

Visible light-driven organic photochemical synthesis in China

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In recent years, visible light-driven organic photochemical synthesis has attracted wide research interest from academic and industrial communities due to its features of green and sustainable chemistry. In this flourishing area, Chinese chemists have devoted great efforts to different aspects of synthetic chemistry. This review will summarize their representative work according to the following categories: C–H functionalization, synthesis of aromatic aza-heterocycles, asymmetric organic photochemical synthesis, transformations of small molecules and biomolecule-compatible reactions.

visible light, photochemical synthesis, C–H functionalization, aromatic aza-heterocycle, asymmetric catalysis, biomolecule-compatible reaction, small molecule

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1 Introduction

Organic photochemical synthesis by mimicking the photosynthesis of plants in nature has been a dream for synthetic communities for more than one hundred years [1]. In the past decade, due to the impressive work of MacMillan, Yoon and Stephenson [2], organic photochemical synthesis, especially the one driven by visible light, has undergone a conspicuous renaissance [3]. More significantly, many photoactivation modes, such as the direct photo-excitation of substrates, reagents or their complex, photo-SET (single electron transfer) and ET (energy transfer), PCET (proton-coupling electron

transfer), etc., have seeded a number of updated or unprecedented chemical transformations under mild and user-friendly conditions for organic synthesis. Here, we would like to highlight the impressive and representative work in this research area contributed by Chinese scientists from the following five aspects: (1) photoredox catalyzed C–H bond functionalization; (2) visible-light-induced synthesis of privileged aromatic aza-heterocycles; (3) visible-light-induced asymmetric organic photochemical synthesis; (4) visible light-induced transformations of small molecules; (5) visible-light-induced reactions under biomolecule-compatible conditions.

2 Photoredox catalyzed C–H bond functionalization

C–H bond functionalization is an essential topic in organic

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synthetic chemistry. Over the past several years, visible-light-induced photocatalysis has become a powerful method for the direct functionalization of C–H bonds. In this section, representative examples of visible-light photocatalytic sp^3 and sp^2 C–H bond functionalization will be discussed.

2.1 Visible-light mediated $C(sp^3)$ –H bond functionalization

Tertiary amine scaffolds are important synthetic synthons and widely exist in numerous organic compounds. Functionalization of a $C(sp^3)$ –H bond adjacent to the nitrogen atom provides a practical strategy for the modification of *N*-containing compounds. In 2010, Stephenson and coworkers [2c] first realized direct $C(sp^3)$ –H functionalization of *N*-aryl tetrahydroisoquinolines using visible-light photoredox catalysis. Since then, many examples of the functionalization of a $C(sp^3)$ –H bond adjacent to a nitrogen atom under photoredox catalysis have been reported.

Tandem reactions have proven to be a superior strategy for the rapid construction of intricate molecular architectures. In 2011, the Xiao's group [4] described a highly efficient method for the construction of biologically important pyrrolo [2,1,0]isoquinolines using a visible-light-induced tandem C (sp^3)–H oxidation/[3+2] cycloaddition/oxidative aromatization process. The substrate **1** undergoes the SET process under photoredox catalysis conditions to generate a 1,3-dipole that undergo [3+2] cycloaddition with dipolarophile components, leading to **6**. Subsequently, the intermediate **6** can be oxidized to pyrrolo[2,1,0]isoquinolines in good to excellent yields (Scheme 1).

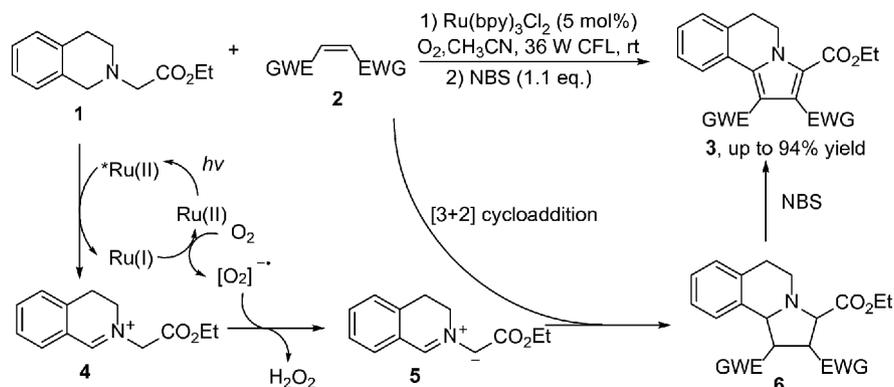
In 2012, the Xia's group [5] applied enol silanes as nucleophiles to trap the iminium ion generated through photoredox catalysis (Scheme 2). A variety of tetrahydroisoquinolines underwent a Mannich-type reaction smoothly, leading to the desired coupling products in almost quantitative yield.

The high emission quantum yields and long-lived triplet excited state of organogold(III) complexes with strong-field

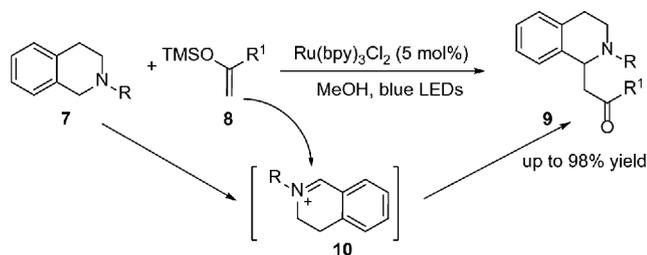
ligands make them appealing species for photocatalysis. In 2012, Che and coworkers [6] applied a highly phosphorescent NHC-gold(III) complex as a photocatalyst to accomplish direct $C(sp^3)$ –H functionalization of secondary and tertiary amines by irradiation with a 300 W xenon lamp under an oxygen atmosphere. The oxidation of secondary amines to imines or the oxidative cyanation of tertiary amines proceeds at a high efficiency with almost 100% conversion and excellent product yields (Scheme 3).

Bicyclic isoxazolidine scaffolds are frequently found in alkaloids. Their wide spectrum of biological activities has made the synthesis of these compounds attractive. However, multiple steps are generally required to construct these important structures. In 2013, the Zhu's group [7] developed an efficient method for obtaining the isoxazolidine derivatives in one process from simple tertiary amines through a C–H activation/retro-aza-Michael/oxidation-cyclization tandem sequence using visible-light. A plausible mechanism was proposed (Scheme 4). Under photoredox catalysis conditions with air as a green oxidant, an iminium ion intermediate was first formed and subsequently underwent a Mannich reaction with ketoesters, yielding intermediate **18**. Then, a retro-aza-Michael process occurred to generate intermediate **19**, which was quickly oxidized to nitrile oxides **20**. The subsequent [3+2] cycloaddition finally produced bicyclic isoxazolidines **16**.

Cross-dehydrogenative coupling can be used to form a C–C bond directly from two different C–H bonds. In 2013, the Wu's group [8] reported a cross-coupling hydrogen evolution reaction between *N*-Ar-tetrahydroisoquinolines and indoles by combining eosin Y and G-RuO₂ as the photosensitizer and the catalyst, respectively. This reaction does not require any sacrificial oxidant and the desired cross-coupling products are generated in excellent yields with H₂ as the only by-product (Scheme 5). Under the coaction of eosin Y and G-RuO₂, the tetrahydroisoquinolines is oxidized to form iminium ion **23** and release hydrogen. Then, the nucleophilic addition to the iminium gives rise to the cross-coupling product **22**.



Scheme 1 Visible-light-induced tandem $C(sp^3)$ –H oxidation/[3+2] cycloaddition/oxidative aromatization process.



Scheme 2 Visible light-induced Mannich reaction with enol silanes.

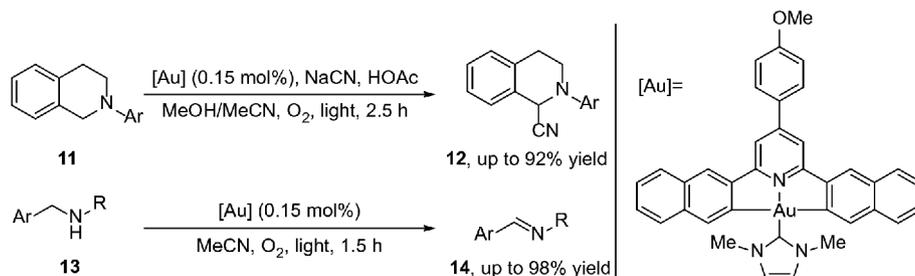
In 2017, the Li's group [9] also reported a visible-light photoredox catalyzed H_2 evolution reaction with various *N*-heterocycles at room temperature by combining photoredox catalysis and cobalt catalysis. This desaturation strategy could be applied to synthesize a wide range of *N*-heteroaromatic compounds (Scheme 6). The potential application of this protocol to hydrogen-storage materials was also demonstrated via the reversible dehydrogenation-hydrogenation of 2-methyl-THQ and 2-methylquinoline on a gram scale.

Recently, the Xu's group [10] reported another example of visible-light induced desaturation of *N*-heterocycles using the simultaneous functionalization of two vicinal $\text{C}(\text{sp}^3)\text{-H}$ bonds. The *in situ* generated cyclic enamine intermediates

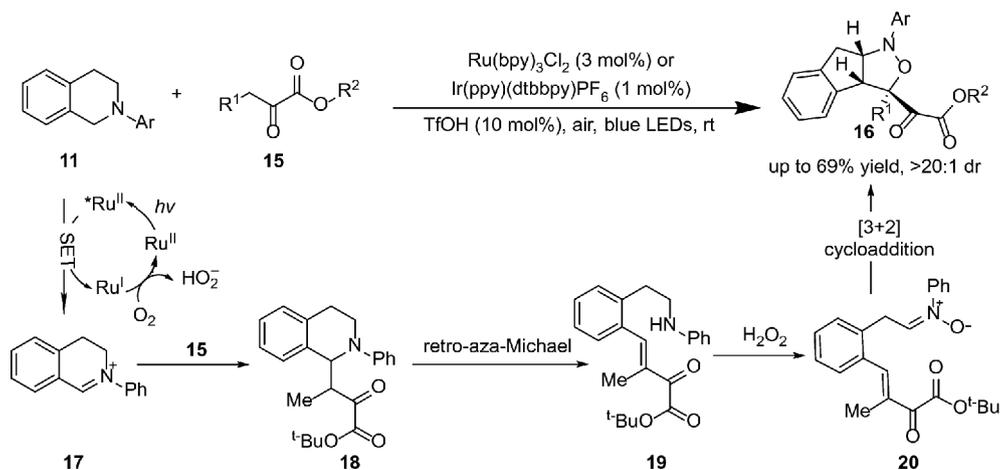
undergo a subsequent [2+2] cycloaddition procedure with acetylene esters to form a wide array of bicyclic amino acid derivatives (Scheme 7).

The α -amino radicals are useful reactive intermediates that can participate in a series of reactions and provide various *N*-containing compounds. Visible-light-induced photocatalysis is a versatile tool for the *in situ* generation of α -amino radicals [11]. The Li's group [12] reported the addition of α -aminoalkyl radicals to isocyanate and isothiocyanate under visible-light-photoredox conditions. A new visible light sensitizer, Ir-based FIrpic, was found to be the best catalyst among the six catalysts screened. Good yields of α -amino amides and α -amino thioamides could be obtained with the assistance of FIrpic (Scheme 8). The authors found that the steric effect of aniline substrates seemed to have a great influence on the reaction yields. For example, the *para*- and *meta*-methyl *N,N*-dimethylanilines gave the desired products in a 75% and 88% yield, respectively, whereas an only 28% yield of the corresponding product was obtained with ortho-methyl *N,N*-dimethylaniline as the substrate.

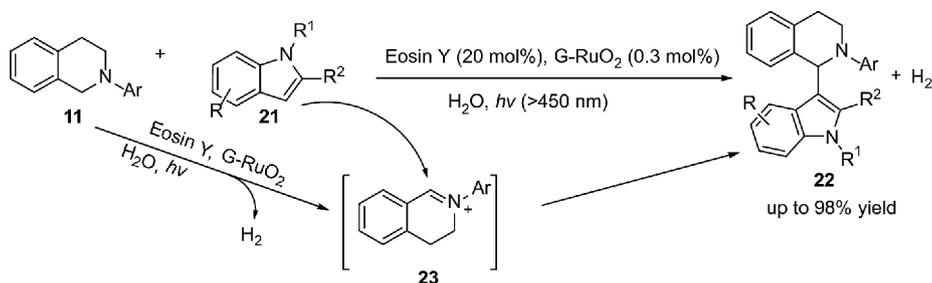
3-Acylindoles, as the core structures of many biologically active heterocyclic compounds, are widely present in numerous bioactive natural products, pharmaceuticals, and agrochemicals. In 2014, Zhou and coworkers [13] reported the visible-light photoredox catalyzed synthesis of 3-acyin-



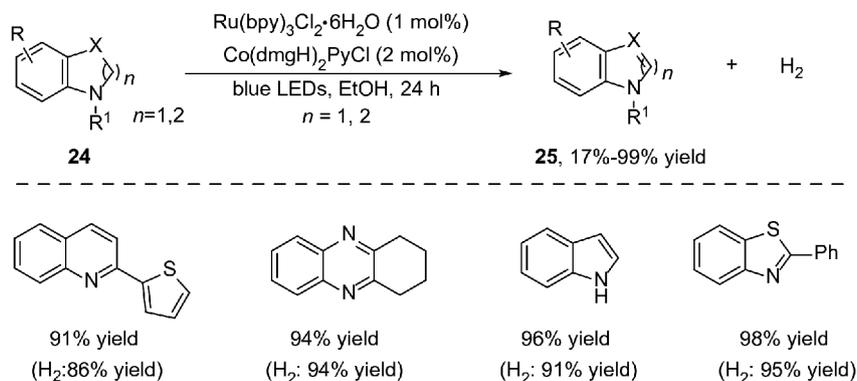
Scheme 3 Luminescent organogold(III) complexes for light-induced oxidative $\text{C}(\text{sp}^3)\text{-H}$ bond functionalization.



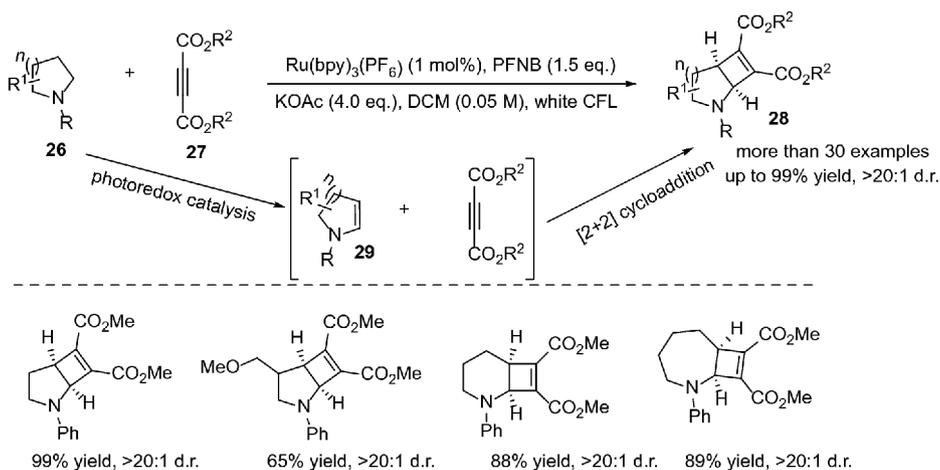
Scheme 4 One step synthesis of bicyclic isoxazolidines via photoredox catalyzed tandem reaction (Wedge bonds were used for the related configuration of products in this section).



Scheme 5 Cross-coupling hydrogen evolution reaction using visible light catalysis.



Scheme 6 Dehydrogenation of *N*-heterocycles by merging visible-light photoredox catalysis and cobalt catalysis.



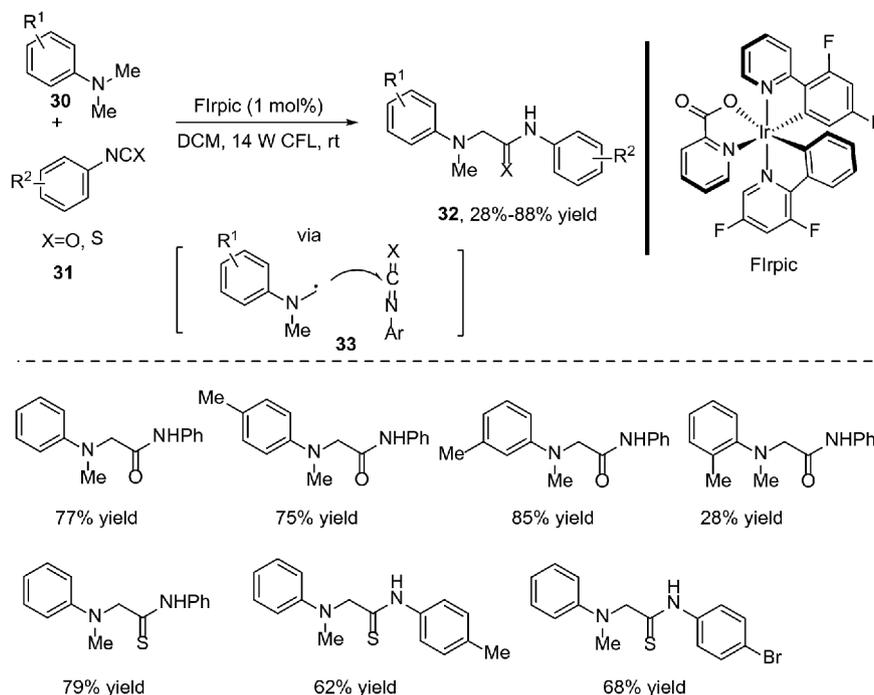
Scheme 7 Dual C(sp³)-H bond functionalization of saturated nitrogen-containing heterocycles.

doles through intramolecular oxidative cyclization. This is the first example of visible-light promoted α -aminoalkyl radical addition to alkynes followed by C–O bond formation. The reaction is environmentally friendly under mild conditions using air as a green external oxidant with water as the only side product (Scheme 9).

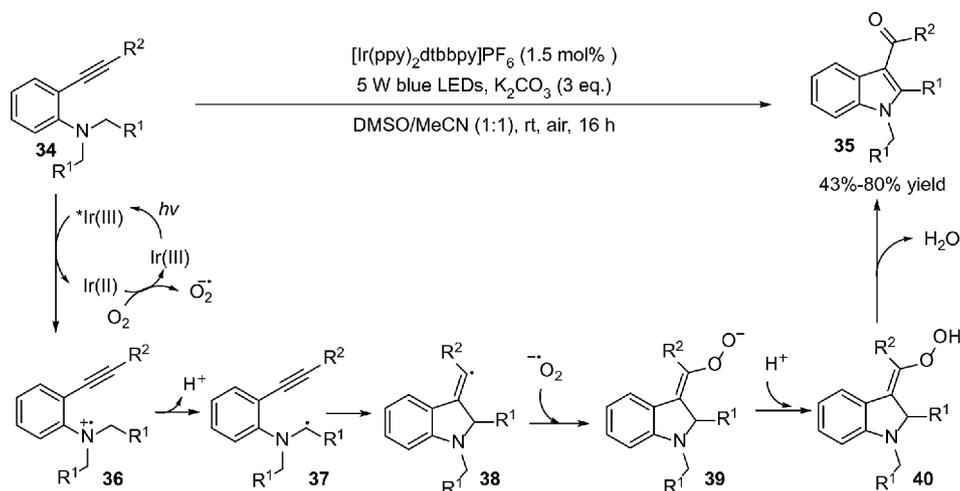
The synthesis of different products from the same starting materials represents a formidable task, especially the efficient control of the radical reaction in such a process. Jiang and coworkers [14] presented an example of a diverse and controllable radical reaction involving *N*-tetrahydrois-

quinolines (THIQs) and *N*-itaconimides catalyzed via visible-light photoredox catalysis. This reaction contains four possible pathways modulated by the reaction medium, temperature, and additive, affording four different products from the same starting materials through the addition/cyclization, addition/elimination, addition/coupling, or addition/protonation pathway (Scheme 10).

In view of the wide presence of nitrogen heterocycles in bioactive products, the construction of multisubstituted *N*-heterocycles with a quaternary carbon center from simple substrates is attractive. In 2016, Zhu and coworkers [15]



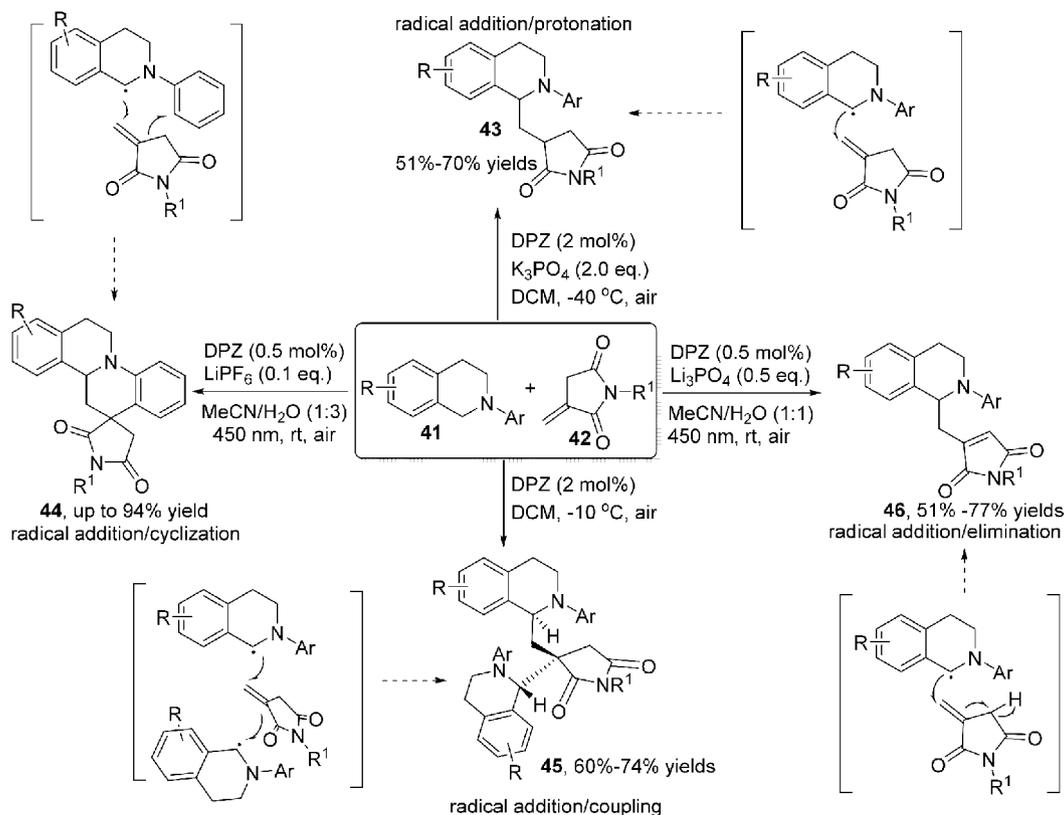
Scheme 8 α -Aminoalkyl radical addition to isocyanate and isothiocyanate under visible-light-photoredox conditions.



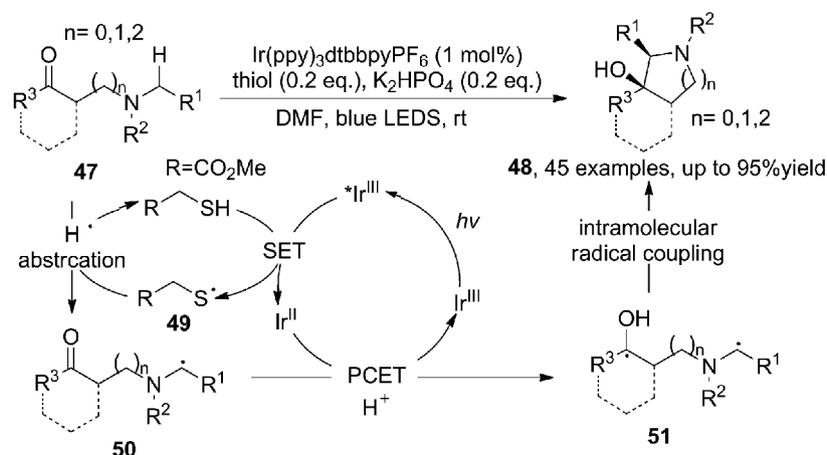
Scheme 9 Synthesis of 3-acylindoles by photoredox catalysis.

presented a visible-light mediated intramolecular biradical cyclization to synthesize four-, five- and six-membered aminated heterocyclic structures. The presence of methyl thioglycolate was essential for the reaction to occur. Methyl thioglycolate was assumed to be a cocatalyst that underwent the SET process with an excited photocatalyst to generate thiyl radical **49**. The thiyl radical intermediate abstracted an H atom from substrate **47**, providing α -amino radical **50**. The ketone part of intermediate **50** could be reduced by Ir^{II} via a PCET process to form biradical intermediate **51**, which underwent intramolecular radical coupling to yield product **48** (Scheme 11).

In contrast to the great achievements in photoredox catalyzed α -amino radical reactions, the generation of an α -oxoalkyl radical under visible light conditions is rarely reported, presumably due to high electronegativity of the O atom, which leads to the difficulty in oxidation of oxygen lone pairs. The radical migration strategy offers a new chance to evaluate selective and mild C–H bond functionalization. In 2016, Chen and coworkers [16] reported alkoxy radical triggered $\text{C}(\text{sp}^3)\text{--H}$ allylation and alkenylation reactions via a 1,5-HAT (HAT=hydrogen-atom transfer) process enabled by visible-light photoredox catalysis. Hantzsch ester was used as the reductant to reductively quench excited



Scheme 10 Diverse and controllable radical reaction via visible-light photoredox catalysis.



Scheme 11 Photoredox catalyzed radical-radical coupling reaction to access multisubstituted nitrogen heterocycles.

photocatalyst. The subsequent single-electron transfer between *N*-alkoxyphthalimide **52** and reduced photocatalyst Ir (II) results in radical anion **55**, which releases phthalimide **56** to facilitate the formation of the alkoxy radical **57**. Finally, the alkoxy radical undergoes exclusive δ -C(sp³)-H activation and subsequent intermolecular carbon radical trapping to yield the C-C bond-coupling adduct (**Scheme 12**).

Recently, Zhu and coworkers [17] reported an example of visible-light photoredox and thiol organocatalyst cocata-

lyzed site-specific umpolung trifluoromethylthiolation of readily available tertiary alkyl ethers, achieving the construction of a tertiary C(sp³)-SCF₃ bond. This transformation was initiated by polarity-matching H-abstraction of C(sp³)-H bonds in alkyl ethers, leading to α -oxoalkyl radical **62**, which underwent site-selective cleavage of the tertiary sp³ C-O ether bond and generated alkyl radical **63**. Then, the intermediate **63** underwent radical-radical coupling with radical anion **64** (generated from the photocatalysis cycle) to afford

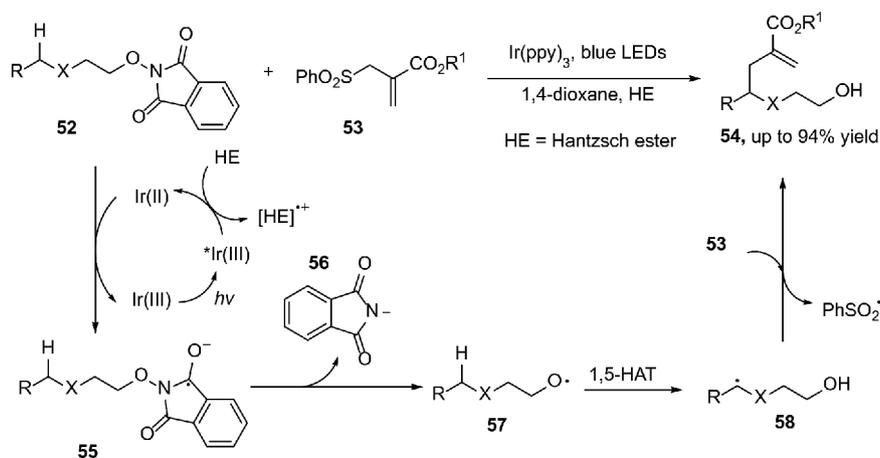
the desired product **61** (Scheme 13).

Direct transformation of unactivated C(sp³)-H bonds is a powerful and step-economic synthetic strategy, but challenges still remain regarding reactivity and selectivity. Radical translocation processes mediated by heteroatom-centered radicals provide an efficient entry for selective and controllable functionalization of inert C(sp³)-H bonds based on radical hydrogen migration, such as 1,5-HAT (HAT=hydrogen-atom transfer) or intermolecular H-atom abstraction. Nitrogen-centered radicals have long been known to trigger distal C-H bond transfer. However, the harsh reaction conditions severely limit its synthetic applications. In 2015, the Yu's group [18] first reported a neutral photoredox catalyzed Hofmann-Löffler reaction for the functionalization of a remote C(sp³)-H bond via 1,5-H transfer at room temperature. A variety of aminated five membered-ring compounds and δ -chlorinated sulfonamide are prepared in good to excellent yields (Scheme 14). In this reaction, amidyl radical **67** is generated by oxidative quenching of excited state *Ir(III) with *N*-chlorosulfonamides. The subsequent 1,5-H transfer/

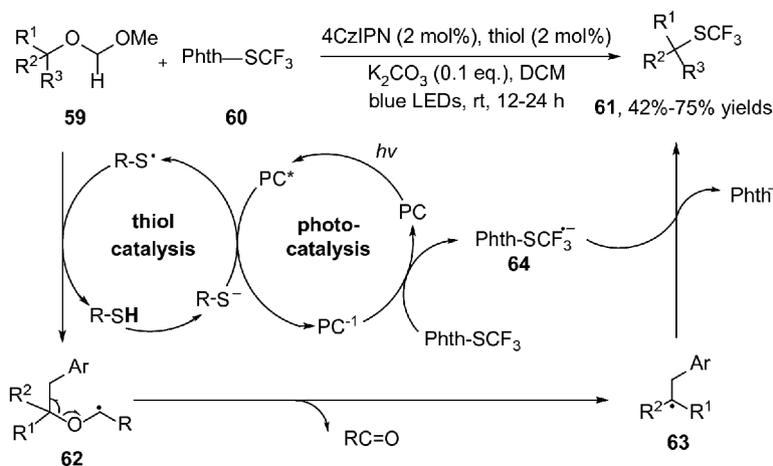
oxidation/cyclization finally leads to the desired products.

The easily handled DABCO•(SO₂)₂ has been recognized as a good coupling reagent with various radicals to generate sulfonyl radicals. In 2017, Wu and coworkers [19] reported visible-light promoted the direct aminosulfonylation of unactivated C(sp³)-H bonds through an iminyl radical initiated 1,5-H atom transfer process without any metals or photoredox catalysts. *O*-Aryl oximes react with DABCO•(SO₂)₂ under blue LED irradiation to generate *N*-radicals that undergo 1,5-H atom abstraction followed by sulfur dioxide insertion and cyclization to produce the desired product in good to excellent yields (Scheme 15).

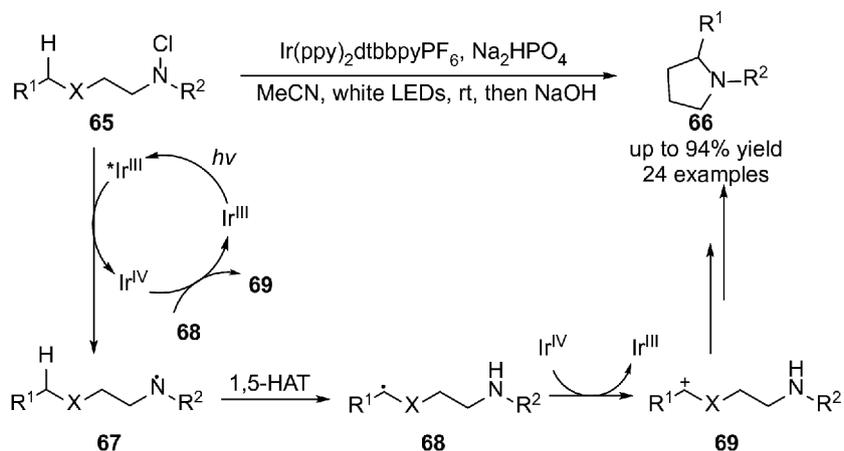
Recently, Zhu and coworkers [20] reported an elegant example of alkoxy radicals directed C(sp³)-H bond functionalization via remote hydrogen atom migration enabled by using visible-light photocatalysis. This reaction was initiated via photoredox catalyzed generation of alkoxy radicals followed using a sequential 1,5-H shift and 1,4-heteroaryl migration process, yielding heteroarylated ketones (Scheme 16). A wide range of functional groups, such as bromide,



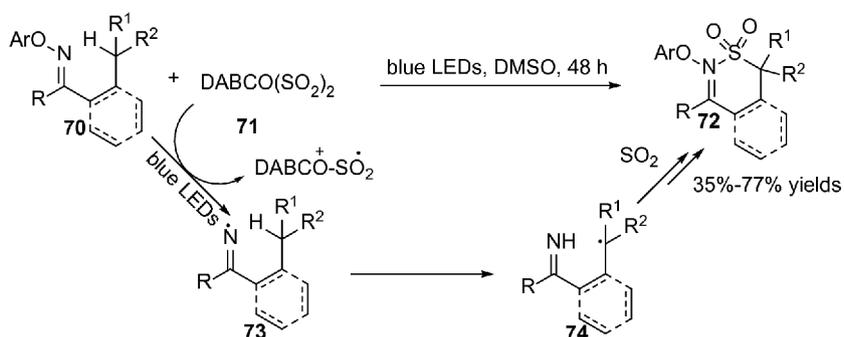
Scheme 12 Alkoxy radical enabled C(sp³)-H functionalization.



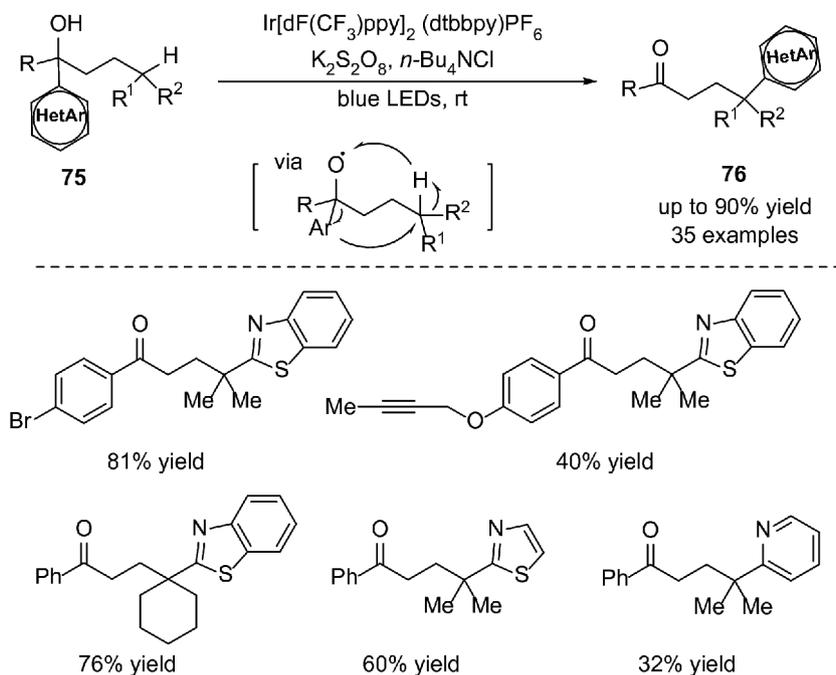
Scheme 13 Organo-photoredox cocatalyzed trifluoromethylthiolation of tertiary ethers.



Scheme 14 Redox-neutral, visible-light-induced Hofmann-Löffler reaction.



Scheme 15 Visible-light promoted direct aminosulfonylation of unactivated $\text{C}(\text{sp}^3)\text{-H}$ bonds.



Scheme 16 Tertiary alcohol-guided heteroarylation of remote $\text{C}(\text{sp}^3)\text{-H}$ bonds.

alkenyl and alkynyl groups, are tolerated.

Almost at the same time, the Zuo's group [21] developed a

platform for the direct generation of alkoxy radicals from alcohols using a visible-light-induced ligand-to-metal charge

transfer mechanism. In this article, simple and abundant primary alcohols were applied to generate alkoxy radicals using inexpensive cerium photocatalyst (Scheme 17). This reaction features a wide substrate scope, high functional-group tolerance, and excellent δ -selectivity. Complex polycyclic molecules can also be selectively functionalized with the nitrogenous functionality, demonstrating the applicability of this manifold to complex molecule synthesis.

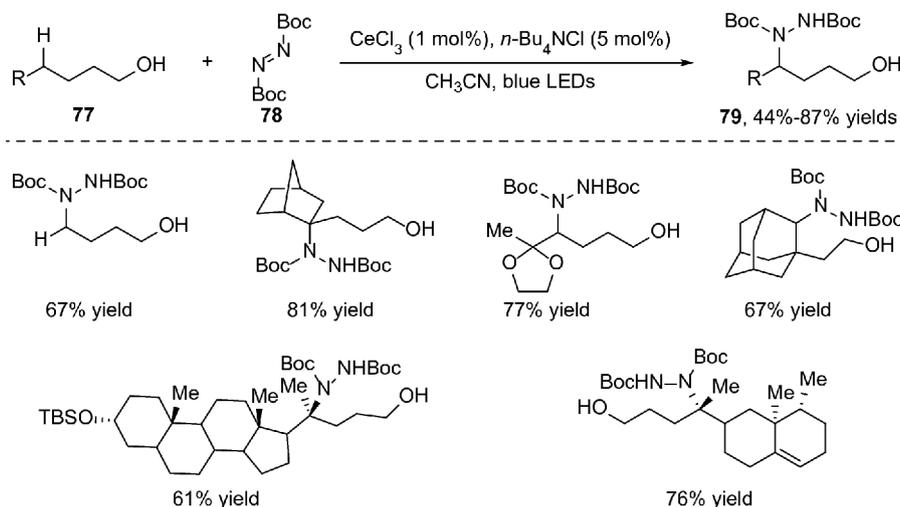
2.2 Visible-light mediated C(sp²)-H bond functionalization

Along with the renaissance of radical chemistry, the functionalization of the C(sp²)-H bond via a radical addition and deprotonation strategy is frequently used to modify mole-

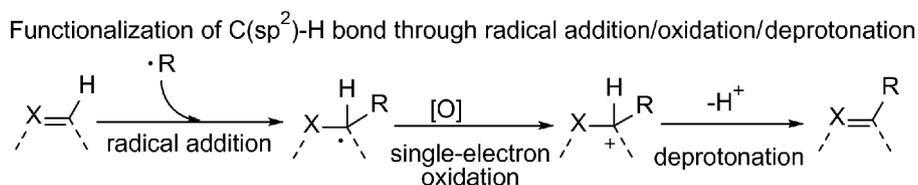
cules with a C(sp²)-H bond (Scheme 18). In this section, we will discuss the radical induced C(sp²)-H bond functionalization enabled via visible-light photocatalysis.

The radical initiated cyclization of 1,6-enynes is a uniquely powerful tool for the synthesis of polysubstituted polycyclic compounds. In 2013, Li and coworkers [22] reported a visible-light photoredox catalyzed tandem radical addition/5-*exo*-cyclization/C(sp²)-H functionalization of 1,6-enyne to construct functionalized 10*a*,11-dihydro-10*H*-benzo[*b*]fluorenes (Scheme 19). With arylsulfonyl chlorides as an aryl radical source, the desired polysubstituted polycyclic products can be obtained in intermediate to good yields.

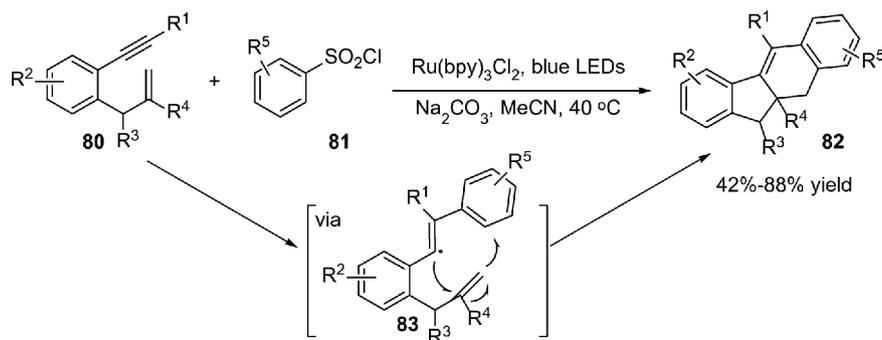
In 2016, Xie and coworkers [23] reported a visible-light mediated boron-functionalization of the sp² C-H bond of



Scheme 17 Visible-light LMCT mediated alcohol δ -C-H functionalization.



Scheme 18 General mechanism of visible-light mediated C(sp²)-H bond functionalization.

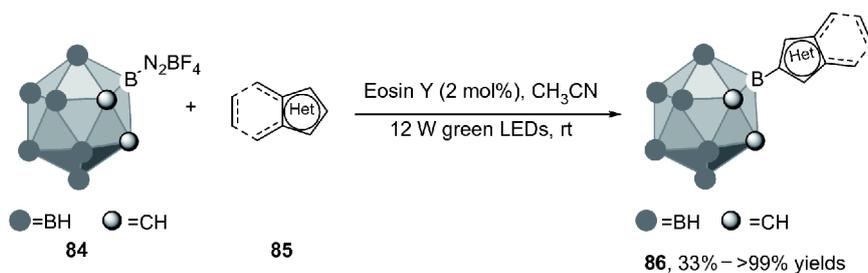


Scheme 19 Tandem cyclization of alkynes with alkenes and ArSO₂Cl.

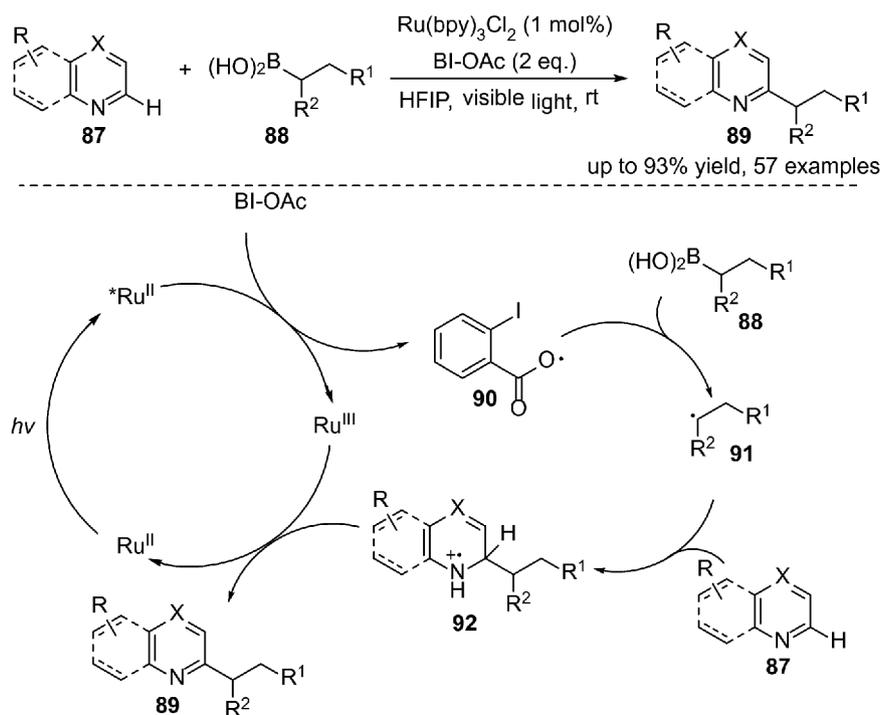
various heteroarenes with 3-diazoniomo-carborane tetrafluoroborate. A boron-centered carboranyl radical can be generated efficiently under photoredox catalysis and reacts with heteroarenes in good to excellent yields. This procedure is the first example of 3-heteroaryl-*o*-carborane synthesis (Scheme 20).

The Minisci C–H functionalization of *N*-heteroarenes is a powerful method for accessing functionalized *N*-heteroarenes. In 2016, the Chen's group [24] reported a photoredox-mediated Minisci C–H alkylation of *N*-heteroarenes with alkyl boronic acids as alkyl radical sources. This protocol provides a facile access to various alkylated *N*-heteroarenes, which are recurrent structural motifs in natural products, drug molecules and organic materials. The authors proposed that the oxidant BI-OAc can be readily reduced by photoexcited Ru(II)* via SET to form radical intermediate **90**, which reacts with boronic acid to form alkyl radical **91**. The intermediate **91** undergoes a nucleophilic addition reaction with *N*-heteroarenes followed by single-electron oxidation and deprotonation, leading to the final C–H alkylated product (Scheme 21).

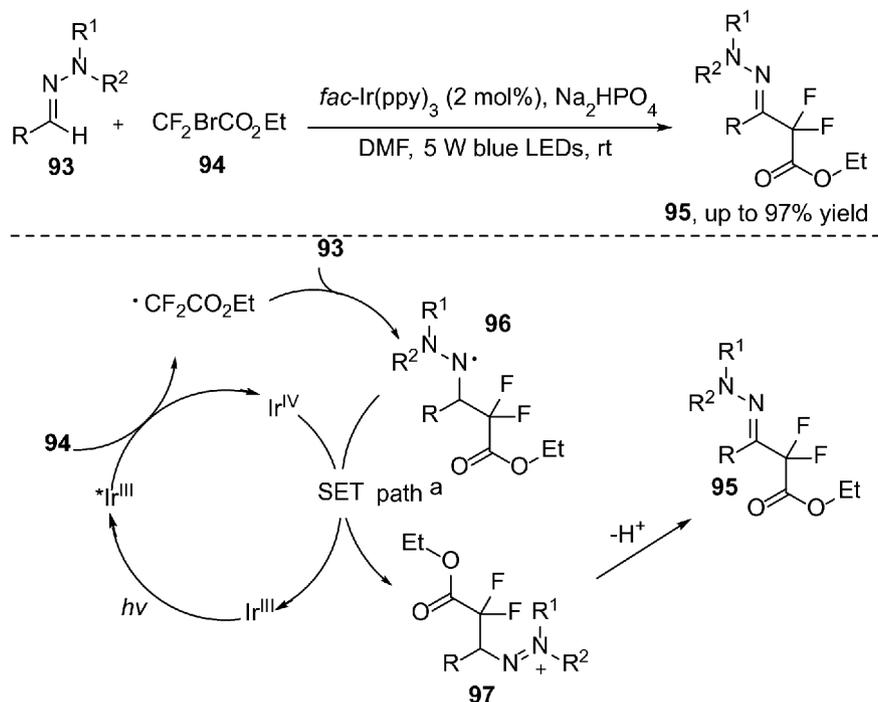
The radical addition to C=C unsaturated structures (arenes, alkenes or alkynes) is well-developed. However, radical C–H addition to a C=N π -acceptor is rarely reported. Hydrazones are valuable and versatile building blocks in synthetic chemistry. In 2016, Zhu and coworkers [25] reported a photoredox catalyzed aminyl radical/polar crossover reaction to synthesize difluorinated hydrazine derivatives via radical C–H difluoroalkylation of carbon-nitrogen π bonds. Mechanistic analyses and theoretical calculations well supported the aminyl radical/polar mechanism. With Ir(ppy)₃ as the photocatalyst under visible-light irradiation, BrCF₂CO₂Et is reduced by the excited-state photocatalyst via a SET process to form a strong oxidant Ir^{IV} and difluoroalkyl radical. Subsequent radical addition to the C=N bond leads to the aminyl radical intermediate **96**. Intermediate **96** can be oxidized by Ir^{IV} to generate intermediate **97**, which is converted to **95** by deprotonation (Scheme 22).



Scheme 20 Photocatalytic B–C coupling via a boron-centered carboranyl radical.



Scheme 21 Photoredox-mediated Minisci C–H alkylation of *N*-heteroarenes.



Scheme 22 Visible-light photoredox-catalyzed C–H difluoroalkylation of hydrazones.

3 Visible-light-induced synthesis of privileged aromatic aza-heterocycles

Aromatic aza-heterocycles occupy a very important position in organic chemistry, material chemistry and pharmaceutical chemistry [26]. To this end, considerable efforts have been devoted to the development of efficient and facile synthetic routes to access these molecules. In particular, the strategy of visible light photocatalysis has been widely applied in their synthesis due to its mild and green conditions, as well as the user-friendly advantage. In this section, we will highlight the representative examples in this impressive research area.

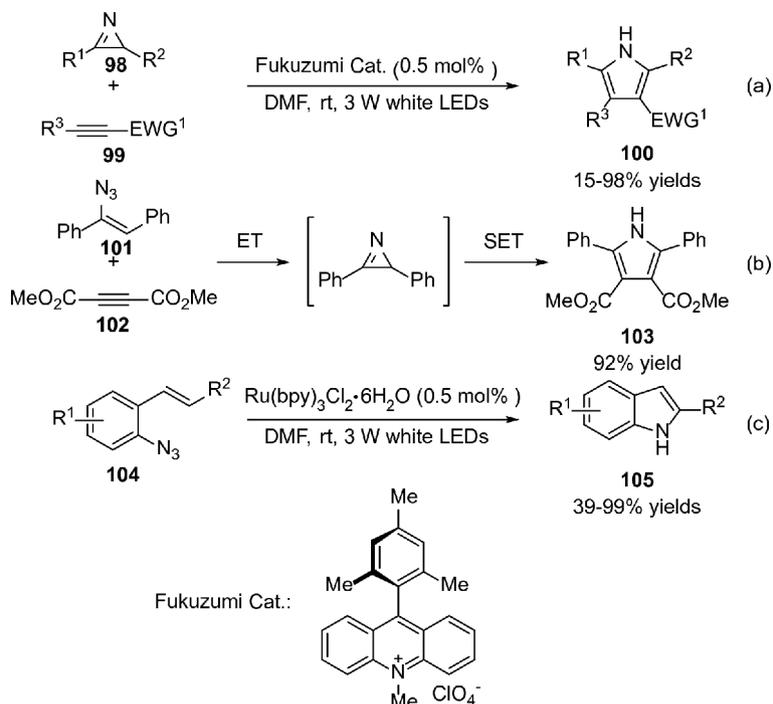
3.1 Visible-light-induced synthesis of pyrrole and indole

Pyrroles and indoles are widespread in many biologically active molecules, pharmaceutical compounds and natural products, thus receiving increasing attention from the synthetic community. Since the first report from the Xiao's group [4] on the photocatalytic synthesis of pyrroles via C–H functionalization in 2011, many research endeavors have been devoted to the synthesis of these aromatic aza-heterocycles.

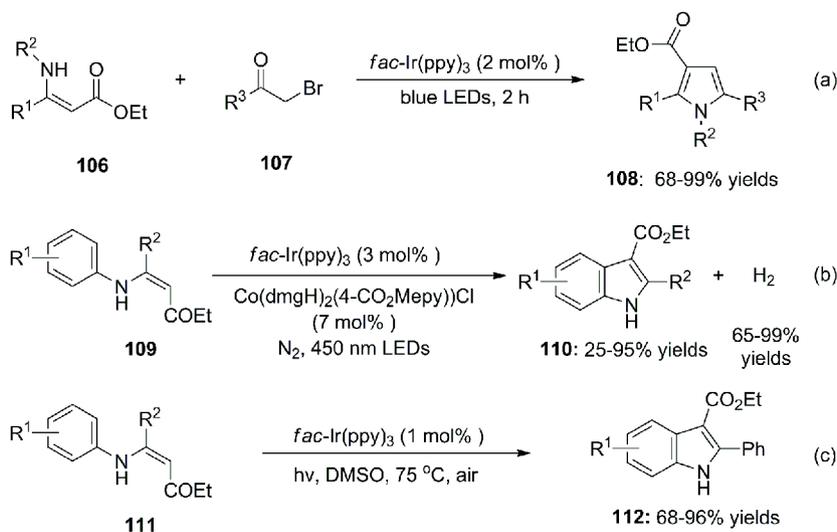
In 2014, Lu, Xiao and coworkers [27] further realized the photocatalytic synthesis of polysubstituted pyrroles through a metal-free visible-light induced [3+2] cycloaddition of 2*H*-azirines with activated alkynes under mild conditions (Scheme 23(a)). In this article, the authors also disclosed the

first example of a sequential reaction of azide olefins and dimethyl propionate by combining energy transfer and the photo-SET process (Scheme 23(b)). Notably, in 2015, a similar photoredox catalysis with the Fukuzumi catalyst was extended to the synthesis of oxazoles via a [3+2] cycloaddition/oxidative aromatization sequence of 2*H*-azirines and aldehydes [28]. In 2014, they further developed a novel protocol for the synthesis of indole products from the 1-azido-2-alkenylbenzenes through the visible light photoredox catalysis with a Ru-based photocatalyst (Scheme 23(c)) [29]. Subsequently, 2*H*-azirine and azide compounds were further applied to the construction of other aromatic aza-heterocycles, such as benzotriazoles, 2-acyl oxazoles and 2-aminothiazoles [30].

In addition to azide substrates, the Wu's group [31] disclosed alternative approaches for the synthesis of poly-substituted pyrroles and indoles from easily available enamine substrates. For example, in 2016, they used enamine **106** and bromide **108** to produce 1,2,3,5-tetrasubstituted pyrroles in good to excellent yields via the photoredox catalytic Hantzsch reaction (Scheme 24(a)). Moreover, the same group also smartly developed an oxidant-free protocol for the synthesis of indoles through intramolecular C–C bond formation under visible light irradiation [32]. This protocol uses cobalt-oxime catalyst in place of an oxidant and the reaction proceeds smoothly to afford indole products with H₂ as the only by-product (Scheme 24(b)). The same strategy of merging visible light photoredox catalysis with cobalt catalysis has been successfully used in the construction of ben-



Scheme 23 Photocatalytic synthesis of pyrroles and indoles from 2H-azirines or azide compounds.



Scheme 24 Photocatalytic synthesis of pyrrole and indoles from enamines.

zothiazoles, quinolines, and many other aromatic systems. Furthermore, in 2017 the Wu's group [33] furnished an indole synthesis by developing a visible-light induced intramolecular radical cyclization of enamines in dimethyl sulfoxide (DMSO) with air as the oxidant and with *fac*-Ir(ppy)₃ as the photocatalyst (Scheme 24(c)).

Photocatalytic transformations of alkynes are a powerful method for indole synthesis. In early 2014, Wang and co-authors [34] reported a cascade reaction consisting of an Au-catalyzed hydroamination, visible-light-promoted electron transfer and dehydrogenative coupling for indole synthesis

(Scheme 25). This protocol provided a novel route to highly functionalized indoles from readily available anilines and alkynes featuring extremely mild conditions and the avoidance of additional photosensitizers and oxidants. Soon afterwards, intramolecular cyclizations of *ortho*-amino or *ortho*-sulfamido alkynes through visible light photoredox catalysis were also developed by other groups for the synthesis of 3-acyl or aryl indoles [13,35].

Very recently, Chen, Xiao and coworkers [36] described the synthesis of indole derivatives through a multicomponent reaction of 2-vinylanilines, halides, and sulfur ylides. The

key to success was believed to be the generation of aza-ortho-quinone methide intermediates under the visible-light photocatalysis system, which could be trapped by sulfur ylides to provide the indoles via a formal [4+1] cycloaddition (Scheme 26).

3.2 Visible-light induced synthesis of pyridines, quinolines, isoquinolines and phenanthridines

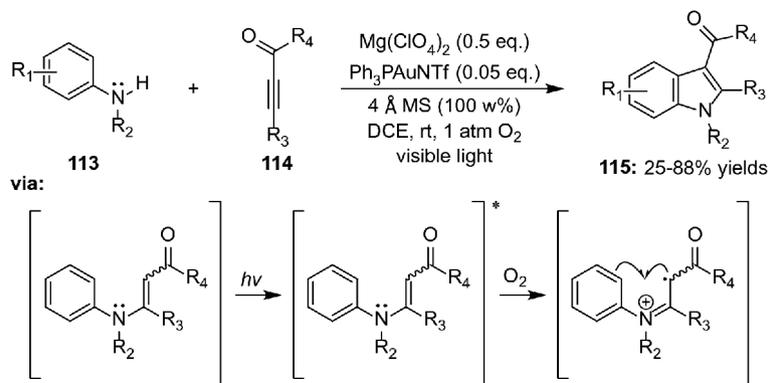
Pyridine and its structurally related aza-aromatic heterocycles, i.e., quinolines, isoquinolines and phenanthridines, are other types of important skeletons that are widespread in many biologically active natural alkaloids and pharmaceutical agents. The development of efficient methods for their synthesis has attracted much attention among organic chemists.

Isoyanides are versatile building blocks in synthetic chemistry, and can undergo serial organic transformations. Early in 1995, Nanni and coworkers [37] reported an unprecedented radical isocyanide insertion of the 2-isocyanobiphenyl and 2-cyanopropyl radicals induced by azodiisobutyronitrile (AIBN) to give 6-substituted phenanthridines. In 2013, Yu and coworkers [38] first described a visible-light-promoted radical isocyanide insertion reaction between 2-isocyanobiphenyl **120** and alkyl bromides to afford 6-alkylated phenanthridine derivatives (Scheme 27). In this protocol, a variety of alkylating reagents were proved to be efficient radical precursors via photocatalytic C–Br bond

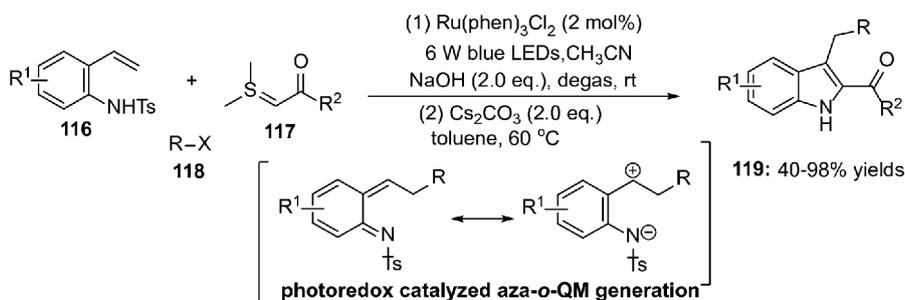
cleavage to initiate the radical cascade and a variety of phenanthridines were assembled under mild reaction conditions. Consequently, a similar photocatalytic cyclization strategy of isocyanides with a range of radicals has been developed as a broad avenue for the construction of phenanthridine and its derivatives [39]. Moreover, Yu and coworkers [40] successfully extended this strategy into other heterocycle syntheses, such as that of isoquinolines, pyridine, and quinazolinones.

Iminyl-radicals have long been recognized as versatile synthetic intermediates that can trigger many chemical transformations. In 2015, Yu and coworkers [41] reported a visible-light promoted SET reduction of acyl oximes to generate iminyl-radicals that undergo intramolecular homolytic aromatic substitution to give the *N*-containing arenes, including phenanthridines, quinolines, and pyridines. It is found that the acyl groups on acyl oximes have great influence on the reaction results (Scheme 28).

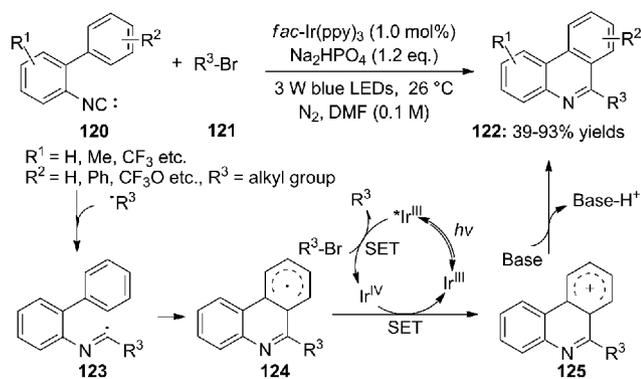
In addition to isocyanide and acyl oxime as the key substrates, other imino substrates were developed for the synthesis of phenanthridine. In 2014, Zou and coworkers [42a] developed an intramolecular radical cyclization of trifluoroacetimidoyl chlorides for the synthesis of 6-(trifluoromethyl)phenanthridines without the extra radical source (Scheme 29(a)). In 2015, Yu and coworkers [43] disclosed another route to phenanthridines through a visible-light-promoted formation of imino nitrogen radicals from acyl oximes (Scheme 29(b)). The photogenerated imino



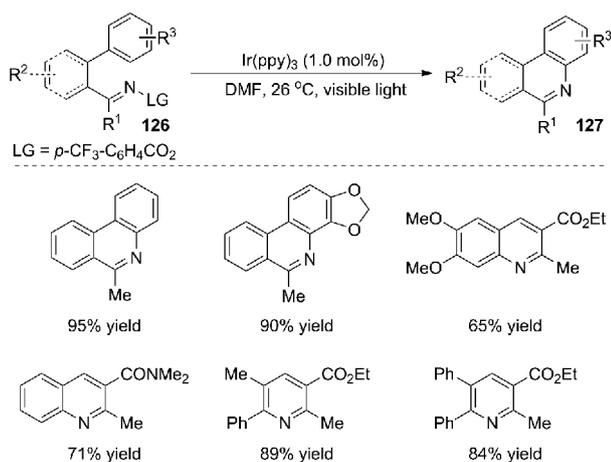
Scheme 25 Visible light-promoted synthesis of functionalized indoles from anilines and alkynes.



Scheme 26 Multicomponent reaction for indole synthesis through visible light photocatalysis.



Scheme 27 Photocatalytic synthesis of phenanthridines from isocyanides.



Scheme 28 Visible-light-promoted synthesis of azarenes via iminyl radicals.

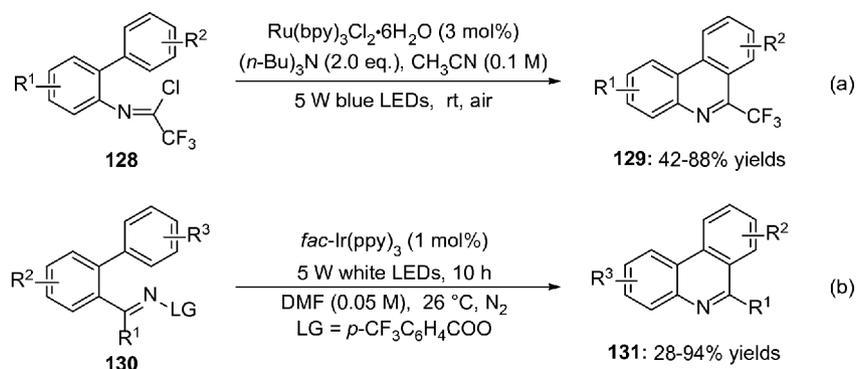
carbon or nitrogen radicals proceeded with a similar cyclization with the isocyanide insertion to provide the phenanthridine products. Notably, the photogenerated imino carbon radicals were also successfully used to synthesize CF₃-substituted isoquinoline through the intermolecular cycloadditions of trifluoroacetamido chlorides and alkynes [42b].

The two main routes for the photocatalytic synthesis of quinolines and isoquinoline are the radical addition/cyclization cascade reaction with olefin or alkyne and the Povarov

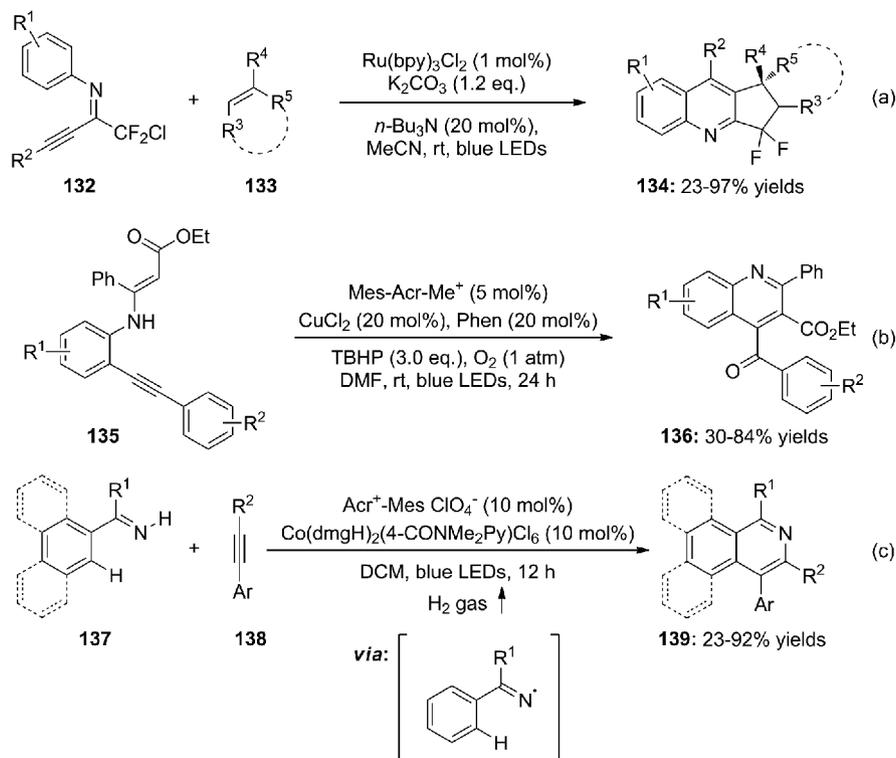
cycloaddition/aromatization cascade reaction. In 2016, Zhou *et al.* [44] facilely synthesized the gem-difluorinated fused quinolines through the cascade reaction of chlorodifluoromethyl- and alkynyl-substituted imines with alkenes (Scheme 30(a)). This protocol induced by visible light featured high synthetic efficiency involving the formation of three C–C bonds in one step. In 2017, using CuCl₂ as a cocatalyst to activate an alkyne component and oxygen gas as the oxidant, Xia and coworkers [45] accomplished a visible light photoredox catalyzed oxidative cyclization of aromatic enamines for the synthesis of multisubstituted quinoline derivatives (Scheme 30(b)). In the same year, the Li's group [46] developed a dehydrogenative [4+2] cycloaddition of imines and alkenes, affording isoquinolines with a high atom economy (Scheme 30(c)). The key points in this transformation are the photocatalytic N–H bond cleavage, the addition of generated iminyl radicals to alkenes and the dehydrogenative oxidation via Co catalysis.

The Povarov reaction is widely used for the efficient synthesis of quinoline via the formal cycloaddition between an aromatic imine and an electron-rich alkene. In 2016, Zhang and coworkers [47] developed a tandem reaction involving visible-light-induced photocatalytic oxidation/intramolecular Povarov cyclization to give the quinoline-fused lactones via a one-step operation (Scheme 31(a)). Substrate **140** is oxidized by oxygen to aromatic imine **143** under photocatalytic conditions, followed by a Lewis acid-catalyzed intramolecular Povarov reaction. The afforded tetrahydroquinolines were further oxidized to the desired quinoline products. Via a similar strategy, the Zhang's group [48] realized an intramolecular Povarov cycloaddition reaction/aromatization sequence, which produced substituted indolizino [1,2-*b*] quinolin-9(1H)-one from finely designed aldehydes and anilines (Scheme 31(b)).

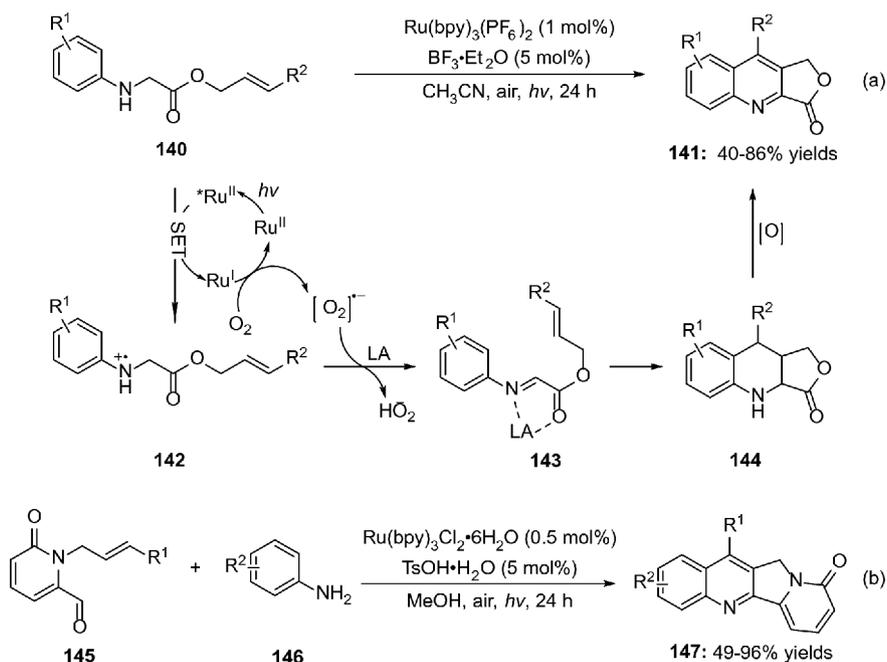
In contrast to previous strategies to construct a pyridine ring, Meng and Wang *et al.* [49] developed a visible-light-promoted three-component cycloaddition of alkynes **148** with nitriles to furnish pyridines (Scheme 32). This [2+2+2] cycloaddition process features high regioselectivity and was built on the unusual photooxidation of alkynes into a reactive



Scheme 29 Photocatalytic synthesis of phenanthridines from imidoyl chlorides and acyl oximes.



Scheme 30 Visible-light-induced cascade radical cyclizations using alkynes.



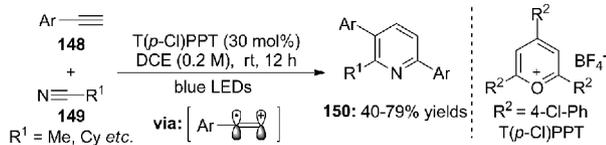
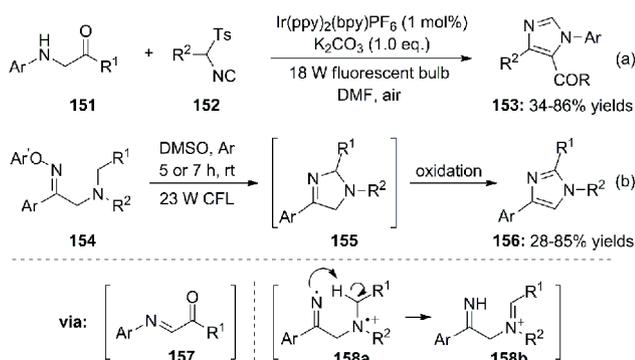
Scheme 31 Visible-light-induced photocatalytic oxidation/Povarov cyclization reaction.

alkene-type radical cation.

3.3 Visible-light-induced synthesis of other aza-aromatic compounds

Aromatic systems bearing two or more nitrogen atoms, such

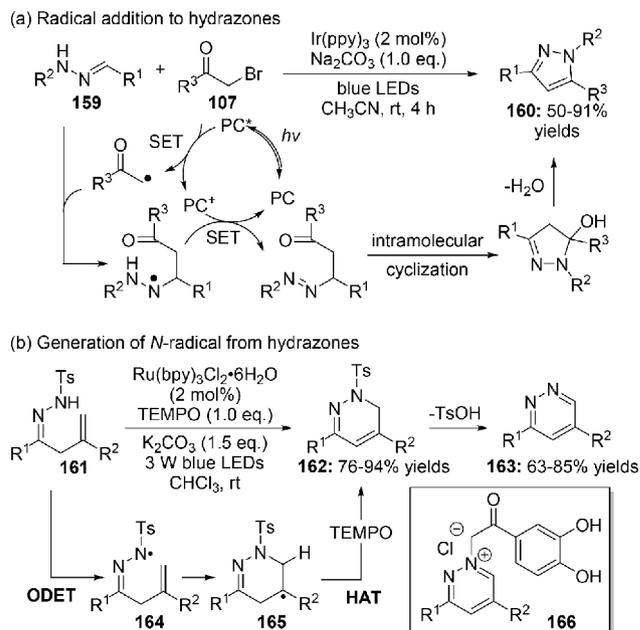
as imidazoles, pyrazols, pyridazines and triazoles, usually have unique biological activities that are popular in agricultural agents. In 2014, the Xiao and Chen's group [50] developed a cascade reaction of secondary amines **151** and isocyanides **152** for imidazole synthesis (Scheme 33(a)). This reaction proceeded via an imine intermediate **157** that

**Scheme 32** Photocatalytic access to pyridines.**Scheme 33** Photocatalytic synthesis of imidazoles from amines.

was generated from amines through visible light photo-oxidation and participated in a subsequent [3+2] cycloaddition/aromatization to deliver the final products (**Scheme 33**(a)). In 2017, Fu and coworkers [51] disclosed a visible-light-mediated intramolecular $\alpha\text{-C}(\text{sp}^3)\text{-H}$ imination/oxidative aromatization reaction with oximes as efficient substrates (**Scheme 33** (b)). Notably, only visible light was required for this transformation, avoiding the use of an oxidant, catalyst, additive, base and acid.

Hydrazones have been established as suitable feedstock for the synthesis of aromatic rings with two vicinal nitrogen atoms. In 2016, the Wu's group [52] reported a visible light photocatalytic protocol to the 1,3,5-trisubstituted pyrazoles using hydrazones and α -bromo ketones as efficient substrates (**Scheme 34**(a)). This reaction was built on a hydrazine addition by the carbon radical that was generated from α -bromo ketones. In the same year, Chen and coworkers [53] developed a photocatalytic cascade reaction for synthesizing pyradazines with high regioselectivity and good yields (**Scheme 34**(b)). Distinguished from Wu's mechanism, this work involved an oxidative deprotonation electron transfer (ODET) process for the generation of *N*-radicals from hydrazones through visible light photoredox catalysis. The corresponding 1,6-dihydropyridazines **164** can be easily transformed into diazinium salts **166** that showed marked *in vitro* antifungal pharmacological activities.

Oxazoline and thiazole are well known as the core backbone of many drug molecules and functional materials. The synthesis of these two classes of compounds has attracted the wide attention of researchers in recent years. In 2011, the Li's group [54] reported a novel photocatalytic synthesis of benzothiazoles via radical cyclization of thioanilides **167**,

**Scheme 34** Photocatalytic synthesis of pyrazoles and pyridazines from hydrazones.

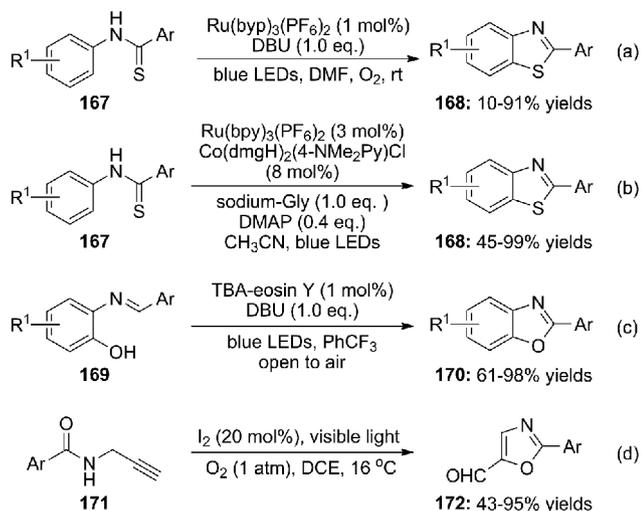
which used oxygen as the terminal oxidant (**Scheme 35**(a)). In 2014, Lei and Wu *et al.* [55] furnished the same transformation through the synergistic photoredox/Co catalysis, avoiding the external oxidant and with H_2 as the only by-product (**Scheme 35**(b)). In the same year, using an organic dye as photocatalyst, the Liu's group [56] reported a visible-light-driven, intramolecular oxidative cyclization/aromatization reaction to achieve 2-substituted benzoxazoles from 2-aminophenol-derived imines (**Scheme 35**(c)). In 2017, using a catalytic amount of I_2 , the Wang's group [57] reported a visible-light-promoted cyclization/aromatization reaction for the production of formyl-substituted oxazoles from *N*-propargyl benzamides (**Scheme 35**(d)).

In addition to intramolecular cyclizations, in 2013, Lei, Lan and coworkers [58] achieved a visible-light-induced oxidative decarboxylative coupling reaction of α -keto acids **173** with amines **174**, providing benzothiazoles and benzimidazoles and benzoxazoles in good reaction efficiency (**Scheme 36**).

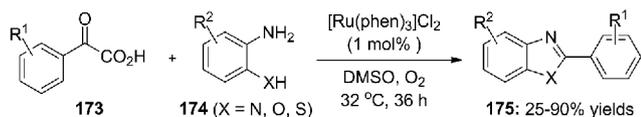
4 Visible-light-induced asymmetric organic photochemical synthesis

4.1 Chiral organocatalyst-assisted asymmetric organic photochemical synthesis

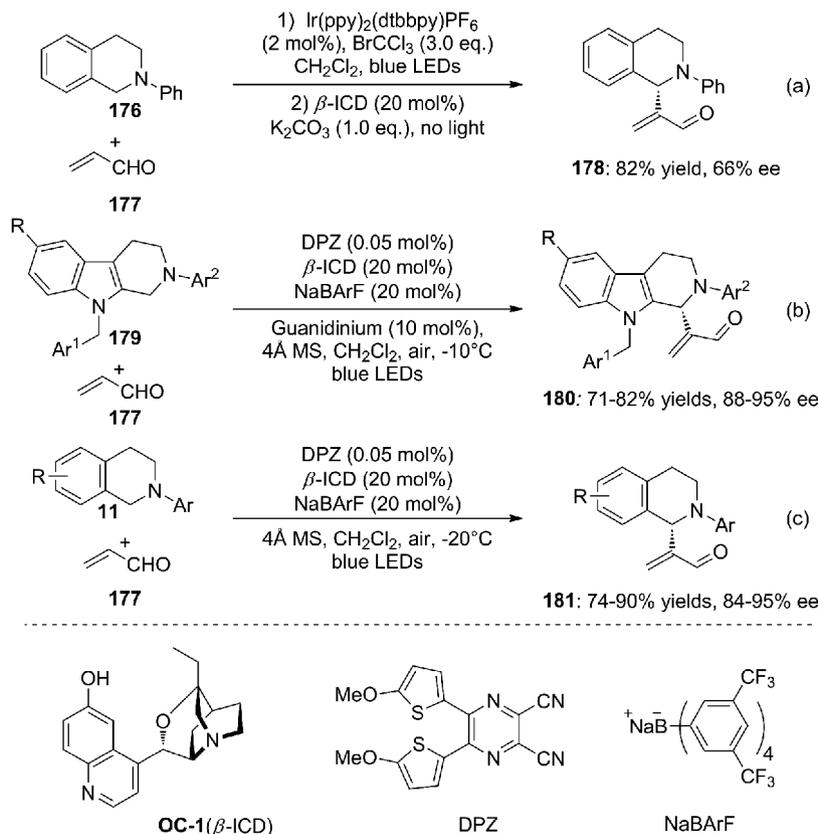
Since the pioneering work of the MacMillan's group [2a], who described the first direct asymmetric alkylation of aldehydes by merging a photoredox catalyst and an imidazolone organocatalyst, the synthetic community has witnessed the rapid development of asymmetric organic



Scheme 35 Photocatalytic synthesis of oxazoline and thiazole via intramolecular cyclizations.



Scheme 36 Photocatalytic synthesis of oxazolines, imidazoles and thiazoles via intermolecular couplings.



Scheme 37 Asymmetric sp^3 C-H acroleination of THIQ and THCs via sequential nucleophilic and photoredox catalysis (Wedge bonds were used for the absolute configuration of products in this section).

synthesis through visible-light-induced photochemical processes. In this research area, many Chinese groups have made important progress through synergetic organic and photoredox catalysis, synergetic Lewis acid and photoredox catalysis, sequential organic and transition metal catalysis, or sequential photoactivation and transition metal catalysis. In this section, we will highlight these impressive advances.

Cross-dehydrogenative coupling (CDC) has continuously flourished as a powerful tool for C–C bond formation. In 2014, Lu, Xiao and coworkers described an isolated example of visible-light-induced catalytic asymmetric sp^3 C–H acroleinations of *N*-aryltetrahydroisoquinolines (THIQ) directly through a sequential catalysis. Using β -isocupreidine (β -ICD) as the chiral nucleophilic catalyst, the reaction afforded the enantioenriched product in good yield and moderate enantioselectivity (**Scheme 37(a)**) [59]. In 2016, the Jiang's group [60] significantly improved the enantiocontrol and extended the substrate scope to tetrahydro- β -carboline (THCs) by applying a dicyanopyrazine-derived chromophore (DPZ) as the photocatalyst, β -ICD as the catalyst, and molecular oxygen as the green oxidant (**Scheme 37(b, c)**). The use of an inorganic salt, NaBARf, as cocatalyst, which could activate the carbonyl group of acrolein substrates and stabilize the reaction intermediates, was important for the good results.

In 2016, Jiang and coworkers [61] disclosed an asymmetric arylation of benzofuran-2(3*H*)-ones through the combination of visible light photocatalysis and bifunctional organocatalysis. Instead of naphthoquinones, cheaper and more easily available 1-naphthols together with oxygen gas as the green oxidant could be applied to afford chiral benzofuranone products in moderate yields and excellent enantioselectivities (Scheme 38).

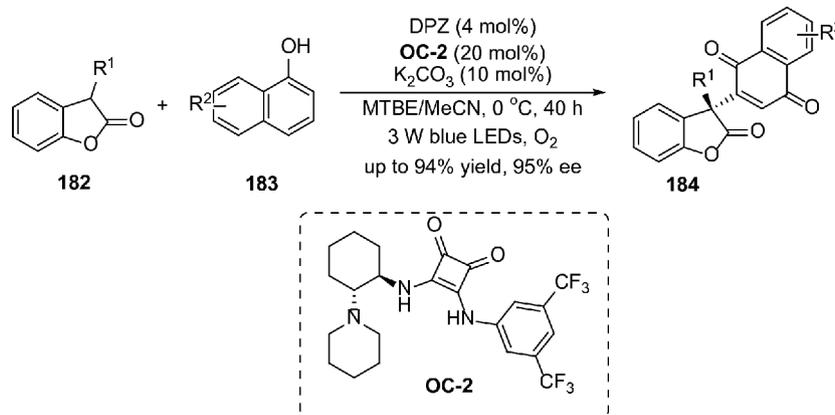
In 2017, Wu and Luo *et al.* [62] described a visible-light-promoted asymmetric CDC-type coupling of tertiary amines to ketones. This unprecedented synergistic multiple catalysis including Ru photocatalyst, a chiral primary amine catalyst and a cobalt catalyst coupled a tertiary amine oxidation process and a subsequent Mannich reaction of the generated iminium cation intermediate. In this article, most of the substrates were converted into the desired tetrahydroisoquinoline derivatives in good to excellent yields with high diastereo- and enantioselectivities (Scheme 39). Later, the Zhang's group [63] proved a novel bifunctional organic sponge photocatalyst that can also catalyze this asymmetric transformation with good enantioselectivities in water.

Enantioselective alkylation reactions are among the most important methods for adding molecular complexity in organic synthesis. In 2014, Luo and coworkers [64a] developed a catalytic asymmetric α -photoalkylation of β -

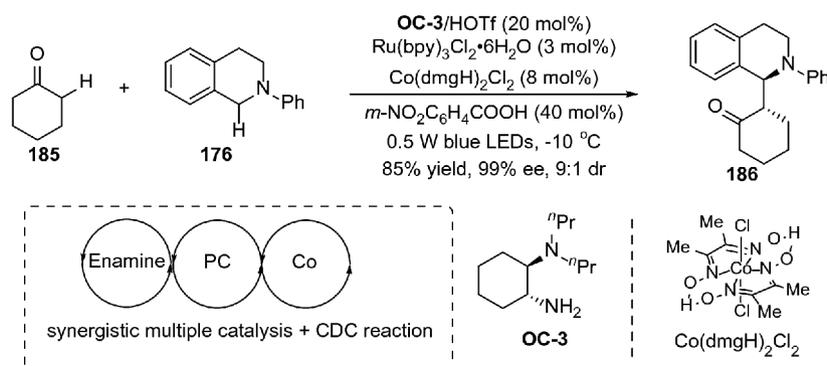
ketocarboxyls using a Ru-based photocatalyst and a chiral primary amine (Scheme 40(a)). This reaction produced a wide range of multiple-carbonyl compounds bearing chiral all-carbon quaternary stereocenters with excellent enantioselectivities. A hydrogen bond between the protonated tertiary amine and the acyl radical intermediate was very important for the high asymmetric induction. Very recently, the same group reported an unprecedented asymmetric α -alkynylation of β -ketocarboxyls to afford corresponding adducts with high enantioselectivities using a similar strategy [64b]. Specifically, they proposed a different amine catalytic mode involving an α -imino radical intermediate followed with an α -radical addition process (Scheme 40(b)).

2,2-Disubstituted indolin-3-one is a core structure of pseudoindoxyl alkaloids. In 2014, Lu, Xiao and coworkers [65] described a concise and efficient route to this synthetically significant scaffold through a visible light-induced aerobic oxidation/semipinacol rearrangement process. With molecular oxygen as the ideal terminal oxidant, chiral phosphoric acid could be applied as an efficient organocatalyst to asymmetrically induce the rearrangement step, thus generating chiral indol-3-one products in good yields with a moderate enantioselectivity (Scheme 41).

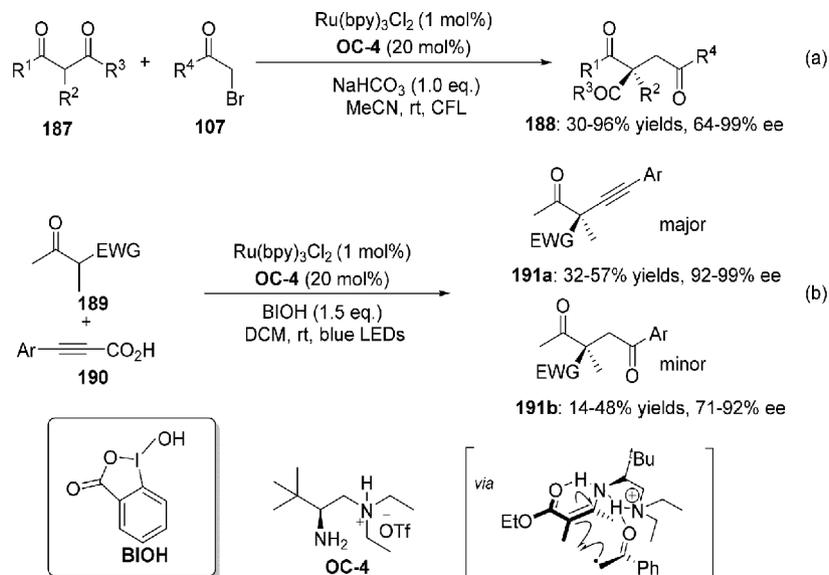
In 2017, the Luo's group [66] developed a novel chiral ion-pair photoredox organocatalyst to facilitate asymmetric anti-Markovnikov hydroetherification of alkenols under the ir-



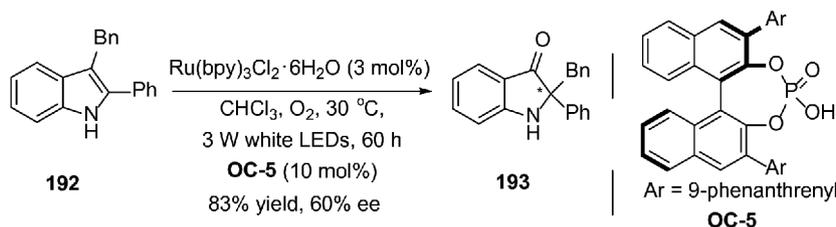
Scheme 38 Asymmetric arylation of benzofuran-2(3*H*)-ones via a cooperative visible light photocatalysis and bifunctional organocatalysis.



Scheme 39 Asymmetric CDC-type coupling of tertiary amines with ketones induced by visible light.



Scheme 40 Asymmetric α -photoalkylations and α -photoalkynylations of β -ketocarboxylates induced via synergistic amine and photoredox catalysis.

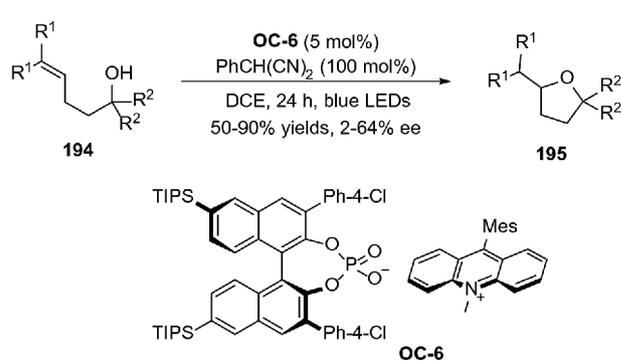


Scheme 41 Visible-light-induced aerobic asymmetric oxidation/semipinacol rearrangement of indoles.

radiation of visible light. Though the enantioselectivity is modest, it proved that the chiral ion pair strategy is feasible for inducing an asymmetric photochemical reaction (Scheme 42).

In 2018, the Jiang's group [67] achieved an enantioconvergent formal substitution of alkyl halides through an asymmetric radical coupling strategy (Scheme 43(a)). The joint use of commercial chiral phosphoric acid catalyst and DPZ photocatalyst can promote the generation of chiral β -amino ketones with good yields and stereoselectivities with racemic bromides and *N*-aryl amino acids as feedstock. In the same year, they finished an enantioselective decarboxylative radical addition reaction of 2-alkenyl quinolines and pyridines with *N*-aryl amino acids through the same synergistic catalysis strategy [68]. For these two transformations, asymmetric H-bonding induction from a chiral Brønsted acid ensure the high stereocontrol for the coupling of two radical species or the protonation of the prochiral carbanion intermediate (Scheme 43(b)).

In 2017, the Jiang's group [69] realized a visible-light-induced, enantioselective photoreduction of 1,2-diketones and α -keto ketimines by combining the DPZ photocatalyst and chiral organocatalyst (Scheme 44). Significant chiral α -hydroxy ketones and α -amino ketones were produced under

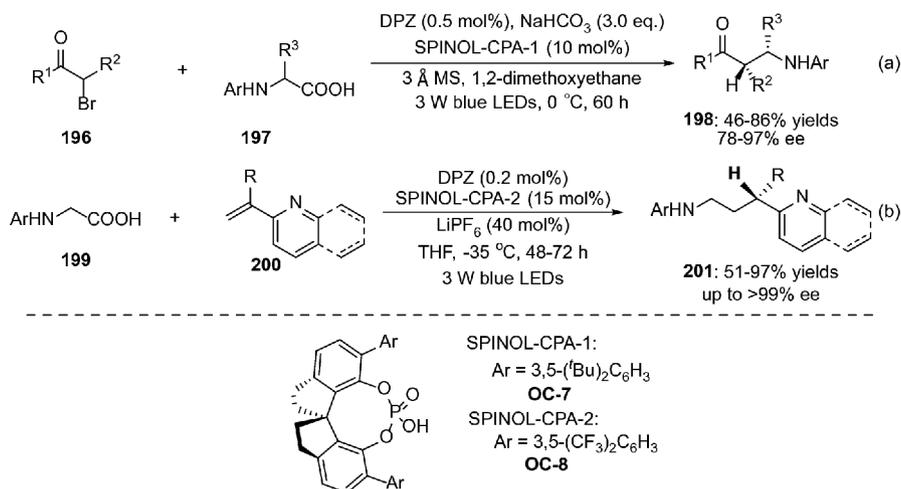


Scheme 42 Asymmetric anti-Markovnikov hydroetherifications of alkenols with a chiral ion-pair photoredox organocatalyst.

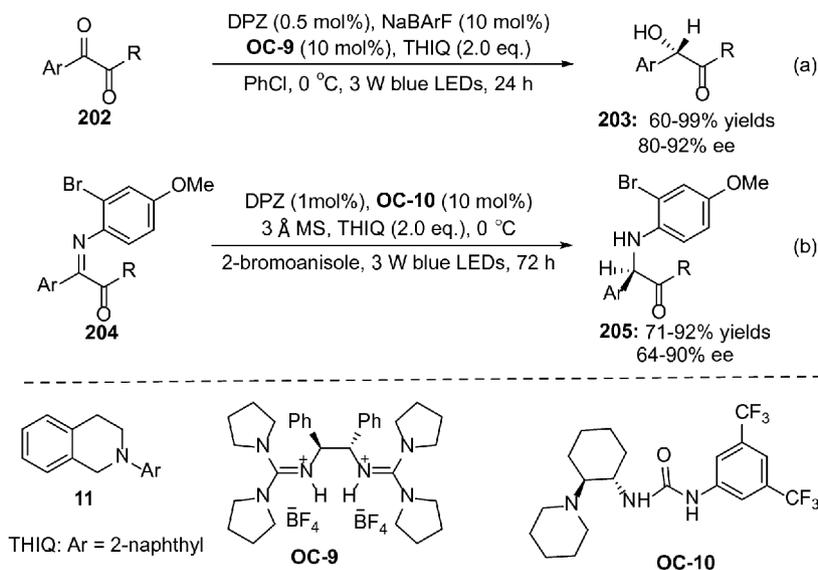
mild conditions with high enantioselectivities. The generation of these two diverse ketones was attributed to the flexible selection of an appropriate chiral Brønsted acid or base catalyst for proton shuttle.

4.2 Chiral organometallic catalyst-assisted asymmetric organic photochemical synthesis

In addition to the combination of visible light photocatalysis and organocatalysis, in recent years, asymmetric transfor-



Scheme 43 Asymmetric photoredox radical substitution and addition reactions via synergistic Brønsted acid and photoredox catalysis.



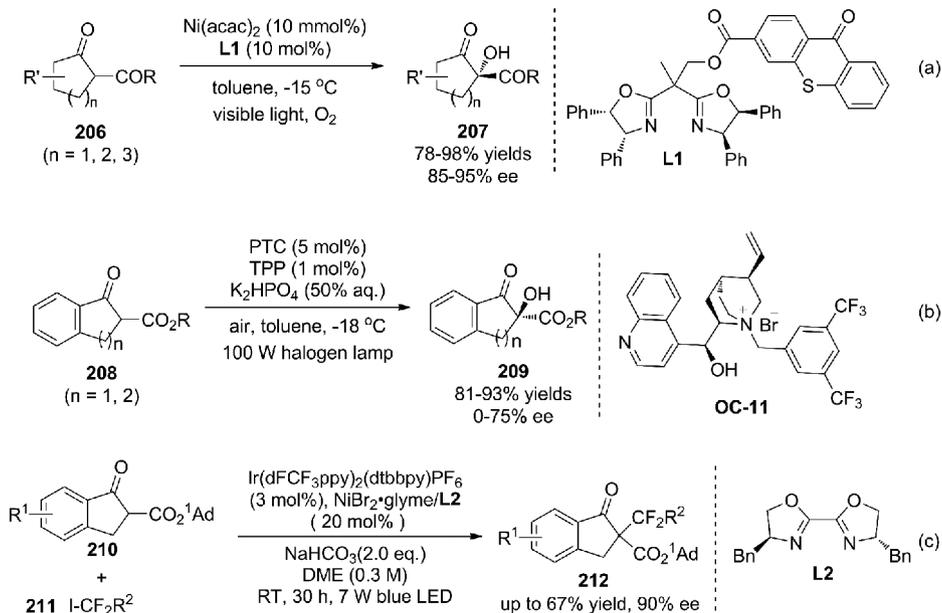
Scheme 44 Asymmetric photoreductions of 1,2-diketones and α -keto ketimines through synergistic visible light photocatalysis and organocatalysis.

mations using cooperative photocatalysis and transition metal (TM) catalysis have flourished as a powerful method for synthesizing chiral compounds [70]. At the beginning of 2017, Xiao and coworkers [71] devised a family of visible-light-responsive chiral ligands by grafting a thioxanthone photosensitizer to chiral bisoxazoline ligands (Scheme 45 (a)). These ligands could be successfully applied in metal-photocatalytic asymmetric aerobic oxidation reactions of cyclic β -ketoesters with molecular oxygen as the green terminal oxidant, affording the hydroxylation products in high yields and enantioselectivities. Interestingly, this hydroxylation process has also been realized by Meng and coworkers [72] through synergistic photocatalysis and asymmetric phase-transfer catalysis using a 100 W halogen lamp (Scheme 45(b)). Soon afterwards, Lu, Xiao and coworkers [73] reported an asymmetric radical difluoroalkylation of β -ketoesters by merging visible light photocatalysis

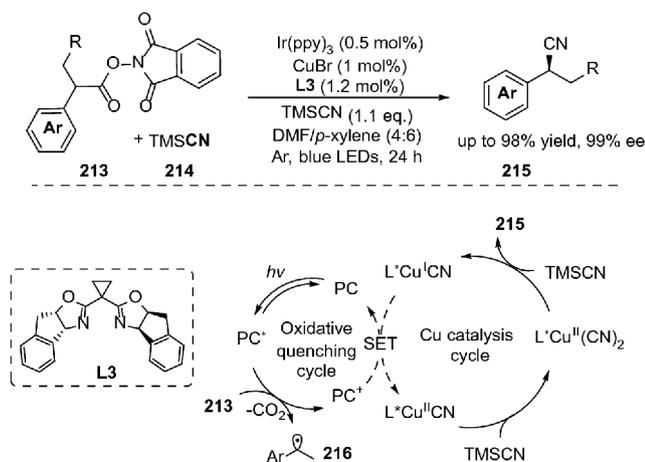
and nickel catalysis. With NiBr₂•glyme as the Lewis acid, fluoroalkylation products containing chiral all-carbon quaternary stereocenters were synthesized with good enantioselectivities. In addition, this strategy could be successfully applied to the perfluoroalkylation of β -ketoesters (Scheme 45(c)).

In 2017, the Liu's group [74] furnished a decarboxylative functionalization of racemic carboxylic acid derivatives by merging photoredox catalysis with asymmetric copper catalysis (Scheme 46). This work provides a useful method to chiral nitriles with high yields and enantioselectivities. Furthermore, this protocol has been demonstrated by its application through a 270-mmol-scale, one-pot reaction with carboxylic acid and *N*-hydroxy-phthalimide as starting materials.

In 2017, Lu and coworkers [75] developed an enantioselective [4+2] cycloaddition reaction of vinyl carbo-



Scheme 45 Asymmetric aerobic oxidation reactions and fluoroalkylation reactions of β -ketoesters induced using visible light.



Scheme 46 Enantioselective decarboxylative cyanation via synergistic photoredox and copper catalysis.

mates with α -diazoketones through the strategy of sequential visible-light photoactivation and palladium catalysis (Scheme 47). By doing so, a variety of chiral quinolinones bearing chiral all-carbon stereocenters were obtained in high yields with excellent enantioselectivities under extremely mild conditions. In particular, reactive ketenes were *in situ* generated from α -diazoketones through a visible-light-induced Wolff rearrangement, which make this transformation tolerate diverse functional groups.

5 Visible light-induced transformations of small molecules

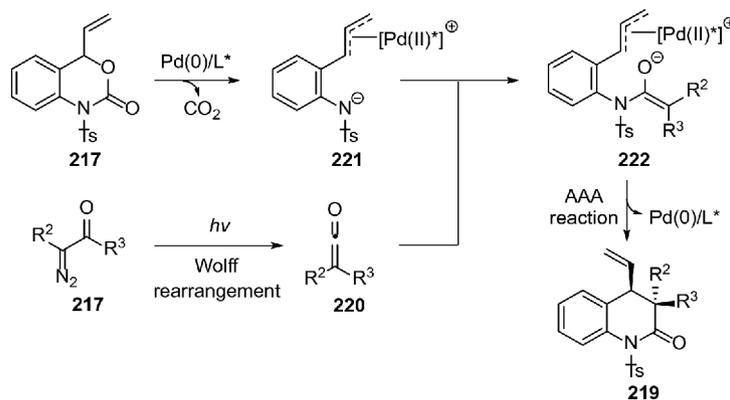
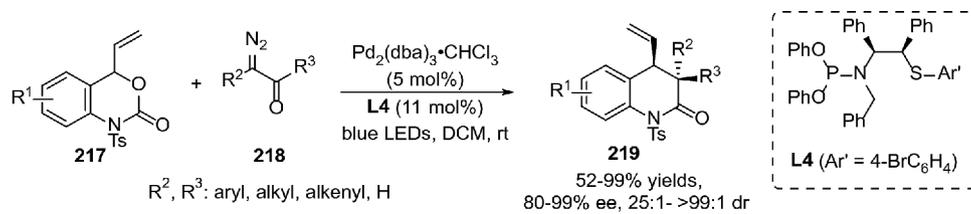
Visible light photoredox catalysis represents a powerful

potential in the transformations of small molecules, such as CO_2 , CO, and CH_4 etc. In this part we highlight the recent advances of this emerging area.

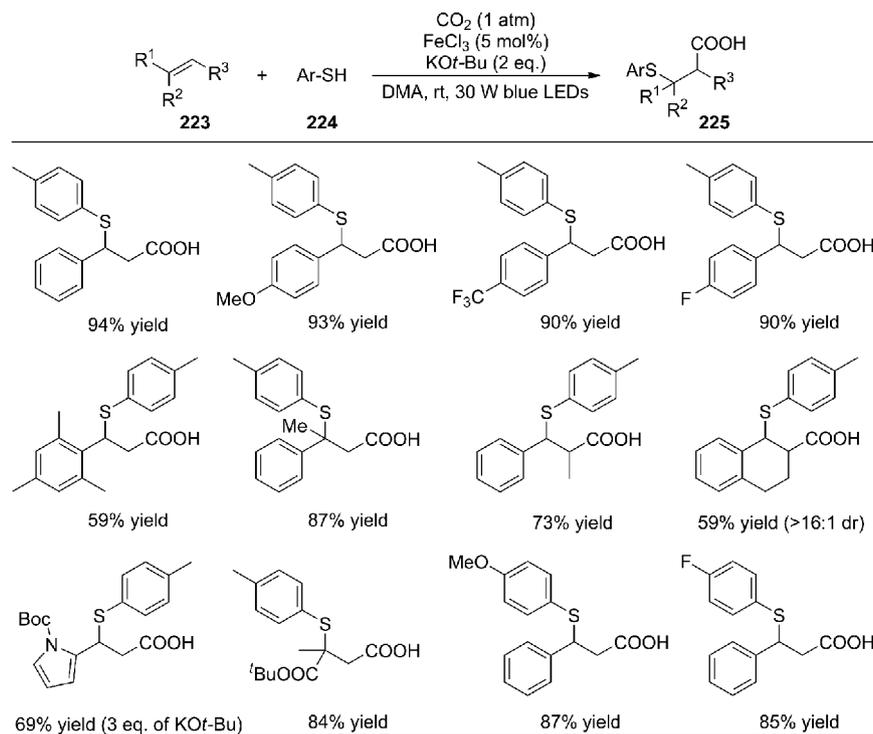
5.1 Visible light-induced transformations of CO_2

Carbon dioxide (CO_2) is an abundant and renewable carbon resource, and was widely used as an ideal C1 building block in chemical synthesis [76]. In the past few years, numerous efforts have been focused on photochemical transformations of CO_2 . This part offers a brief overview about recent examples of visible light-induced organic transformations of CO_2 with organic compounds.

Ultraviolet induced fixation of CO_2 has been reported as early as in 1975. After that, many efforts have been devoted to the transformation of CO_2 by using UV photoreactor (high-pressure mercury lamp, Hg or Xe lamp) [77]. A breakthrough for visible light-induced transformations of CO_2 has not been achieved until very recently. In 2017, Iwasawa and co-workers [78a] reported a visible light-induced hydrocarboxylation of alkenes with CO_2 by merging of Rh catalysis and $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ (bpy=2,2'-bipyridyl) catalysis. In the same year, Martin and co-workers [78b] described a visible light-induced redox-neutral intermolecular dicarbofunctionalization of styrenes with CO_2 to enable multiple C–C bond formations. Meanwhile, Yu and co-workers [79] developed the first thiocarboxylation of styrenes/acrylates and thiols with CO_2 under blue light irradiation by using catalytic iron salts as promoters (Scheme 48). The important β -thioacids were obtained in good to excellent yields with high regioselectivity under the optimal



Scheme 47 Visible-light-induced Pd-catalyzed asymmetric [4+2] cycloadditions of vinyl benzoxazinones with α -diazoketones.



Scheme 48 Photoinduced thiocarboxylation of styrenes and acrylates with CO_2 .

reaction conditions. Notably, the regioselectivity was significantly different from previous hydrocarboxylations and carbocarboxylations. Based on the preliminary mechanistic studies, they speculated that the *in situ* generated Fe/S complex (iron sulfur clusters) might play an important role in this reaction, leading to the generation of CO_2 radical anion via a single-electron reduction process. The unusual regio-

selectivity may result from the addition of CO_2 radical anion to unsaturated double bonds. Recently, König and co-workers [80] have developed an elegant ligand-controlled Markovnikov and anti-Markovnikov hydrocarboxylation protocol based on 4CzIPN (4CzIPN=1,2,3,5-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene) as photosensitizer and Hantzsch ester as non-metallic reductant.

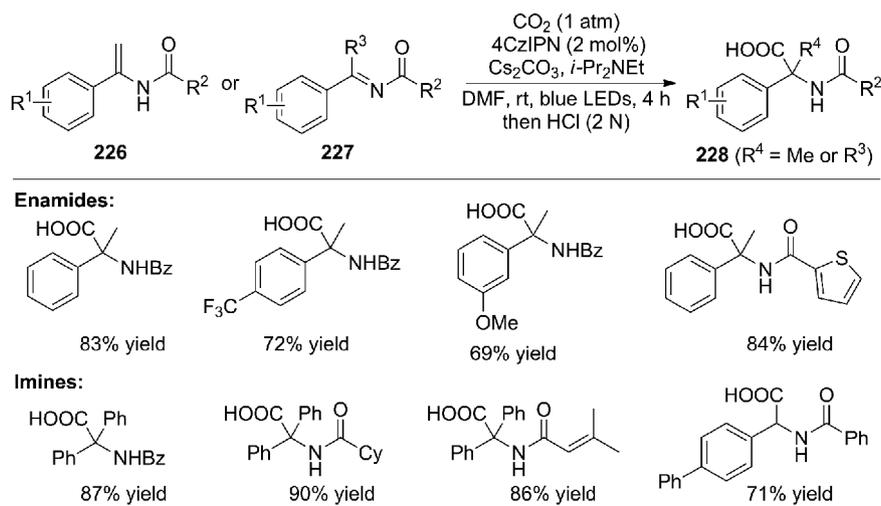
Very recently, Yu and co-workers [81] also developed a catalytic hydrocarboxylation of enamides and imines with CO₂ to generate valuable α,α -disubstituted α -amino acids. This reaction was carried out by using 4CzIPN as photocatalyst and ^tPr₂NEt as non-metallic reductant. Notably, this reaction also has excellent chemo- and regioselectivity, which is significantly different from previous reports on β -carboxylation of enamides, homocoupling or reduction of imines (Scheme 49). For example, when the photocatalyst, reductant, or light was not present, carboxylation occurred at the β -position of enamides in high yields. Mechanistic studies indicate that α -amino carbanion might be the key intermediate in this reaction.

Besides carboxylation to give acids, the carboxylative cyclization with CO₂ is also highly important. Recently, He and co-workers [82] developed an elegant visible light-induced carboxylative cyclization under ambient conditions. A series of perfluoroalkyl 2-oxazolidinones were obtained by the reaction of allyl amines, CO₂ and perfluoroalkyl iodides

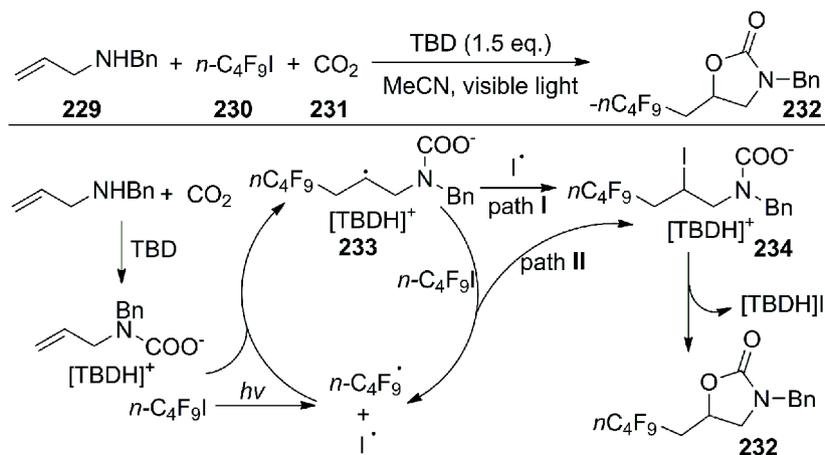
(Scheme 50). Mechanistically, carbamate, perfluoroalkyl radical and iodine radical were involved in the reaction. Control experiments and ¹H NMR analysis revealed that iodo-perfluoroalkylated carbamate could be the intermediate of this reaction.

Yu and co-workers [83] independently reported an efficient method for the selective oxy-difluoroalkylation of allylamines with CO₂. This method is environment-friendly to generate various difluoroalkylated 2-oxazolidinones skeleton under mild conditions (Scheme 51). Mechanistically, the reductive quenching of the excited Ru* catalyst by DABCO was the key initial step, where the generated Ru(I) triggered the generation of CF₂COOEt radical. Then, benzylic radical was obtained by the addition of CF₂COOEt radical to the alkene moiety of carbamate. Further single electron oxidation by the excited *Ru(II) species and following intramolecular cyclization process afforded the final products.

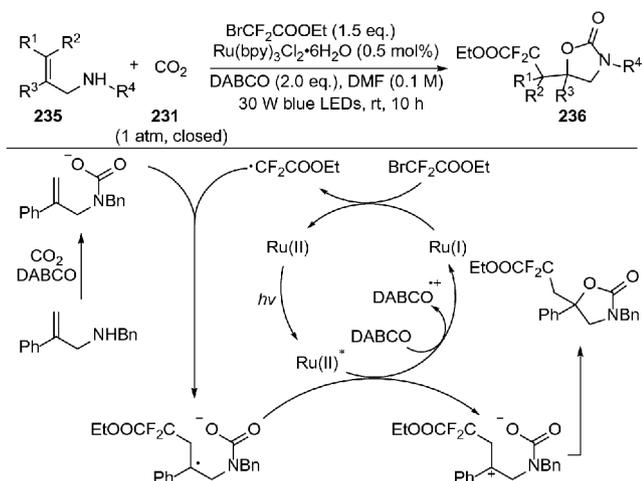
Compared with activated perfluoroalkyl iodides and difluoroalkyl bromides, simple unactivated alkyl halides show



Scheme 49 Catalytic hydrocarboxylation of enamides and imines with CO₂.



Scheme 50 Visible light induced carboxylative cyclization of allyl amines.

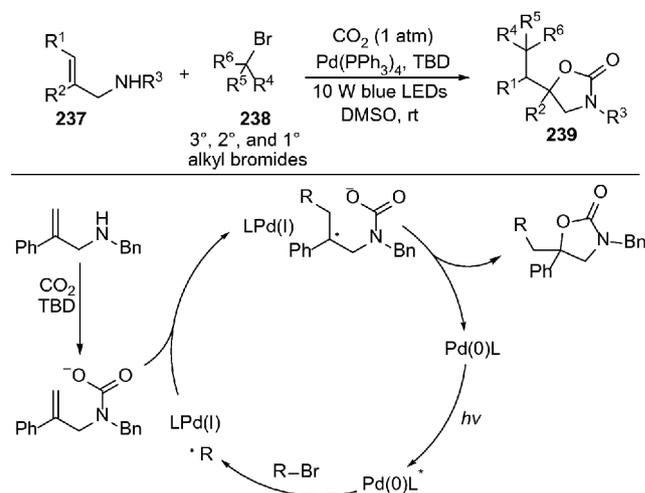


Scheme 51 Visible light induced selective oxy-difluoroalkylation of allylamines.

lower reactivity under visible light photoredox catalysis and could not be employed in such transformations. Very recently, Yu and co-workers [84] have also reported another selective oxy-alkylation of allylamines with diverse unactivated alkyl bromides and CO₂ via visible light-induced palladium catalysis. Commercially available Pd(PPh₃)₄ is employed as the sole catalyst in this three-component reaction, which enabled the use of less unactivated alkyl bromides in such a transformation compared with their previous method (Scheme 52). In this study, atmospheric CO₂ could be efficiently transferred into the valuable alkylated 2-oxazolidinones with high yield and selectivity under irradiation of blue LEDs. Radical trapping experiments and radical clock experiments revealed that the reaction may proceed via a radical pathway.

As we know, the reductive carboxylation of electrophiles with CO₂ always precedes in the presence of stoichiometric metal as reductants [85]. In 2018, Zhao and Wu *et al.* [86] reported an elegant visible light-induced hydrocarboxylation of alkynes by using CO₂ as carboxyl source via an iridium/cobalt dual catalysis system. The reaction was carried out by using CoBr₂/dcype [dcype=bis(dicyclohexylphosphino)ethane] as catalyst, Ir(ppy)₂(dtbbpy)PF₆ as photocatalyst, and ^tPr₂NEt as non-metallic reductant, respectively (Scheme 53), affording the hydrocarboxylated products with low selectivity. However, a high degree of regioselectivity was achieved when the two substituents were sterically differentiated, providing the sole regioisomer, where CO₂ was inserted adjacent to the less sterically hindered substituent.

Moreover, they discovered that the coumarin derivatives could be obtained by a one-pot synthesis via the sequential procedure of hydrocarboxylation/alkene isomerization/cyclization (Scheme 54). The key of the reactions is the use of the alkynes which bore a MOM-protected hydroxyl group at the *ortho* position on the aromatic ring. Firstly, hydrocarboxylation reaction proceeded under the same reaction



Scheme 52 Visible light-induced selective oxy-alkylation of allylamines.

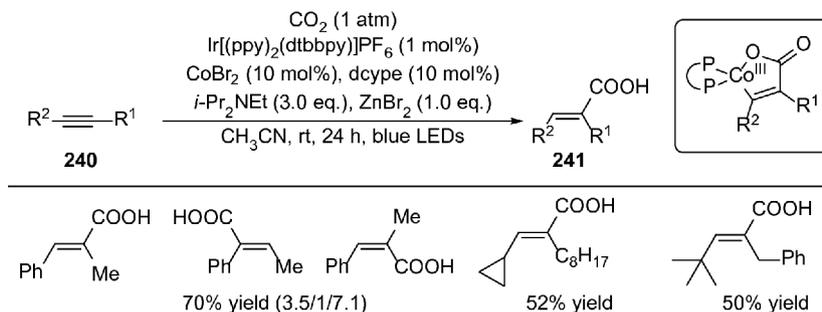
conditions as described in Scheme 54. After adding of TsOH, the reaction mixture was further stirred under irradiation of blue LED. In the latter step, Ir-photocatalyst played an important role in promoting energy transfer in the alkene isomerization. The corresponding coumarin derivatives were obtained in moderate to good yields. In addition, 2-quinolones were obtained when alkyne bearing a Boc-protected carbamate in place of the MOM protected ether was used.

Furthermore, this protocol could be expanded to the synthesis of γ -hydroxybutenolides by using *ortho*-esters substituted aryl alkynes (Scheme 55). Various alkynes were converted to the corresponding products in good yields.

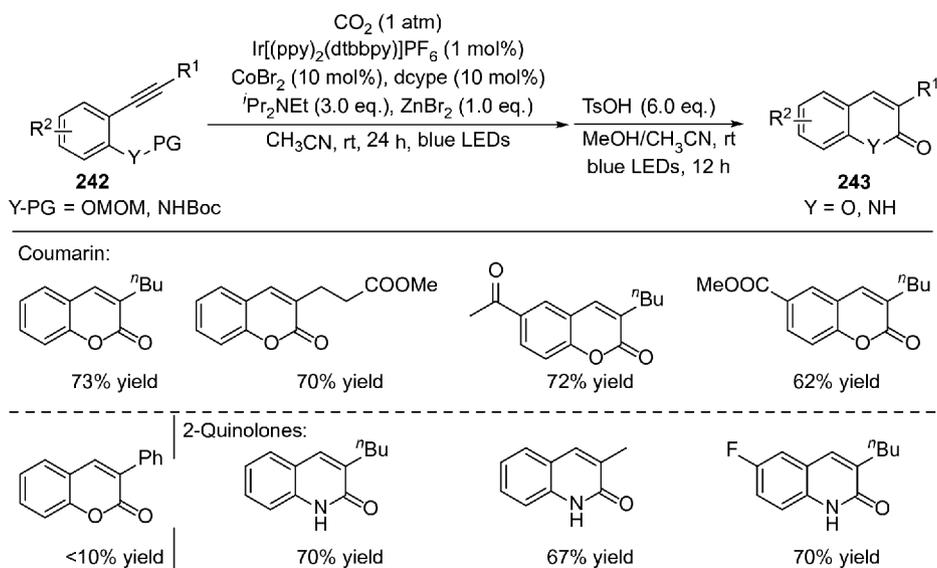
5.2 Visible light-induced transformation of CO

Carbon monoxide (CO) is one of the most important C1 building blocks for the production of chemicals and fuels in industry. For decades, significant effort has been devoted to transition-metal-catalyzed and light-induced CO chemistry [87]. In this part, we mainly introduce visible light-induced carbonylation with CO.

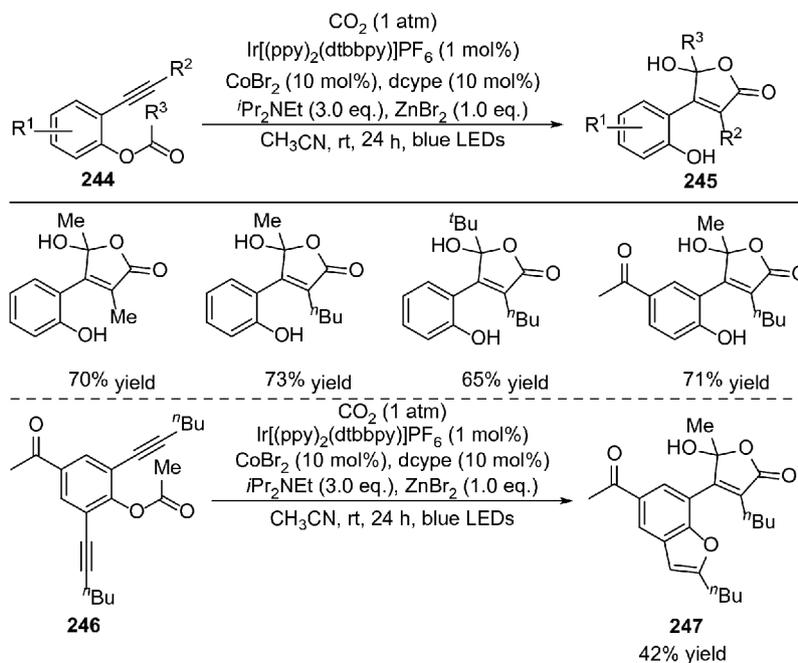
In 2012, Yin and Jia *et al.* [88] reported the carbonylation of aryl bromides via Co(OAc)₂ and PhCOPh dual catalysis in the presence of basic additive under visible light irradiation conditions. A wide range of methyl aryl carboxylates were obtained in the presence of MeOH. In 2015, Xiao's group [89] and von Wangelin's group [90] independently reported visible light-induced alkoxy-carbonylation of aryldiazonium salts to synthesize aromatic esters (Scheme 56). Their reaction conditions were similar among different photocatalysts. The Xiao's group chose fluorescein as photocatalyst along with a 16 W blue light-emitting diode (LED), while von Wangelin's group used eosin Y as photocatalyst and green LED as light source. High concentration of CO was critical to this transformation, as it could significantly inhibit the formation of unwanted homocoupling (Ar–Ar) and reduction



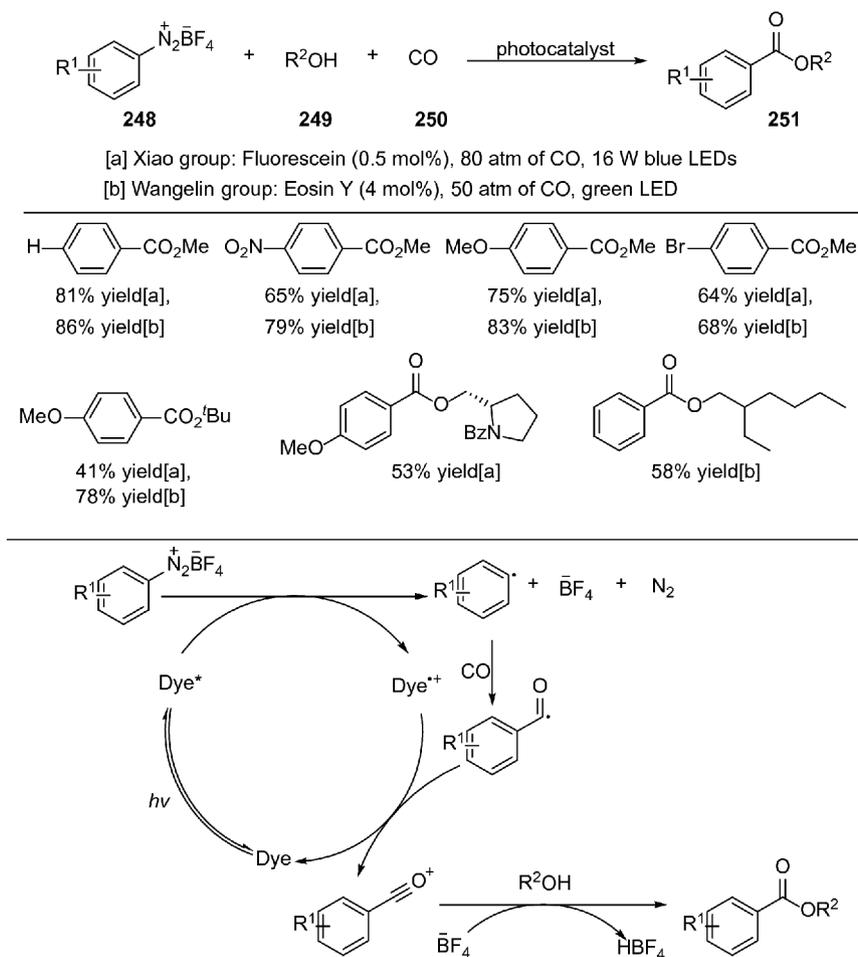
Scheme 53 Visible light-induced hydrocarboxylation of alkynes with CO_2 .



Scheme 54 Synthesis of coumarin derivatives and 2-quinolones.



Scheme 55 Synthesis of γ -hydroxybutenolides.



Scheme 56 Visible light-induced alkoxy carbonylation of aryldiazonium salts.

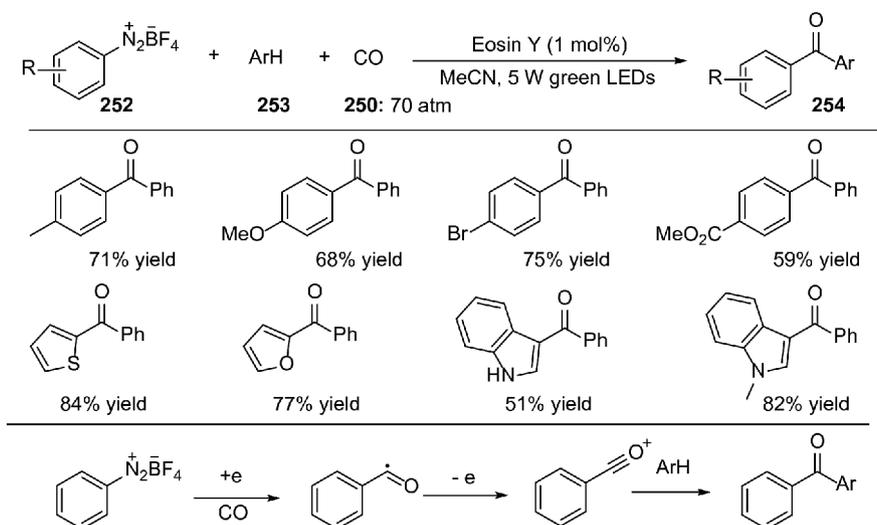
(Ar-H) product. Radical quenching experiments with 2,2,6,6-tetramethylpiperidinoxy (TEMPO) confirmed that the reaction proceeds by a radical mechanism. DFT calculations indicated that oxidation of acyl radical by [dye] radical cation is thermodynamically favorable while oxidation of aryl radical to an aryl cation is not. Based on these results, a common mechanism was shown. Firstly, the SET between aryl diazonium salts and the excited organic dye results in the release of nitrogen (N_2) and generation of aryl radical, which can rapidly react with CO to afford acyl radical. The acyl radical then undergoes oxidation to give the highly electrophilic acylium ion. Finally, nucleophilic attack of the alcohol to the acylium ion affords the final product.

In the same year, Gu and co-workers [91] reported a radical carbonylation of aryldiazonium salts with arenes and indoles as nucleophilic reagents (Scheme 57). A wide range of aryl ketones and indol-3-yl aryl ketones were obtained in good yields. The reactions are thought to proceed through a pathway similar to the work of Xiao *et al.* and von Wangelin *et al.* [89,90], expect for the final step with capture of acylium ion by (hetero)arenes.

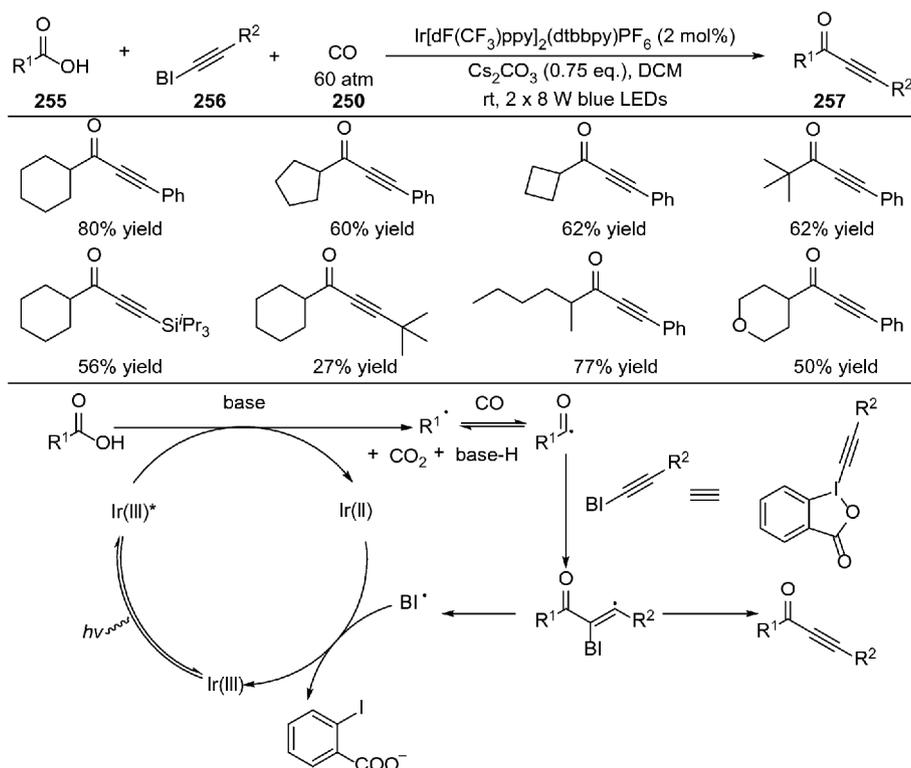
In 2015, the Xiao and Lu's group [92] developed the first

decarboxylative and carbonylative alkylation of carboxylic acids with CO and ethynylbenziodoxolone (EBX) reagents (Scheme 58). A series of valuable alkynones were obtained in good yields. The radical clock experiments implied the radical mechanism was involved in this reaction. With detailed mechanistic studies, a plausible reaction pathway was proposed. First, the carboxylate is oxidized by the excited Ir(III) catalyst to generate an alkyl radical, and reacts with CO to form an acyl radical. The following radical addition to EBX and elimination yield the desired product.

In 2016, Li, Liang and coworkers [93] also reported a visible light-induced procedure for the synthesis of indol-3-yl aryl ketones by using arylsulfonyl chlorides as the robust aryl radical precursors. In 2016, the Lei's group [94] reported an aerobic intramolecular oxidative carbonylation of enamides via palladium and visible light photoredox dual catalysis (Scheme 59). In this process, the purpose of the photocatalyst is to oxidize Pd(0) into the Pd(II) species. Ac_2O could inhibit the possible reduction of the active Pd(II) intermediate by CO to give inactive Pd(0) complex. Mechanically, the vinylpalladium intermediate generated through a Pd(II)-catalyzed alkenyl C-H activation and underwent coordination



Scheme 57 Visible light-induced carbonylation of aryldiazonium salts.



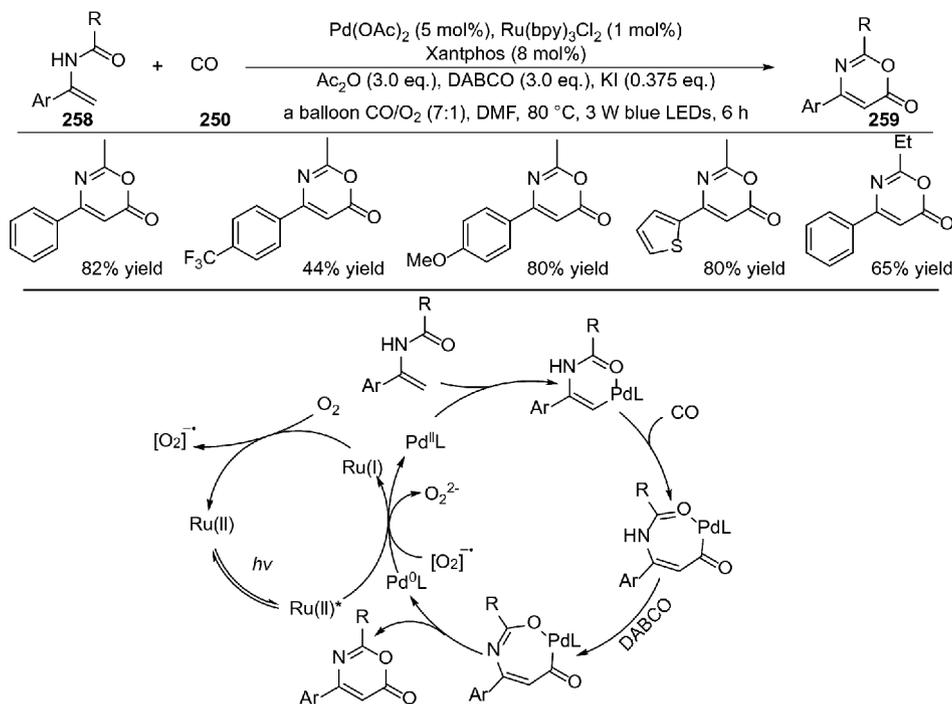
Scheme 58 Visible light-induced carbonylative alkylation of carboxylic acids.

and insertion of CO to afford the acylpalladium intermediate. Subsequent deprotonation by DBACO and reductive elimination afforded the desired 1,3-oxazin-6-ones products and Pd(0) species.

5.3 Visible light-induced transformations of CH₄

Very recently, Zuo and co-workers [95] have reported an elegant photocatalytic amination, alkylation and arylation of

inert C(sp³)-H bonds in methane, ethane, and higher alkanes under visible light irradiation (Scheme 60). This protocol exhibits high catalytic efficiency (TON up to 2900 for methane and 9700 for ethane) and selectivity. Importantly, this mild protocol was realized by using inexpensive cerium salts as photocatalysts. The alkoxy radicals, *in situ* generated from simple alcohols through ligand-to-metal charge transfer (LMCT), acted as hydrogen atom transfer catalysts. The highly electrophilic alkoxy radicals intermediate might ab-



Scheme 59 Visible light-induced oxidative carbonylation of enamides.

struct hydrogen from methane. The generated alkyl radicals could react with some electrophilic reagents to afford the final products. Furthermore, the mixed phase gas/liquid reaction was adapted to continuous-flow, enabling the efficient use of gaseous feedstocks in scalable photocatalytic transformations.

6 Visible-light-induced reactions under biomolecule-compatible conditions

The visible-light-induced biomolecule-compatible reactions were developed before the recent boom in visible light photoredox catalysis in 2008. In 1999, Kodadek and coworkers [96] pioneered the visible-light-induced oxidative cross-linking reaction of protein tyrosine residues using persulfates under 150 W white xenon irradiation. However, the biocompatibility is compromised with the strongly oxidative persulfates and high-energy light irradiation conditions required [97]. Recently, with the emerging use of low-energy CFL and LED light sources and the development of various photoredox catalysis methods, the visible-light-induced biomolecule-compatible reactions have flourished and are widely studied.

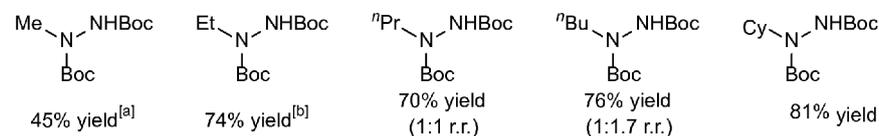
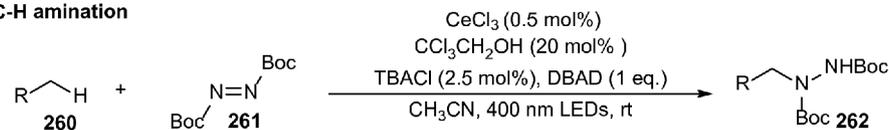
In 2011, Liu and coworkers [98] discovered a visible-light-induced biomolecule-compatible azide-reduction reaction from a DNA-encoded reaction discovery system (Scheme 61). This azide reduction reaction is highly chemoselective and is compatible with various functional groups including

alcohols, phenols, acids, alkenes, alkynes, aldehydes, alkyl halides, alkyl mesylates and disulfides. The azide reduction is applicable to nucleic acid and oligosaccharide substrates without detectable occurrence of side reactions, and protein enzyme activity is not affected under the reaction conditions. The visible-light-induced photouncaging of amine and carboxylate functional groups can be achieved on nucleic acids without ultraviolet irradiation.

In 2014, Chen and coworkers [99] discovered a visible-light-induced deboronative alkynylation reaction with biomolecule compatibility (Scheme 62). The reaction is enabled by hydroxylbenziodoxole (BI-OH), a hypervalent iodine(III) reagent, which acts as an effective oxidative quenching agent and was previously reported to be chemically inert. Primary, secondary and tertiary alkyl trifluoroborates or boronic acids are all applicable to generate aryl, alkyl and silyl substituted alkynes under mild and redox-neutral conditions. This reaction is highly chemoselective and compatible with alkenes, alkynes, aldehydes, ketones, esters, nitriles, azides, aryl halides, alkyl halides, alcohols, and indoles. This reaction can be performed in neutral aqueous conditions, and the presence of amino acids, nucleosides, oligosaccharides, nucleic acids, proteins, and cell lysates does not affect the reaction.

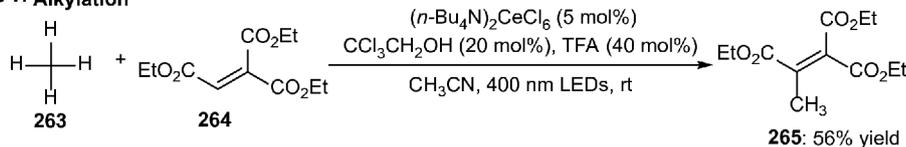
In 2014, Chen and coworkers [100] reported a visible-light-induced decarboxylative alkynylation to construct aryl, alkyl and silyl substituted alkynes at room temperature in organic solvents or neutral aqueous solutions (Scheme 63 (a)). This reaction is enabled by the ascorbates acting as biocompatible reductants, which are also effective reductive

C-H amination

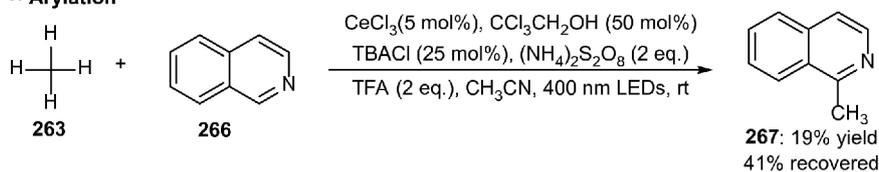


[a] $\text{Ce}(\text{OTf})_4$ as cerium catalyst. [b] With diisopropyl azodi-carboxylate.

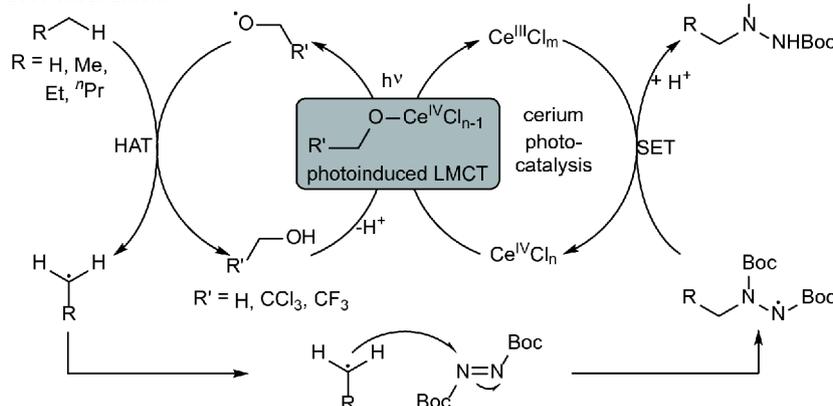
C-H Alkylation



C-H Arylation



proposed mechanism



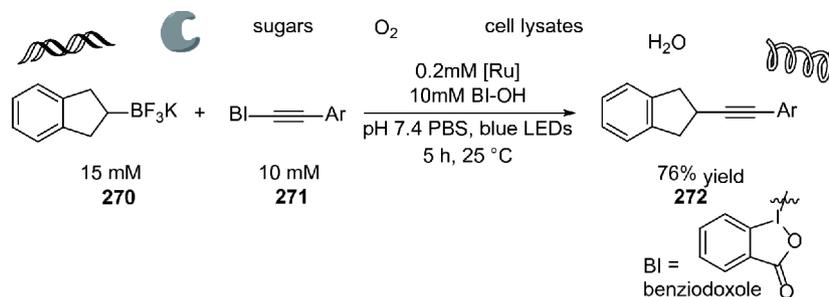
Scheme 60 Photocatalytic C-H alkylation and arylation of methane.



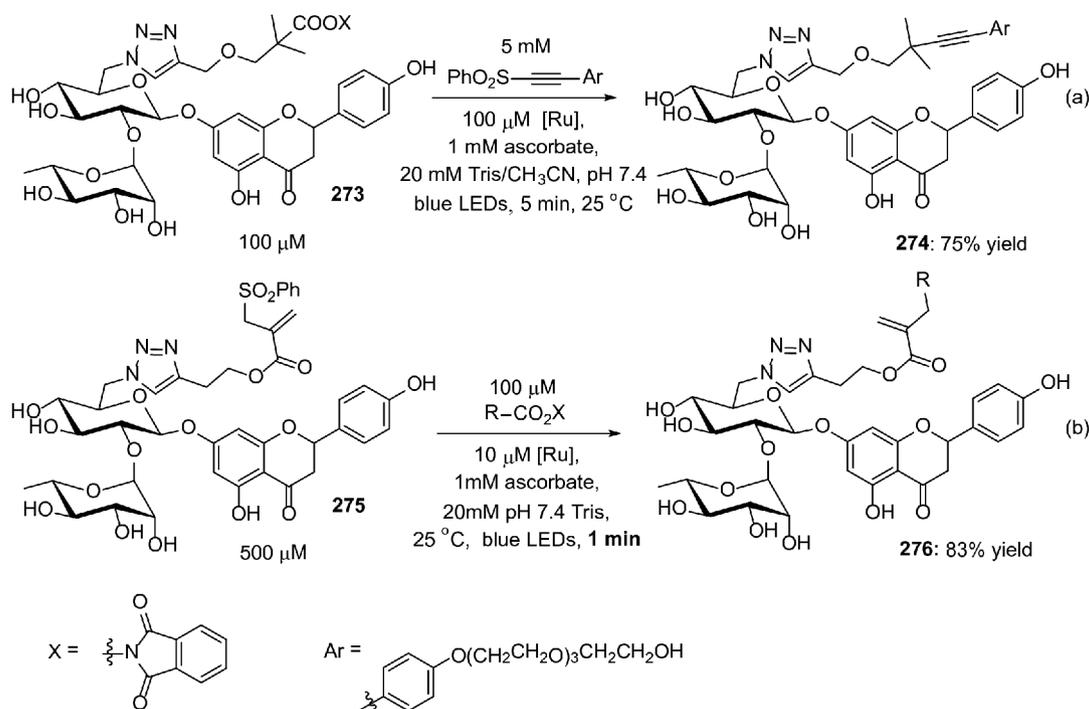
Scheme 61 Biomolecule-compatible visible-light-induced azide reduction on oligonucleotide and oligosaccharide substrates.

quenching reagents. This reaction is performed chemoselectively on substrates containing alkenes, alkynes, aldehydes, ketones, esters, amides, azides, aryl/alkyl halides, alcohols, phenols, carboxylic acids, and indoles. The remarkable functional group compatibility and mild conditions of the reaction enabled an oligosaccharide alkynylation in 75% yield within minutes under neutral aqueous condition, and the addition of various endogenous and exogenous biomolecules did not affect the reaction. This reaction also

occurred in the presence of a protein enzyme without loss of its enzymatic activity. In 2015, Chen and coworkers [101] developed a visible-light-induced decarboxylative allylation with ultrafast reaction kinetics (Scheme 63(b)). This reaction works for primary, secondary, tertiary, benzyl, and α -heteroatom-substituted alkyl *N*-acyloxyphthalimides and can be run in organic solvents and neutral aqueous solutions. The reaction completes in minutes at room temperature with a rate constant of $10^6 \text{ M}^{-1} \text{ s}^{-1}$. The decarboxylative allylation



Scheme 62 Visible-light-induced chemoselective deboronative alkylation enabled by hypervalent iodine(III) reagents under biomolecule-compatible conditions.

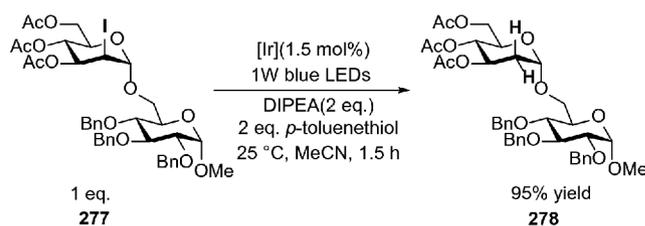


Scheme 63 Visible-light-induced reductive decarboxylative alkylation and allylation in low concentrations with fast reaction kinetics under biomolecule-compatible conditions.

demonstrates excellent chemoselectivity and is compatible with sensitive functional groups. A functional-group-rich oligosaccharide modification with decarboxylative allylation is demonstrated in neutral aqueous conditions.

In 2014, Wan and coworkers [102] described a visible-light-induced reductive deiodination to construct 2-deoxy- α -glycosides with glycosides compatibility (Scheme 64). This visible-light-mediated tin-free reductive deiodination uses diisopropylethylamine as the reductant and free thiol as the hydrogen donor to enable the 2-deoxy sugar synthesis. The postglycosylation deiodination strategy can be applied to various *mono*-, *di*-, *tri*-, *tetra*- and *pentadeoxy*saccharides with excellent stereo- and chemoselectivity. This strategy can be used for the synthesis of a 2-deoxy-tetrasaccharide containing four α -linkages.

In 2015, Chen and coworkers [103] described a visible-light-induced deboronative/decarboxylative alkenylation in



Scheme 64 Stereoselective synthesis of α -linked 2-deoxy glycosides enabled using visible-light-mediated reductive deiodination.

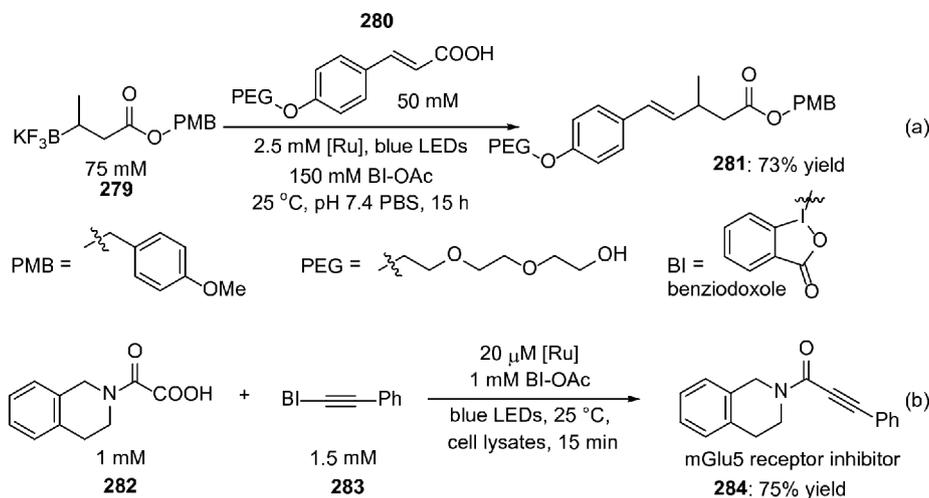
organic solvents and neutral aqueous conditions at room temperature (Scheme 65(a)). A novel benziodoxole-vinyl carboxylate reaction intermediate is isolated and this represents the first hypervalent-iodine-enabled radical decarboxylative alkenylation reaction. The aryl and acyl substituted alkenes can be effectively constructed to contain various sensitive functional groups. The PEG-conjugated

vinyl carboxylic acid gave a 73% yield in a neutral aqueous buffered condition and suggested future biomolecule applications. Later in 2015, Chen and coworkers [104] reported a decarboxylative ynylation with dual hypervalent iodine (III)/photoredox catalysis under mild reaction conditions (Scheme 65(b)). Various ynones, ynamides, and ynoates can be constructed at room temperature with the compatibility of sensitive/reactive functional groups. This reaction can be used to synthesize an mGlu5 receptor inhibitor under neutral aqueous conditions or in cell lysate at 1 mM concentration in 15 min.

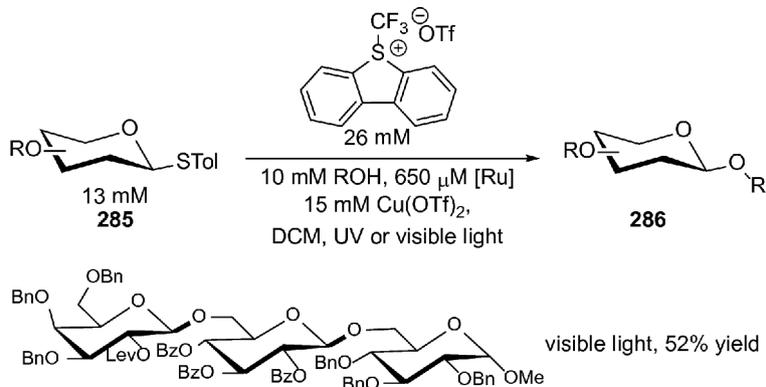
In 2016, Ye and coworkers [105] developed a light-induced glycosylation reaction from thioglycosides via the trifluoromethyl radical intermediate (Scheme 66). The reaction can be run under UV or visible light irradiation with copper catalysis and many common protecting groups are tolerated. A rapid one-pot sequential assembly of oligosaccharides is demonstrated with this glycosylation protocol. Later in 2016, the Ye's group [106] reported the *O*-sialylation using the thiosialoside donors under similar reaction conditions with a ruthenium photocatalyst.

In 2017, Wang and coworkers [107] developed a visible-light-induced thiol-ene reaction for the synthesis of glycoconjugates between carbohydrates and peptides (Scheme 67 (a)). The organic photocatalyst 9-mesityl-10-methylacridinium tetrafluoroborate was used for the reaction and applicable to terminal alkenes and various thiols. In 2018, Wang and coworkers [108] reported the synthesis of 2-deoxyglycosides from glycols by photoacid catalysis (Scheme 67 (b)). With phenol-conjugated acridinium-based organic photoacids, synthetic glycols can couple with a range of alcohols to afford 2-deoxyglycosides with excellent α -selectivity.

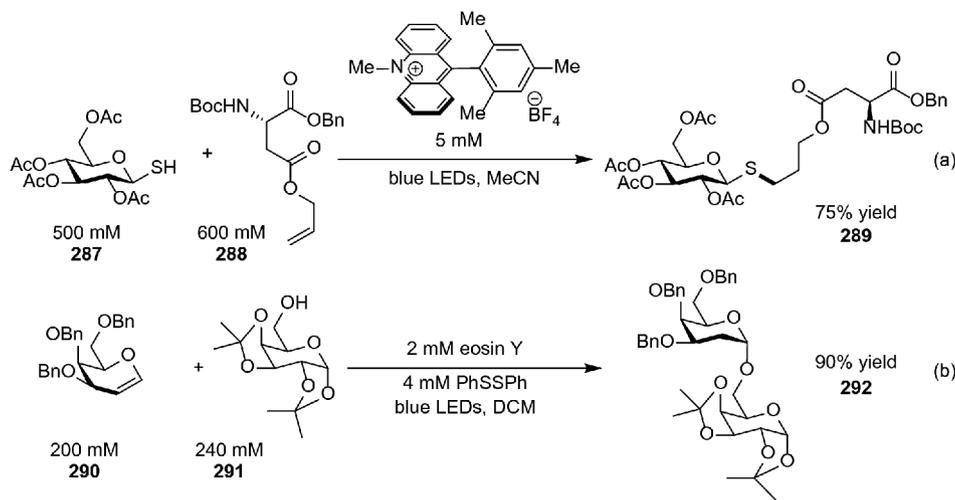
In 2018, Zhu, Xie, and coworkers [109] reported a deoxygenation method to synthesize ketones from aromatic carboxylic acids and alkenes (Scheme 68). This reaction can be run in aqueous solution to construct structurally diverse ketones using triphenylphosphines. This reaction can be used for the late-stage modification of several complex molecules, and for the construction of macrocycloketones. The presence of amino acids, nucleosides, oligosaccharides, nucleic acids, and proteins does not affect the reaction.



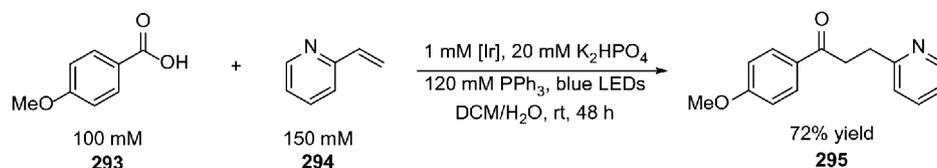
Scheme 65 Hypervalent iodine reagents enable chemoselective alkenylation and ynylation under neutral aqueous conditions and in cell lysates.



Scheme 66 Light-driven glycosylation reaction from thioglycosides.



Scheme 67 Visible-light-mediated thiol-ene reaction and photoacid catalysis for glycoconjugates synthesis.



Scheme 68 Visible-light-induced ketone synthesis by deoxygenation in neutral aqueous conditions.

7 Summary

In the past decade, visible light-driven organic photochemical reactions have been established as a powerful tool for synthetic chemistry. As we shown in this review, Chinese chemists have devoted a great number of endeavors to this field from different aspects, especially on direct C–H functionalizations, synthesis of aromatic aza-heterocycles, catalytic asymmetric organic photochemical reactions, transformations of small molecules and biomolecule-compatible reactions. Obviously, the utility of visible light photoactivation or photocatalysis strategy not only provides chances to develop new transformations that are impossible or not easy through the traditional ground-stated chemistry, but also makes these processes that have drawn wide attention from industry more user- and environment-friendly. Despite these advances, there are still many challenging problems in this area. For example, though the merging of visible light photocatalysis with organometallic catalysis has been widely used to forge a variety of chemical bond formations, there is still a long way to develop asymmetric processes due to the lack of specific and general chiral ligands. More recently, the continuous flow photoreaction has been developed as a potential technology to realize the scale-up production of industrial products; while, the solid/liquid biphasic reaction is still difficult. We anticipate that, in the future the cooperation among photochemical scientists, synthetic chemists and engineers may resolve these problems

well and further promote the development of visible light-driven organic photochemical synthesis.

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Conflict of interest The authors declare that they have no conflict of interest.

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