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Recent advances in visible light-mediated chemical transformations of enaminones

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ABSTRACT

Enaminones, which possesses both the nucleophilic enamine as well as electrophilic enone structures, are well known versatile building blocks in organic synthesis. Meanwhile, visible light-mediated reactions have emerged as useful synthetic strategy with enhanced sustainability. Around the last decade, various photochemical transformations of enaminones have been developed to construct cyclic or acyclic compounds. In this review, we describe the recent advances in visible light-mediated chemical transformations of enaminones. Detailed discussion on the reaction mechanism of the related reactions is given to provide guide to the reader. Finally, a summary on the existing challenges and the future outlook towards the development of practical photocatalytic reactions of enaminones is also presented.

1. Introduction

Enaminones or enaminoesters, which consist of an amino group linked through a carbon-carbon double bond to a carbonyl or ester group, are important and powerful synthons [1–7]. Owing to the amine-alkene-carbonyl conjugated structural features, they combine the triple nucleophilicity (C-2, amino and carbonyl oxygen) with the ambident electrophilicity of enones (C-1 and C-3) (Fig. 1). Enaminones have been utilized as versatile building blocks in organic the synthesis of carbocyclic [8–11], heterocyclic [12–18] as well as acyclic compounds [19–23] under proper reaction conditions. The known transformations usually take place in the unit of "enamines" or "enones" in the presence of one or more other reaction partners, enabling the construction of heterocycles though tandem cyclization under proper environments [24–27], the functionalization of the internally activated vinyl C–H bond under the catalyst of transition metal [28–30,27], iodide [31–34] or other oxidants [35,36], C–H bond functionalization of aryl ring in the aromatic ketone or aryl amine moiety [37–39], the synthesis of acyclic compounds through the cleavage of the C=C double bond by means of different pathways of transformation [40–43], the functionalization of the C–N bond to different enones [44,20], as well as some other novel reactions in enaminones [45–49]. The results, especially the ones reported over the last decade by us and others, have opened new frontiers in the enaminone-based synthetic chemistry.

Following the daily increasing emphasis on sustainable synthesis, the visible light-mediated reactions has won significant attention and advances [50–52] since the pioneer reports by MacMillan [53–55], Yoon [56,57], Stephenson [58–60] and Nicewicz [61–63]. By employing visible light photocatalysis, a large variety of new synthetic reactions have been established to deliver diverse organic products *via* mild, easy to handle, and environmentally benign operations. Such reactions are more favorable than conventional heating protocols from the perspective of green chemistry. In this regard, applying photocatalysis to the chemical transformations of enaminones could be valuable approaches for organic synthesis. Actually, during the last decade, a broad range of synthetic works on the functionalization of enaminones under visible light catalysis have been published. However, no review work on the photocatalytic reactions of enaminones is currently available. Thus, we present herein an overview on the progress of visible light-mediated chemical transformations of enaminones, in hope of bring some guides to the development of more environmentally friendly synthesis by the transformation of enaminones.

2. Direct α-C(sp^2)-H bond functionalization

In recent years, the direct functionalization of the alkenyl α-C(sp^2)-H bond in enaminones has gained extensive attention be-

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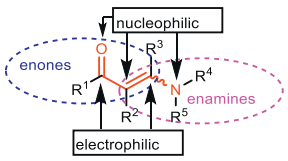
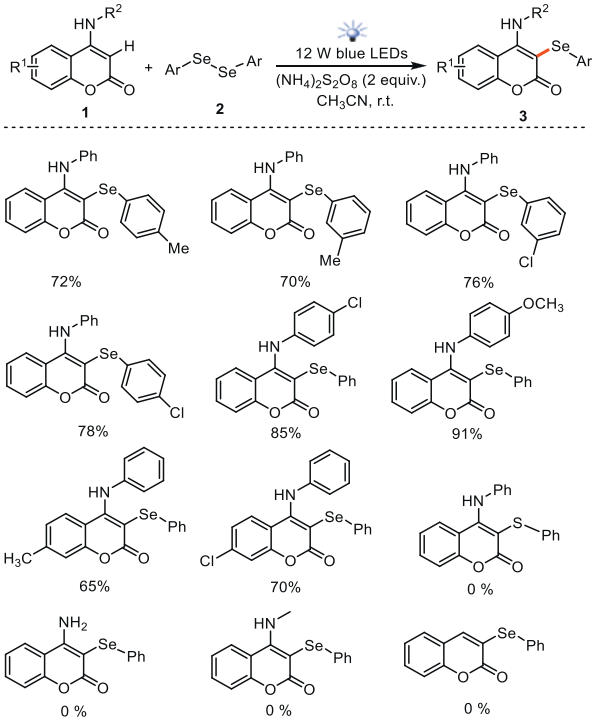


Fig. 1. Structure of enaminones.

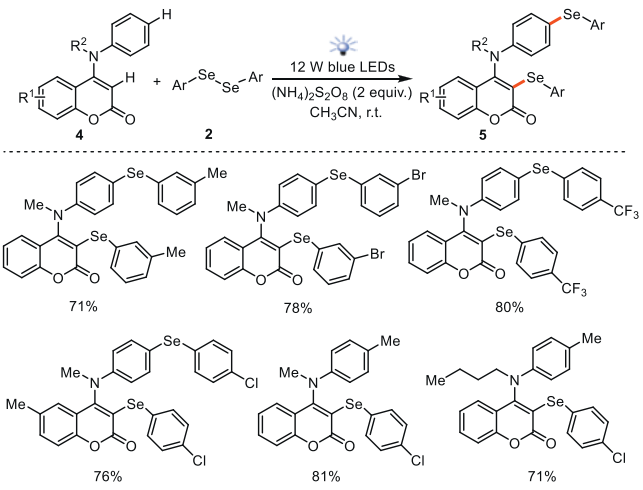
cause of its highly versatile reactivity and widespread application in designing the synthesis of biologically active molecules and pharmaceutical substances. Among these approaches, visible light-mediated direct α-C(sp^2)-H bond functionalization is definitely one of the simple and ideal methods. Recently, several direct α-functionalization reactions of enaminones such as α-selenylation, α-fluoroalkylation and α-thiocyanation have been developed.

2.1. Photocatalytic α-C-H selenylation of enaminones

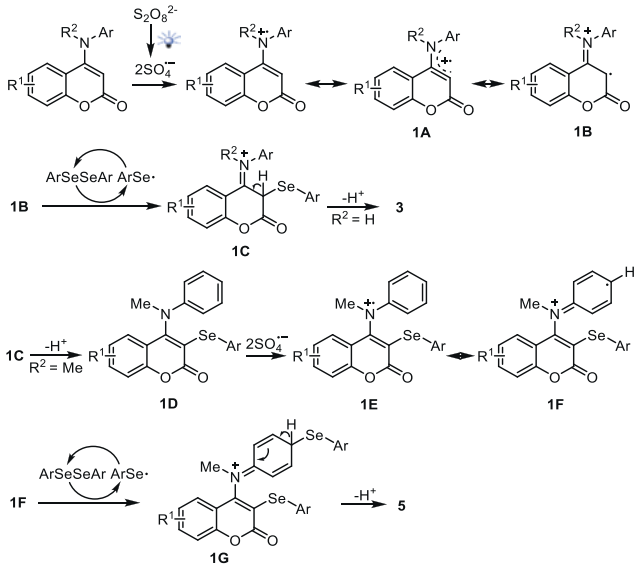
In 2018, Yang and coworkers reported the direct C(sp^2)-H α-selenylation of coumarin derivatives under metal- and photocatalyst-free visible light catalysis [64]. The reactions were run with the conditions of $(NH_4)_2S_2O_8$ as the oxidant, CH_3CN as the solvent under air atmosphere as well as the irradiation of 12 W blue LEDs visible light at room temperature. As shown in Scheme 1, aryl selenium could be smoothly incorporated to various coumarin derivatives at α-site. A wide array of diselenides and coumarin derivatives, bearing either electron-withdrawing or electron-donating groups, were tolerated in this reaction, leading to the desired product in generally good to excellent yields. It is worth noting that as to *N*-substituted 4-(phenylamino)−2*H*-chromen-2-ones **4**, the dual selenylated products were selectively generated in 71%–81% yields (Scheme 2). When the *para*-site of the 4-phenylamino group was substituted, only C-3 selenylated products were obtained. Two possible mechanisms to rationalize the formation of **3** and **5** were illustrated (Scheme 3). First, the *in situ* generated active radical anion $SO_4^{\bullet-}$ from $(NH_4)_2S_2O_8$ occurred under the irradiation of visible light. Then, a single electron



Scheme 1. Visible-light-promoted regioselective selenylation of 4-(phenylamino) coumarins.



Scheme 2. Visible-light-induced selenylation of *N*-substituted 4-(phenylamino) coumarins.

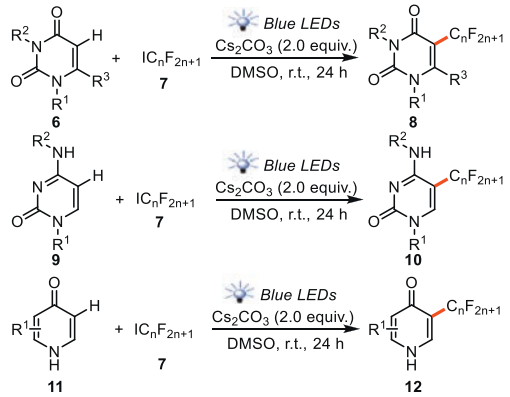


Scheme 3. Proposed mechanisms for the formation of **3** and **5**.

transfer (SET) process between **1** and $SO_4^{\bullet-}$ to delivered the radical cation **1A** or **1B**, which further reacted with diselenides **2** to form the intermediate **1C**. Finally, if R^2 was H atom, the final product **3** was obtained by the elimination of H^+ from **1C**. If R^2 was methyl, the reaction of intermediate **1C** with diselenides **2** led to the C-3 selenylated species **1D**. Subsequently, a SET process took place between **1D** with $SO_4^{\bullet-}$ to give radical cation **1E** or **1F**, which was then captured by ArSe· to afford the intermediate **1G**. The deprotonation of **1G** afforded the final product **5**.

2.2. Photocatalytic α-C-H perfluoroalkylation of enaminones

Incorporation of fluoroalkyl groups into a molecule is important because such elaboration can dramatically alter the chemical and physical properties of the molecules and results in various applications in pharmaceuticals, agrochemicals, and functional materials [65]. In 2018, He *et al.* reported catalyst-free and visible light promoted trifluoromethylation and perfluoroalkylation of uracils, cytosines and pyridiones in the α-C-H bond of the enaminone fragments (Scheme 4) [66]. The reactions were conducted with 12 W blue LED irradiation at room temperature using Cs_2CO_3 as base and DMSO as solvent. The negatively ionized uracil **5A** was first generated in the presence of Cs_2CO_3. A fluoroalkyl radical could

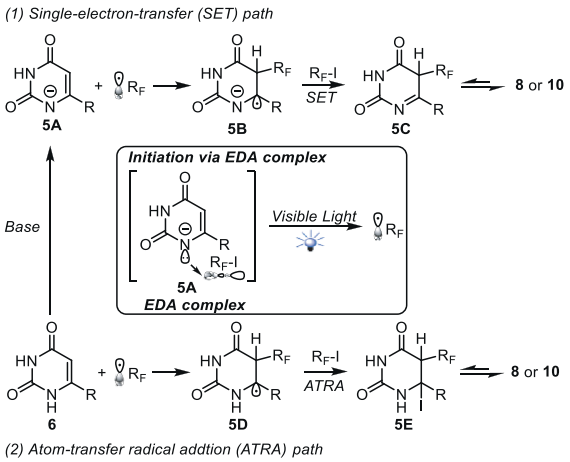


Scheme 4. The synthesis of α-perfluoroalkylated uracils, cytosines and pyridiones.

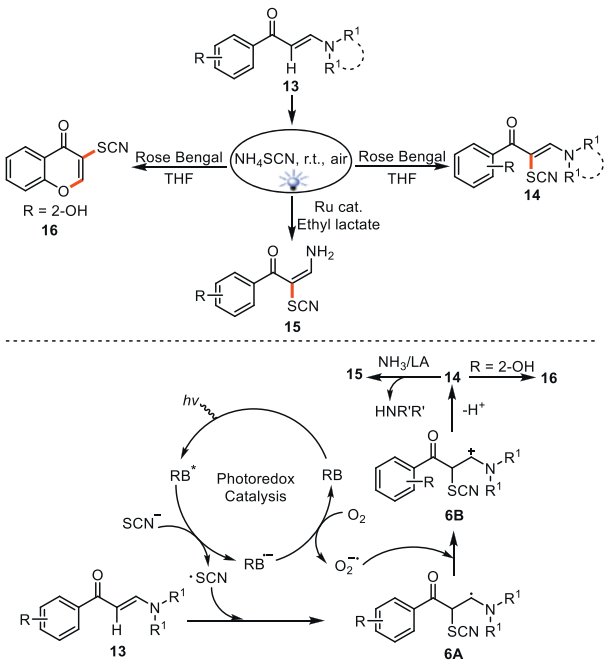
be formed under the irradiation of blue LEDs *via* the EDA complex. Then two pathways might be involved in the propagation step: (1) fluoroalkyl radical reacted with **5A** to produce intermediate **5B**, which accessed to intermediate **5C** *via* a SET process in the influence of fluoroalkyl iodides. Finally, the desired product **8** or **10** were formed by 1,3-hydrogen migration process with the help of Cs_2CO_3. (2) The R_f radical might add to uracils **6** and generate the carbon radical intermediate **5D**, which abstracted an iodine atom from R_fI to afford **5E**. The final products **8** or **10** were obtained *via* the fast re-aromatization of **5E** *via* HI elimination (Scheme 5).

2.3. Photocatalytic α-C-H thiocyanation of enaminones

Organic thiocyanates are moieties possessing plentiful biological and pharmaceutical activities in both synthesized and naturally occurring molecules [67]. Among the reported strategies on organic thiocyanate synthesis, the direct C–H thiocyanation is more practical and cost-effective because such a method allows for the synthesis of organic thiocyanates using those prevalently available C–H bond donors. In 2019, our group realized the first vinyl C–H bond thiocyanation reaction of tertiary enaminones under metal-free, photocatalytic conditions in the presence of Rose Bengal, which enables the synthesis of thiocyanated alkene derivatives and chromones using NH_4SCN as the thiocyano source under an aerobic atmosphere [68]. Besides, employing $Ru(bpy)_3Cl_2{\cdot}H_2O$ as the photocatalyst switches the reaction pathway to provide NH_2-functionalized thiocyanated enamines. As shown in Scheme 6, the reactions might start from the quenching of NH_4SCN to the excited RB* species generated from the visible light irradiation to the RB catalyst, which gave rise to the SCN free radical. Meanwhile, the



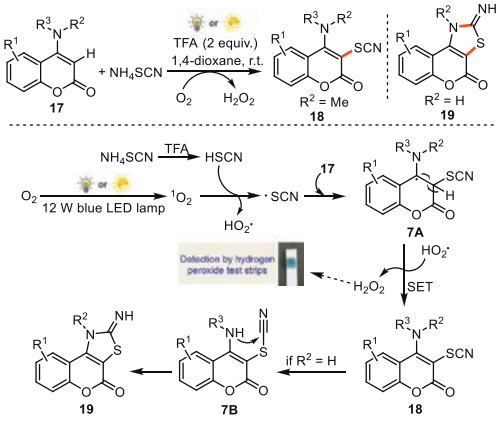
Scheme 5. Proposed mechanisms for the formation of **8** and **10**.



Scheme 6. Photocatalytic synthesis of polyfunctionalized alkenes and thiocyano chromones.

$RB^{\cdot -}$ formed therein could be regenerated to RB by the oxidation of molecular oxygen. Subsequently, the addition of the SCN· to the C=C double bond in **13** provided the free radical intermediate **6A**, which was further oxidized to carbon cation **6B**. The deprotonation on **6B** then yielded thiocyanated product **14**. when the Ru-catalyst is employed, a transamination between the tertiary enaminones and the ammonium was promoted to form products **15**, wherein the Ru-catalyst might act also as a Lewis acid (LA) catalyst. In addition, when *o*-hydroxylphenyl-functionalized enaminones were used as substrates, the successive chromone annulation took place to give thiocyanated chromones **16**.

After our work, Yang *et al.* reported the photocatalyst-free C–H thiocyanation of 4-anilinocoumarins by visible light irradiation (Scheme 7) [69]. The reactions started from ammonium incorporation of thiocyanate and TFA forming thiocyanic acid (HSCN). Under the visible light irradiation, oxygen was converted to singlet oxygen which subsequently abstracting an electron from HSCN to generate $HO_2{\cdot}$ and ·SCN. The selective addition of thiocyano free radical to the coumarin derivatives **17** gave the intermediate **7A**. The SET processes from $HO_2{\cdot}$ to the intermediate **7A** donated the desired products **18** by releasing H_2O_2. If R^2 was H, the intramolecu-



Scheme 7. Photocatalyst-free regioselective C–H thiocyanation of 4-anilinocoumarins.

lar nucleophilic addition of NH to CN afforded the cyclization products **19**.

Despite the fact that *N*,*N*-disubstituted and *N*-mono substituted enaminones have been successfully used as the C–H bond donors for C–H thiocyanation by photocatalysis, equivalent photocatalytic C–H thiocyanation reactions of the free NH_2-enaminones kept inapplicable in the aforementioned systems. In 2022, our group reported the first α-C-H thiocyanation of NH_2-enaminones with air oxygen as the oxidant *via* visible light photocatalysis [70]. By using NH_2-enaminones **20** and NH_4SCN as starting materials, the synthesis of α-thiocyanated NH_2-enaminones **21** could be accessed by means of blue LEDs irradiation in the presence of $Ru(bpy)_3Cl_2{\cdot}6H_2O$ photocatalyst. The reactions were initiated by the Ru-based photocatalyst enabling the formation of ·SCN and PC anionic radical. The free radical addition of ·SCN to the enaminone C=C double bond in **20** donated **8A**. Meanwhile, the coupling of the PC anionic free radical to O_2 leads to the generation of an oxygen anionic free radical accompanied by PC regeneration. Intermediate **8A** captured oxygen anionic free radical (observed by HRMS) afforded intermediate **8B** in the presence of an ammonium cation. Further, the elimination of hydrogen peroxide in intermediate **8B** generated thiocyanated NH_2-enaminones **21**. When base was used following the photocatalytic process, the tandem cyclization and tautomerization processes took place to give 2-aminothiazoles **22**. On the other hand, when NH_2-enaminones **21** are employed in aqueous acidic conditions, 2-thiazolinones **23** were obtained *via* cyclization, hydrolysis, and the elimination of ammonium (Scheme 8).

3. Functionalization reactions *via* C=C double bond cleavage

Scissoring the C=C bond of enaminones constitutes one of the irreplaceable tools of modern organic synthesis in the form of either partial [71–74] or full bond cleavage [75–77]. Among them, visible-light-mediated C=C bond cleavage of enaminones have been also identified as useful synthetic approaches.

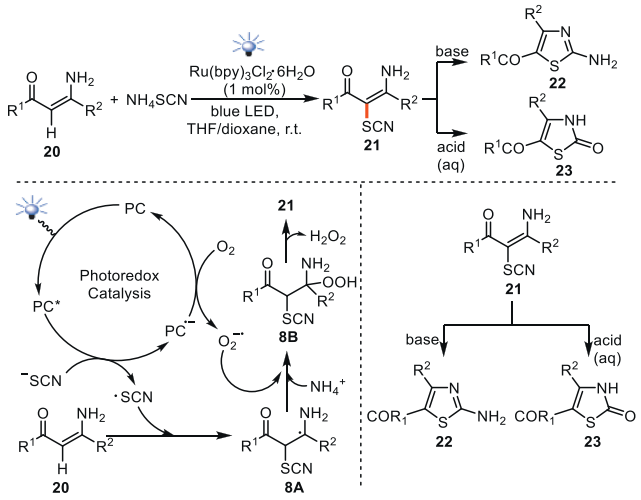
3.1. Synthesis of 1,2-diketone or its derivatives

As early as in 1970s, Wasserman and Ives firstly revealed that 1,2-diketones can be obtained from enaminones *via* C=C double bond cleavage under the conditions of 650 W lamp heating at −78 °C to room temperature [78,79]. In these reactions, the C=C bonds of enamines were cleaved through [2 + 2] cycloaddition procedure to give two carbonyl compounds. In 2015, our group developed a facile method for the synthesis of 1,2-diketones *via* C=C bond cleavage of enaminones under ambient conditions through visible-light photocatalysis in presence of Rose Bengal (RB) [80]. By employing enaminones **24** as the substrate, as shown in Scheme 9, with visible light irradiation, RB was converted into the excited RB*, which further reacted with $^3O_2$ to regenerate the stage of RB and produce singlet oxygen $^1O_2$. The singlet oxygen then incorporated to the enaminone **24**, giving peroxide intermediates **9A**. The subsequent decomposition of **9A** gave the 1,2-diketones **25**, which could be captured by diamine to afford quinoxalines **26** *via* stepwise operation.

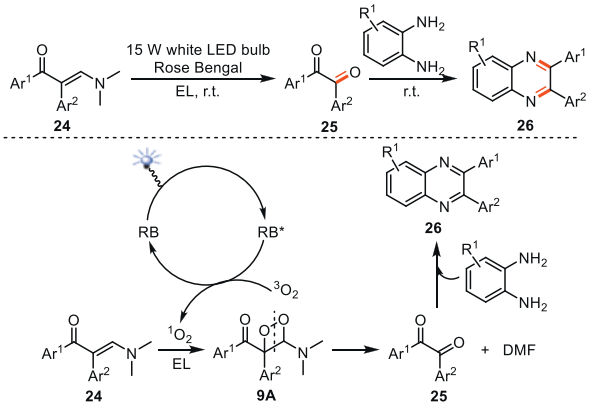
Interestingly, by employing enaminones **27** to react with alcohols **28** under the irritation of 20 W green LEDs in the presence of Rose Bengal, our group further developed a facile method for the synthesis of useful α-ketoesters [81]. This method showed general tolerance to the aryl group of enaminones and primary/secondary alcohols. Analogously, the visible light irradiation to RB gave rise to excited RB* species, which further activates $^3O_2$ to the active singlet oxygen $^1O_2$. The highly active singlet oxygen $^1O_2$ then coupled the C=C double bond of enaminone to offer 1,2-dioxetane **10A** which was further converted to intermediate **10B** through the ring opening and a subsequent N–O bond formation process. Next, alcohol acted as nucleophilic reagent to attack the C–O bond in intermediate **10B**, delivering zwitterion intermediate **10C**. The successive decomposition afforded the final product α-ketoester **29** and **10D**. The hemiaminal **10D** might be further oxidized to DMF under the titled oxidative conditions (Scheme 10).

3.2. Synthesis of quaternary amino acid derivatives

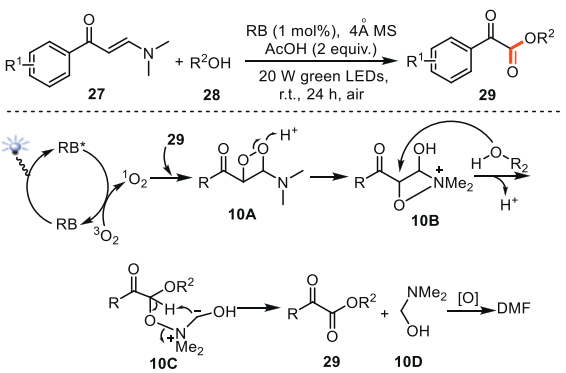
In 2014, Li and co-workers reported a visible-light-promoted transformation involving the ene-type reaction of secondary enam-



Scheme 8. Photocatalytic C–H thiocyanation of NH_2-enaminones.



Scheme 9. Synthesis of 1,2-diketones and quinoxalines *via* C=C bond cleavage of enaminones.



Scheme 10. Synthesis of α-ketoester *via* C=C bond cleavage of enaminones.

ino ketones with singlet oxygen, followed by a 1,2-acyl migration, affording quaternary amino acid derivatives [82]. The reaction pathway was distinctively different from the previous reports of C=C bond cleavage by singlet oxygen. As shown in Scheme 11, under the irradiation of 14 W CFL, ruthenium(II) is converted into a high-energy excited singlet $^1Ru^{II*}$, which underwent intersystem crossing (ISC) to triplet $^3Ru^{II*}$. Then the triplet $^3Ru^{II*}$ species reacted with $^3O_2$ *via* intermolecular energy transfer process to regenerate the ground-state Ru^{II} and produced the reactive $^1O_2$ species. Next, an ene-type reaction happened between **30** and $^1O_2$ to yield the intermediate **11A**. The dehydration of **11A** gave **11B**, and a nucleophilic addition of alcohol to **11B** led to **11C**. With subsequent 1,2-acyl migration and protonation, the products **31** were formed (Scheme 11). It should be noted that a fluorescence emission quenching study and the redox potential of the substrate **30** measured by cyclic voltammetry experiments were carried out to support the proposed mechanism.

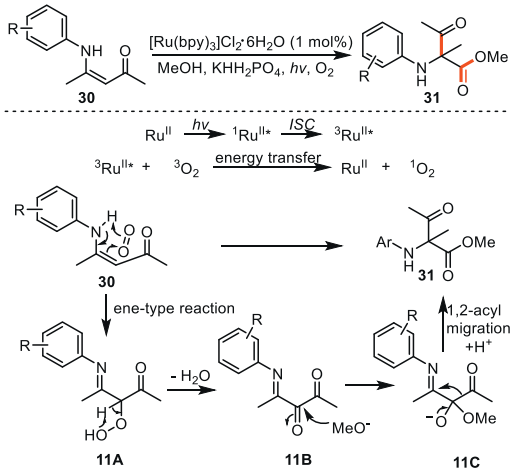
3.3. Synthesis of α-substituted γ-ketoesters

In 2022, Jin and co-workers developed a blue visible-light-promoted approach for the synthesis of α-substituted γ-ketoester derivatives *via* C=C bond partial cleavage of enaminones by using enaminones **32** and diazoesters **33** as the substrate [83]. The blue visible light irradiation induced the selective photolysis of aryl diazoesters **33** to give free carbene species with by releasing nitrogen gas. The *in situ* formed free carbene species was captured by enaminones **32** to provide the cyclopropane intermediate **12B**. Due to the stronger electron-withdrawing effect of arylcarbonyl group than that of ester carbonyl group, path a instead of path b could occur *via* ring opening driven by nitrogen atom, affording the intermediate **12C** which might be further converted into α-formyl aryl γ-ketoeser **34** *via* hydrolysis. Then, with the help of Al_2O_3 Lewis acid, the final product α-substituted γ-ketoester **35** could be obtained by decarbonylation of **34** (Scheme 12). This strategy broadened the methods available for accessing the α-formyl aryl γ-ketoester or α-aryl γ-ketoester derivatives.

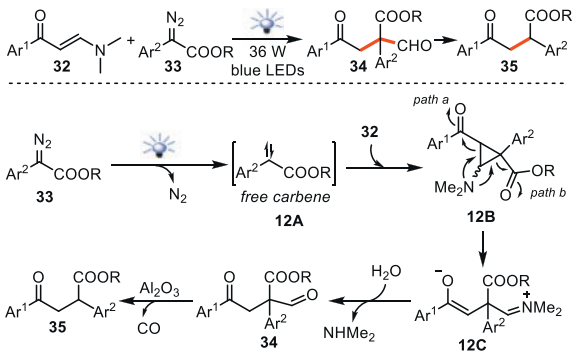
4. Annulation reactions for the synthesis of heterocyclic and carbocyclic scaffolds

4.1. Synthesis of five-membered N-heterocycles

As a typical five-membered *N*-heterocycles, the indole motif is a well-documented core structure of numerous natural products



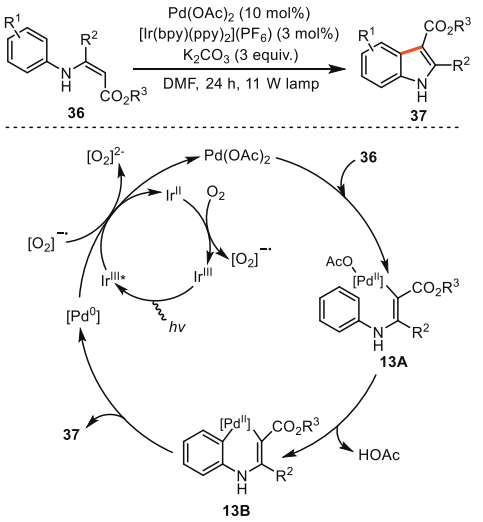
Scheme 11. Visible-light-mediated the partial cleavage of enaminone C=C double bond.



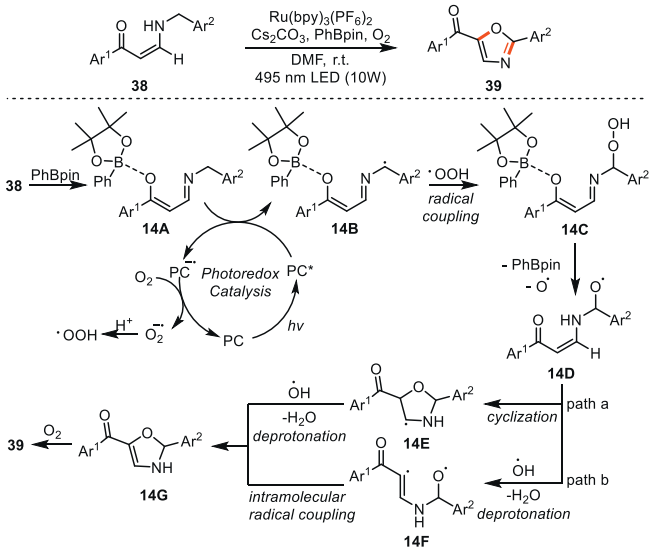
Scheme 12. Synthesis of α-substituted γ-ketoesters *via* C=C bond cleavage of enaminones.

and bioactive compounds. In addition to the Fischer indole syntheses, many different synthetic approaches using modern transition-metal catalysis are known. The enaminone annulations leading to indoles *via* intramolecular C–H activation by transition metal catalysis have been known for long period, but the reliance on stoichiometric chemical oxidant and heating at elevated temperature are limits of such methods. In 2014, Rueping *et al.* reported the enaminone-based indole synthesis using a new combination of palladium and photoredox catalysis [84]. With catalytic amount of the photoredox catalyst in the presence of visible light, the typical high loadings of external oxidants could be avoided. In the first step, the C–H bond activation of the olefin of **36** took place *via* Pd(II) insertion, giving the intermediate **13A** which further underwent the arene C–H bond to form the six-membered cyclopalladium intermediate **13B**. After reductive elimination, indoles **37** were produced and the resulting Pd(0) was re-oxidized to Pd(II) by either the photoredox catalyst or the *in situ* formed superoxide anion (Scheme 13).

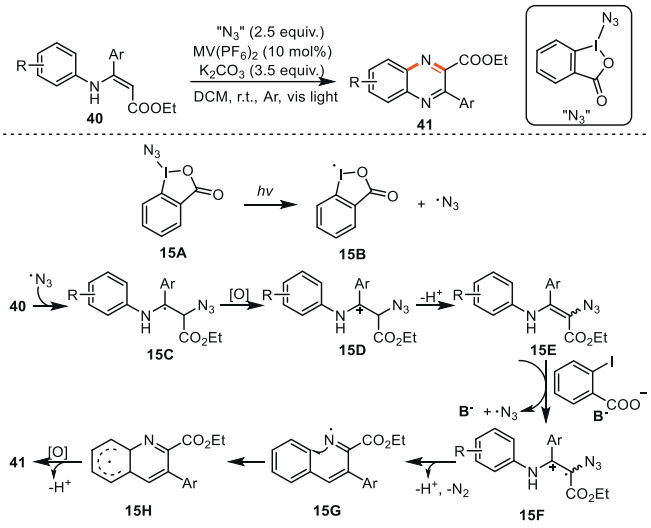
Very recently, Baell and Huang *et al.* established a protocol for the synthesis of polysubstituted oxazoles through photocatalytic benzylic C–H oxidation/cyclization of enaminones with molecular oxygen as an ideal and green oxidant [85]. This strategy featured broad substrate scope and good functional group tolerance. Based on the results of control experiments and the DFT computations, the authors proposed a plausible mechanism (Scheme 14). Firstly, the $Ru(bpy)_2(PF_6)_2$ was excited by 495 nm LEDs to form $Ru(bpy)_2(PF_6)_2^*$ which underwent a SET with the benzylic C–H bond of B-O complex **14A** to give $Ru(bpy)_2(PF_6)_2^{\bullet-}$ and benzyl rad-



Scheme 13. Synthesis of indoles *via* intramolecular annulation reactions of enamine ester.



Scheme 14. Synthesis of polysubstituted oxazoles from enaminones.



Scheme 15. Synthesis of quinoxalines *via* tandem azidation/cyclization of *N*-arylenamines.

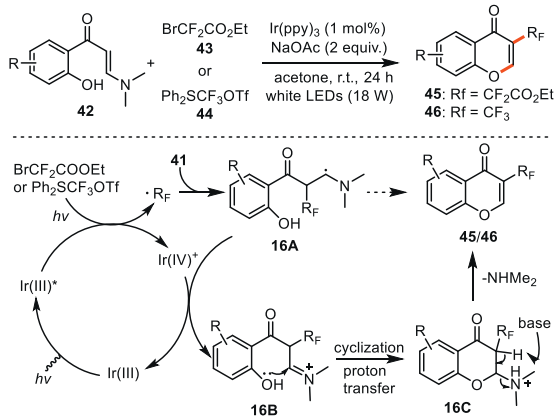
ical **14B**. The $Ru(bpy)_2(PF_6)_2^{\bullet-}$ is subsequently oxidized by molecular oxygen to regenerate $Ru(bpy)_2(PF_6)_2$ and release superoxide radical anion $O_2^{\bullet-}$. The superoxide anion coupled proton to generate ·OOH. The benzyl radical **14B** coupled with ·OOH to access adduct **14C** which could be further transferred into oxygen radical **14D** by losing PhBpin and hydroxyl radical. Then, two possible reaction pathways could occur. On the one hand, the 2,3-dihydrooxazole skeleton **14G** was formed *via* intramolecular cyclization of oxygen radical intermediate **14D** and a deprotonation process (path a, Scheme 14). On the other hand, diradical species **14F** could be obtained *via* deprotonation, and the subsequent intramolecular radical-radical coupling gave **14G** (path b, Scheme 14). Finally, the desired oxazole product **39** was afforded through further oxidation and deprotonation process under O_2. Due to the high electro-negativity of oxygen in the hydroxyl radical, it is relatively unstable and tends to react with the C–H bond to form a more stable carbon radical, path a was hypothesized as the more favorable route.

4.2. Synthesis of six-membered N-heterocycles and O-heterocycles

In 2018, Yu and co-workers achieved the synthesis of quinoxalines *via* tandem azidation/intramolecular C–H amination under visible light irradiation by using 1-azidyl-1,2-benziodoxole as the azidating agent with *N*-arylenamines [86]. Under the irradiation of visible light, the I-N bond of **15A** cleaved to yield the azidyl radical **15B**, which subsequently added to the C=C double bond in *N*-arylenamines to form the intermediate **15C**. The **15C** was further oxidized to carbocation intermediate **15D**, which was then converted into vinyl azide **15E** *via* oxidative deprotonation. Vinyl azide **15E** was more prone to be oxidized to imine radical **15G** because the azide group would render the C=C double bond in **15E** electronically richer than the one in **40**. Subsequent cyclization of **15G** followed by oxidation and deprotonation afforded the final products **41** (Scheme 15). It was worth mentioning that the substituent at β-site in *N*-arylenamines **40** exhibited crucial influence on the reaction, and the conditions were needed to be modified for the reactions of different substrates. For example, $Cu(OAc)_2$ was required for the preparation of 3-(trifluoromethyl)quinoxalines, whereas $Ru(bpy)_3Cl_2$ along with $Cu(OAc)_2$ combination was found to be more favorable for the synthesis of 2,3-diarylquinoxalines (Scheme 15).

Currently, the annulation reactions of *N,N*-disubstituted 2-hydorxyphenyl enaminones has been widely used in the construction of diversely functionalized chromones, especially for the synthesis of 3-substituted chromones. Among these methods, photoredox catalysis has won particular attention as options of the enhanced sustainability. In 2017, Yang and Chen reported a visible-light-driven, radical-triggered tandem cyclization of *o*-hydroxyaryl enaminones for the synthesis of 3-CF_2/CF_3-chromones [87]. At first, the irradiation of the catalyst [Ir(ppy)$_3$] under visible light generated the excited state Ir(ppy)$_3$* which was then oxidized by $BrCF_2COOEt$ or Ph_2SCF_3OTf to generate $[Ir(IV)(ppy)_3]^+$ complex and R_F free radical species. Subsequently, the R_F radical added to the C=C double bonds of substrate **42** regioselectively to give radical intermediate **16A**. Further oxidation to this intermediate by $[Ir(IV)(ppy)_3]^+$ provided **16B** with the concurrent regeneration of [Ir(ppy)$_3$]. Next, the hydroxyl group on benzene ring attacked the iminium cation to give intermediate **16C**. Ultimately, the *N,N*-dimethyl group was eliminated to furnish the desired product **45**/**46** (Scheme 16). Ten 3-CF_2COOEt and ten 3-CF_3 substituted chromones were obtained in acetone at room temperature in good to excellent yields.

In the same year, Zhang *et al.* developed an efficient method for the synthesis of 3-CF_2-chromones *via* a ruthenium reduction

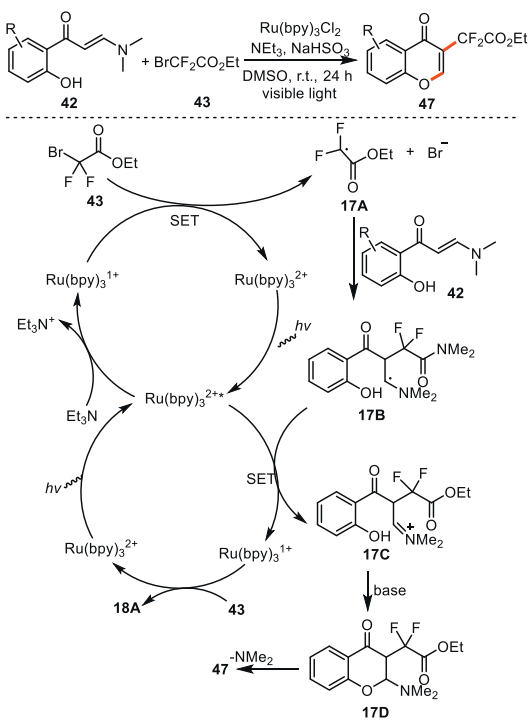


Scheme 16. Synthesis of 3-CF_2/CF_3-containing chromones *via* tandem cyclization of *o*-hydroxyaryl enaminones.

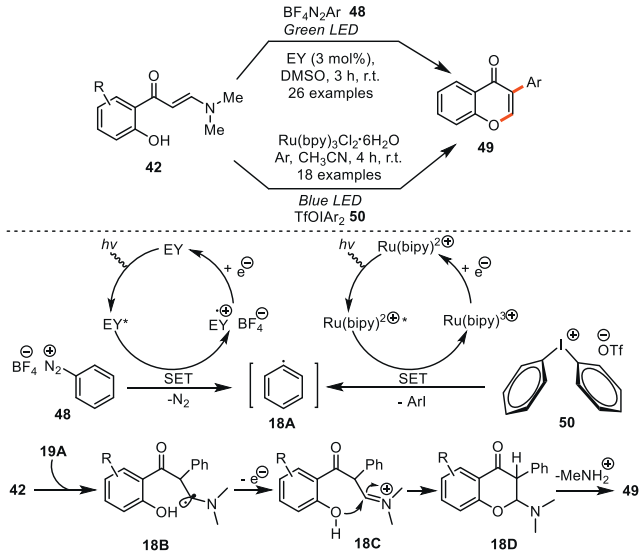
cycle from the similar substrates [88]. The catalyst $[Ru(bpy)_3]^{2+}$ was firstly converted into the excited state $[Ru(bpy)_3]^{2+*}$ under visible light, and enabled the oxidation of Et_3N to generate the $[Ru(bpy)_3]^{1+}$ species. Then the electron-rich metal complex $[Ru(bpy)_3]^{1+}$ underwent a SET process with the cleavage of C-Br bond in $CF_2BrCOOEt$ to afford an electron-deficient radical **17A** and regenerate $[Ru(bpy)_3]^{2+}$. Intermediate **17A** added to the C=C double bond in substrate **42** to give radical **17B**. The SET between **17B** and $[Ru(bpy)_3]^{2+*}$ provided iminium cation intermediate **17C** and the metal complex $[Ru(bpy)_3]^{1+}$. Finally, the chromones **47** were obtained *via* intramolecular annulation and a subsequent elimination of dimethylamine (Scheme 17).

In 2020, Iaroshenko and Mkrtchyan developed two facile routes to synthesis diverse 3-arylchromones through photo-arylation reactions of *ortho*-hydroxyarylenaminones by using aryldiazonium tetrafluoroborates and diaryliodonium triflates as aryl sources, respectively [89]. Initially, the irradiation of Eosin Y and Ru(II) generates their excited states by an appropriate light source. Aryl radicals **18A** could be formed from aryldiazonium tetrafluoroborates and diaryliodonium triflates catalyzed by the corresponding excited *Eosin Y and *Ru(II) species. The aryl radicals **18A** formed thereby attacked promptly on the enaminone to afford the radical intermediate **18B** which was oxidized afterwards to carbocation **18C**. The annulation on this intermediate then gave intermediate **18D**. Finally, the 3-arylchromones **49** were furnished by Et_2NH elimination (Scheme 18).

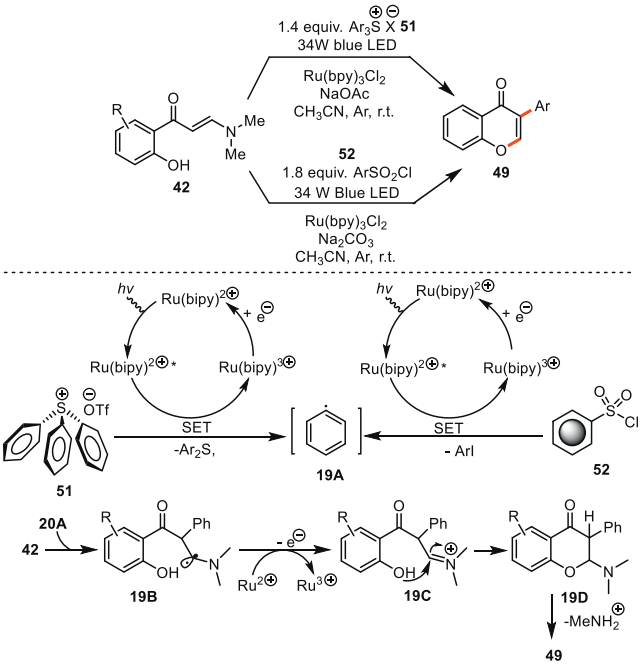
In 2021, the same group disclosed different methods for the synthesis of 3-arylchromones by arylation of *ortho*-hydroxyarylenaminones by photocatalysis by employing sulfonium salts and arenesulfonyl chlorides as the aryl radical precursors [90]. These two routes showed good efficiency and were feasible for the preparation of 3-arylchromones in good to excellent yields. Analogously, the pathways were commenced by a SET oxidation initiated by the excited state Ru(II)*, which coupled with triarylsulfonium and arenesulfonyl chlorides to afford aryl radical (Ar·). The addition of the free radical to the enaminone moiety gave



Scheme 17. Synthesis of 3-CF_2-containing chromones *via* radical cascade reaction of *o*-hydroxyaryl enaminones.



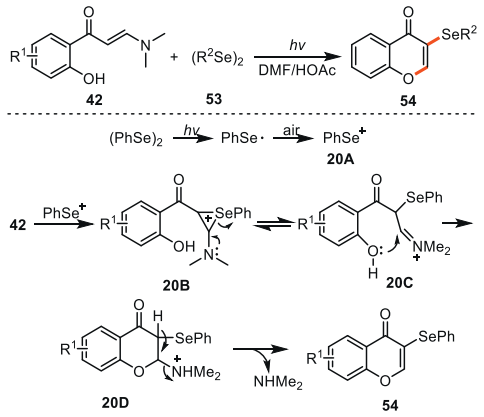
Scheme 18. Visible-light-mediated arylation of *o*-hydroxyaryl enaminones by BF_4N_2Ar and $TfOIAr_2$.



Scheme 19. Visible-light-mediated arylation of *o*–hydroxyl aryl enaminones by sulfonium salts and arenesulfonyl chlorides.

carbon-centered radical **19B** which could be further be converted into the final products **49** *via* nucleophilic annulation and amine elimination (Scheme 19).

In 2021, Xu *et al.* developed a visible light-promoted, metal-free selenylation/cyclization cascade between *ortho*-hydroxyaryl enaminones and diselenides for the synthesis of 3-selanylchromones under mild conditions [91]. Notably, no transition metal catalyst, photocatalyst or additional oxidant were required in the reactions. The final products could be easily converted into selenyl-functionalized pyrimidines by reacting with benzamidines. As for mechanism, the light irradiation to diphenyl diselenide **53** produced phenylselenyl radicals which could be further oxidized to phenylselenyl cation **20A** by air. Subsequently, the phenylselenyl cation **20A** coupled the C=C bond in the enaminone **42** to afford cycloselenium ion **20B** on which a ring-opening driven by lone pair electrons of NMe_2 took place to give rise to imine cation intermediate **20C**. Then the

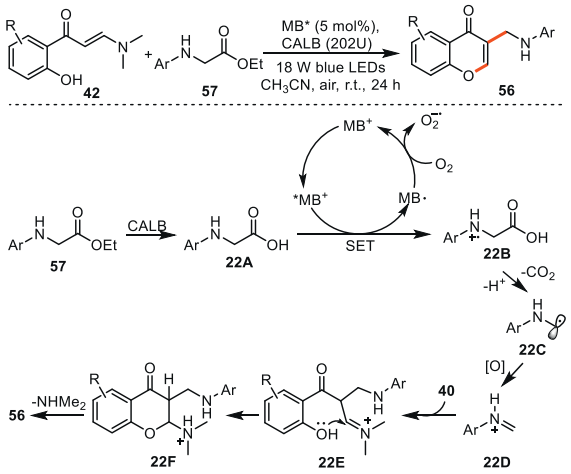


Scheme 20. The photocatalytic synthesis of 3-selenochomones.

intramolecular cyclization of **20C** and a following elimination of dimethylamine delivered the final products **54** (Scheme 20).

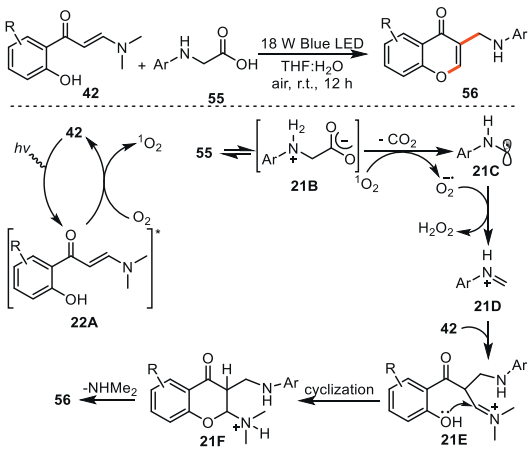
In 2022, Le *et al.* disclosed a method for the synthesis of 3-aminoalkyl chromones from *o*-hydroxyphenyl enaminone and *N*-aryl glycines **55** under visible light catalysis [92]. This synthetic method required no photocatalyst or additive, and proceeded to products with good functional group tolerance. The reactions were proposed to be initiated by the light irradiation to enaminones **42**, affording the excited state **21A** (**42***), which acted as the photocatalyst to provide singlet oxygen ($^1O_2$) from molecular oxygen through energy transfer process. The singlet oxygen ($^1O_2$) interacted with ammonium-carboxylate salt **21B**, an isomeric form of *N*-arylglycine **55**, to give the α-amino radical intermediate **21C** and superoxide radicals ($O_2^{-\cdot}$). Intermediate **21C** was further oxidized and deprotonated to form the imine specie **21D** which was subsequently captured by substrate **42** *via* nucleophilic addition to provide iminium intermediate **21E**. The intramolecular cyclization of **21E** by intramolecular nucleophilic addition of OH group to imine cation gives intermediate **21F**. The elimination of dimethylamine then led to the desired products **56** (Scheme 21).

In the same year, the group reported another approach for the synthesis of 3-aminoalkyl chromones **56** using *N*-arylglycine esters as the alkylating agents by the cooperative catalysis of visible light and an enzyme. By utilizing Methylene Blue (MB) as the photocatalyst [93]. This approach avoided the synthesis of acids from esters in a separate step, since *N*-aryl glycines were derived from *N*-aryl glycine salts under strong basic conditions. As shown in Scheme 22, Firstly, *N*-aryl glycine ester **57** was hydrolyzed into *N*-arylglycine **22A** with the help of Lipase B Candida antarctica (CALB). Then radical cation **22B** could be formed from *N*-aryl glycine **22A** *via* SET oxidation by the excited photocatalyst MB^{+*}. The 3-aminoakyl chromones **56** could be obtained by similar photoredox decarboxylation of *N*-arylglycine **22A**, oxidation of aminoalkyl radicals **22D**, Mannich reaction, intramolecular nucleophilic cyclization and subsequent amine elimination.

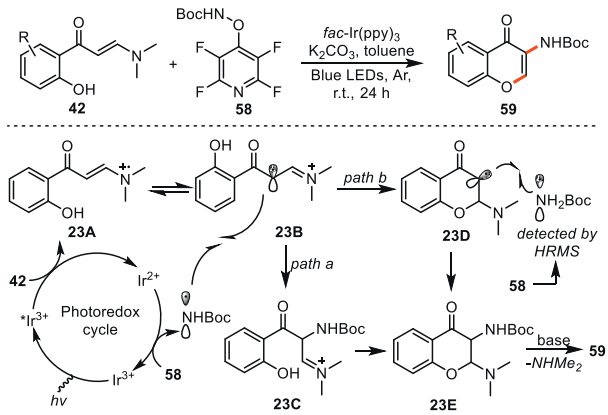


Scheme 22. The combined enzyme and photoredox catalysis for the synthesis of 3-aminoalkyl chromones.

In 2022, Yang and Xiang *et al.* established a new cascade protocol for the assembly of 3-aminochromones **42** with *o*-hydroxyaryl enaminones and *O*-perhalopyridin-4-yl hydroxyl amine **58**, a versatile amidyl-radical precursor [94]. This protocol featured with mild reaction conditions, synthetic simplicity, and scalability. In the reactions, the photocatalyst *fac*-Ir(ppy)$_3$ was first excited to generate its active species *fac*-Ir(ppy)$_3$* under the blue LEDs irradiation. The subsequent quenching of the exited photocatalyst by enaminone **42** generated the nitrogen-centered radical **23A** and Ir^{2+} *via* SET process. The highly reactive Ir^{2+} was immediately oxidized by **58** to furnish amido radical ·NHBoc along with regeneration of the Ir-photocatalyst. A facile radical transposition of **23A** delivered the isomeric carbon-center radical **23B**. The species could be quickly trapped by amido radical ·NHBoc to give intermediate **23C** prior to the cyclization process (path a). Alternatively, the cyclic radical **23D** might be formed *via* intramolecular cyclization of **23B** under in the presence of base (path b). Radical cross-coupling of **23D** with ·NHBoc led to the intermediate **23E**. The final products **59** were provided *via* the elimination of dimethylamine (Scheme 23).



Scheme 21. The photocatalytic synthesis of 3-aminoalkyl chromones.

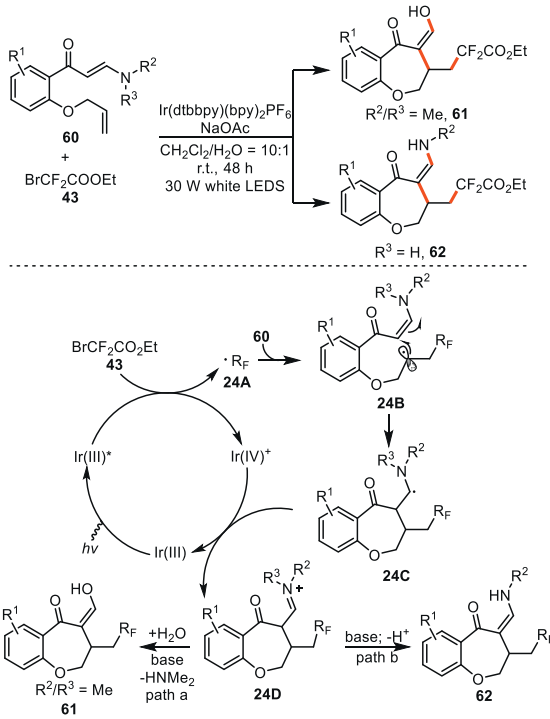


Scheme 23. The synthesis of 3-aminated chromones from *o*-hydroxyarylenaminones.

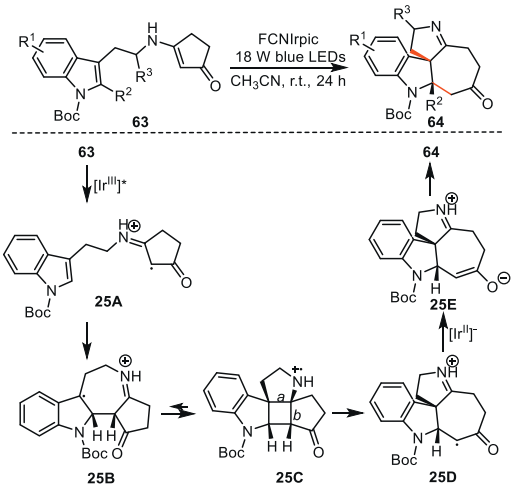
4.3. Synthesis of seven-membered O-heterocycles and carbocycles

In 2018, Yang and Chen developed a practical protocol accessing benzoxepines **61**/**62** by using functionalized enaminones **60** and ethyl bromodifluoroacetate **43** as starting materials with white LEDs irradiation in the presence of Ir(dtbbpy)(bpy)$_2$PF$_6$ [95]. In the formation of these fused seven-membered scaffolds, the excited state Ir(III)* occurred from Ir(III) under visible-light irradiation. The further reaction with BrCF$_2$COOEt **43** gave Ir(IV)$^+$ species and R_F radicals **24A**. Subsequently, the free radical addition of **24A** to the olefin unit in substrate **60** and a sequential radical addition cascade process generated radical intermediate **24C**. The quick oxidation by Ir(IV)$^+$ yielded iminium intermediate **24D** and regenerated Ir(III). When *N*,*N*-dimethyl enaminones (R^2/R^3 = Me) were used, the intermediate **24D** was quickly hydrolyzed by water to furnish products **61** (path a). In the case of the monosubstituted iminium ion (R^3 = H), the deprotonation and tautomerization processes took place to afford the corresponding enamine **62** (path b) (Scheme 24).

In 2021, Yang *et al.* developed a method for the synthesis of cyclohepta[*b*]indoles **64** *via* highly functionalized enaminones **63** [96]. This approach involves a visible-light-induced cascade of [2 + 2] cycloaddition and retro-Mannich-type reaction of enaminones. As shown in Scheme 25, radical cation intermediate **25A** was first formed by single electron oxidation of substrate **63** in the presence of excited-state FCNIrpic ([Ir^{III}]*). The oxidized enaminone moiety in intermediate **25A** readily underwent radical addition to the indole ring to furnish benzylic radical intermediate **25B** which then added to the iminium moiety to deliver radical cation **25C**. The resulting intermediate **25C** was unstable and tended to either go back to **25B** (breaking bond a) or forward to **25D** (breaking bond b). The species **25D** would subsequently be reduced by previously generated [Ir^{II}] species to zwitterion **25E**. The final products **64** were afforded *via* an intermolecular proton transfer in **25E**.



Scheme 24. The photocatalytic synthesis of CF_2-containing benzoxepine derivatives.



Scheme 25. The photocatalytic synthesis of cyclohepta[*b*]indoles.

5. Multicomponent reaction for heterocycle construction

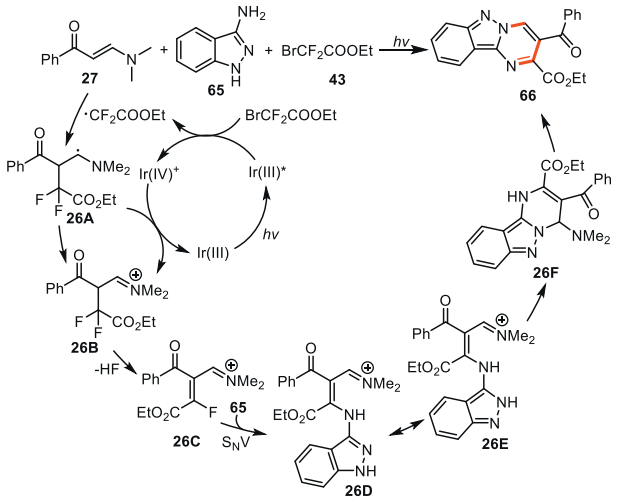
Multicomponent reactions (MCRs) are powerful tools in current organic synthesis due to their irreplaceable advantages in simple starting materials, step economy, product diversity and fast construction of molecular diversity [97,98]. Designing enaminone-based MCRs with photocatalyst would inarguably benefit the synthetic chemistry by providing highly sustainable routes toward highly diversified organic products.

5.1. Synthesis of pyrimido[1,2–b]indazole derivatives

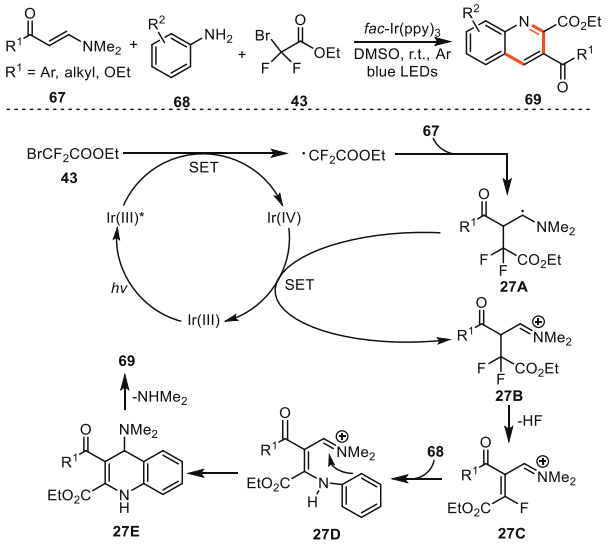
In 2021, Wang and co-workers reported a visible-light-driven three-component cyclization for the synthesis of pyrimido[1,2-*b*]indazole derivatives **66** from enaminones **27**, 3-aminoindazoles **65** and ethyl bromodifluoroacetate **43** [99]. The reactions were proposed to start from a metal-to-ligand charge transfer (MLCT) process from the photocatalyst *fac*-[Ir^{3+}(ppy)$_3$] to generate excited state Ir^{III}* under blue LEDs irradiation, enabling the C-Br bond cleavage of in **43** *via* SET reduction process to give alkyl radicals (·CF$_2$COOEt). The alkyl radicals subsequently added to the electron-rich olefin in the enaminone moiety and led to carbon radicals intermediate **26A**. The further oxidation on this intermediate by Ir^{IV} accessed to imine cation **26B** Subsequently, the intermediate **26B** underwent an elimination of HF to afford 1,3-vinylimine ion intermediate **26C** which was trapped by 3-aminoindazoles *via* addition-elimination process (SNV reaction) to form intermediate **26D** or its isomer **26E**. Afterwards, the intramolecular addition of the nucleophilic NH group to the iminium site gave tricyclic intermediate **26F**. The elimination of dimethyl amine from the amino dihydropyrimidine ring provided products **66** (Scheme 26).

5.2. Synthesis of 2, 3-difunctionalized quinolines

In 2022, Wang's group reported another three-component protocol for the synthesis of 2,3-difunctionalized quinolines **69** *via* the reactions of enaminones **67**, aryl amines **68** and ethyl bromodifluoroacetate **43** with the irradiation of blue LEDs in the presence of *fac*-Ir(ppy)$_3$ [100]. The reaction mechanism was familiar with the former one in Scheme 26. The difference was that when 1,3-vinyl imine ion intermediate **27C** was formed, it was rapidly trapped by aryl amine to give intermediate **27D** which underwent an intramolecular cyclization and amine elimination to provide products **69** (Scheme 27).



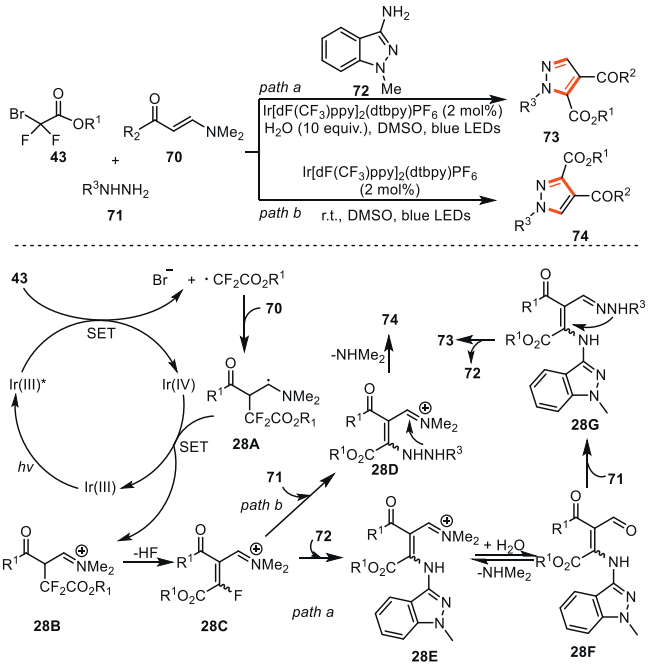
Scheme 26. Visible-light-driven three-component cyclization for the synthesis of pyrimido[1,2-*b*]indazole derivatives.



Scheme 27. Photoinduced three-component cyclization for the synthesis of 2,3-difunctionalized quinolines.

5.3. Synthesis of trisubstituted pyrazoles

Recently, Wang and Geng *et al.* again developed a multicomponent method for the tunable synthesis of pyrazoles **73** and **74** by employing bromodifluoroalkyl acetates **43**, enaminones, and hydrazines as starting materials with blue LEDs photocatalysis [101]. In these reactions, 1-methylindazol-3-amine acted as a traceless mediator in switching the regionselectivity of 1,3,4-trisubstituted and 1,4,5-trisubstituted pyrazole formation. Mechanically, the active 1,3-vinylimine ions intermediate **28C** was first formed through similar transformation processes as in the above works. This intermediate was then trapped by 1-methylindazol-3-amine **72** to form **28E**. Intermediate **28E** might further undergo hydrolysis to deliver intermediate **28F**, and subsequently reacted with hydrazine to provide **28G**. The sequential intramolecular cyclization/deamination processes then took place to afforded 1,4,5-trisubstituted pyrazoles **73**. On the other hand, when the traceless mediator **72** was not added, R_3NHNH_2 was directly captured 1,3-vinylimine ions **28C**, giving intermediate **28D** *via* an SNV process. The similar intramolecular cyclization/deamination process then led to the formation of 1,3,4-trisubstituted pyrazoles **74** (Scheme 28).



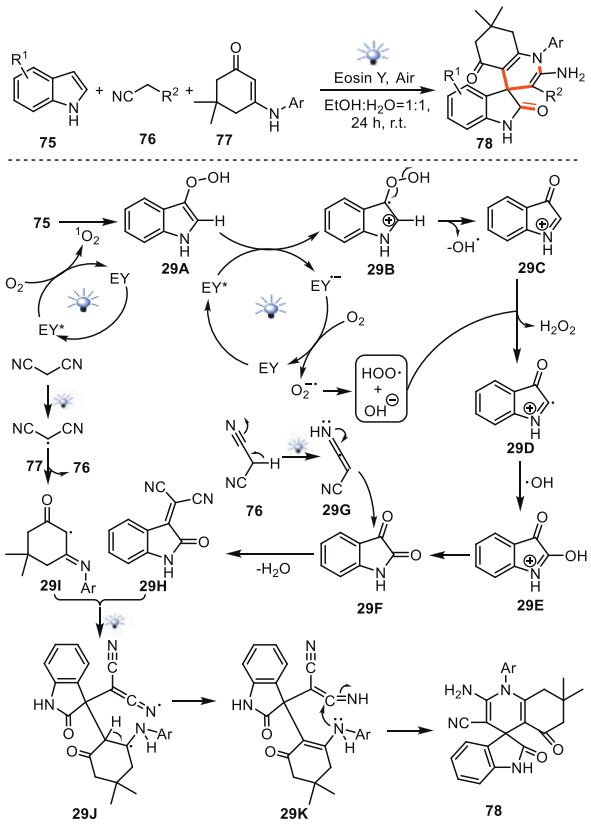
Scheme 28. Photoinduced switchable multicomponent cyclization for the synthesis of adjustable multi-substituted pyrazoles.

5.4. Synthesis of spiro[indoline-3,4′-quinoline] derivatives

Very recently, Singh *et al.* reported the visible light-mediated three-component synthesis of spiro[indoline-3,4′-quinoline] derivatives **78** *via* the reactions of indoles **75**, methylene nitriles **76** and enaminones **77** under the irradiation of a 22 W LED lamp [102]. In the formation of these spiroheterocyclic products, the initially irradiation of light to Eosin Y led to the excited state EY* which promoted the transformation of molecular oxygen to singlet oxygen. Indoles captured the singlet oxygen to afford peroxo species **29A**, and a subsequent oxidation by EY* led to **29B** By the O–O homolytic cleavage in **29B**, the cation **29C** and hydroxyl radical were created. The C2-site hydrogen atom in **29C** could be abstracted by the peroxyl free radical to deliver intermediate **29D**. The rapid coupling of **29D** with hydroxyl radical gave **29E**, and **29E** could further isomerize into **29F**. Meanwhile, the light irradiation to substrate **76** led to intermediate **29G**. The reaction of **29F** with **29G** provided **29H**. On the other hand, the free radical intermediate **29I** was formed *via* the promotion of malononitrile and visible light irradiation. The addition of **29I** to **29H** led to the formation of **29J**. After a sequential hydrogen radical transfer and intramolecular cyclization process, the final products **78** were provided (Scheme 29).

6. Conclusions and perspectives

Herein, we reviewed for the first time the advances in the visible light-mediated chemical transformations of enaminones. The modes of transformations, including the direct C(sp^2)-H α-functionalization, C=C double bond functionalization, annulation toward heterocyclic and carbocyclic scaffolds, as well as enaminone-based multicomponent reactions have been covered. These interesting results illustrate the power of combining enaminone chemistry and photocatalysis in the designation and application of energy economic, mild and diversity-oriented organic reactions. However, challenges remain yet in this research area. For example, the frequent application of noble-metal photocatalyst, limited generality in the application of different free radical reac-



Scheme 29. Visible light triggered three-component cyclization for the synthesis of spiro[indoline-3,4′-quinoline].

tion designation with most of the currently known model, and switchable control of the site selectivity in analogous sites such as the two vinyl C–H bonds are yet non-negligible restrictions. Therefore, in developing more novel and applicable photocatalytic enaminone-based synthesis, extensive efforts are still highly desirable. The discovery on more novel and different transformation and catalytic modes, tuning the chemo-selectivity, application in other important synthesis such as asymmetric synthesis, target-oriented synthesis, are directions worthy of more attention.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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