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Heterocycles from cyclopropenones

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Great attention has been paid to cyclopropenones as they are present in many natural sources. Various synthesized cyclopropenone derivatives also show a wide range of biological activities. The cyclopropenone derivatives undergo a variety of reactions such as ring-opening reactions, isomerization reactions, C–C coupling reactions, C–H activation, cycloaddition reactions, thermal and photo-irradiation reactions, and acid–base-catalyzed reactions under the influence of various chemical reagents (electrophiles, nucleophiles, radicals, and organometallics) and external forces (heat and light). Many previous reviews have dealt with the chemistry and reactions of cyclopropenones. However and to the best of our knowledge, the utility of cyclopropenones in the synthesis of heterocycles has not been reported before. Therefore, it would be interesting to shed light on this new topic. The present review article provides, for the first time, a comprehensive compilation of synthetic methods for the synthesis of various heterocyclic ring systems, as a significant family in the field of organic chemistry.

1 Introduction

Cyclopropenone is an important building block for the construction of a large number of skeletons.[1] Very recently, new developments have been made using cyclopropenone and its heteroanalogues, such as [3 + *n*] annulation reactions, acylation, organocatalytic reactions, metal catalytic reactions, base-mediated reactions, nucleophilic substitution reactions, light-induced reactions, σ-bond cross-exchange reactions and C–H activation reactions for the synthesis of diverse heterocycles. Besides, they are used as catalysts in a few reactions. The activation of C–C bonds is a powerful concept for the reorganization or coupling of organic scaffolds, yet it is a relatively challenging process to achieve in the context of synthetic methodology because of their inherent stability.[2] In order to enable such methods, one can use C–C-strained, often cyclic, building blocks that are consequently spring-loaded for C–C bond activation.[3–22]

This review highlights the recent applications of cyclopropenone ring-expansion reactions aiming to synthesize various products (essentially various classes of heterocycles). Since there is no extensive comprehensive review concerned with the chemistry of cyclopropenone derivatives in the construction of heterocycles, the present study would be of great interest.

2 Chemistry

Cyclopropenone (**1a**) (Fig. 1) is a cyclic organic ketone with the molecular formula C_3H_2O composed of a cyclopropene with a ketone functional group. Cyclopropenone (**1a**) is an aromatic compound that polymerizes at room temperature.[23]

The stability of 2,3-diphenylcyclopropenone (**1b**) increases when the substituents are aryl groups. The possible resonance structures of 2,3-diphenylcyclopropenone (**1b**) (Fig. 2) are shown in **A–C** (equivalent to **D**), which contain a three-membered ring of sp^2 carbon coupled to the electron-donor phenyl group in order to stabilize these structures (Fig. 2).[24,25]

Since the first synthesis of cyclopropenone (**1**) was done by Breslow,[26] organic chemists have been quite interested in it. Cyclopropenones are commonly employed as electrophile-trapping agents.[27,28] Due to their high strain[29,30], cyclopropenones easily participate in cycloaddition,[31] ring-opening,[32–34] and ring-enlargement[35–37] reactions. They are also used as organocatalysts in the conversion of aldoximes to nitriles.[38] In addition, they are used as Lewis bases for the organocatalytic transformation of alcohols into alkyl chlorides.[39] The effect of UV irradiation on cyclopropenones and their analogues results in efficient decarbonylation and the generation of the corresponding alkynes.[40–45] Visible light

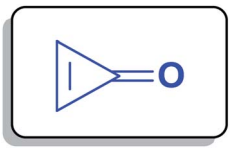

Fig. 1 Structure of cyclopropenone (**1a**).

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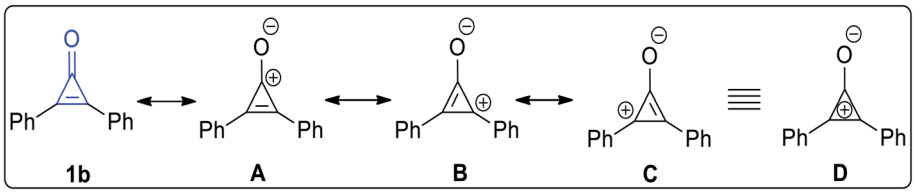


Fig. 2 Resonance structures of 2,3-diphenylcyclopropenone (**1b**).

causes cyclopropenones to undergo decarbonylation and form alkynes.[46] Cyclopropenones can form metal complexes *via* chelation with transition metals at the oxygen center or at the double bond.[47]

2.1. Natural products containing cyclopropenone (1) and biological investigation of cyclopropenones

Numerous extracted natural products have cyclopropenone moieties such as 2-(hydroxymethyl)-cycloprop-2-enone (penitricin) (**A**),[48] 2-((8*S*,8*aR*)-8,8*a*-dimethyl-1,2,3,4,6,7,8,8*a*-octahydronaphthalen-2-yl)cycloprop-2-enone (**B**) and 2-((2*R*,4*aR*,8*aS*)-4*a*-methyl-8-methylenedecahydronaphthalen-2-yl)cycloprop-2-enone (**C**) (Fig. 3).[49] Compound **A** was extracted from *Penicillium aculeatum*, whereas compounds **B** and **C** were extracted from plant sources. It was found that penitricin (**A**) is the only one that showed biological activity as an antibiotic agent.[50]

Besides, alutacenoic acid A (**D**) and alutacenoic acid B (**E**) (Fig. 4) are naturally occurring molecules that contain cyclopropenone structures. They were isolated from common fungi such as *Eupenicillium alutaceum*.[51]

Other types of isolated naturally occurring products **F**, **G** and **H** (Fig. 5) having cyclopropenone moieties are 2-(1-hydroxypropyl)cycloprop-2-enone (**F**), 2-(1-hydroxyoctyl)-cycloprop-2-enone (**G**), and 2-(1-hydroxyhexyl)cycloprop-2-enone (**H**) (Scheme 5). Such compounds showed antibacterial activity more than penitricin (**A**).[52]

Some studies reported in the literature illustrated the utility of diphenylcyclopropenone derivatives for dermatological treatments such as *alopecia areata*, *alopecia totalis*, and *alopecia universalis*.[53,54] Moreover they were used for the treatment of *recalcitrant warts*,[55] and others showed antitumor activities in the treatment of B16 melanoma.[56,57]

2.2. Synthesis of cyclopropenone (1) and its derivatives

2.2.1. From acetals or their formation. Synthesis of cyclopropenone (**1a**) was achieved *via* selective dechlorination using $(C_4H_9)_3SnH$ on perchlorocycloprop-1-ene (**2**) to give 3,3-dichloro-cycloprop-1-ene (**3**). Hydrolysis of **3** led to the formation of compound **1a** in 46% yield (Scheme 1).[58]

The most effective procedure for the synthesis of cyclopropenones was found during the treatment of compounds **4a–e** with equal amounts of boron trifluoride (BF_3) as a Lewis acid in ether to yield substituted cyclopropenones **1c–g** in moderate to excellent yields (Scheme 2).[59]

Another convenient method was known to obtain substituted cyclopropenones **1** in 70–96% yield, *via* the hydrolysis of 6,6-dimethyl-4,8-dioxaspiro[2.5]oct-1-ene derivatives **5** (cyclopropenone acetals) using Amberlyst-15 in acetone or in aqueous tetrahydrofuran (THF) at room temperature (Scheme 3).[60]

Breslow *et al.* also reported on the synthesis of diphenylcyclopropenone (**1b**) by treatment of (2,2-dimethoxyvinyl)benzene (**6**) with (dichloromethyl)benzene in the presence of potassium

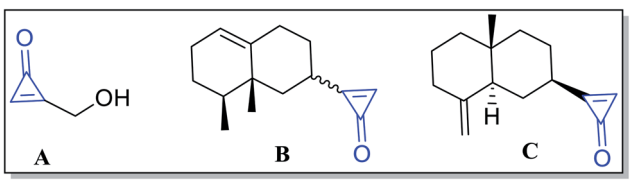


Fig. 3 Naturally occurring compounds A–C containing cyclopropenone molecules.

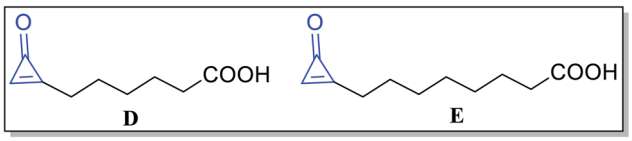


Fig. 4 Naturally occurring acids containing cyclopropenone structures.

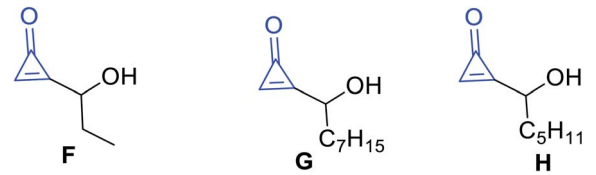
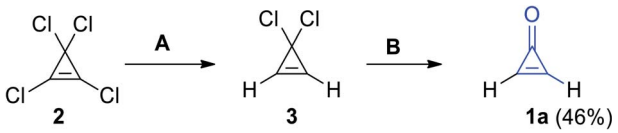
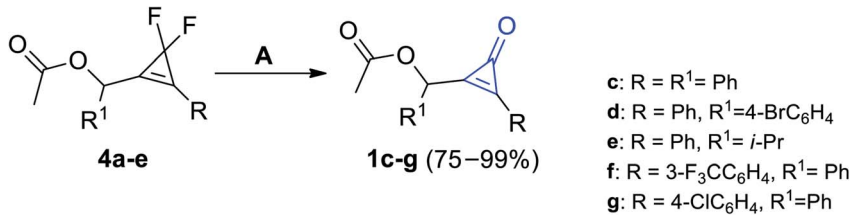


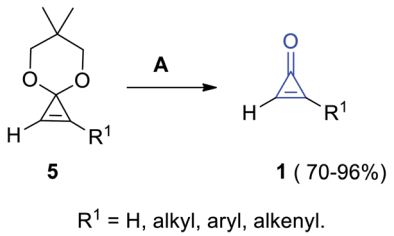
Fig. 5 Structures of naturally occurring compounds F–H.



Scheme 1 Synthesis of cyclopropenone (**1a**) from perchlorocycloprop-1-ene (**2**). *Reagents and conditions*: A = $(C_4H_9)_3SnH$, B = H_2O.



Scheme 2 Synthesis of substituted cyclopropenones **1c–g** using BF_3. *Reagents and conditions*: A = BF_3, Et_2O.



Scheme 3 Hydrolysis of 6,6-dimethyl-4,8-dioxaspiro[2.5]oct-1-ene derivatives **5** into **1**. *Reagents and conditions*: A = Amberlyst-15, MeCOMe or aq. THF, rt.

tert-butoxide (KO-*t*-Bu) to obtain 3,3-dimethoxy-1,2-diphenylcyclopropene (**7**) as an intermediate, which was converted by hydrolysis to give **1b** in 80% yield (Scheme 4).[25]

An alternative method for the synthesis of **1b** was applied during the cycloaddition of phenylmethoxy-acetylene (**8a**) with (dichloromethyl)benzene in the presence of KO-*t*-Bu (Scheme 5).[61]

Cyclopropenones **1h,i** were formed in a low yield (4–7%) *via* the reaction between acetylenes **8b,c** and sodium trichloroacetate (Cl_3COONa) using dimethylethane (DME), as shown in Scheme 6.[62]

McGarrity *et al.* used a rapid injection NMR technique to observe the formation of the cyclopropenium intermediate (**9**) *via* hydrolysis of 1,1-diethoxy-2,3-diphenylcycloprop-2-ene (**7**) in slightly acidic aqueous acetone to obtain diphenylcyclopropenone (**1b**) (Scheme 7).[63]

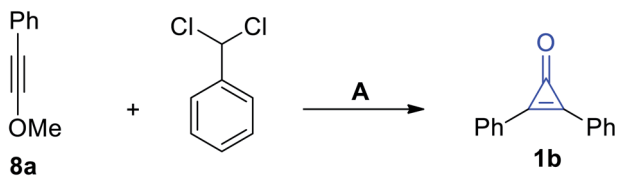
2.2.2. Bromination and/or elimination reaction of bromoketonic compounds. Various substituted cyclopropenones **1j** were synthesized during the reaction of 1-phenyl-2-butanone (**10**) with bromine in DCM and Et_3N. As an example, 2-methyl-3-phenylcycloprop-2-enone (**1**) was obtained in 45% yield (Scheme 8).[64]

The Favorskii reaction was also used to synthesize 2,3-diphenylcyclopropenone (**1b**) in 45% yield during elimination of HBr by the action of Et_3N on dibromodibenzyl ketone (**11a**). The reaction mechanism was the formation of intermediates **12** and **13** (Scheme 9).[65]

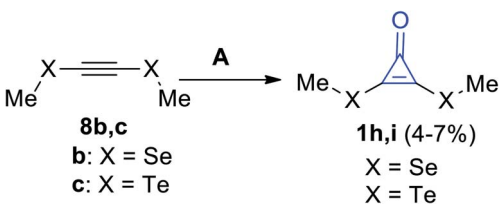
Previously, Curnow *et al.* reported that 2,3-diisopropylcycloprop-2-enone (**1k**) was also obtained in a low yield (18%), *via* dehydrobromination of 3,5-dibromo-2,6-dimethylheptan-4-one (**11b**) using NaH in THF as a solvent, followed by treatment with aqueous HCl (Scheme 10).[66]

2.2.3. Different methods of preparation. 2,3-Bis(methyl-(phenyl)-amino)cycloprop-2-enone (**1l**) was formed in 22% yield (Scheme 11) *via* the hydrolysis of *N*-(2,3-bis(methyl(phenyl) amino)cyclopropylidene)-*N*-methylbenzenaminium (**14**) using aqueous KOH. The reaction was proceeded *via* the formation of intermediate **15**.[67]

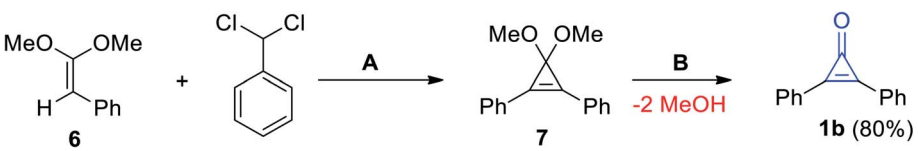
The reaction mixture of **2** with naphthalene and ferrocene in DCM in the presence of aluminum chloride ($AlCl_3$) afforded



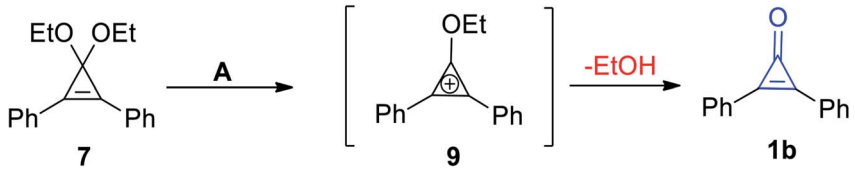
Scheme 5 Synthesis of **1b** from the cycloaddition of phenylmethoxy-acetylene (**8a**) with (dichloromethyl)benzene. *Reagents and conditions*: A = (i) KO-*t*-Bu, (ii) H_2O/H^+.



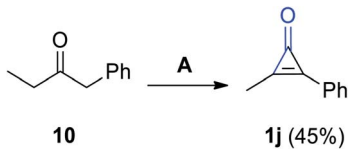
Scheme 6 Formation of cyclopropenone **1h,i** *via* the reaction of acetylenes **8b,c** with Cl_3COONa. *Reagents and conditions*: A = (i) $Cl_3CCOONa$, DME, reflux, (ii) H_2O.



Scheme 4 Synthesis of 2,3-diphenylcyclopropenone (**1b**). *Reagents and conditions*: A = KO-*t*-Bu, B = H_2O/H^+.



Scheme 7 Synthesis of cyclopropenone **1b**. *Reagents and conditions*: A = MeCOMe, H_2O/H_3O^+.



Scheme 8 Synthesis of 2-methyl-3-phenylcycloprop-2-enone (**1j**). *Reagents and conditions*: A = Br_2, CH_2Cl_2, Et_3N, 0 °C.

among other products, diferrocenylcyclopropenone (**1m**) in 41% yield (Scheme 12).[68]

During heating of 1,2,3-trichlorocycloprop-2-en-1-ylium aluminum(III) chloride (**16**) in a mixture of benzene/H_2O, 2,3-diphenylcyclopropenone (**1b**) was obtained in 67% yield (Scheme 13).[69] As compound **16** underwent an electrophilic aromatic substitution (Friedel–Crafts alkylation) during reaction with benzene, which upon heating, *gem*-dichlorodiphenylcyclopropene was obtained. Then, the formed intermediate underwent hydrolysis (during workup) to afford 2,3-diphenylcyclopropenone (**1b**).

Decomposition of 1,3-bis(diazo)-1,3-diphenylpropan-2-one (**17**) in methanol in the presence of Ag_2O yielded compounds **18** and **19**, in addition to 2,3-diphenylcyclopropenone (**1b**), in a 11% yield (Scheme 14).[70]

2.3. Utility of cyclopropenone derivatives in the synthesis of various heterocyclic compounds

2.3.1. Synthesis of four-membered rings with one heteroatom. An example of heterocyclic ring containing an heteroatom was reported.[71] For example, the cyclization reaction of 2-(2-hydroxypropan-2-yl)-3-methylcycloprop-2-enone (**1n**) in CD_3OD and triphenylphosphine (PPh_3) yielded 3-ethylidene-4,4-dimethyloxetan-2-one (**20**) in 60% yield, whereas substituted furanone **21** was also formed as a side product with 39% yield (Scheme 15).[71]

2.3.2. Synthesis of five-membered rings with one heteroatom

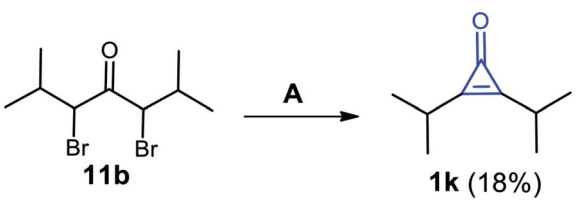
2.3.2.1. Synthesis of pyrrolones. Under microwave (MW) irradiation, the reaction of primary enaminone derivatives **22a–g** with **1b** catalyzed by $Bi(NO_3)_3 \cdot 5H_2O$ afforded the corresponding 2-pyrrolinone derivatives **23a–g** in 42–80% yield. The reaction was performed in toluene in the presence of bismuth nitrate $Bi(NO_3)_3$ as a catalyst (Scheme 16).[72]

The suggested mechanism involves the formation of pyrrolinones **23a–g** initiated *via* coordination between Bi(III) and the oxygen atom in **1b** (Scheme 17). Then, the nitrogen atom of enaminone **22** would attack on carbonyl carbon of (**1**) *via* hard–hard interaction **A**.[72] Proton shift to adduct **B** then occurred to yield intermediate **C**. Thereafter, adduct **C** underwent simultaneous ring expansion and Michael reaction, resulting in the formation of enol **D**, which finally gave 2-pyrrolinones **23a–g** (Scheme 17).[72]

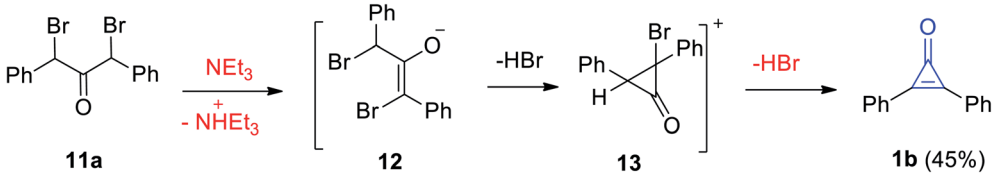
Reaction of (*Z*)-4-((2,2-dimethoxyethyl)amino)pent-3-en-2-one (**24**) and **1b** in refluxing toluene for 6 d, proceeded to give 1-(2,2-dimethoxyethyl)-5-methyl-5-(2-oxopropyl)-3,4-diphenyl-1*H*-pyrrol-2(5*H*)-one (**25**) in 71% yield (Scheme 18).[73]

3-Pyrrolinone derivatives **27a–c** were successfully synthesized in a moderate yield of 42–67%, *via* the reaction of diimines **26a–c** with 2,3-diphenylcyclopropenone (**1b**) in dry ethanol for 2–5 h (Scheme 19).[74]

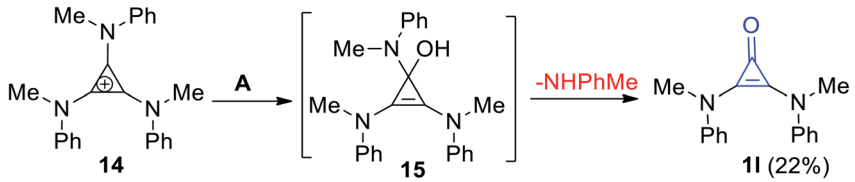
The mechanism of the formation of 3-pyrrolinone **27a–c** is proposed and illustrated in Scheme 20. First, one of the imino



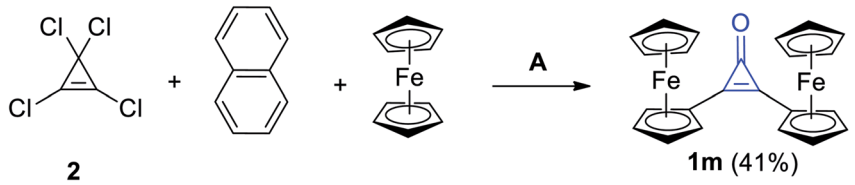
Scheme 10 Synthesis of 2,3-diisopropylcycloprop-2-enone (**1k**). *Reagents and conditions*: A = (i) NaH, THF, (overnight) and (ii) HCl/H_2O.



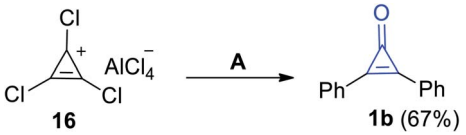
Scheme 9 Synthesis of diphenylcyclopropenone (**1b**) from dibromodibenzyl ketone (**11a**).



Scheme 11 Formation of 2,3-bis(methyl(phenyl)-amino)cycloprop-2-enone (**1l**). *Reagents and conditions*: A = KOH/H_2O, MeOH, rt, 40 h.



Scheme 12 Synthesis of diferrocenylcyclopropenone (**1m**). *Reagents and conditions*: A = $AlCl_3$, CH_2Cl_2, H_2O.



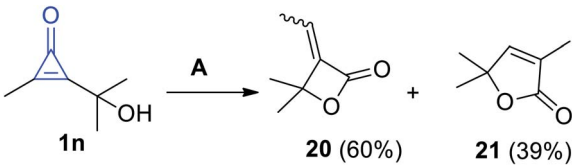
Scheme 13 Synthesis of 2,3-diphenylcyclopropenone (**1b**) from (**16**). *Reagents and conditions*: A = benzene, H_2O.

nitrogen atoms of **26a–c** was added to C-2 of **1b** to obtain the intermediate (**A**). The ketene intermediate (**B**) was then obtained after ring opening, and then imines (**C**) were formed by cyclization *via* the ketene attack on iminium function, and finally, 3-pyrrolinones **27a–c** were formed.[74]

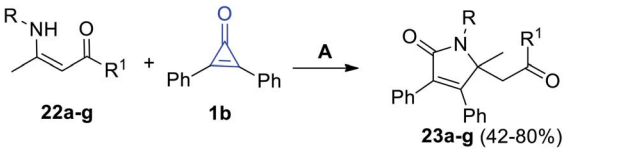
Haito and Chatani used [Rh(OAc)(cod)]$_2$ as a catalyst in the reaction between *N*-(pyridin-2-ylmethyl)pentanamide (**28a**) and 2,3-diphenylcyclopropenone (**1b**). The reaction was performed in toluene in the presence of 2-phenylbenzoic acid (2-PhC_6H_4-COOH) to produce 5-butyl-5-hydroxy-1-(pyridin-2-ylmethyl)-1*H*-pyrrol-2(5*H*)-one (**29a**) as a major product and also gave 5-butylidene-1-(pyridin-2-ylmethyl)-1*H*-pyrrol-2(5*H*)-one (**29b**) as a side product (Scheme 21).[75]

In continuation to the methods dealing with the synthesis of five-membered rings with one heteroatom, using cyclopropenone (**1**), Haito and Naoto Chatani reacted *N*-(pyridin-2-ylmethyl)benzamide (**28b**) with diphenylcyclopropenone (**1b**) in the presence of [Rh(OAc)(cod)]$_2$ as a catalyst. 3,4,5-Triphenyl-1-(pyridin-2-ylmethyl)-1*H*-pyrrol-2(5*H*)-one (**29c**) and 5-hydroxy-3,4,5-triphenyl-1-(pyridin-2-ylmethyl)-1*H*-pyrrol-2(5*H*)-one (**29d**) were obtained in 80% and 9% yields, respectively (Scheme 22).[75]

In 2020, Nanda *et al.* have reported that the reaction of **1b** with various anilines **30a–q** in the presence of palladium acetate

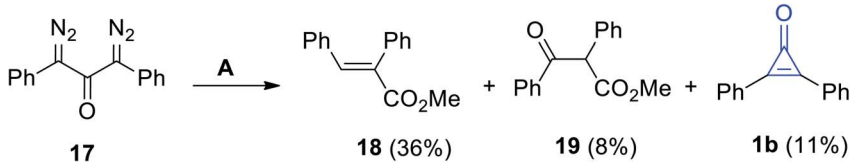


Scheme 15 Synthesis of 3-ethylidene-4,4-dimethyloxetan-2-one (**20**). *Reagents and conditions*: A = PPh_3 (5 mol%), CD_3OD, 25 °C.

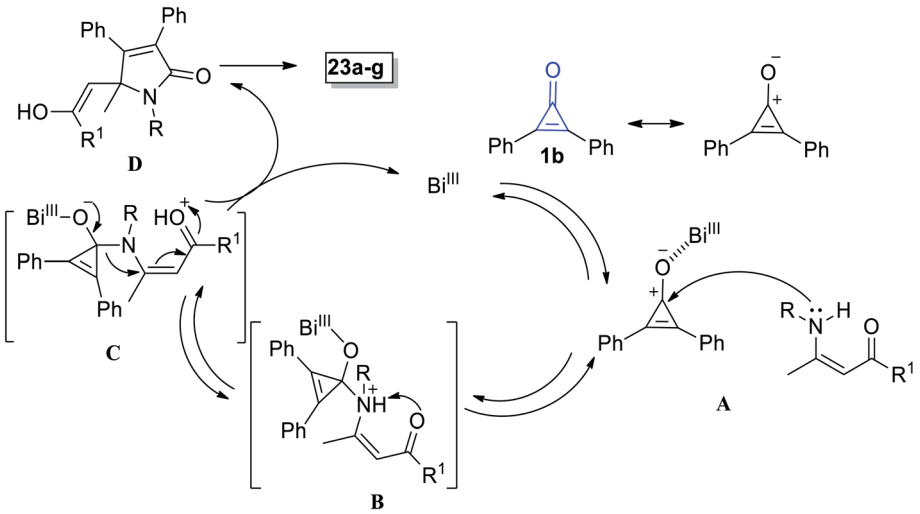


22 and **23**
a: R = H, R^1 = Me
b: R = H, R^1 = OMe
c: R = H, R^1 = OEt
d: R = n-Bu, R^1 = Me
e: R = C_6H_{11}, R^1 = Me
f: R = CH_2CH_2OH, R^1 = Me
g: R = CH_2CH_2OH, R^1 = OEt

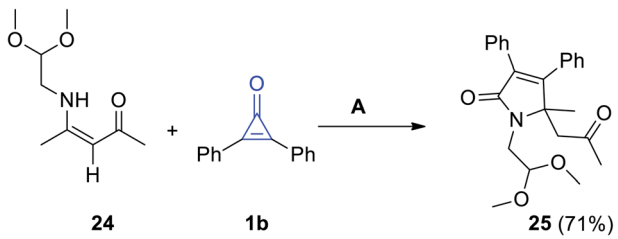
Scheme 16 Synthesis of 2-pyrrolinones **23a–g**. *Reagents and conditions*: A = MW, toluene, $Bi(NO_3)_3 \cdot 5H_2O$, 30–90 min.



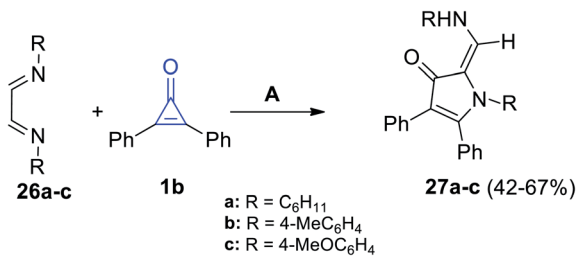
Scheme 14 Oxidation of **17** into diphenylcyclopropenone (**1b**), **18** and **19**. *Reagents and conditions*: A = MeOH, Ag_2O.



Scheme 17 Mechanism of the formation of 2-pyrrolinones **23a–g**.



Scheme 18 Synthesis of compound **25**. *Reagents and conditions*: A = toluene, reflux, 6 d.



Scheme 19 Synthesis of 3-pyrrolinones **27a–c**. *Reagents and conditions*: A = EtOH, 2–5 h.

as the catalyst, tetrabutylammonium bromide as an additive, and sodium acetate as the base at 120 °C for 12 h in DMF (0.25 M) gave substituted pyrroles **31a–q** in 38–80% yield (Scheme 23).[76]

When 1-arylideneamino-2,2,2-trichloroethanols **32a–f** were subjected to **1b** at room temperature in methanol, the reaction produced 2,2′-diaryl-4,4′,5,5′-tetraphenyl-1,1′,2,2′-tetrahydro-3*H*,3′*H*-2,2′-bipyrrole-3,3′-diones **35a–f** in 23–84% yield (Scheme 24), through the formation of intermediates **33** and **34**, respectively.[77]

2.3.2.2. Synthesis of furanones. A series of substituted butenolides were successfully synthesized *via* the reaction between **1b** and β-ketoester derivatives **36a–m** in DME and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as an organocatalyst to produce the substituted 2-furanone derivatives **37a–m** in 41–92% yield (Scheme 25).[78]

Another organocatalyzed synthesis of substituted 2-furanones was achieved by Reitel *et al.* As the chiral compound **39** was used as a catalyst in the reaction between ethyl-3-oxo-3-phenyl-propaneperoxoate (**38**) and **1b** to yield 5-((ethylperoxy)-methyl)-3,4,5-triphenylfuran-2(5*H*)-one (**40**) in 60% yield (Scheme 26).[79]

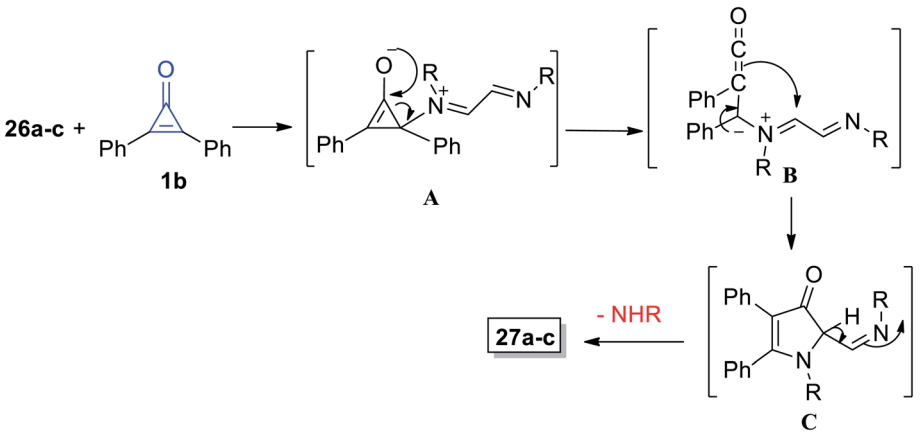
In 2018, Matsuda *et al.* succeeded in synthesizing trisubstituted 2-furanones by using another convenient method. The reaction between formamides **41** and **1b** (10–20 equiv.) was performed for refluxing chlorobenzene, which was catalyzed with silver trifluoromethane-sulfonate (AgTOf) to give diphenylfuranone derivatives **42a–d** in 31–98% yield (Scheme 27).[80]

The suggested mechanism is illustrated as follows: diphenylcyclopropenone underwent ring-opening [3 + 2] annulation and the corresponding formamides **42** were formed (Scheme 28). The carbonyl oxygen atom of **1** was coordinated to Ag^+ to form **A,** C-1 atom of **A** was attacked by the carbonyl oxygen atom of **41** and then the intermediate **B** was obtained. The final step afforded the furane ring *via* ring expansion and regenerated Ag^+.[80]

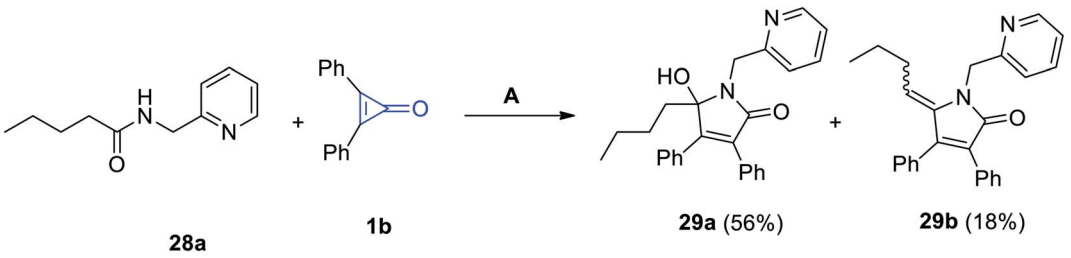
Ren *et al.* in 2018, used silver catalysis to afford other furanone derivatives **42a–m** in 28–92% yield, *via* the reaction between cyclopropenone derivatives **1b,j,o–s** and formamides **41** using silver hexafluoroantimonate(v) $AgSbF_6$ at 80 °C (Scheme 29).[81]

Triphenylphosphine (TPP) mediated the reaction developed by Nguyen *et al.* The reaction occurred between the substituted cyclopropenones **1t** in methanol and TPP at 23 °C to yield butenolides **44a–l** in 36–91% yield *via* the formation of triphenylphosphine ylidene intermediate **43** (Scheme 30).[71]

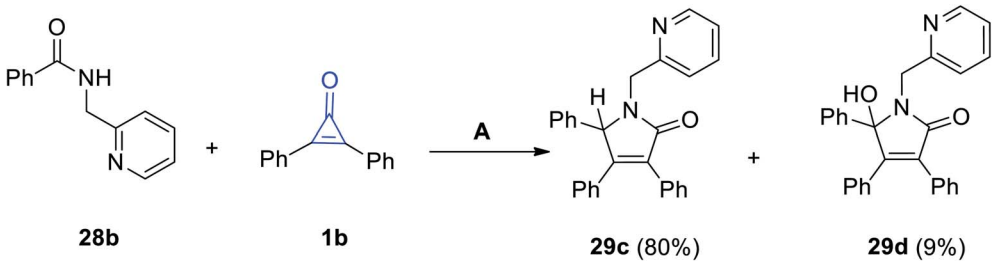
γ-Alkenylbutenolide **47** was synthesized by Bai *et al. via* cycloaddition reaction between **1b** and enones **45** at room



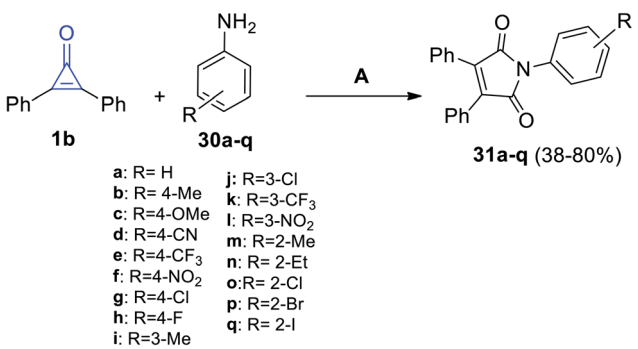
Scheme 20 Mechanism of the formation of 3-pyrrolinone derivatives **27a–c**.



Scheme 21 Synthesis of *N*-pyridymethyl-pyrrol-3-ones **29a** and **29b**. *Reagents and conditions*: A = $[Rh(OAc)(cod)]_2$ (5 mol%), toluene, 140 °C, 12 h.



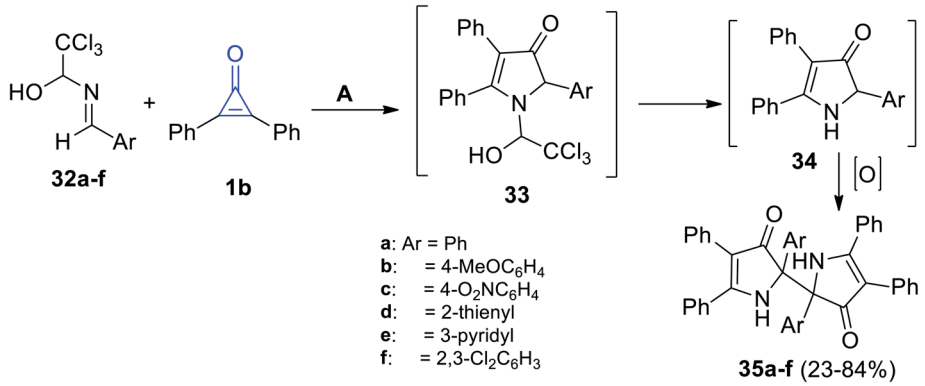
Scheme 22 Synthesis of pyrrol-2-ones **29c**,**d**. *Reagents and conditions*: A = $[Rh(OAc)(cod)]_2$ (10 mol%), toluene 2 ml, 140 °C, 1 h.



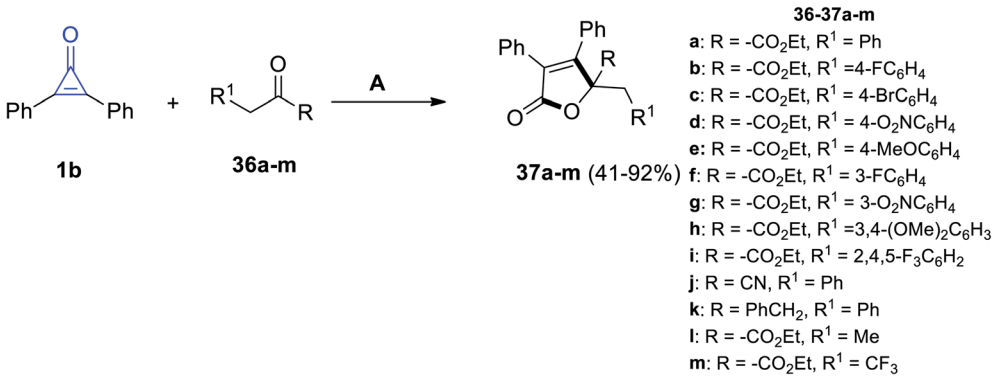
Scheme 23 Palladium-catalyzed synthesis of maleimides **31a–q**. *Reagents and conditions*: A = $Pd(OAc)_2$ (15 mol%), KOAc (4 equiv.), Bu_4NBr (1 equiv.), $K_2S_2O_8$ (1.5 equiv.), DMF (0.25 M), 120 °C, 1 h.

temperature in the presence of Ni complex **46** as an organic catalyst (Scheme 31).[82]

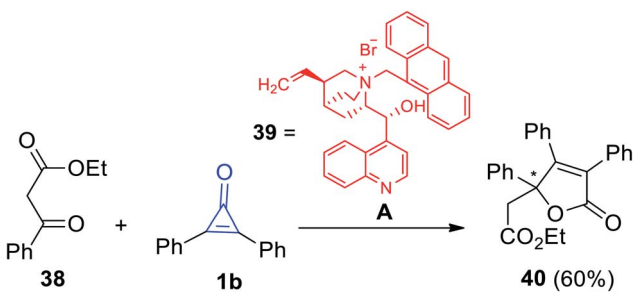
The plausible reaction mechanism was proposed in Scheme 32, as intermediate **A** was obtained by oxidative addition of **1b** to Ni^0. The intermediate **A** was then thought to migrate into the C=O bond *via* intermediate **B** and enantioselective Ni–C(acyl) migratory insertion occurred (path a). The Ni^2–allyl intermediate **C** that resulted reductively removed the final product **47**, allowing the catalyst to be regenerated. Alternatively, or even more probable, the intermediate **B** may go through a concerted 4,1-insertion of the Ni–acyl into the enone, yielding an 8-membered nickelacycle **D** that was a direct predecessor of **C** (path b). The olefin unit is involved in both pathways to allow for allyl stabilization (Scheme 32).[82]



Scheme 24 Synthesis and mechanism describing the formation of compounds **35a–f**. *Reagents and conditions*: A = MeOH, rt.

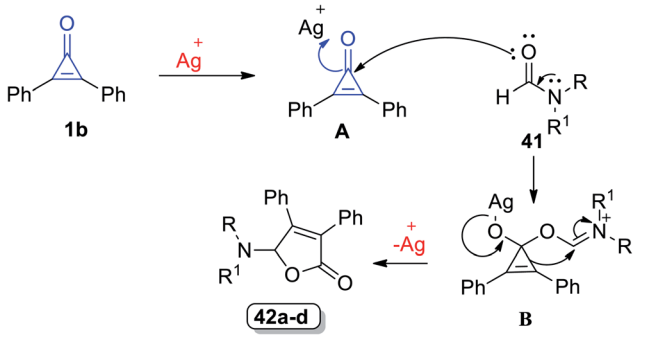


Scheme 25 Synthesis of substituted butanolides **37a–m**. *Reagents and conditions*: A = DBU (20 mol%), DME, rt, 24 h.

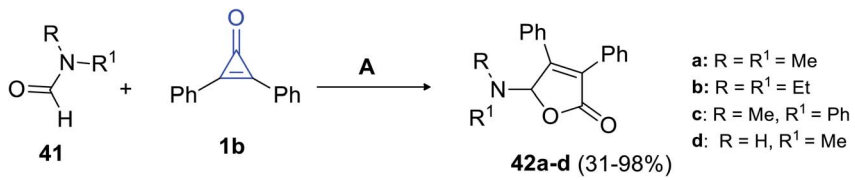


Scheme 26 Synthesis of 5-((ethylperoxy)-methyl)-3,4,5-triphenylfuran-2(5*H*)-one (**40**). *Reagents and conditions*: A = CH_2Cl_2, 50% aq KOH (1 equiv.), rt, 1 h, **39** (20 mol%).

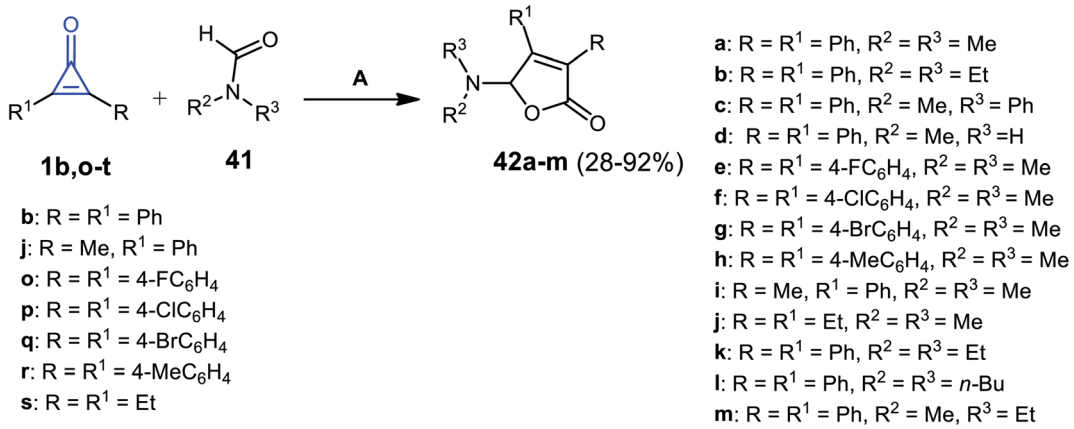
2.3.2.3. Synthesis of various classes of five-membered rings with one heteroatom. 2-(5-(2,3-Diarylcycloprop-2-en-1-ylidene)-2,5-dihydrothiophen-2-yl)malononitriles **49a,b** were obtained in good yield *via* the reaction of 2-(thiophen-2-yl)malononitrile (**48**) with diarylcyclopropenones **1u,v** in refluxing acetic anhydride (Scheme 33).[83]



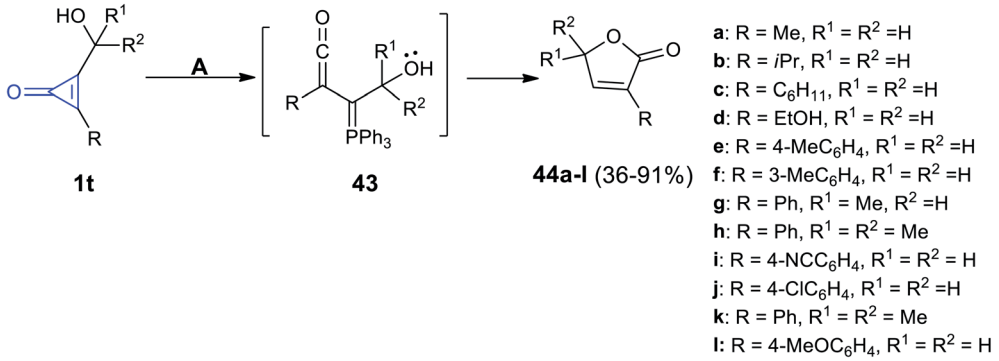
Scheme 28 Mechanism of the formation of diphenylfuranones **42a–d**. *Reagents and conditions*: A = AgTOf (10 mol%), C_6H_5Cl, 130 °C, 2 h.



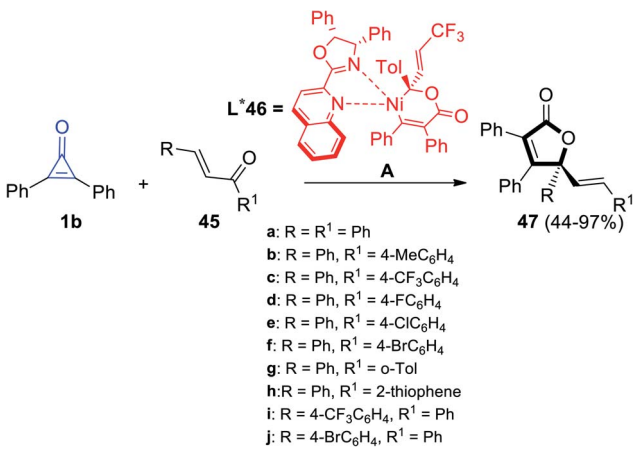
Scheme 27 Synthesis of substituted diphenylfuranones **42a–d**. *Reagents and conditions*: A = AgTOf (10 mol%), PhCl, 130 °C, 2 h.



Scheme 29 Synthesis of compound **42a–m**. *Reagent and conditions*: A = $AgSbF_6$ (10 mol%), 80 °C, 20 h.



Scheme 30 TPP mediated the synthesis of **44a–l**. *Reagents and conditions*: A = PPh_3 (5 mol%), MeOH, 23 °C.



Scheme 31 Synthesis of γ-alkenylbutenolide **47** from enones **45** and **1b**. *Reagents and conditions*: A = $Ni(cod)_2$ (1–2 mol%), L* **46** (2–3 mol%), toluene, rt, 1–24 h.

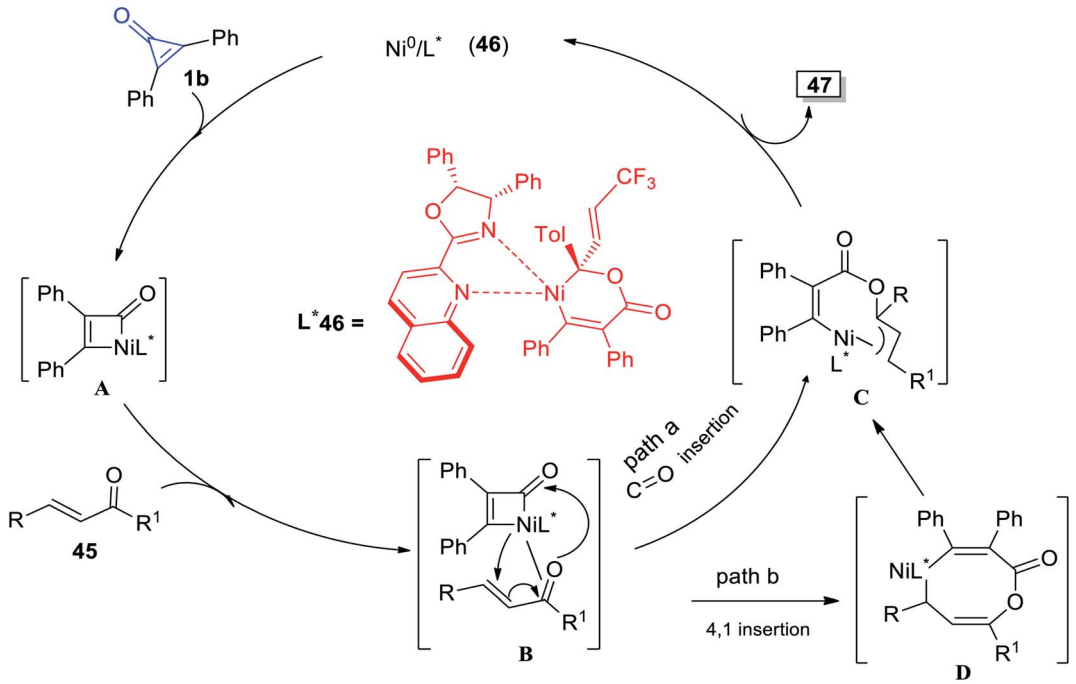
2.3.2.4. Spirocyclic heterocycles with one heteroatom. Spirocyclic heterocycles with one heteroatom were established *via* the reaction of cyclopropenones **1** with organic compounds having various heteroatoms.

Matsuda and Sakurai used gold catalysis in their reaction between 4-methyl-*N*-(3-methylbut-2-en-1-yl)-*N*-(prop-2-yn-1-yl) benzene-sulfonamide (**50**) and cyclopropenone **1j,s,w,x**. The former reaction was carried out in DCM, at room temperature, and in the presence of (IPr)$AuNTf_2$ to give the spiro compounds **51a–d** in 85–97% yield, as shown in Scheme 34.[84]

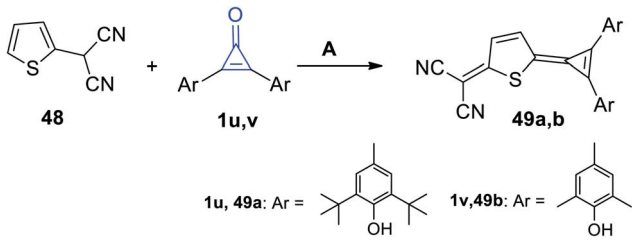
Xu *et al.* succeeded to synthesize the spiro heterocyclic compounds **53** and **54** from the reaction between cyclopropenone derivatives **1b,o,p,q,y** and isatines **52** (Scheme 35). The reaction was carried out in toluene and 4-dimethylaminopyridine (DMAP) as a catalyst at 50 °C. The two isomers of spiro furano-indolinone **53a–h** and **54a–h** were formed in 5–50% and 10–99% yield, respectively.[85]

Previously, Cunha and Rocha had reported that 1,6-diisopropyl-2,7-diphenyl-4-oxaspiro-[2.4]hepta-1,6-dien-5-one (**55**) was synthesized in 48% yield, *via* refluxing 2-isopropyl-3-phenyl-cycloprop-2-en-1-one (**1z**) in dioxane in the presence of copper chloride (CuCl) for 12 h, as shown in Scheme 36.[86]

In 2014, Rivero *et al.* have reported that the reaction between substituted cyclopropenones **1b,a′** and trisubstituted cyclopropanes **56a–j** in DCM catalyzed by scandium(III) trifluoromethane-sulfonate $Sc(OTf)_3$ for 4 h gave the spiro heterocyclic compounds **57a–j** (Scheme 37).[87]



Scheme 32 Mechanism describing the synthesis of γ-alkenylbutenolide **47**.

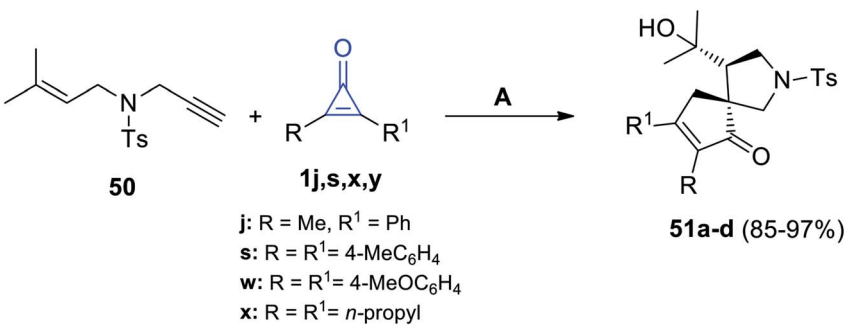


Scheme 33 Reaction of 2-(thiophen-2-yl)malononitrile (**48**) with diarylcyclopropenones **1u,v**. *Reagents and conditions*: A = Ac_2O, reflux.

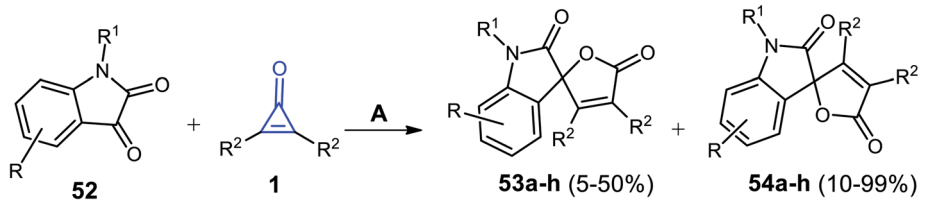
1,2-Bis(2-methoxy-5-methylphenyl)-6,7-diphenyl-4-oxaspiro [2.4]hepta-1,6-dien-5-one (**59**) was obtained in 70% yield *via* the reaction of two derivatives of cyclopropenones **1b** and **1b′** together with compound **2** in the presence of CuBr as a catalyst. One of these cyclopropenones was synthesized from the reaction of **58** with **2** in $AlCl_3/CH_2Cl_2$ at −20 °C (Scheme 38).[88] The reaction was due to the formation of **1c′** (Scheme 38).[88]

Then, we proceeded to the formation of fused compounds such as indoles **61a–g**, which were obtained in 45–85% yield, *via* the reaction between *N*-nitrosoanilines **60** and cyclopropenones **1b,r,d′** in the presence of $[RhCp^*(OAc)_2]$ and $AgNTf_2$ in DCE at 120 °C for 24 h (Scheme 39).[89]

The interesting approach to prepare compounds containing indole moieties is outlined in Scheme 40. The strategy started with treatment compound **62** with trimethylsilyl trifluoromethanesulfonate (TMS-OTf), Et_3N and $TiCl_4$ (method **A**). Oxidation of **63** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in $CHCl_3$ (method **B**) afforded compound **64**. Rearrangement of **64** using methyl trifilate (MeOTf) (method **C**) gave the corresponding compound **65** (Scheme 40).[90] Upon heating **65** with cyclopropenone (**1a**) in MeCN (method **D**), the reaction gave the target products **66a** in 89% yield together with its



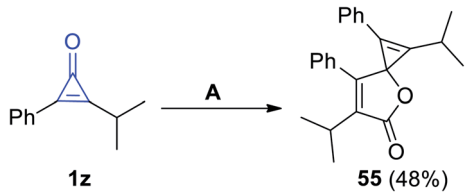
Scheme 34 (IPr)$AuNTf_2$-catalyzed synthesis of compounds **51a–d**. *Reagents and conditions*: A = (IPr)$AuNTf_2$ (2 mol), DCM, rt.



b: R^2 = Ph
o: R^2 = 4-FC_6H_4
p: R^2 = 4-ClC_6H_4
q: R^2 = 4-BrC_6H_4
y: R^2 = *n*-BuC_6H_4

53-54a-h
a: R = Bn, R^1 = H, R^2 = Ph
b: = Me, R^1 = H, R^2 = Ph
c: = Boc, R^1 = H, R^2 = Ph
d: = R^1 = H, R^2 = Ph
e: = Bn, R^1 = 5-OMe, R^2 = 4-*n* BuC_6H_4
f: = Bn, R^1 =5-F, R^2 = 4-FC_6H_4
g: = Bn, R^1 = 5-Cl, R^2 = 4-ClC_6H_4
h: = Bn, R^1 =5-Br, R^2 = 4-BrC_6H_4

Scheme 35 Synthesis of spiro furano-indolinone **53a–h** and **54a–h**. *Reagents and conditions*: A = DMAP (20 mol%), toluene, 50 °C, 6 h.

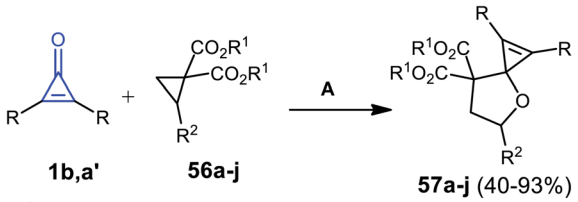


Scheme 36 Synthesis of the spiro compound **55**. *Reagents and conditions*: A = dioxane, CuCl, 12 h.

diastereomer **66b** (Scheme 40). The two diastereomers **66a,b** were used as precursors in the synthesis of (±) Aspergilline A.[90]

Cunha *et al.* reported on a direct path to obtain pyrrolizidine **68** and indolizidine **69** by the reaction of **67** with **1b** in refluxing toluene (Scheme 41).[91]

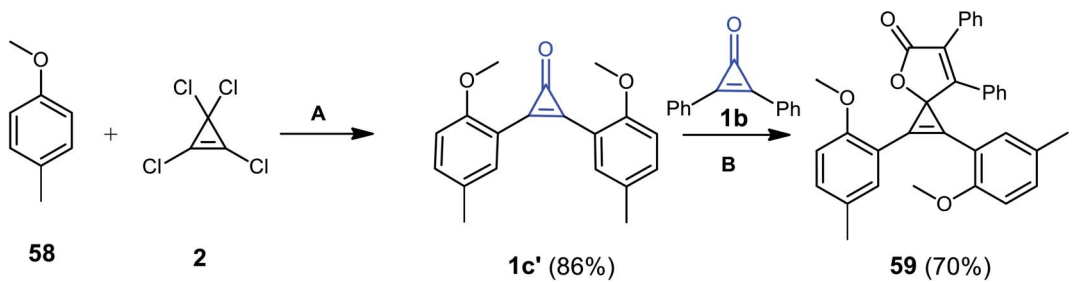
Recently, in 2021, Yao *et al.* reacted dimethyl 2-(1,11-diphenylundeca-1,3,8,10-tetrayn-6-yl)malonate (**70**) with cyclopropenone derivatives **1j,o,p,r** under the stream of O_2 to give the



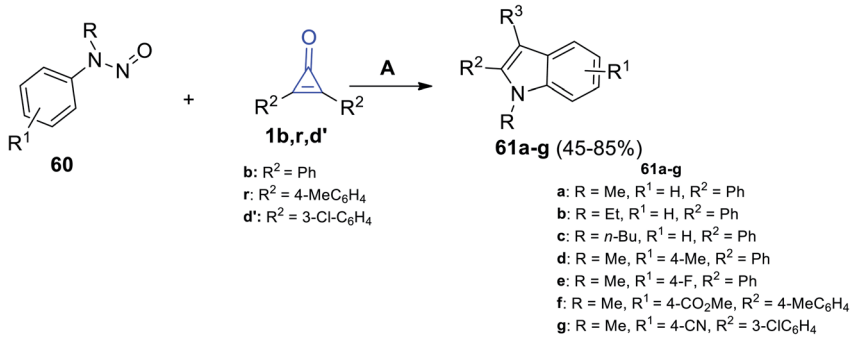
b: R = Ph
a': R= Et

57a-j
a: R = R^2 = Ph, R^1= Et
b: R = R^2 = Ph, R^1= Me
c: R = Ph, R^1= Me, R^2= 4-$MeOC_6H_4$
d: R = Ph, R^1= Me, R^2= 4-FC_6H_4
e: R = Ph, R^1= Me, R^2= 4-BrC_6H_4
f: R = Ph, R^1= Me, R^2= 4-NC-C_6H_4
g: R = Ph, R^1= Me, R^2= 4-$O_2NC_6H_4$
h: R = Ph, R^1= Et, R^2= isoindoline-1,3-dione
i: R = Ph, R^1= Me, R^2= isoindoline-1,3-dione
j: R =Et, R^1= Me, R^2= isoindoline-1,3-dione

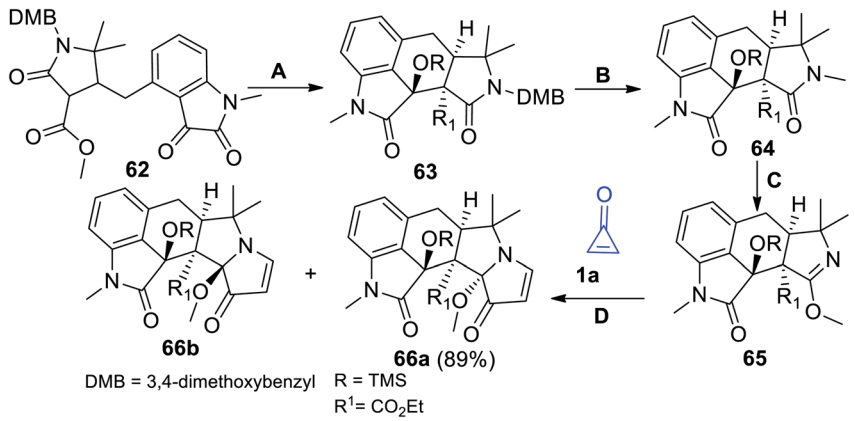
Scheme 37 $Sc(OTf)_3$ mediated the synthesis of **57a–j**. *Reagents and conditions*: A = $Sc(OTf)_3$ (10 mol%), DCM, 25 °C 4 h.



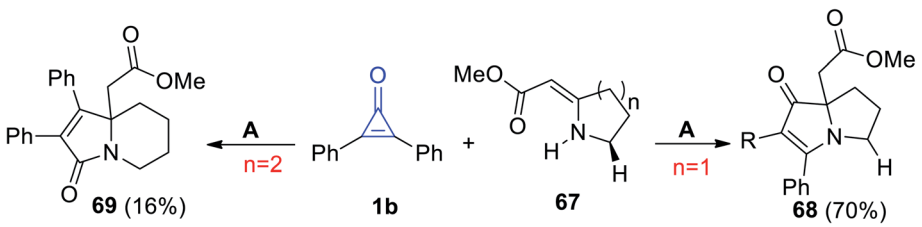
Scheme 38 Synthesis of 1,2-bis(2-methoxy-5-methylphenyl)-6,7-diphenyl-4-oxaspiro[2.4]hepta-1,6-dien-5-one (**59**). *Reagents and conditions*: A = (i) $AlCl_3$, CH_2Cl_2, −20 °C, 45 min; (ii) H_2O; B = CuBr, CH_2Cl_2, 70 °C, 12 h.



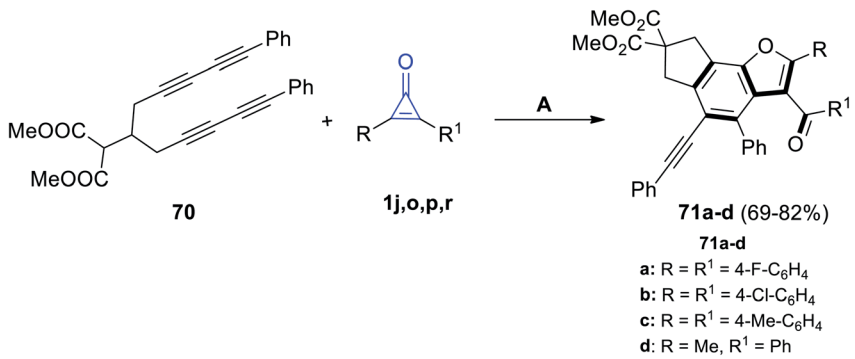
Scheme 39 Synthesis of indoles **61a–g**. *Reagents and conditions*: A = [RhCp*(OAc)$_2$], AgNTf$_2$, DCE, 120 °C, 24 h.



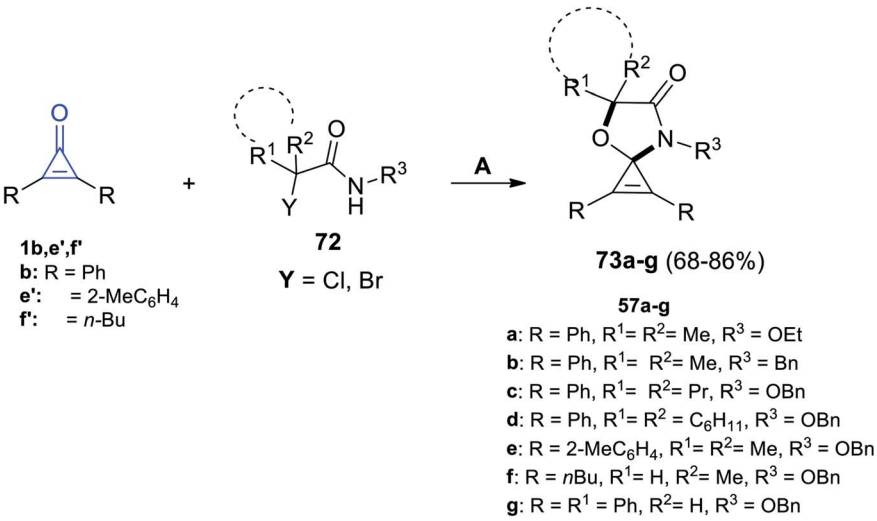
Scheme 40 Synthesis of compounds **66a**,**b**. *Reagents and conditions*: A = TMS-OTf, Et$_3$N, DCM, TiCl$_4$, 0–35 °C; B = CHCl$_3$, DDQ, H$_2$O, 70 °C; C = MeOTf, CH$_2$Cl$_2$; D = MeCN, 50 °C.



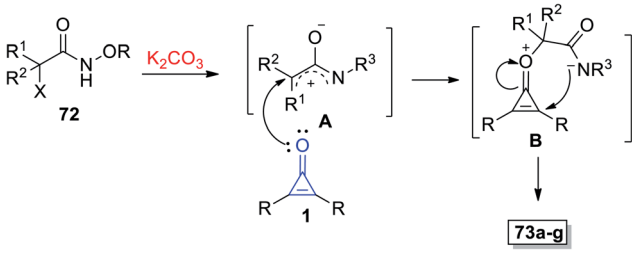
Scheme 41 Synthesis of pyrrolizidine **68** and indolizidine **69**. *Reagents and conditions*: A = toluene, reflux.



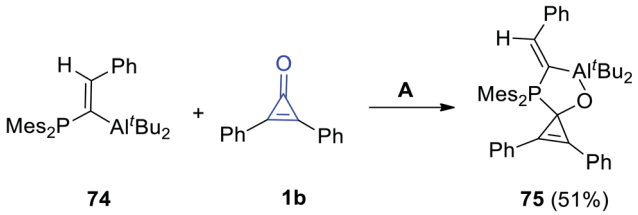
Scheme 42 Synthesis of benzo[*b*]furane derivatives **71a–d**. *Reagents and conditions*: A = O$_2$, MeCN, reflux, 12 h.



Scheme 43 Synthesis of spiro oxazoles **73a–g**. *Reagents and conditions*: A = K_2CO_3 (0.8 mmol), HFIP (2 ml), 50 °C, 12 h.



Scheme 44 Mechanism illustrating the formation of spiro oxazoles 73a–g.



Scheme 45 Synthesis of spiro compound **75**. *Reagents and conditions*: A = *n* pentane, −40 °C, overnight.

benzo[*b*]furan derivatives **71a–d** in 69–82% yield, as shown in Scheme 42.[92]

2.3.2.5. Five-membered rings with two heteroatoms. Using hexafluoroisopropanol (HFIP) and potassium carbonate (K_2CO_3) in the reaction between cyclopropenone derivatives **1b,e′,f′** and α-halohydroxamate **72** afforded the spiro oxazoles **73a–g** in 68–86% yield (Scheme 43).[93]

The mechanism described the formation of **73a–g** as an initiation step using K_2CO_3, and **72** was converted *in situ* into azaoxyallyl cation intermediate **A.** Thereafter, the azaoxyallyl cation **A** gave the zwitterionic intermediate **B** after addition of carbonyl oxygen in the cyclopropenone **1.** Finally, the spirocyclic oxazoles **73** were obtained by intramolecular nucleophilic addition of **B**, as illustrated in Scheme 44.[93]

When (*E*)-di-*t*-butyl(1-(dimesitylphosphino)-2-phenylvinyl) aluminum (**74**) reacted with **1b** in *n*-pentane at −40 °C, the spiro product **75** was produced in 51% yield (Scheme 45).[94]

In 2020, Wu *et al.* had reported that the reaction between diaryl cyclopropenones **1j,g′–o′** and elemental sulfur in dimethylformamide (DMF) at room temperature for 12 h provided disubstituted dithiolone derivatives **76a–j** in 25–98% yield, as shown in Scheme 46.[95]

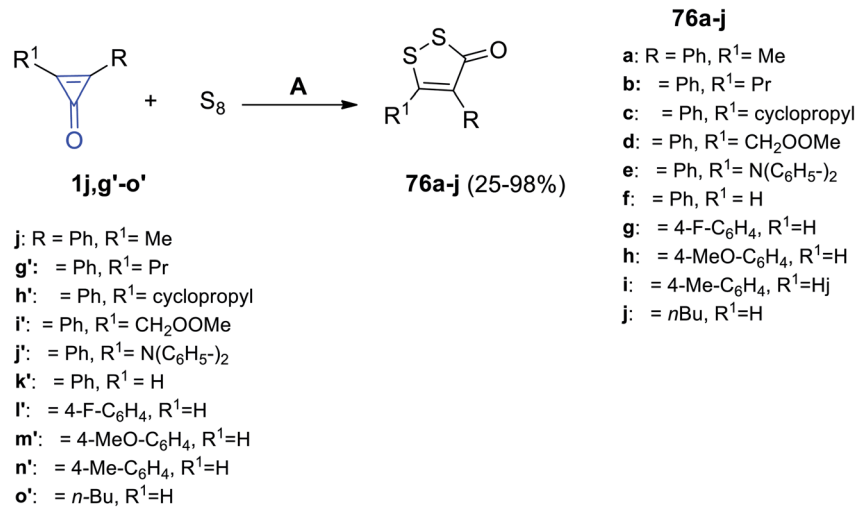
[1,2]Dithiolo[5,1-*e*][1,2]dithiole derivatives **78a–d** were successfully synthesized in 40–51% yield, by refluxing two moles of cyclopropenones **1** in DCM at 70 °C in the presence of CuBr, the spironolactone intermediate **77** was formed and then reacted with elemental sulfur in DMF at 50 °C for 5 h to give the targeted compounds (Scheme 47).[95]

Similarly, Wu *et al.* also succeeded to obtain diselenolone derivatives **79a–f** in 76–85% yield (Scheme 48), *via* the reaction between cyclopropenones **1** and elemental selenium in dimethylsulfoxide (DMSO) at 120 °C under N_2 flow for 12 h.[95]

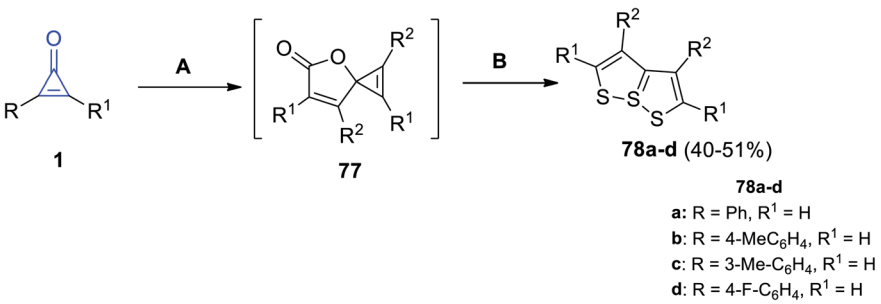
2.3.2.6. Five-membered rings with three heteroatoms. When 4-phenyl-1-tosyl-1*H*-1,2,3-triazole (**80**) reacted with of 2,3-diphenylcyclopropenone (**1b**) in DCE for 2.5 h, 2,2′-(2,3-diphenylcycloprop-2-ene-1,1-diyl)bis(4-phenyl-2*H*-1,2,3-triazole) (**81**) was obtained in 97% yield (Scheme 49).[96]

Hassan *et al.* reported that a series of thiadiazoles **83a–p** were obtained in 69–84% yield, *via* a catalyst-free reaction between **1b** and alkenylidene hydrazine carbothioamides **82a–p** in dry ethanol.[97]

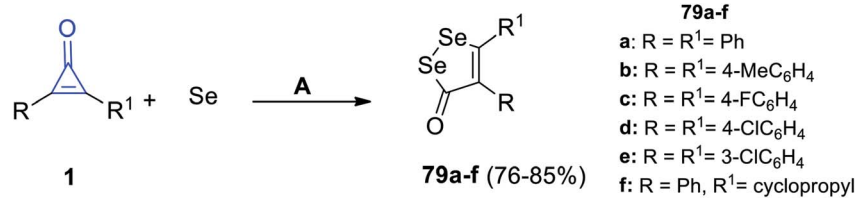
The reaction mechanism was explained by the attack of the azomethine (CH=N) nitrogen atom of compound **82** to the carbonyl group of **1b.** The mechanism of the reaction was explained by the formation of intermediate **B** *via* a spontaneous



Scheme 46 Synthesis of dithiolone derivatives **76a–j**. *Reagents and conditions*: A = KF, DMF, air, rt, 12 h.

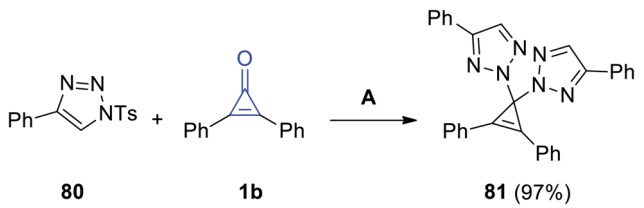


Scheme 47 Synthesis of [1,2]dithiolo[5,1-*e*][1,2]dithioles **78a–d**. *Reagents and conditions*: A = CuBr (5 mol%), DCM, 75 °C, N_2,12 h, B = KF (2 equiv.), S_8, DMF, 50 °C, air, 5 h.



Scheme 48 Synthesis of diselenolone derivatives **79a–f**. *Reagents and conditions*: A = DMSO, N_2, 120 °C, 12 h.

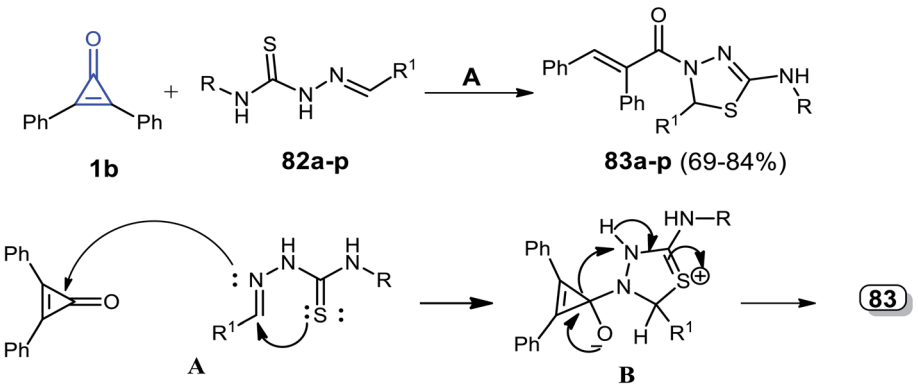
intramolecular nucleophilic attack of the sulfur atom lone pair on the CH=N group. That was followed by cyclization, *via* the formation of intermediate **B**, which rearranged to the final product **83** (Scheme 50 and Table 1).[97]



Scheme 49 Synthesis of 2,2′-(2,3-diphenylcycloprop-2-ene-1,1-diyl) bis(4-phenyl-2*H*-1,2,3-triazole) (**81**). *Reagents and conditions*: A = DCE, 80 °C, 2.5 h.

Aly *et al.* reported that the reaction mixture of **1b** and ylidene-*N*-phenylhydrazine-carbothioamides **84a–e** in glacial acetic acid at room temperature afforded 2,5,6,7-tetrasubstituted-pyrrolo [2,1-*b*](1,3,5-oxadiazolyl)-2-amines **85a–e** in 60–76% yield (Scheme 51).[98]

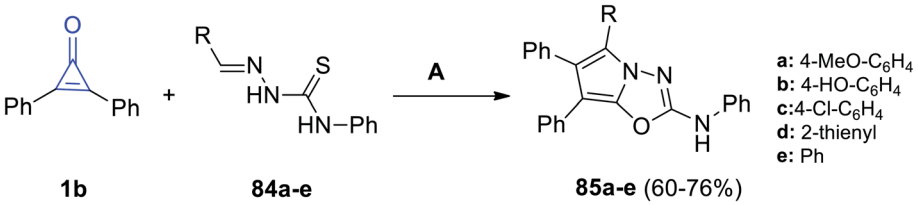
The suggested mechanism is explained as follows: the afforded product structures supported the formal [2 + 3] cycloaddition pathway proposed by Eicher to generate the adducts (**A**). This was followed by cyclization of intermediate (**B**) with aromatization of the pyrrole ring. Eventually, intermediate **B** lost a molecule of hydrogen sulfide and the final product **85** was formed, as shown in Scheme 52.[98]



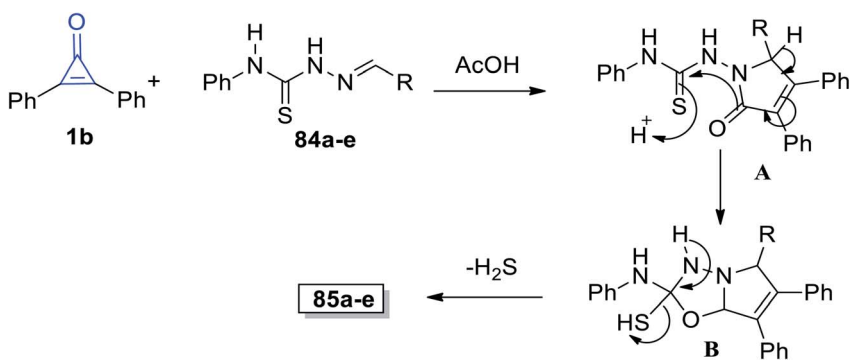
Scheme 50 Synthesis and mechanism of thiadiazoles **83a–p**. *Reagents and conditions*: A = EtOH, 4–8 h.

Table 1 Substituents and the yield of thiadiazoles **83a–p**

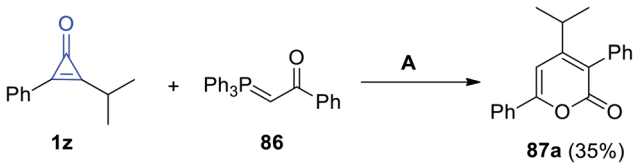
	R	R^1	Yield (%)
a	Ph–	C_6H_5–CH=CH (*E*)	82
b	Bn–	C_6H_5–CH=CH (*E*)	75
c	CH_2=CH–CH_2–	C_6H_5–CH=CH (*E*)	70
d	Ph–	2- MeO–C_6H_4–CH=CH (*E*)	72
e	Bn–	2- MeO–C_6H_4–CH=CH (*E*)	76
f	CH_2=CH–CH_2–	2- MeO–C_6H_4–CH=CH (*E*)	68
g	Ph–	C_6H_5–CH=C–Me_2 (*E*)	84
h	Ph–	Me–$(CH_2)_2$–CH=CH– (*E*)	83
i	Bn–	Me–$(CH_2)_2$–CH=CH– (*E*)	65
j	CH_2=CH–CH_2–	Me–$(CH_2)_2$–CH=CH– (*E*)	71
k	Ph–	Me–CH=CH– (*E*)	75
l	Bn–	Me–CH=CH– (*E*)	71
m	CH_2=CH–CH_2–	Me–CH=CH– (*E*)	67
n	Ph–	Me_2–CH–	76
o	Bn–	Me_2–CH–	74
p	CH_2=CH–CH_2–	Me_2–CH–	69



Scheme 51 Synthesis of pyrrolo[2,1-*b*](1,3,5-oxadiazolyl)-2-amines **85a–e**. *Reagents and conditions*: A = AcOH, 4–8 h.



Scheme 52 Mechanism of the formation of pyrrolo[2,1-*b*](1,3,5-oxadiazolyl)-2-amines **85a–e**.



Scheme 53 Synthesis of 4-isopropyl-3,6-diphenyl-2*H*-pyran-2-one (**87a**). *Reagents and conditions*: A = benzene, reflux, 5 h.

2.3.3. Synthesis of six-membered rings

2.3.3.1. Six-membered rings with one heteroatom. On reacting 2-isopropyl-3-phenylcycloprop-2-en-1-one (**1z**) with 1-phenyl-2-(triphenyl-phosphoranylidene)ethanone (**86**) in benzene for 5 h, 4-isopropyl-3,6-diphenyl-2*H*-pyran-2-one (**87a**) was obtained in 35% yield (Scheme 53).[86]

Furthermore, Zhou *et al.* reported on the synthesis of a series of 2-pyranone derivatives **87b–j** in 52–93% yield, that was achieved by the reaction between β-ketosulfoxonium ylides **1b** in MeCN at 100 °C for 12 h, and dichloro(pentamethyl-cyclopentadienyl)-rhodium(III) dimers $(Cp^*RhCl_2)_2$ (Scheme 54).[99]

The reaction between 2-arylcycloprop-2-enones **1** and substituted 2-indolones **89** at 25 °C in acetonitrile for 1 h and DABCO was used as an organic catalyst to form compound **90a–n** in 67–92% yield (Scheme 55).[100]

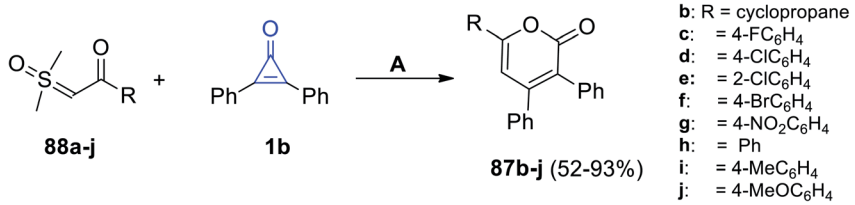
The mechanism was described as follows. First, DABCO subtracts one proton from two to form the nucleophile **A**, on the less sterically hindered side. Thereafter, 1,4-addition of the C=C bond of **1** was initiated *via* nucleophile **A**, yielding the enolate intermediate **B**. The intermediate **B** was then added intermolecularly to another molecule of **1** to form intermediate **C**, which was converted to intermediate **D** by a concerted process after the ring-opening process and intramolecular nucleophilic addition; after that, it was passed through another ring-opening step to produce intermediate **E**, which after protonation gave the final product **90**, and the catalyst was regenerated (Scheme 56).[100]

A series of substituted diaryl spiro[cycloprop[2]ene-1,9′-xanthene] derivatives **92a–j** were successfully synthesized in 40–80% yield, *via* the reaction between compound **91a–d** (2.5 equiv.) and diaryl cyclopropenones **1** (1 equiv.) (Scheme 57). The reaction was performed in MeCN using cesium fluoride (CsF) as a catalyst at 30 °C for 24 h.[101]

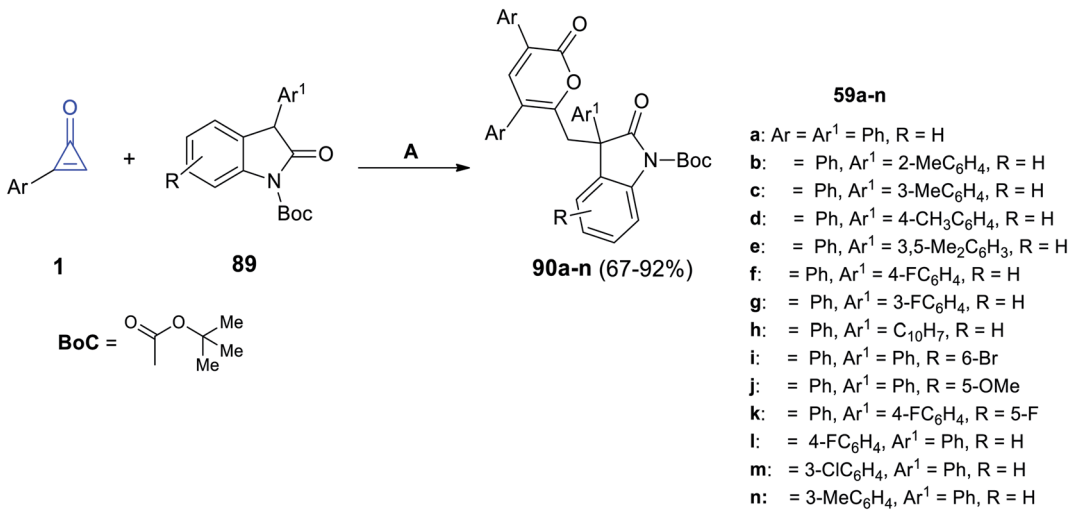
The rhodium-catalyzed reaction occurred between substituted *N*-nitrosoanilines **60** and **1b** in the presence of $AgBF_4$ and DCE at 100 °C for 12 h. The quinoline-4-one derivatives **93a–f** were produced in 46–70% yield, as shown in Scheme 58.[102]

Moreover, in 2020, Shi *et al.* reacted with **1b** with *N*-nitrosoanilines **60** using $[RhCp^*(OAc)_2]$, $[Rh(COD)Cl]_2$ and $AgBF_6$ in DCM and yielded 4-quinolones **93a–h** in 51–85% yield (Scheme 59).[89]

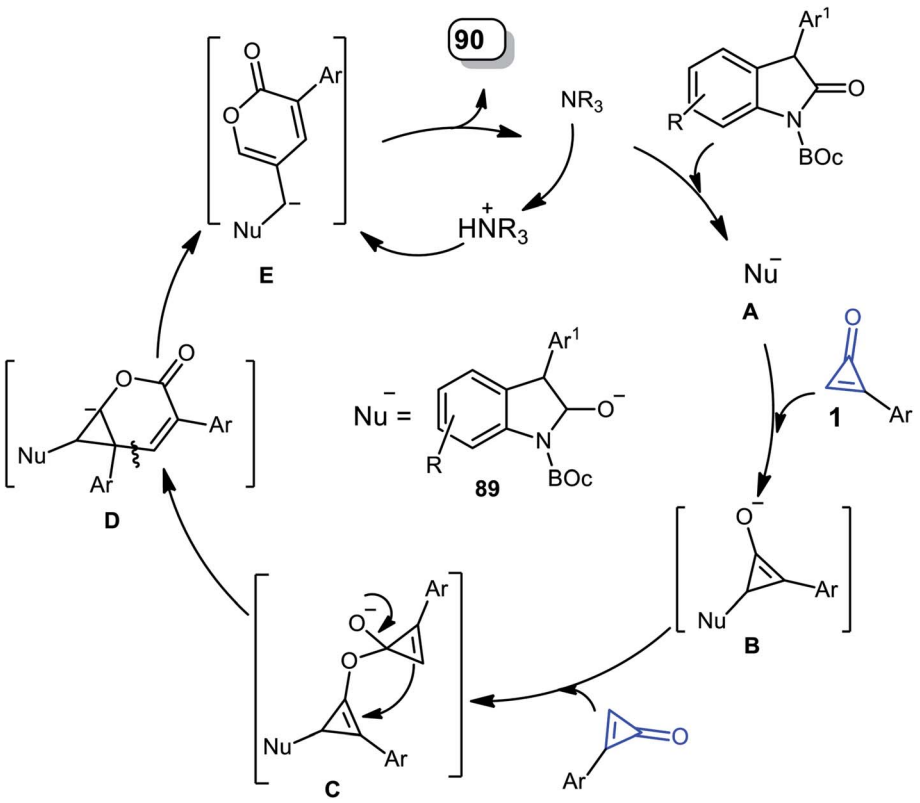
(3*S*,4*aS*,9*bS*)-Diethyl-3-methyl-4-oxo-4*a*-phenyl-1,4,4*a*,9*b*-tetrahydrobenzofuro[3,2-*b*]pyridine-2,2(3*H*)-dicarboxylates **96a–**



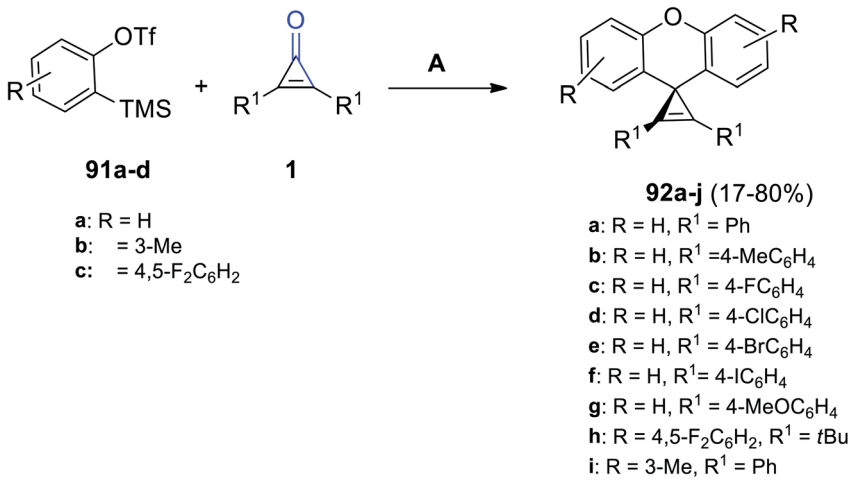
Scheme 54 Synthesis of 2-pyranone derivatives **87b–j**. *Reagents and conditions*: A = $(Cp^*RhCl_2)_2$, NaOAc, MeCN, 100 °C, 12 h.



Scheme 55 Synthesis of compound **90a–n**. *Reagents and conditions*: A = DABCO (20 mol%), MeCN, 25 °C, 1 h.



Scheme 56 Mechanism describing the formation of **90a–n**.



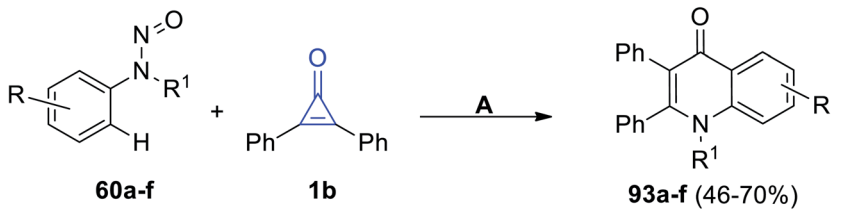
Scheme 57 Synthesis of substituted diaryl spiro[cycloprop[2]ene-1,9′-xanthene] derivatives **92a–j**. *Reagents and conditions*: A = CsF, MeCN, 30 °C, 24 h.

d were synthesized *via* the reaction of (*E*)-diethyl 2-((2-hydroxybenzylidene)amino)malonate derivatives (**94**) with **1j** at room temperature in the presence of the catalyst **95** (Scheme 60).[103]

In 2020, it was reported that phenanthridine derivatives **98a–d** were synthesized in 67–82% yield, *via* refluxing [1,1′-biphenyl]-2-amine (**97**) with substituted cyclopropenones **1** in DCM for 48 h and in the presence of $[Ru(p\text{-cymene})Cl_2]_2$ and Ag_2CO_3 (Scheme 61).[104]

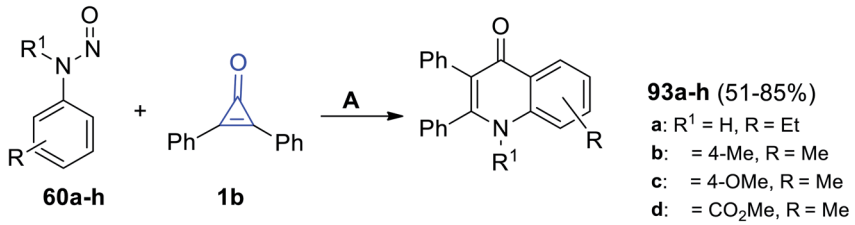
Substituted pyrido[3,4-*b*]indoles **99a–j** could react easily with cyclopropenone derivatives **1** at room temperature in absolute ethanol for 5–50 h. The reaction yielded compounds **100a–j** in 39–93% yield (Scheme 62).[105]

Refluxing diarylcyclopropenones **1** in pyridine at 100 °C in the presence of cupric acetate ($Cu(OAc)_2$) afforded biindolizines **101a–b**, as shown in Scheme 63.[106]



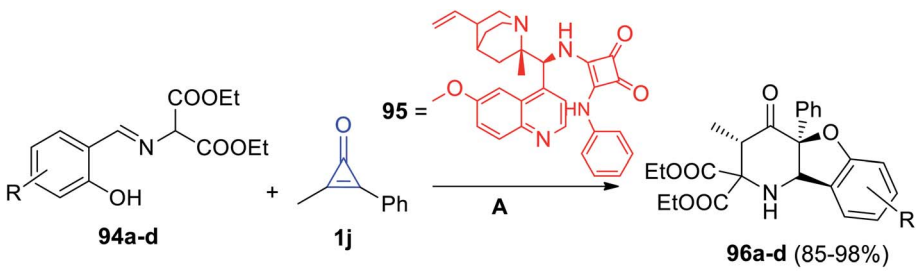
a: R = H, R^1 = Et
b: = 4-Me, R^1 = Me
c: = 4-OMe, R^1 = Me
d: = COOMe, R^1 = Me
e: = 4-F, R^1 = Me
f: = H, R^1 = *n*Bu

Scheme 58 Rhodium(III)-catalyzed synthesis of quinoline-4-one derivatives **93a–f**. *Reagents and conditions*: A = $(Cp^*RhCl_2)_2$ (2 mol%), $AgBF_4$ (1.2 equiv.), NaF, DCE, 100 °C, 12 h.



a: R^1 = H, R = Et
b: = 4-Me, R = Me
c: = 4-OMe, R = Me
d: = CO_2Me, R = Me
e: = 4-F, R = Me
f: = H, R = *n*Bu
g: = H, R = Me
h: = Me, R = 4-CN

Scheme 59 Synthesis of 4-quinolones **93a–h**. *Reagents and conditions*: A = $[RhCp^*(OAc)_2]$ (0.5 mol%), $[Rh(COD)Cl]_2$, $AgBF_6$ (0.02 mmol), DCM, 120 °C, 36 h.



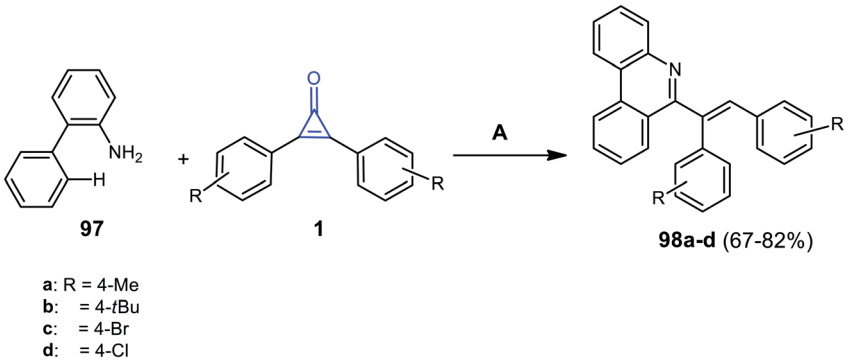
94 and **96a-d**
a: R = 8-Cl
b: = 8-Br
c: = 8-Me
d: = 7-OMe

Scheme 60 Synthesis of compounds **95a–d**. *Reagents and conditions*: A = mesitylene, rt, cat **96**.

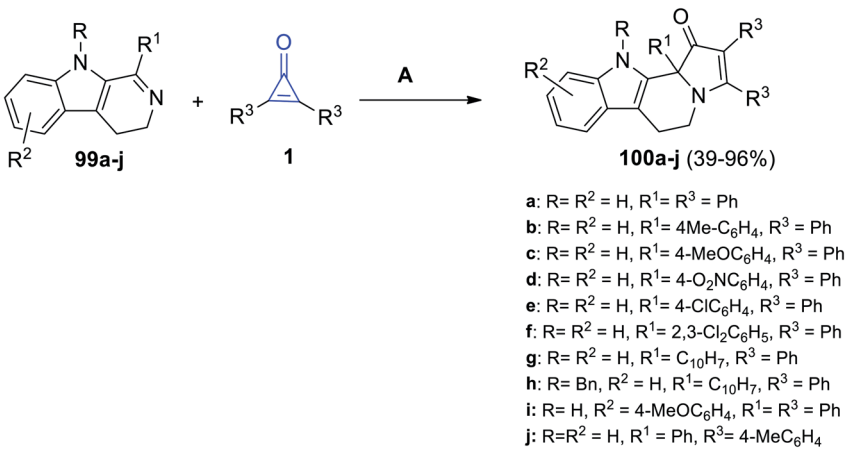
7-Methyl-1-phenyl-3,4-dihydrobenzo[*b*][1,7]naphthyridine (**102**) easily reacted with cyclopropenones **1** without using any catalyst at room temperature in EtOH to afford 2,3-disubstituted-9-methyl-12*b*-phenyl-5,6-dihydrobenzo[*b*]pyrrolo[1,2-*h*][1,7]naphthyridin-1(12*bH*)-ones **103a–b** in 45–56% yield, as shown in Scheme 64.[105]

Carbonylation of symmetrical cyclopropenones **1** with alkynes **8c–e** occurred in refluxing toluene for 20 h. The reaction was mediated by triruthenium dodecacarbonyl $Ru_3(CO)_{12}$ and yielded pyranopyrandiones **104a–c** in 54–82% yield (Scheme 65).[107]

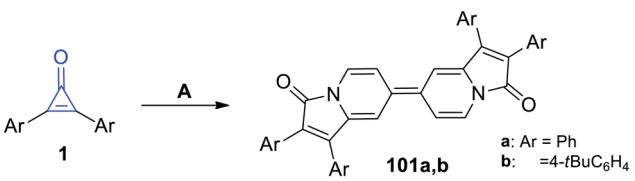
Zhu *et al.* in 2021, have developed a palladium-catalyzed three-component reaction of substituted iodochromen-4-ones **105a–h**, (1*R*,4*S*)-bicyclo[2.2.1]hept-2-ene (**106**) and **1b** in fluorobenzene in the presence of tris-(4-trifluoromethyl-phenyl) phosphine $P(4\text{-}CF_3\text{-}C_6H_4)_3$ at 100 °C for 24 h.



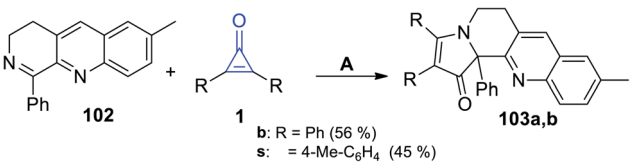
Scheme 61 Synthesis of phenanthridine derivatives **98a–d**. *Reagents and conditions*: A = $[Ru(p\text{-cymene})Cl_2]_2$, Ag_2CO_3, H_3BO_3, DCM, reflux, 48 h.



Scheme 62 Synthesis of **100a–j**. *Reagents and conditions*: A = EtOH, rt, 5–50 h.



Scheme 63 Synthesis of biindolizines **101a,b**. *Reagents and conditions*: A = pyridine, $Cu(OAc)_2$, 15 min.



Scheme 64 Synthesis of the fused heterocyclic compounds **103a,b**. *Reagents and conditions*: A = EtOH, rt.

(6*aR*,7*S*,10*R*,10*aS*)-6*a*,7,8,9,10,10*a*-Hexahydro-7,10-methanoindeno[2,1-*b*]chromene-6,11-diones **107a–h** were obtained in 65–70% yield (Scheme 66).[108]

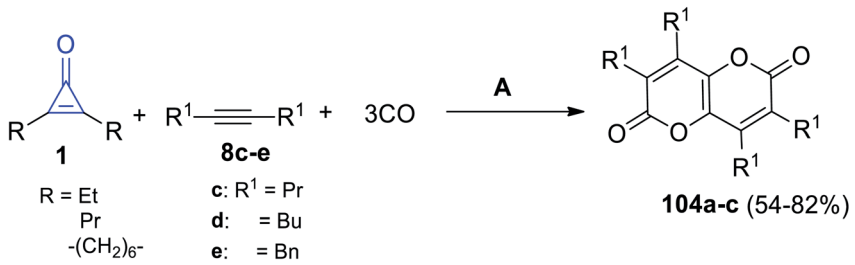
In 2021, Chen *et al.* successfully synthesized a series of tetrasubstituted pyrano[2,3-*b*]indol-2(9*H*)-ones **109a–l** in 65–91% yield *via* the reaction between substituted isatines **40** and diaryl cyclopropenones **1** at 110 °C in toluene and in the presence of lanthanide amides $[(Me_3Si)_2N]_3La(\mu\text{-}Cl)Li(THF)_3$ and ligand **108** as a catalyst (Scheme 67).[109]

2.3.3.2. Six-membered rings with two heteroatoms. (5*S*,6*R*)-5,6-Diphenyl-2-(((*R*)-1-phenylethyl)amino)-5,6-dihydropyrimidin-4(1*H*)-one (**113**) was successfully synthesized by Ahmed *et al. via* the reaction between (*R*)-1-(1-phenylethyl)guanidine (**112**) and **1b**. The reaction was performed at room temperature in benzene and EtOH (Scheme 68).[110]

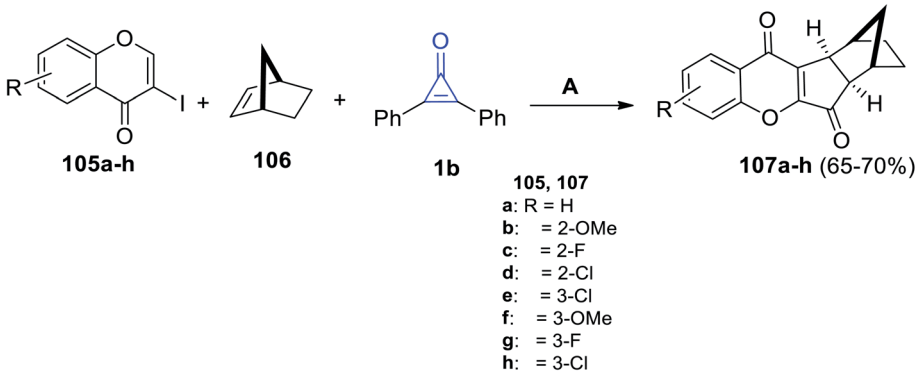
A catalyst-free reaction between *N*-carbamoyl sulfilimines **114a–f** and **1b** in toluene at 110 °C for 13 h afforded the two isomers of diphenyl pyrimidinediones **115a–f** in 51–94% yields, as shown in Scheme 69.[111]

Aly *et al.* in 2016, successfully synthesized pyrimidines **117a–f** in 67–87% yield, *via* the reaction between **116a–f** and **1b** in EtOH and Et_3N (Scheme 70).[112]

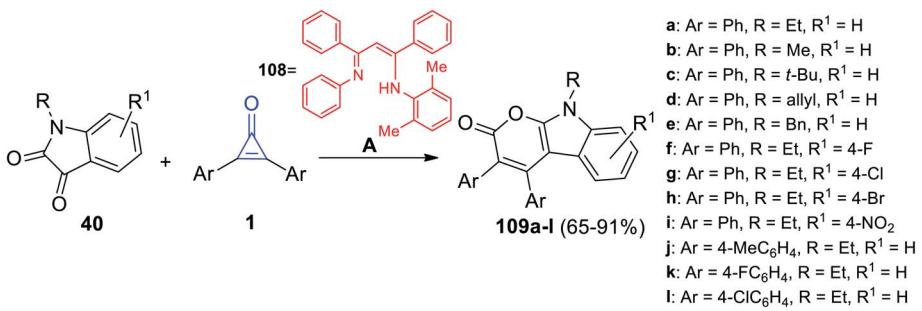
The proposed reaction mechanism is illustrated in Scheme 71; the carbonyl group of cyclopropenone was attacked by the hydrazine nitrogen atom yielding intermediate **B**, following which an amidine-like reaction of N-3 to carbonyl may occur to obtain salt **C**. Nucleophilic addition to positively charged



Scheme 65 Synthesis of pyranopyrandiones **102a–c**. *Reagents and conditions*: A = toluene, $Ru_3(CO)_{12}$, Et_3N, 150 °C, 20 h.



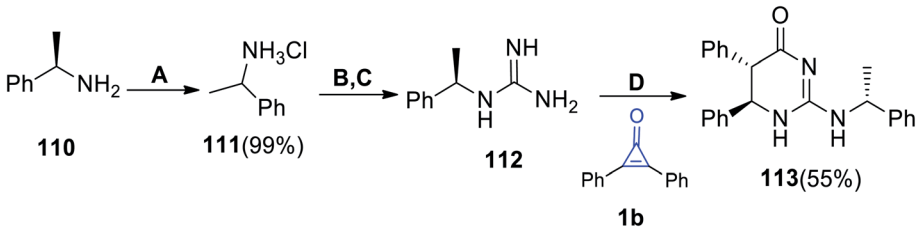
Scheme 66 Synthesis of compounds **107a–h**. *Reagents and conditions*: A = $PdCl_2$, $P(4\text{-}CF_3\text{-}C_6H_4)_3$ (20 mol%), Cs_2CO_3, C_6H_5F, 100 °C, 24 h.



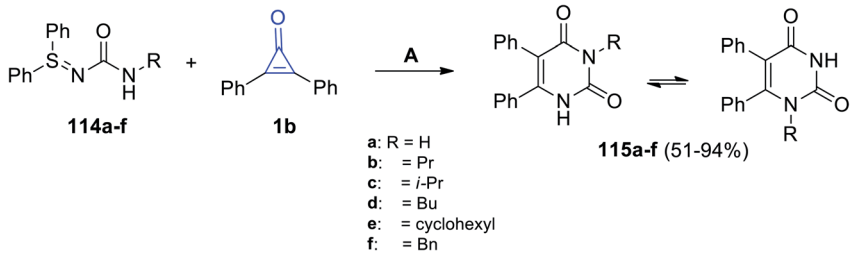
Scheme 67 Synthesis of tetrasubstituted pyrano[2,3-*b*]indol-2(9*H*)-ones (**109a–l**). *Reagents and conditions*: A = $[(Me_3Si)_2N]_3La(\mu\text{-}Cl)Li(THF)_3$, toluene, 110 °C, 2.5 h, (108), $HOP(OEt)_2$.

nitrogen *via* ring opening followed by proton transfer would afford **D**, and the final product **117** was obtained by losing ammonia from **D** (Scheme 71).[112]

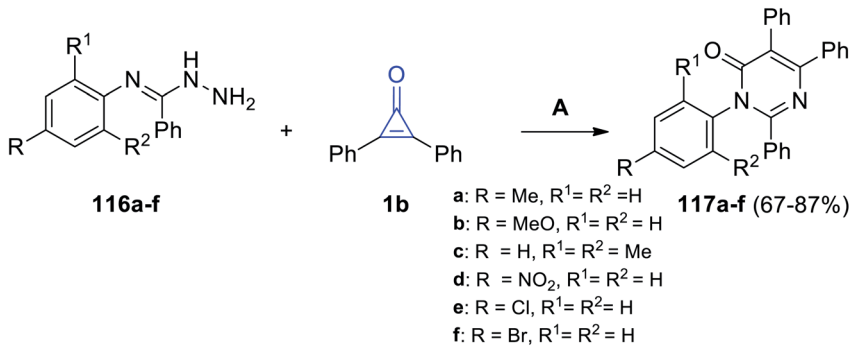
Aly *et al.* also reported that the reaction between (*E*)-*N*′-aryl-*N*-(phenylcarbamothioyl)-benzimidamides **118** and **1b** in EtOH produced substituted 3-aryl-2,5,6-triphenylpyrimidin-4(3*H*)-ones **119a–e**, as shown in Scheme 72.[113]



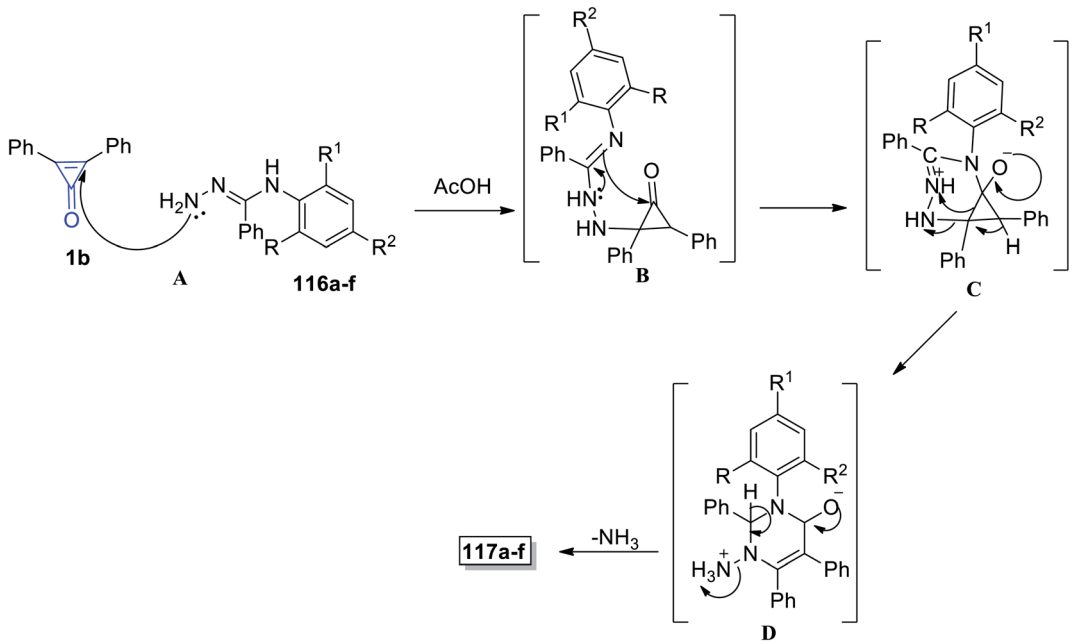
Scheme 68 Synthesis of 5,6-dihydropyrimidine **113**. *Reagents and conditions*: A = conc. HCl, 1,4 dioxane, 20 °C; B = NH_2CN, pH 8–9, H_2O, reflux, 5 h; C = passed through Amberlite IRA-401 (hydroxide form); D = benzene : EtOH (1 : 1), rt, 18 h.



Scheme 69 Synthesis of diphenyl pyrimidinediones **115a–f**. *Reagents and conditions*: A = toluene, 110 °C, 13 h.



Scheme 70 Synthesis of pyrimidines **117a–f**. *Reagents and conditions*: A = EtOH, Et_3N, reflux 6–10 h.

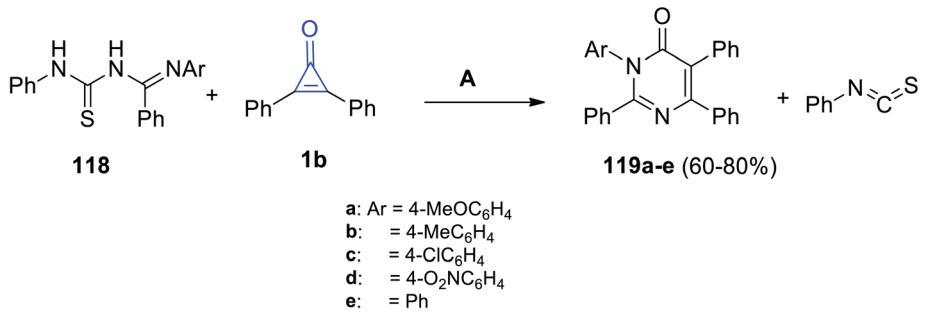


Scheme 71 Mechanism of the formation of pyrimidines **117a–f**.

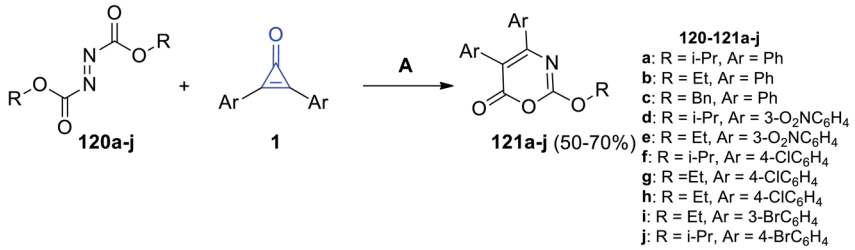
Mohan and Jose, in 2017, have reported that reaction between (*E*)-disubstituted diazene-1,2-dicarboxylates **120a–j** and diarylcyclopropenone **1** in DCM at room temperature. The reaction was catalyzed by PPh_3 to afford substituted 1,3-oxazin-6-one **121a–j** in 50–70% yield (Scheme 73).[114]

The reaction was initiated *via* PPh_3 attack on **120** to give **A** and Huisgen zwitterion's nucleophilic attack on cyclopropenone (**1**) in step **B**; the intermediate (**C**) was formed followed by internal cyclization of **D** to generate 1,3-oxazin-6-ones **121a–j**, as illustrated in Scheme 74.[114]

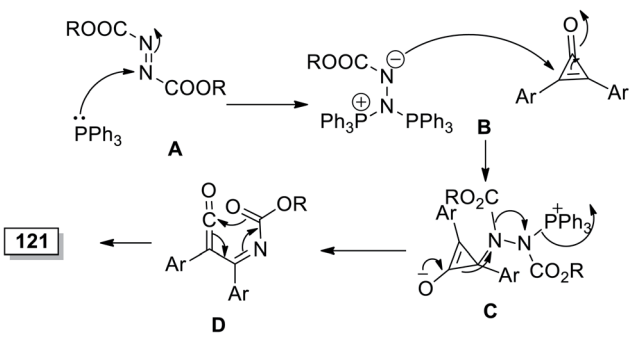
Via the reaction of equal amounts of amide derivatives **124a–i** with 2,3-diphenylcyclopropenones (**1**) in DCE using CsOAc as a catalyst, the substituted 1,3-oxazin-6-ones **121k–q** were obtained in 50–93% yield (Scheme 75).[115]



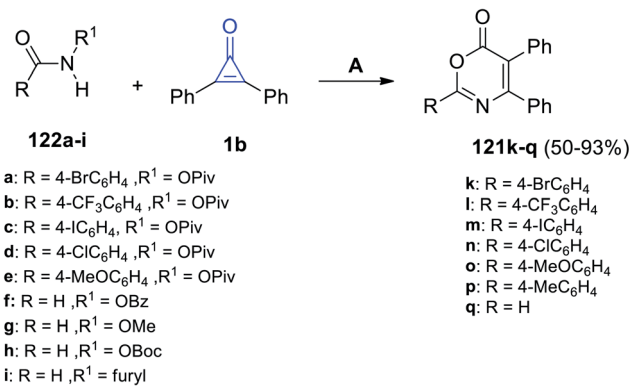
Scheme 72 Synthesis of substituted 3-aryl-2,5,6-triphenylpyrimidin-4(3*H*)-ones (**119a–e**). *Reagents and conditions*: A = EtOH, reflux, 10–16 h.



Scheme 73 Synthesis of substituted 1,3-oxazin-6-ones **121a–j**. *Reagents and conditions*: A = PPh_3 (1 equiv.), DCM, rt, 15 min.



Scheme 74 Mechanism of the formation of substituted 1,3-oxazin-6-ones **121a–j**.



Scheme 75 Scandium-catalyzed synthesis of substituted 1,3-oxazin-6-ones **121k–q**. *Reagent and conditions*: A = CsOAc (1 equiv.), DCE, rt, 6 h.

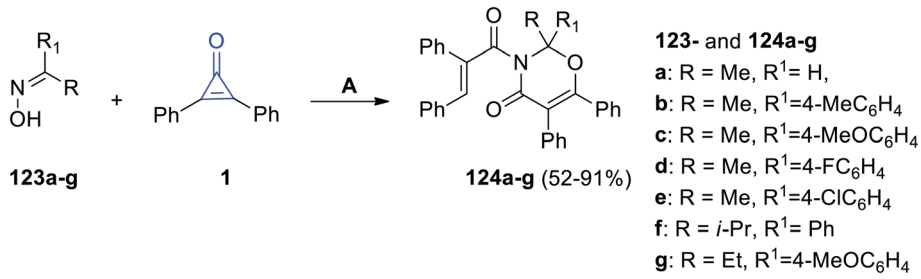
Recently, it has been reported that the oxime derivatives **123a–g** reacted with 2,3-diphenyl-cyclopropenones (**1**) to give substituted 1,3-oxazine-4-ones **124a–g** in 52–91% yield (Scheme 76). The reaction was performed at 80 °C in cyclohexane for 18 h, and Ag_2O was also used as a catalyst.[116]

The reaction mechanism is illustrated in Scheme 77. At first, the resonance structure of cyclopropenone was nucleophilically attacked by oximes, yielding intermediate **A**. Subsequently the intermediate **A** was fragmented into intermediates **B** and **C**. Accordingly, the intermediate **D** was obtained *via* a [4 + 2] cycloaddition between **B** and **C**. Then, a reaction occurred between **D** and another cyclopropenone to generate intermediate **E**, and the intermediate **F** was subjected to a rearrangement/protonation process to form compound **124**.[116]

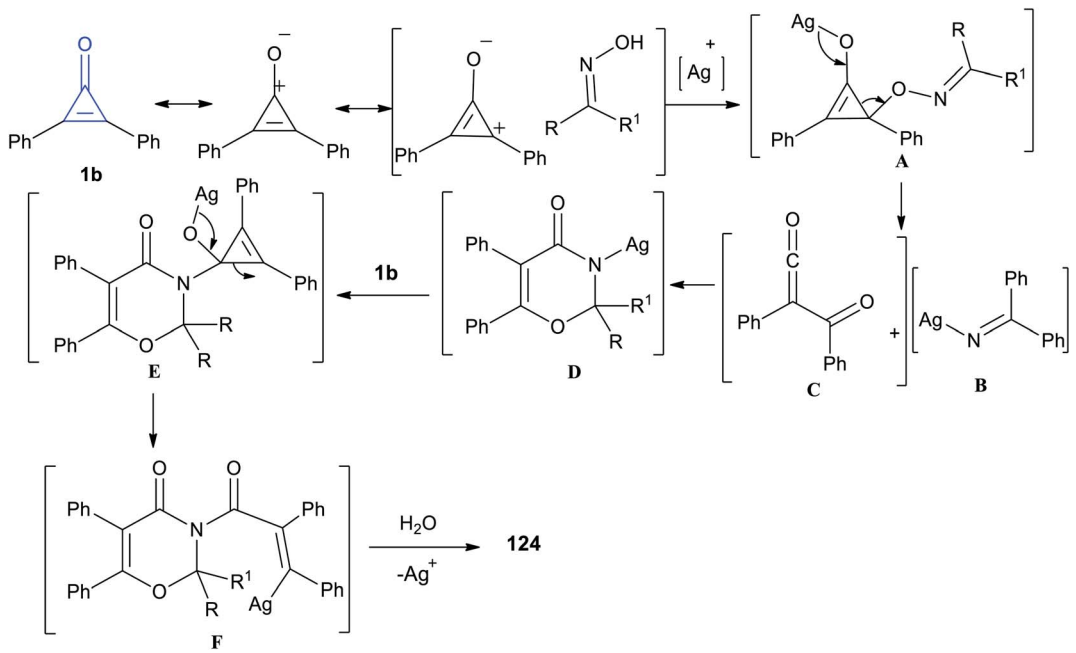
In 2021, Sizhan, *et al.* successfully synthesized substituted 1,3-oxazin-6-ones **121r–y** in 55–93% yield, *via* the reaction between α-halogenated hydroxamates **125a–g** and **1b** in DCM and Et_3N (Scheme 78).[117]

2,4,5-Triphenyl-6*H*-1,3-oxazin-6-one (**121z**) was obtained in 95% yield by reacting *N*-(pivaloyloxy)benzamide (**126**) with 2,3-diphenylcyclopropenone (**1**) at 60 °C in THF using K_2CO_3. The mechanism of the reaction was explained by the nucleophilic attack of the nitrogen atom of amide **26** on **1b** and intermediate **B** was then formed in the presence of base. During the ring opening, **B** lost a pivalate anion to give ketene **C**, which rearranged to form the final structure (**121z**), *via* a 6π electrocyclization process, as shown in Scheme 79.[118]

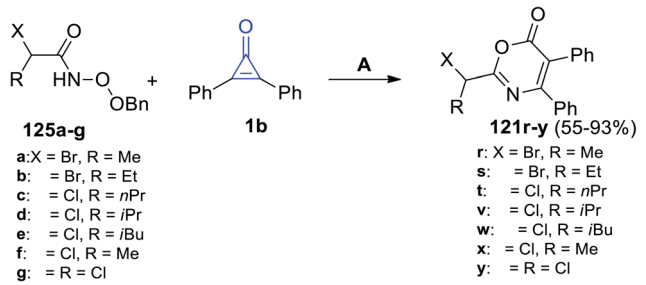
In 2019, substituted thiazinane derivatives **128a–e** were successfully synthesized by Hassan *et al.* in 2019. It was achieved during the reaction of hydrazinecarbothioamide derivatives **127a–e** with **1b** in refluxing EtOH (Scheme 80). The



Scheme 76 Synthesis of 1,3-oxazine-4-ones **124a–g**. *Reagents and conditions*: A = Ag_2O, cyclohexane, 80 °C, 18 h.



Scheme 77 Mechanism describing the formation of 1,3-oxazine-4-ones **124a–g**.



Scheme 78 Synthesis of substituted 1,3-oxazin-6-ones **123r–y**. *Reagents and conditions*: A = DCM, reflux, Et_3N, 2 h.

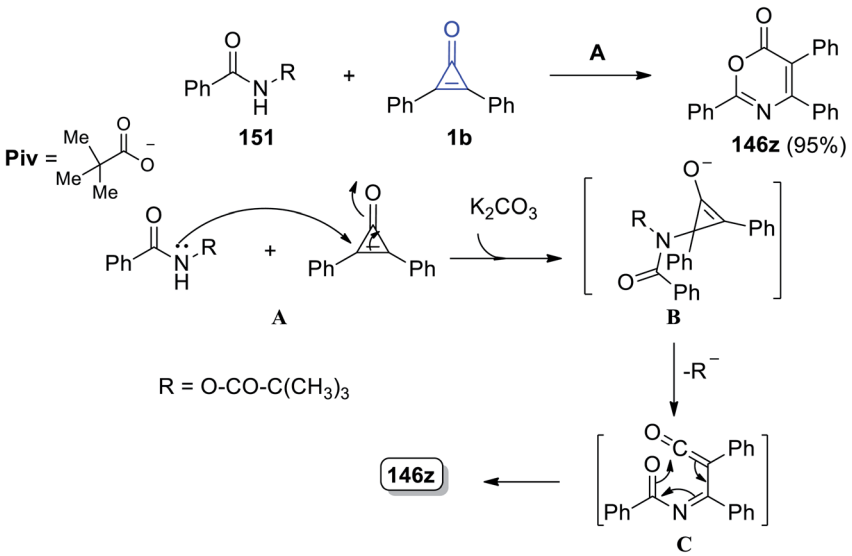
reaction afforded compounds **128a–e**, as well as a side product **129**.[119]

The reaction mechanism could be simply described as the conjugate double bond of **1b** was attacked by the sulfur atom generating intermediate **A.** The intermediate **B** was formed *via* the intramolecular nucleophilic attack of N4–H on C=O, which rearranged to generate **128.** However, the carbonyl group of **1** was attacked by N4–H, resulting in the formation of the product **128** *via* intermediate **D** (Scheme 81).[119]

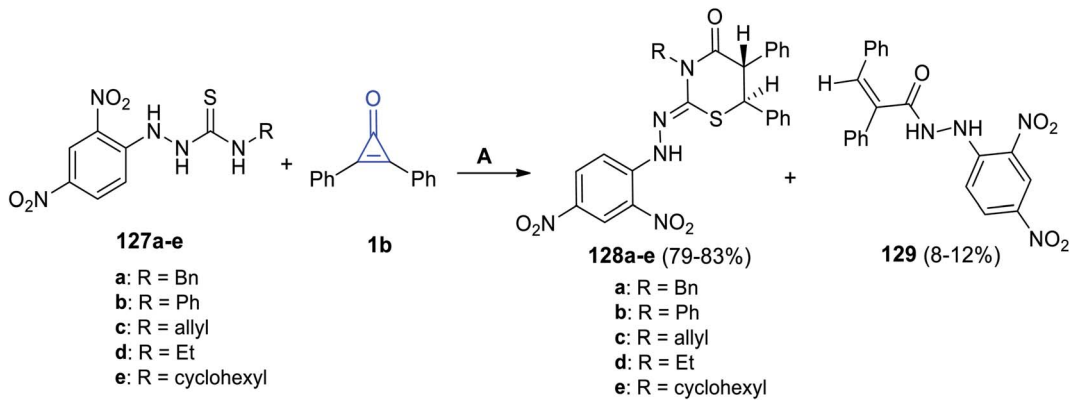
When pyrazolylthioureas **130a–c** were subjected to **1b**, the reaction proceeded to give compounds **131a–c** in 75–90% yield (Scheme 82). The reaction was performed in ethanol for 4–7 h in the presence of DDQ as the oxidizing agent.[120]

Moreover, in 2021, Shi *et al.* succeeded to synthesize the heterocyclic substituted 2-phenyl-10′*H*-spiro[indene-1,12′-isoindolo[1,2-*b*]quinazolin]-10′-ones **133a–j** in 58–87% yield by reacting 2-phenylquinazolin-4-ones **132a–j** with cyclopropenones **1** in refluxing DCE for 24 h, and a (cymene)-ruthenium dichloride dimer $[Ru(p\text{-cymene})Cl]_2$ was used as a metal catalyst (Scheme 83).[121]

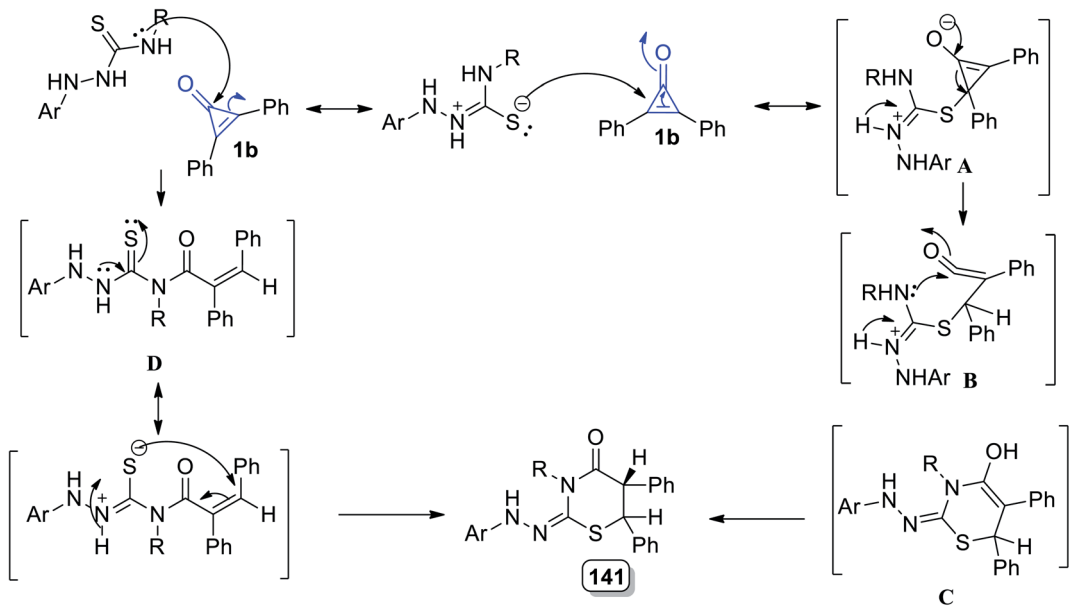
Shi *et al.* also reacted substituted 2-phenylquinazolin-4-ones **134a–f** with **1b** to obtain compounds **135a–f** in 62–82% yield. The reaction was performed in trifluoroethanol (TFE) at 110 °C for 48 h. Subsequently, treatment of compound **135a–f** with trifluoroacetic acid (TFA) at 140 °C and in the presence of Rh [Cp*(OAc)] and Ag_2O yielded compounds **136a–f** (Scheme 84).[121]



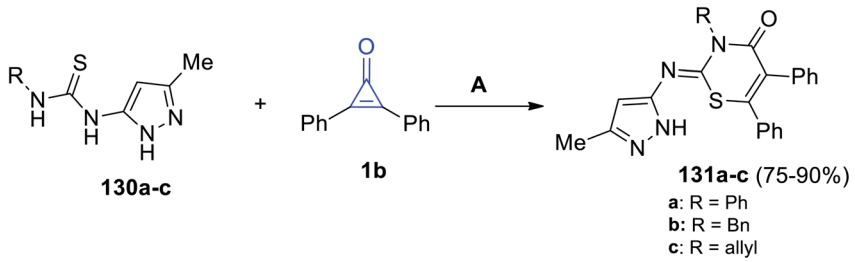
Scheme 79 Synthesis of 2,4,5-triphenyl-6*H*-1,3-oxazin-6-one (**123z**). *Reagents and conditions*: A = K_2CO_3 (0.5 equiv.), THF, 60 °C, 2 h.



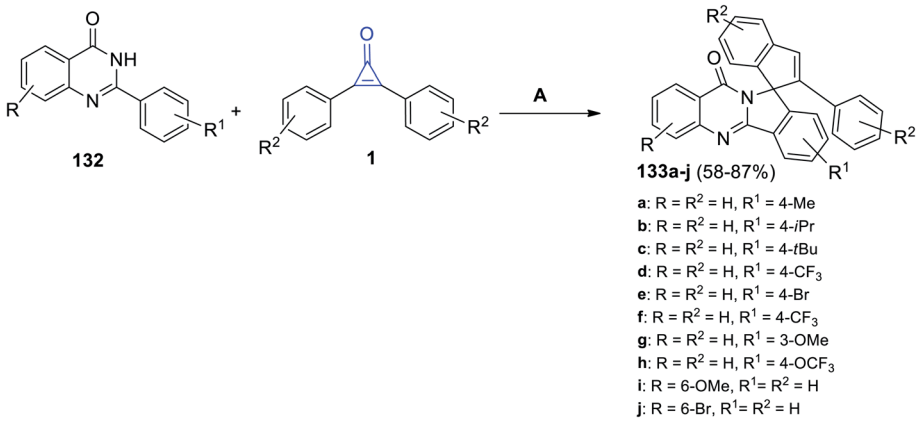
Scheme 80 Synthesis of thiazinanes **128a–e**. *Reagents and conditions*: A = EtOH, reflux.



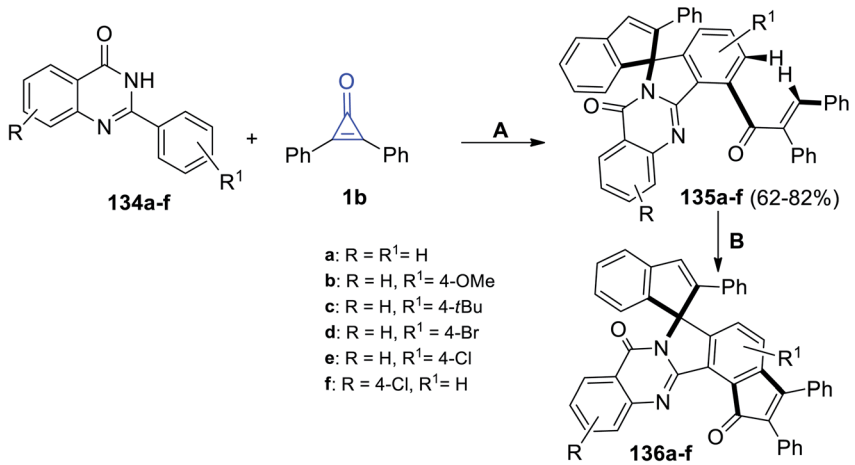
Scheme 81 Mechanism of the formation of thiazinanes **128a–e**.



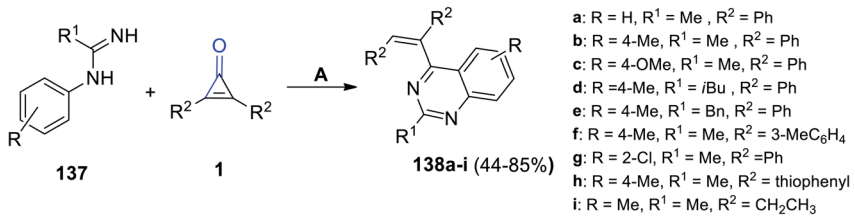
Scheme 82 Synthesis of thiazines **131a–c**. *Reagents and conditions*: A = DDQ, EtOH, reflux, 4–7 h.



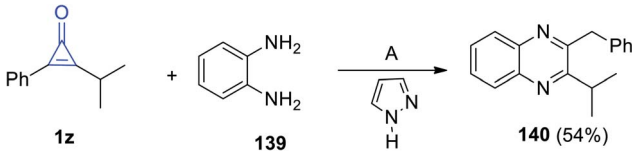
Scheme 83 Synthesis of substituted quinazolin-ones **133a–j**. *Reagents and conditions*: A = [Ru(*p*-cymene)Cl]$_2$, AgSbF$_6$, AdCOOH, DCE, reflux, 24 h.



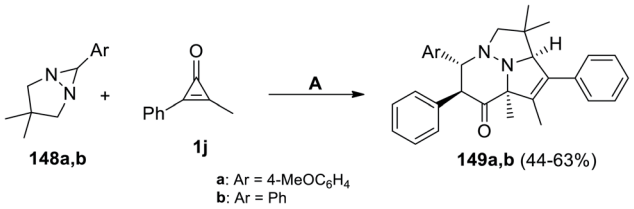
Scheme 84 Synthesis of compounds **135a–f** and **136a–f**. *Reagents and conditions*: A = Rh[Cp*(OAc)], TFE, 110 °C, 48 h; B = Pd(OAc)$_2$, Ag$_2$O, TFA, 140 °C, 24 h.



Scheme 85 Synthesis of quinazoline derivatives **138a–i**. *Reagents and conditions*: A = (Cp*RhCl$_2$)$_2$, AgSbF$_6$, DCM, reflux, 36 h, O$_2$.



Scheme 86 Synthesis of 2-benzyl-3-isopropylquinoxaline (**140**). *Reagents and conditions*: A = Et_2O, 8 h.



Scheme 89 Synthesis of pyridazines **149a,b**. *Reagents and conditions*: A = *p*-xylene, reflux, 138 °C, 20 min.

Refluxing **137** with 2,3-substituted cyclopropenones **1** in DCM yielded quinazoline derivatives **138a–i** in 44–85% yield. The reaction was catalyzed using $(Cp^*RhCl_2)_2$ and $AgSbF_6$, as shown in Scheme 85.[122]

2-Benzyl-3-isopropylquinoxaline (**140**) was synthesized *via* reacting 2-isopropyl-3-phenylcycloprop-2-en-1-one (**1z**) with benzene-1,2-diamine (**139**) in diethyl ether for 8 h and in the presence of 1*H*-pyrazole as a catalyst (Scheme 86).[86]

6,7-(Diphenylpyrrolo[1,2-*b*]pyridazin-5-yl)acetate (**143**) was successfully synthesized in 55% yield *via* a cyclization reaction between pyridazine (**141a**) and **1b** in DCE at the reflux temperature. Subjecting the formed intermediate **142** with acetic anhydride and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) as a base catalyst gave the final product **143** (Scheme 87).[122]

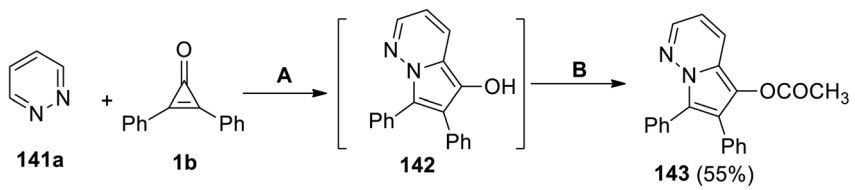
The reaction between pyridazine-4,5-dicarbonitrile (**141b**) and **1b** in acetone at 110 °C afforded 1-oxo-2,3-diphenyl-1*H*-pyrazolo[1,2-*a*]pyridazine-6,7-dicarbonitrile (**145**) in 38% yield *via* the formation of intermediate **144** (Scheme 88). In addition to the formation of **145**, [(*E*)-3,4-dicyano-6,7-diphenylpyrrolo [1,2-*b*]pyridazin-5-yl]-2,3-diphenylacrylate (**147**) was also obtained in 47% yield. The formation of **147** can be explained as due to the cyclization process of intermediate **144** into **146**, which tautomerized and reacted with another molecule of **1** to give **147** (Scheme 88).[123]

Molchanov *et al.* have developed on the synthesis of pyridazines **149a,b** during refluxing a mixture of 6-aryl-3,3-dimethyl-1,5-diazabicyclo[3.1.0]hexanes **148a,b** with 2-methyl-3-phenylcycloprop-2-enone (**1j**) in *p*-xylene for 20 min (Scheme 89).[124]

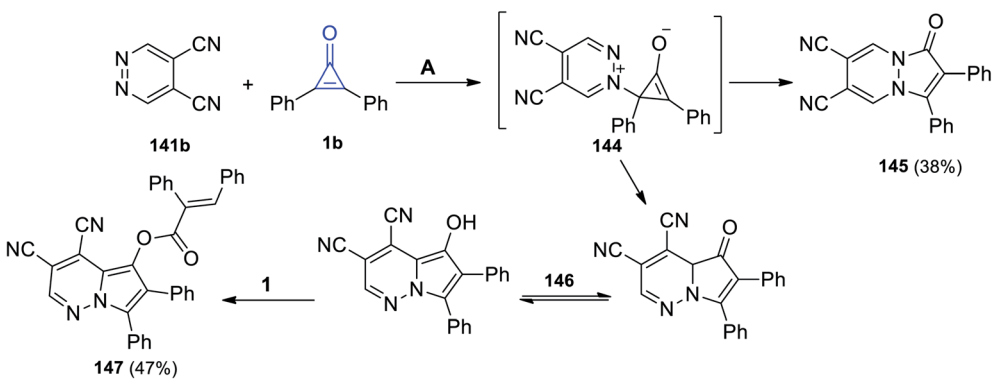
Aly's group reacted **1b** with hydrazinecarbothioamides **138a–c** in MeOH.[125]

The reaction yielded substituted triazolopyridazines **150a–d**. However, when 1,2-diphenyl-hydrazinecarbothioamide (**129h**) was used, the reaction gave only (*Z*)-1,4,5-triphenyl-6-(phenylimino)-1,6-dihydropyridazine-3(2*H*)-thione (**151**) (Scheme 90).[125]

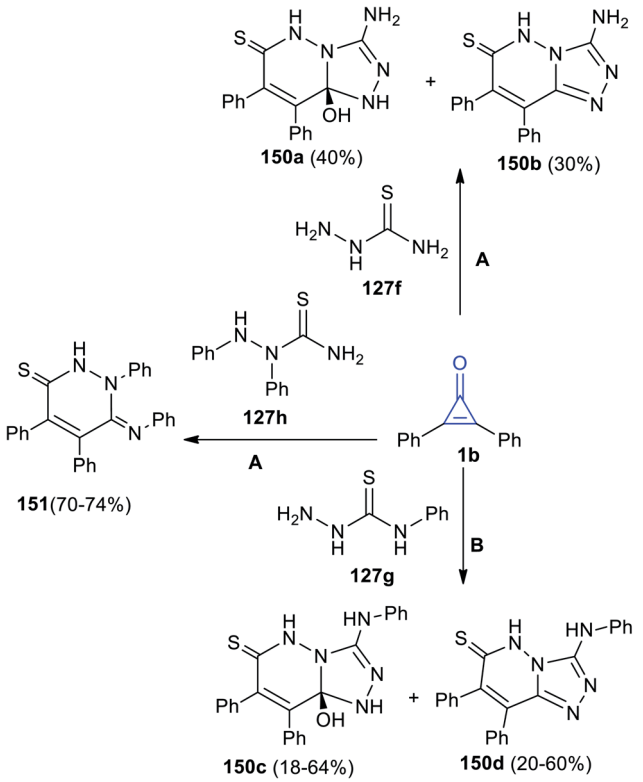
2.3.3.3. Six-membered rings with three heteroatoms. When cyclopropenone **1** was treated with Et_3OBF_4 and CH_2Cl_2 *in situ*, the intermediate **152** was suggested to be formed (Scheme 91). Accordingly, upon addition of Et_2NH *in situ* to the salt **152**, the intermediate **153** was suggested to be formed. Finally, after *in situ* addition of sodium azide (NaN_3) in DMF to **153**, the reaction



Scheme 87 Synthesis of 6,7-diphenylpyrrolo[1,2-*b*]pyridazin-5-yl acetate (**143**). *Reagents and conditions*: A = DCE, reflux, B = Ac_2O, DMAP.



Scheme 88 Synthesis of pyridazines **145** and **147**. *Reagents and conditions*: A = MeCOMe, 110 °C, 48 h.



Scheme 90 Synthesis of pyridazines **150**, **151**. *Reagents and conditions*: A = MeOH, reflux, 48 h, B = MeOH, reflux, 6–12 h.

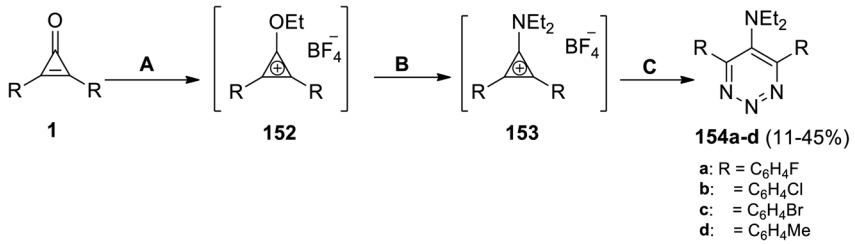
proceeded to yield the triazines **154a–d** in 11–45% yield (Scheme 91).[126]

2.3.4. Synthesis of seven-membered-ring heterocycles. Tetrasubstituted-6,7-dihydro-1*H*-silepin-4(5*H*)-ones **156a–h** were obtained in 65–89% yield by refluxing 1,1-disubstituted siletanes **155a–h** with cyclopropenone derivatives **1** in toluene at room temperature for 48 h, and $Pd(OAc)_2$ (Scheme 92).[127] The reaction was initiated *via* bond cleavage of silacyclobutane (**155**): the C–Si bond of silacyclobutane was broken through an oxidative addition, which was proposed to give palladacycle **A** as the first step. Then, after a series of oxidative additions to the C–C bond of cyclopropenone **1b**, intermediate **C** was formed (Scheme 93). The eight-membered palladacycle **D** was formed *via* the reductive elimination of intermediate **C**, which might go through a second reductive elimination step to produce the final product **156** and form the palladium (0) catalyst again. The possibility of path b could not be completely excluded, which would first involve the cleavage of the C–C σ-bond of cyclopropenone (**1**) (Scheme 93).[127]

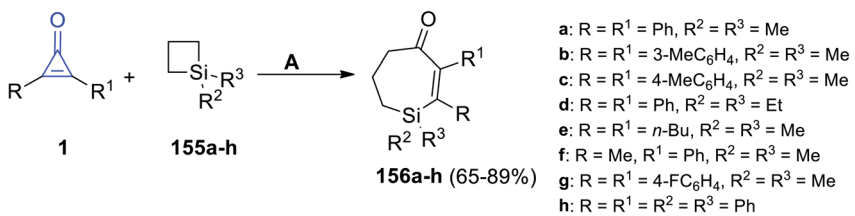
2.3.5. Synthesis of nine-membered-ring heterocycles. When compounds **157a–c** reacted with 2,3-diphenylcyclopropenone (**1b**) in absolute ethanol, intermediate **158** was formed followed by the formation of nine-membered-ring bicyclic products **159a–c** in 51–62% yield (Scheme 94).[128]

3 Conclusion

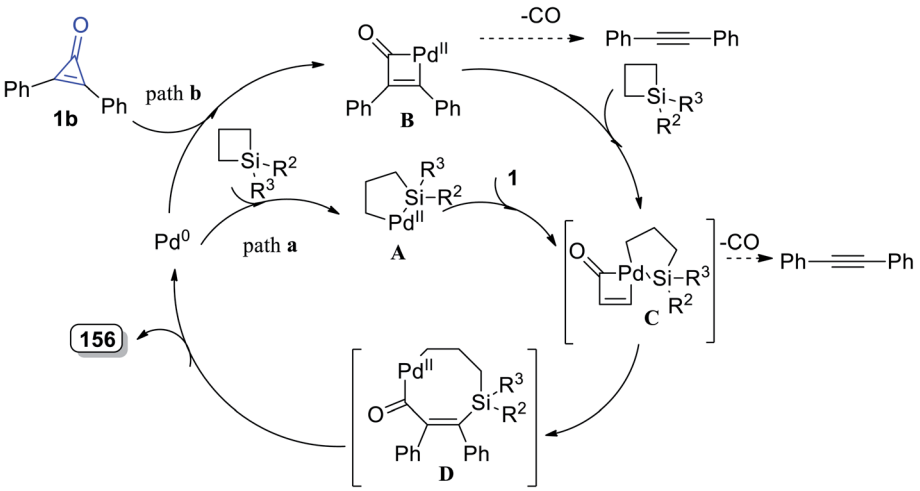
In summary, the use of cyclopropane derivatives for the construction of various heterocycles can provide a practical alternative to traditional methods for the preparation of such compounds. Since cyclopropenones have high strain, they easily participated in various reactions and, therefore, in the construction of various organic molecules. In that review, we consider the utility of cyclopropenones in the synthesis of heterocycles, especially those of prospective biologically active compounds. The reactions of cyclopropenones are described as highly regioselective, often stereoselective, and permit the synthesis of a variety of heterocyclic systems, both saturated



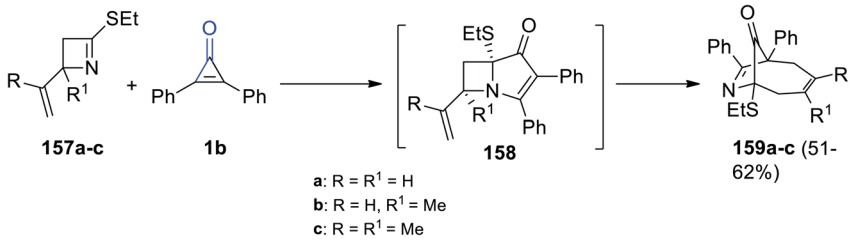
Scheme 91 Synthesis of triazines (**154a–d**). *Reagents and conditions*: A = Et_3OBF_4, CH_2Cl_2; B = Et_2NH; C = NaN_3, CH_2Cl_2, DMF.



Scheme 92 Synthesis of tetrasubstituted-6,7-dihydro-1*H*-silepin-4(5*H*)-ones **156a–h**. *Reagents and conditions*: A = (1 mol%), $Pd(OAc)_2$ toluene, rt, 48 h.



Scheme 93 Mechanism of the formation of 6,7-dihydro-1*H*-silepin-4(5*H*)-ones **157a–h**.



Scheme 94 Synthesis of compounds **159a–c**. *Reagents and conditions*: A = EtOH, reflux.

and unsaturated. The substrates employed in most cases are simple (and often commercially available), making the methods amenable to the rapid construction of diverse collections of compounds.

Author contributions

A. A. Aly (conceptualization, writing, editing, and submitting), Alaa A. Hassan, Sara M. Mostafa (supervision), Asmaa. H. Mohamed (editing of revision), Esraa M. Osman (methodology and writing a draft). A. A. Nayl (editing of revision). All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

The authors declare no conflicts of interest.

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