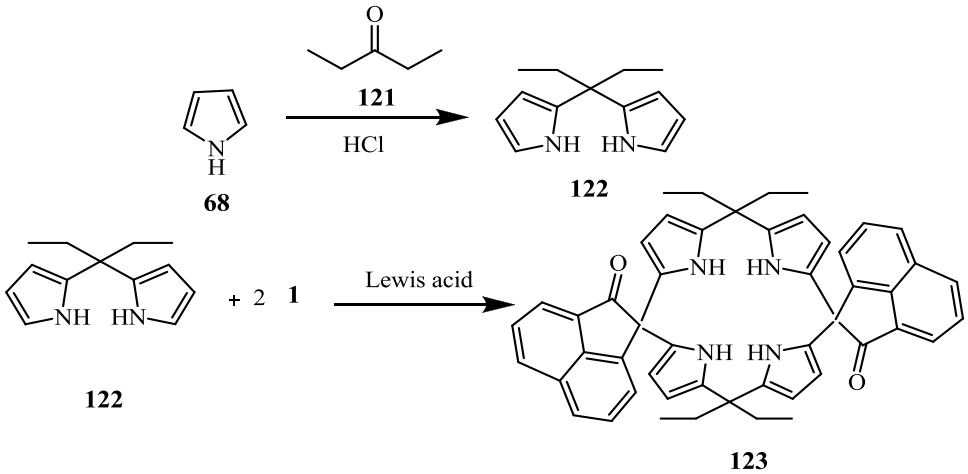


118 **113** **119** **120**

Scheme 35

5. SUBSTITUTION REACTIONS OF ACENAPHTHENEQUINONE

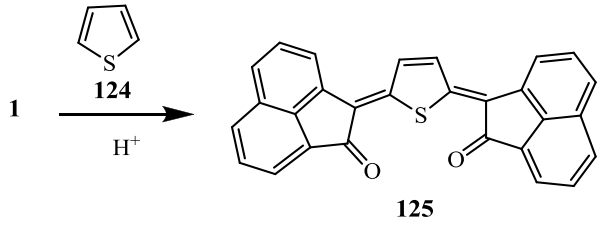
Synthesis, structure and anion binding of a new acenaphthenequinone-based calix[4]pyrrole **123** have been studied.[43] A novel calix[4]pyrrole type anion receptor containing two anti-symmetrically meso-situated acenaphthenequinone moieties has been achieved by a one-pot facile four component synthesis (**Scheme 36**).



68 **122** **122** **123**

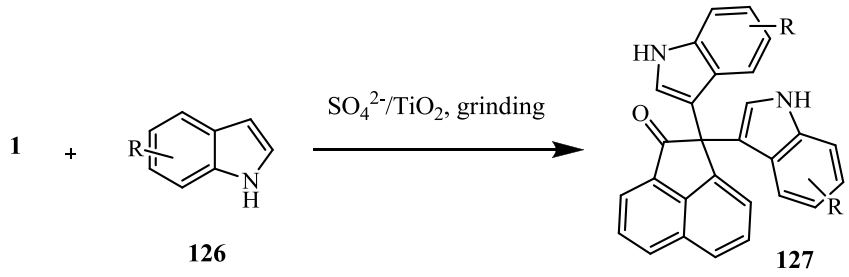
Scheme 36

Harrison et al. reported coloured compounds **125** production from adding concentrated sulphuric acid dropwise during 8 h to a stirred mixture of thiophene **124,** acenaphthene-1,2-dione **1** and acetic acid. In this report thiophene **124** and acenaphthenequinone **1** react in acidic solution to construct a red compound **125** (**Scheme 37**).[44]



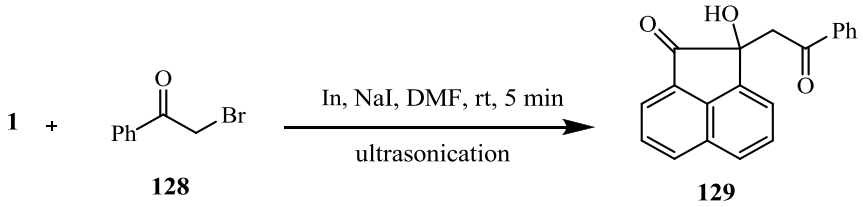
Scheme 37

As demonstrated in **scheme 38** an efficient synthesis of symmetrical 2,2-bis(1*H*-indol-3-yl)-2*H*-acenaphthen-1-one **127** was achieved in high yields by electron-donating substitution of indole **126** and acenaphthenequinone **1** under grinding for 30-60 min at room temperature catalyzed by recyclable solid superacid SO_4^{2-}/TiO_2.[45]



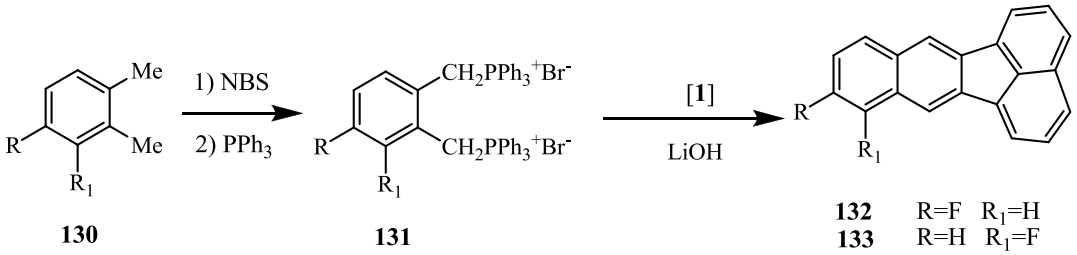
Scheme 38

The reaction of acenaphthenequinone **1** with phenacyl bromide **128** was found to be fast under ultrasonication condition. This reaction performed in the presence of sodium iodide and indium under ultrasonication condition to give α-hydroxy keto compounds **129** in very high yield (**Scheme 39**).[46]



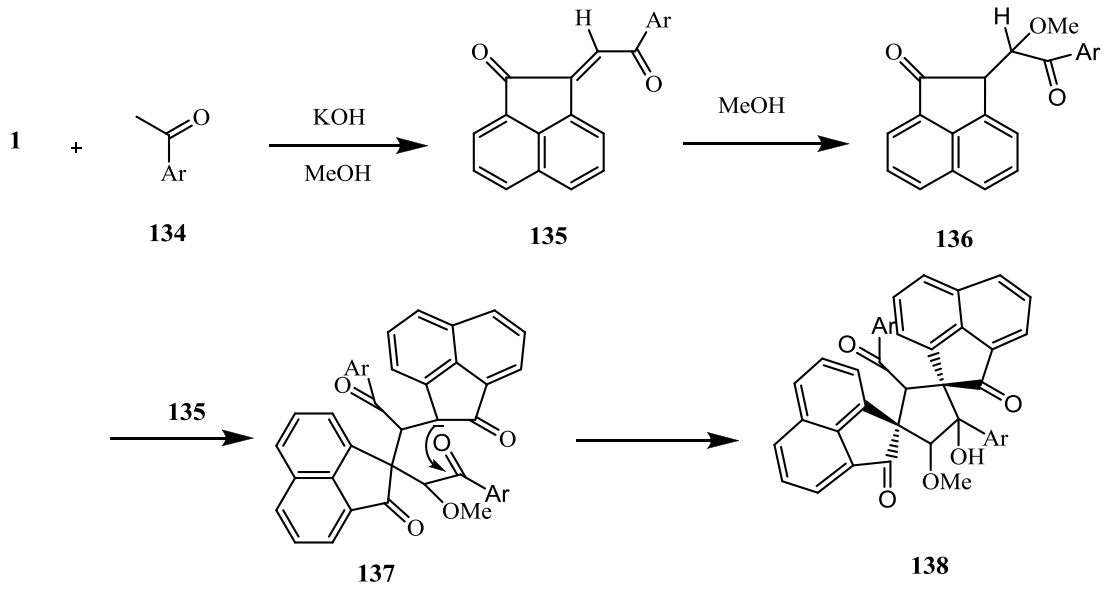
Scheme 39

The synthesis of 8- and 9-fluorobenzo[*k*]fluoranthenes **132**, **133** have been organized by Wittig reaction of the 1,2-bis[(triphenylphosphonio)methyl] salt of the proper fluorobenzene **131** with acenaphthenequinone **1** under phase-transfer conditions. The phosphonium salts are active both as reagents and as phase-transfer catalysts for the two-phase reaction with lithium hydroxide. The yields for synthesis were low (2% for **132** and 15% for **133**), but the reactions can be performed on large scale with only minimum byproduct formation. These compounds **132** and **133** are active as tumorigenic agents (**Scheme 40**).[47]



Scheme 40

A novel solvent-assisted domino Michael-aldol reaction of acenaphthenequinone **1** with acetophenones **134** was reported in methanol in the presence of KOH by heating at about 60 ºC for 12 h to afford dispiro compounds **138** (**Scheme 41**). Acenaphthenone-2-ylidene-ketone **135** was achieved from the condensation between acenaphthenequinone **1** and acetophenone **134**, which undergoes Michael-type addition with a molecule of methanol to give the intermediate **136**. Michael addition of **136** to another molecule of **135** pursued by cyclisation formed **138**. Thus, the mechanism involved catalysed aldol condensation, dehydration, solvent addition, and Michael addition reactions respectively.[48]



Scheme 41

6. CONCLUSION

In conclusion, acenaphthenequinone could provide versatile examples of heterocycles prevalently found in a wide variety of compounds known to exhibit potential biological properties. Important advances in the synthesis from acenaphthenequinone are summarized in detail, with classification in to four types: (a)

pericyclic, (b) ring opening, (c) multicomponent, (d) Substitutions of acenaphthenequinone. Also development of the acenaphthenequinone reactions is to be continued.

7. ACKNOWLEGEMENTS

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