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Photoredox Catalysis

Visible-Light Photoredox Catalysis

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heterocycles · homogeneous catalysis · photocatalysis · radicals · synthetic methods

In the last few years, visible-light initiated organic transformations have attracted increasing attention. The development of visible-light-promoted photocatalytic reactions, which enable rapid and efficient synthesis of fine chemicals, is highly desirable from the viewpoint of cost, safety, availability, and environmental friendliness. In this Minireview, recent advances made in this fast developing area of research are discussed.

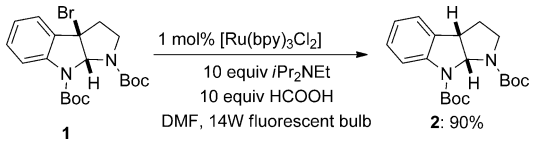
1. Introduction

The use of visible-light photoredox catalysis to initiate organic transformations has evoked interest since the 1970s.[1] However, only in the last few years have spectacular advancements been made in this area. Owing to its natural abundance, ease of use, and fascinating potential of applications, visible-light photoredox catalysis is emerging as a powerful tool in synthetic organic chemistry.[2] Since 2008, various chemical reactions promoted by irradiation with visible light have been elegantly devised and developed into practical synthetic methods. In addition, purely organic dyes have also been successfully utilized as photocatalysts in visible-light-induced organic transformations.

Several comprehensive reviews of this field have been published thus far.[3] Consequently, this Minireview will focus mainly on the new processes described in the past year and is organized by reaction type.

2. Visible-Light-Mediated Radical Addition and Cycloaddition Reactions

Reductive dehalogenation reactions, mediated by visible-light photoredox catalysis, were pioneered by Kellogg and co-workers, as well as others since 1978,[4] and these processes were additionally investigated recently by Stephenson and co-workers (Scheme 1).[5a] Compared with those that employ conventional radical-based methods, visible-light-mediated dehalogenation reactions not only provide the desired products in excellent yields under mild reaction conditions, but also exhibit superior chemoselectivity and excellent functional-group tolerance. Moreover, the utilization of free radicals,[6] which are generated by reductive cleavage of C–X bonds mediated by visible-light photoredox catalysis, for C–C bond formation has also been documented by the groups of Stephenson,[7] Gagné,[8] Reiser,[9] Masson,[10] and Yu.[11]



Scheme 1. A visible-light-mediated reductive dehalogenation reaction. bpy = 2,2′-bipyridine, DMF = *N*,*N*′-dimethylformamide.

Importantly, visible-light photoredox catalysis was used to execute a key C–C bond-forming step in an elegant approach to the synthesis of gliocladin C, a C3–C3′ indole alkaloid which exhibits a broad range of potent biological activities (Scheme 2).[12] By effectively blocking the C2′-position of the indole **5** using a formyl group, visible-light-mediated coupling with the bromopyrroloindoline **4** led to formation of the desired C3–C3′ coupling product. Starting with commercially available Boc-D-tryptophan methyl ester (**3**), gliocladin C was prepared in 10 steps in 30% overall yield. This example strongly illustrates the fact that visible-light photoredox catalysis not only serves as a viable method to promote simple organic transformations, but can also be employed in routes to construct complex natural product architectures.

The use of visible-light to induce the generation of free radicals has been commonly limited to enones and activated organohalogen substrates. Inspired by the work of Hasegawa and co-workers,[13] Fensterbank, Ollivier, and co-workers recently observed that epoxides and aziridines containing an α-carbonyl moiety are also effective radical sources. These substrates undergo epoxide and aziridine ring-opening reac-

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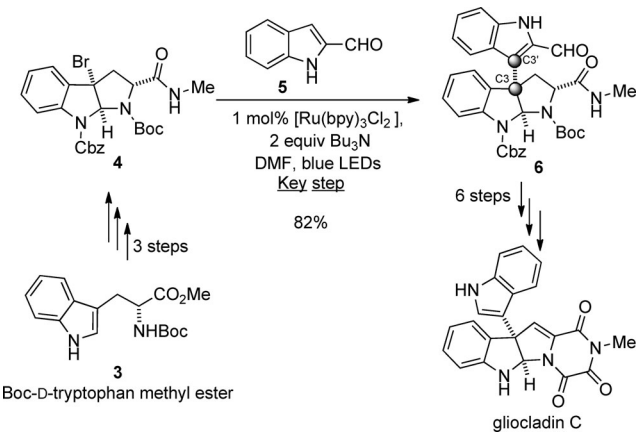
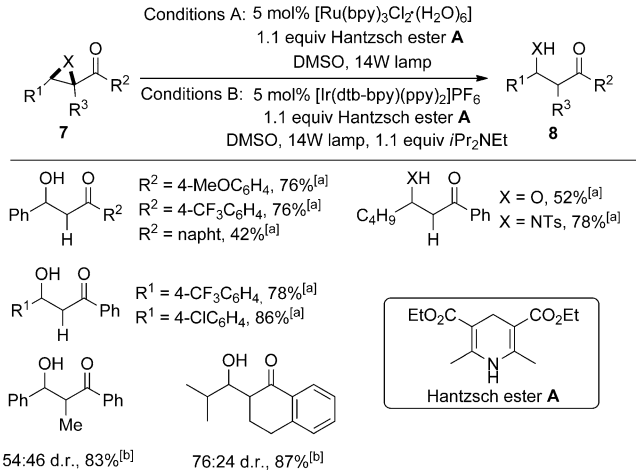


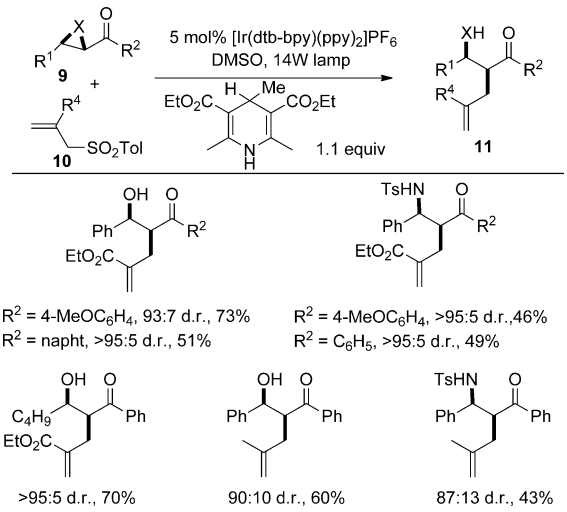
Scheme 2. Total synthesis of (+)-gliocladin C enabled by visible-light photoredox catalysis. Boc = *tert*-butoxycarbonyl, Cbz = carbobenzyloxy, LED = light-emitting diode.

tions through visible-light-mediated, electron-transfer pathways (Conditions A and B in Scheme 3).[14] Conditions B, employing $[Ir(dtb\text{-}bpy)(ppy)_2]PF_6$ as a single-electron transfer (SET) photosensitizer, was utilized to bring about the ring-opening reactions of the sterically hindered β epoxyketones



Scheme 3. Visible-light mediated ring opening of epoxides and aziridines. DMSO = dimethylsulfoxide, dtb-bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, ppy = 2-phenylpyridine, Ts = 4-toluenesulfonyl.

(Scheme 3). More importantly, by the judicious use of the Hantzsch esters to moderate the balance between direct reduction and radical addition, photogenerated radicals derived from these substrates undergo C–C bond-formation reactions with allylsulfone and occur through a highly diastereoselective tandem radical ring-opening/allylation process (Scheme 4). It is important to note that a similar radical allylation reaction would be unlikely when classical titanocene chemistry is utilized because a two-electron reduction would take place rapidly to generate a keto/enolate.[15]



Scheme 4. A visible-light-mediated tandem ring opening/allylation process.

The mechanism proposed by the authors for this process is shown in Scheme 5. Reductive quenching of the photoexcited state ML_3^{n+*} by Hantzsch's ester (HE) affords $ML_3^{(n-1)+}$, a strong reductant which then donates an electron to the substrate **9** to generate the radical anion **14**. Subsequent ring opening of **14** then forms radical anion intermediate **15**. The simple reduction of **15** by the cation radical **13** through a proton transfer/SET proton transfer route provides the product **16** and pyridine **17**. In competition, trapping of **15** by addition to the allylsulfone derivative **10** gives rise to the allylation product **11**.

Previous studies carried by Yoon and co-workers on visible-light photocatalytic [2+2] cycloaddition reactions of

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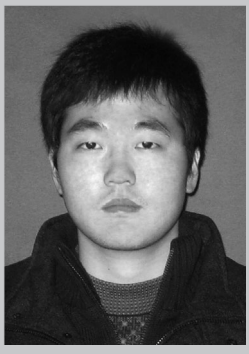

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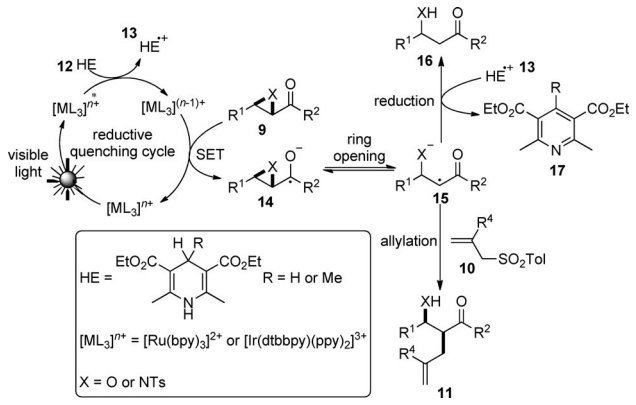
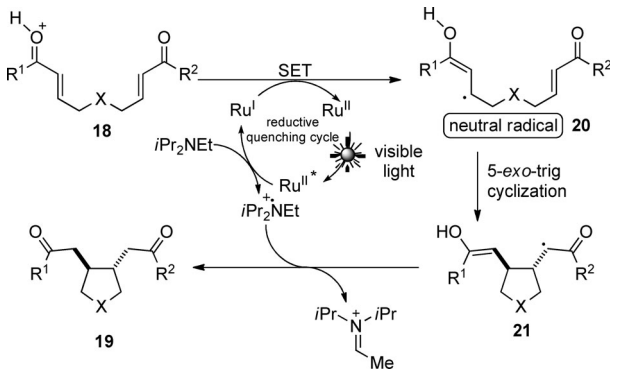
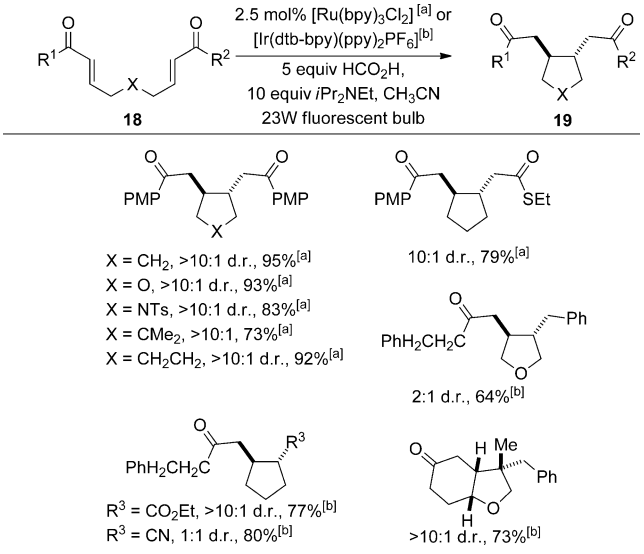


Scheme 5. Proposed mechanism for the visible-light-mediated ring opening/allylation reaction.



Scheme 7. Plausible mechanism for photocatalytic reductive cyclization of enones.

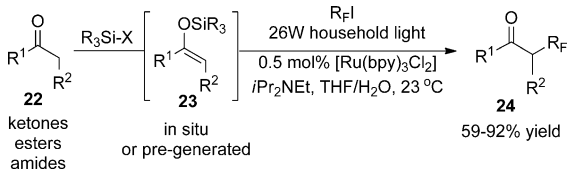
enones demonstrated that lithium salts function not only as Lewis acids to activate the enones, but also to stabilize the key radical anion intermediates.[16a–c,17] Recent work in the same group revealed that the replacement of Lewis acids by Brønstead acids dramatically alters the reactivity of enones. Under these reaction conditions, a net two-electron reductive coupling reaction occurs through a neutral radical intermediate (Scheme 6).[18] Both symmetrical and unsymmetrical enones participate in this process and provide reductive coupling products in satisfactory yields and diastereoselectivities. Moreover, a variety of heteroatoms can be included in the tether linking the enone moieties. Finally, substrates containing less activated olefin moieties, such as styrenes, are also suitable for this process.



Scheme 6. Photocatalytic reductive cyclization of enones. PMP = *para*-methoxyphenyl.

It is believed that the mechanistic pathway for this reaction begins with reductive quenching of the photoexited state Ru^{II}* by iPr_2NEt to give Ru^{I} and an amine radical cation (Scheme 7). SET from Ru^{I} to the protonated enone **18** provides the key neutral radical intermediate **20**, which subsequently undergoes 5-*exo*-trig cyclization to furnish radical **21**. Finally, proton transfer from amine radical cation to **21** yields the reductive cyclization product **19**.

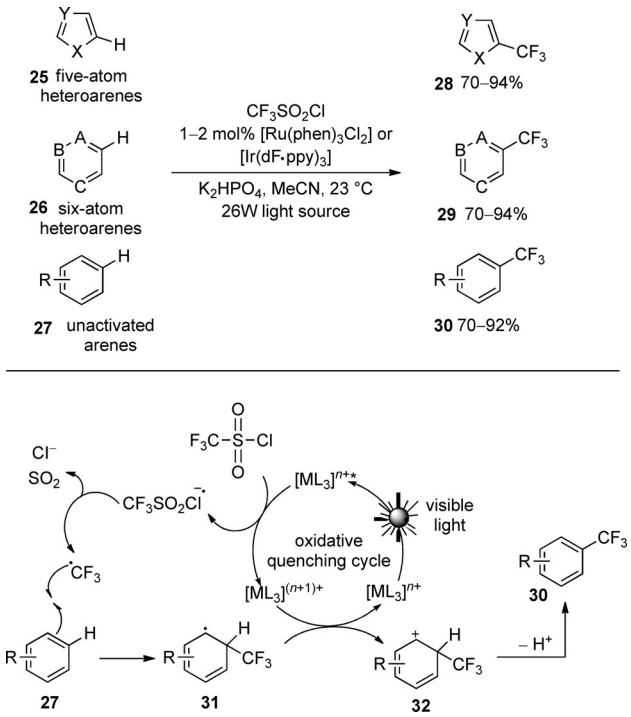
MacMillan and co-workers have conducted an extensive series of studies probing photoredox-catalyzed α-alkylation reactions of aldehydes.[19a,20] Recently, this group has devised a photoredox-based, direct α-trifluoromethylation reaction involving carbonyl compounds, including ketones, esters, and amides (Scheme 8).[21] In a manner that is different from their previously developed methods, enolsilanes, silylketene acetals, and N,O-acetals are used as enolate replacements which act as enolic substrates to combine with electrophilic coupling partners. The iPr_2NEt in the reaction mixture is thought to serve both as a sacrificial reductant and to remove hydroiodic acid which is formed during the reaction.



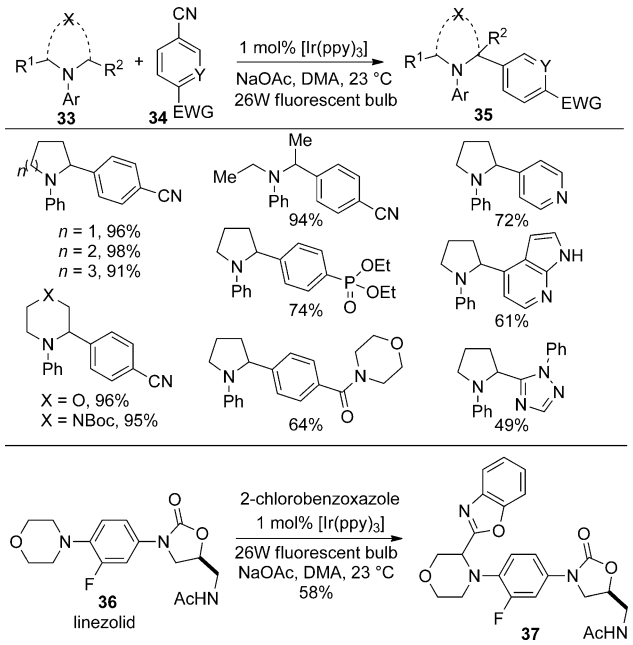
Scheme 8. Photocatalytic α-trifluoromethylation, or α-perfluoroalkylation of carbonyl compounds. THF = tetrahydrofuran.

Following this success, MacMillan and co-workers recently described a photocatalytic trifluoromethylation reaction of arenes and heteroarenes (Scheme 9).[22] It is important to note that TfCl (Tf = trifluoromethanesulfonyl) is employed as a replacement for the commonly used CF_3I as the trifluoromethane radical source to diminish competition from aryl iodination. A wide range of arenes and heteroarenes serve as appropriate substrates for this photocatalytic trifluoromethylation process, which affords coupling products in good to excellent yields.

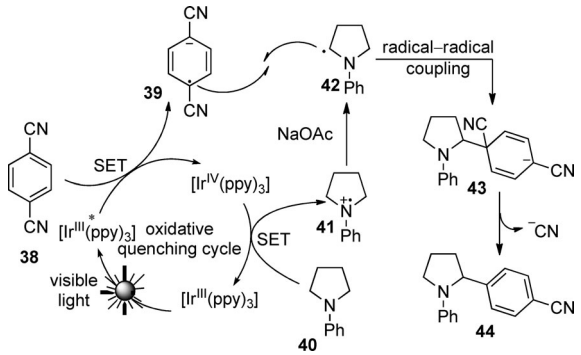
A plausible mechanism for the trifluoromethylation reaction, involving oxidative quenching cycles, has been proposed by MacMillan and co-workers (Scheme 9). Single-electron reduction of TfCl by photogenerated ML_3^{n+} provides $ML_3^{(n+1)+}$ and the CF_3SO_2Cl radical anion, which subsequently collapses to generate the CF_3 radical. This electron-



Scheme 9. Photocatalytic trifluoromethylation reaction of arenes and heteroarenes. phen = 1,10-phenanthroline, dF-ppy = 2-(2,4-difluorophenyl)pyridine.



Scheme 10. Photocatalytic α-amino C–H arylation reaction. DMA = *N*,*N*′-dimethylacetamide.



Scheme 11. Proposed mechanism for photocatalytic α-amino C–H arylation reaction.

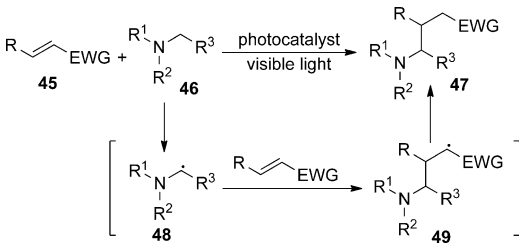
deficient radical then adds to the most electron-rich position of the arene or heteroarene to give the radical **31**. Single-electron oxidation and subsequent deprotonation of the resulting cation generates the trifluoromethyl-substituted arene or heteroarene products.

At around the same time, an interesting α-amine arylation reaction, designed using an accelerated serendipity strategy, was reported by the MacMillan group (Scheme 10).[23] The novel C–H arylation process of amines appears to be quite general with respect to both the amine and aryl components. Apart from its broad applicability, the specific use of this process in the direct derivatization of pharmaceutical agents is well demonstrated by its utilization in a moderate-yielding heteroarylation reaction of the antibiotic linezolid (Scheme 10).

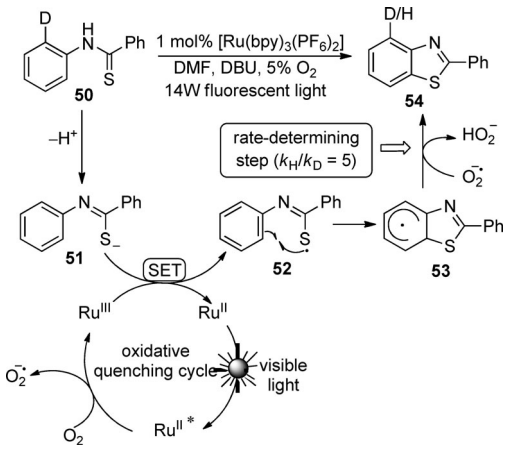
The mechanistic pathway for the arylation reaction proposed by the authors involves initial visible-light excitation of $[Ir(ppy)_3]^{3+}$ to generate the excited state $[Ir(ppy)_3]^{3+*}$, which participates in SET from the arene substrate to form the radical anion **39** (Scheme 11). The generated $[Ir(ppy)_3]^{4+}$ is then reduced by the amine to afford the amine radical cation **41** and regenerated photocatalyst. Deprotonation of the amine radical cation **41** assisted by NaOAc gives the α-amino radical intermediate **42**.[24,25] Then C–C bond formation through radical coupling between **39** and **42** furnishes the anion **43**, which eliminates cyanide to afford the α-arylated product .

Later, the use of a visible-light photocatalytic strategy to generate α-amino radicals and subsequent addition to electron-deficient alkenes was independently reported by Reiser and co-workers[26] and Nishibayashi and co-workers[27] at almost the same time (Scheme 12). Moreover, Stephenson and co-workers also developed another more efficient and versatile approach to trap iminium intermediates, which were formed through an α-amino radical by using $BrCCl_3$ as the stoichiometric oxidant.[28]

In a recent publication, Li and his co-workers described a photocatalytic strategy for the preparation of 2-substituted benzothiazoles starting with thioanilides and takes place through a C–H functionalization/C–S bond-formation sequence (Scheme 13).[29] Compared with the conventional methods, the process is characterized by its high efficiency, unique selectivity, excellent functionality tolerance, and environmental benign nature. Based on observations made in this study and in earlier efforts, the mechanism depicted in Scheme 13 appears to be plausible. The route begins with quenching of the $[Ru(bpy)_3]^{2+*}$ by oxygen to produce the strong oxidant $[Ru(bpy)]^{3+}$. At the same time, thioanilide is deprotonated to give anion **51**. SET from **51** to $[Ru(bpy)]^{3+}$



Scheme 12. Visible-light-mediated addition of α-amino alkyl radicals to electron-deficient alkenes. EWG = electron-withdrawing group.

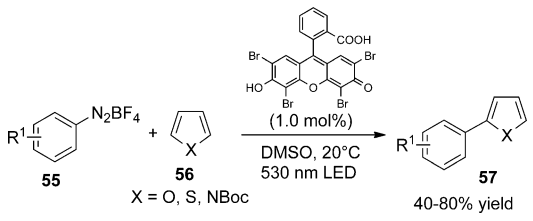


Scheme 13. Visible light photoredox catalytic synthesis of 2-substituted benzothiazoles. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

gives the radical **52**. Cyclization of **52** followed by sequential oxidation of the resulting radical **53** and deprotonation yields the benzothiazole product. Alternative mechanisms for this process are possible and cannot be ruled out at the current time.[29]

The aryl diazonium salts, which were first used in visible-light-mediated organic transformations by Cano-Yelo and Deronzier,[30] are well-known oxidative quenchers in photoredox chemistry. In contrast, they are also an excellent source of aryl radicals owing to their relatively high reduction potentials.[31] Based on these properties, König and co-workers recently reported a metal-free, visible-light-mediated direct intermolecular C–H arylation of heteroarenes by the use of aryl diazonium salts (Scheme 14).[32] In contrast to the well-known metal-catalyzed C–H arylation of heteroarenes, this reaction proceeds smoothly at room temperature without the use of any transition-metal catalysts or bases.

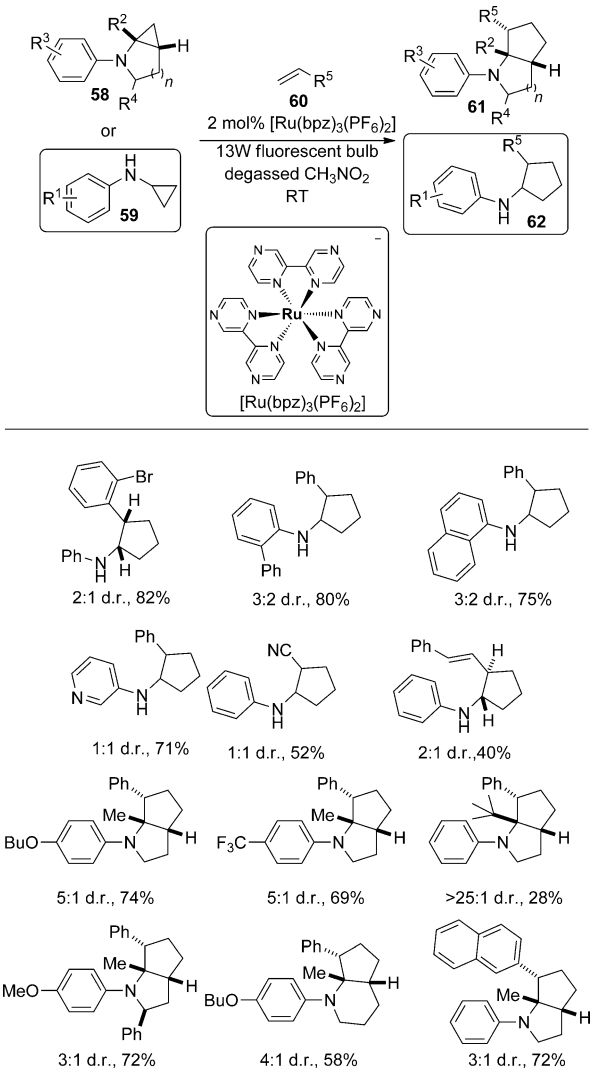
Zheng et al. developed a novel visible-light-promoted photocatalytic intermolecular [3+2] cycloaddition reaction



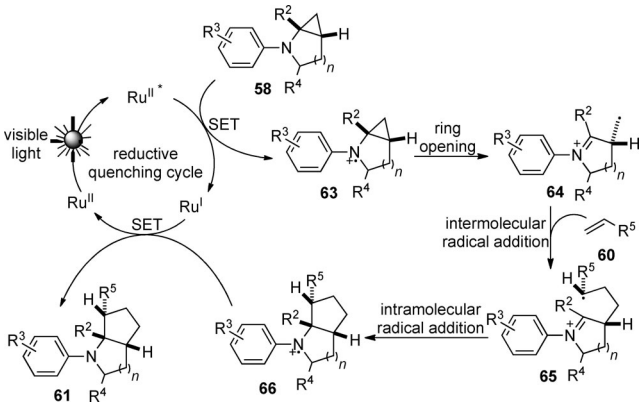
Scheme 14. Photocatalytic direct C-H arylation of heteroarenes.

between cyclopropylamines and olefins which generates aminocyclopentanes (Scheme 15).[33] Interestingly, cyclopropylamines not only act as sacrificial electron donors to initiate the process, but also as substrates. It was observed that degassing the reaction mixture leads to a sharp increase in yield because oxygen-promoted decomposition of the cyclopropylamines is minimized. Both monocyclic and bicyclic cyclopropylamines participate in this cycloaddition reaction and the desired products are formed in moderate to good yields, albeit with only moderate levels of diastereoselectivity. Finally, the studies demonstrated that styrene, acrylonitrile, naphthalene, and the conjugated diene all serve as olefin substrates in this reaction.

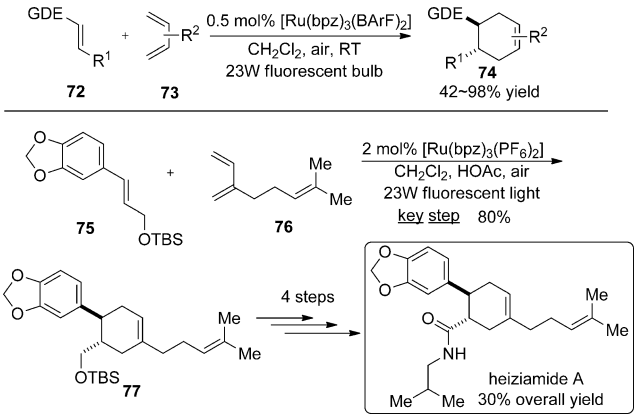
As depicted in Scheme 16, the mechanistic pathway in this process is initiated by reductive quenching of Ru^{II}* by the cyclopropylamine **58** to form Ru^{I}. The generated cyclopropylamine radical cation **63** undergoes ring opening to give the β-carbon radical iminium ion **64**, which subsequently adds to the olefin to provide radical cation **65**. Intramolecular radical addition to the iminium ion moiety in **65** furnishes radical



Scheme 15. Visible-light-mediated intermolecular cycloaddition of cyclopropylamines with olefins. bpz = 2,2′-bipyrazine.



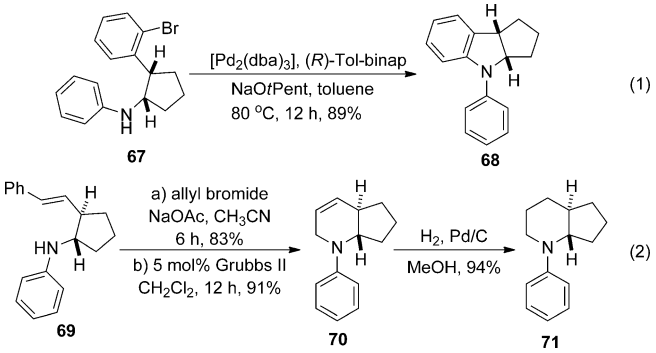
Scheme 16. Proposed mechanism for visible-light-induced intermolecular cycloaddition of cyclopropylamines with olefins.



Scheme 18. Radical cation Diels–Alder cycloadditions by using visible-light photocataysis. BArF = tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate, TBS = *tert*-butyldimethylsilyl.

cation **66**, which is sequentially reduced by Ru^{I} to give the final product and the regenerated photoredox catalyst.

The synthetic usefulness of this photocatalytic cycloaddition reaction was showcased by employing the aminocyclopentane products in sequences leading to N-heterocyclic products. The importance of this application is exemplified by the palladium-catalyzed Buchwald–Hartwig amination reaction of **67** to furnish fused indoline **68** and a three-steps synthesis of fused heterocycle **71** beginning with **69** (Scheme 17).

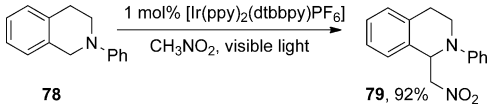


Scheme 17. Synthetic transformation of the cycloaddition products. binap = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl, dba = dibenzylideneacetone.

Based on the previous success on visible-light photoredox catalytic cycloadditions of electron-rich olefins,[16d] Yoon and co-workers developed an electronically mismatched radical-cation-type Diels–Alder cycloaddition reaction occurring between electron-rich coupling partners (Scheme 18).[34a] The reaction takes place efficiently using $[Ru(bpz)_3(BArF)_2]$ as the photocatalyst and is general with respect to both dienes and dienophiles. Furthermore, heiziamide A, an amide natural product, was synthesized by using the photocatalytic radical cation Diels–Alder cycloaddition between the styrene derivative **75** and diene **76** as the key step.

3. Visible-Light-Mediated Functionalization of Iminium Ions

In 2010, Stephenson et al. described a visible-light-mediated aza-Henry reaction that occurs through C–H functionalization of amines (Scheme 19).[35] In this process, an iminium ion is generated under photoredox conditions and is efficiently trapped by appropriate nucleophiles,[28] such as nitromethane.

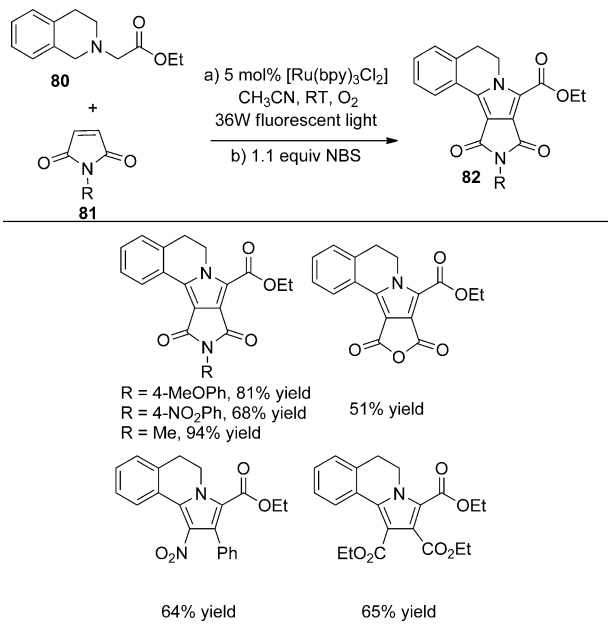


Scheme 19. Visible-light-mediated *aza*-Henry reactions.

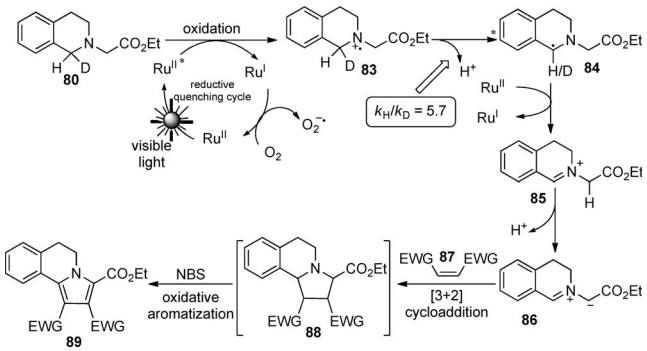
Ensuing work by the groups of Rueping,[36] Xiao,[37] König,[38] Wu,[25] and Tan[39] on α-C–H oxidations of tertiary amines using photoredox catalysis further extended this methodology and demonstrated that it is a powerful synthetic tool.

In a program aimed at utilizing photoredox catalysis in the construction of functionalized heterocycles, Xiao and co-workers developed a photocatalytic cascade strategy to prepare pyrrolo[2,1-*a*]isoquinolines (Scheme 20).[37a] This process, carried out with equal efficiency in the presence of either pure oxygen or air, involves addition of maleimides **81** to the azomethine ylide intermediate generated from tetrahydroisoquinoline **80**. The reaction was observed to be quite general with respect to both dipolarophile and dipole components and the pyrrolo[2,1-*a*]isoquinolines products are produced in moderate to excellent yields.

According to the recent mechanistic investigations,[23,25–28] an updated reaction mechanism for this reaction is depicted in Scheme 21. The photoinduced electron transfer from **80** to the photoexcited species Ru^{II}* results in the formation of the cation radical **83**, which subsequently undergoes a deprotonation/oxidation sequence to give the iminium ion **85**, which is then transformed into the azomethine **86** through a deproto-



Scheme 20. Photocatalytic cascade strategy to construct pyrrolo[2,1-*a*]isoquinolines. NBS = *N*-bromosuccinimide.

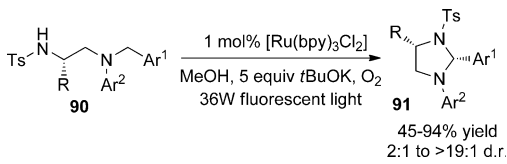


Scheme 21. Plausible mechanism for photocatalytic cascade strategy to construct pyrrolo[2,1-*a*]isoquinolines.

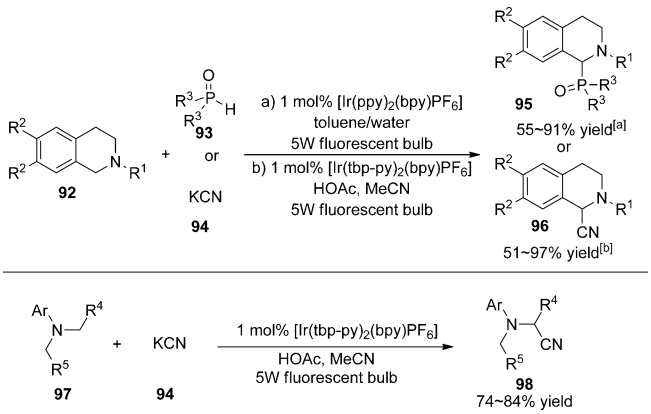
nation process. Dipolar cycloaddition reaction of **86** with a dipolarophile component provides **88**, which is sequentially oxidized to form the pyrrolo[2,1-*a*]isoquinoline product. The kinetic isotopic effect studies show that the deprotonation of the radical cation **83** is 5.7 times faster than the release of deuterium.

In an effort focused on extending this methodology, Xiao et al. applied the photocatalytic oxidation/functionlization strategy to asymmetric construction of tetrahydroimidazoles by a route involving intramolecular cyclization of chiral diamines (Scheme 22).[37b] Interestingly, excellent diastereoselectivities were observed when these reactions were carried out over prolonged time periods, which results in the isomerization of the *trans* product into the thermodynamically more stable *cis* form.

In addition, Rueping and co-workers recently observed novel oxidative phosphonylation and cyanation processes (Scheme 23).[36b,d] In these reactions, various N-aryl-tetrahydroisoquinolines are transformed into their α-phosphono and



Scheme 22. Visible-light-induced asymmetric synthesis of tetrahydroimidazoles.



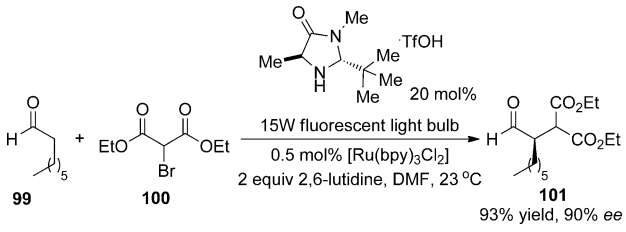
Scheme 23. Photoredox catalyzed oxidative phosphonylation and cyanation reactions. tbp-py = 2-(4-(*tert*-butyl)phenyl)pyridine.

α-cyano derivatives. The oxidative cyanation reaction was observed to be applicable to both cyclic benzylic amines as well as simple, acyclic tertiary amines.

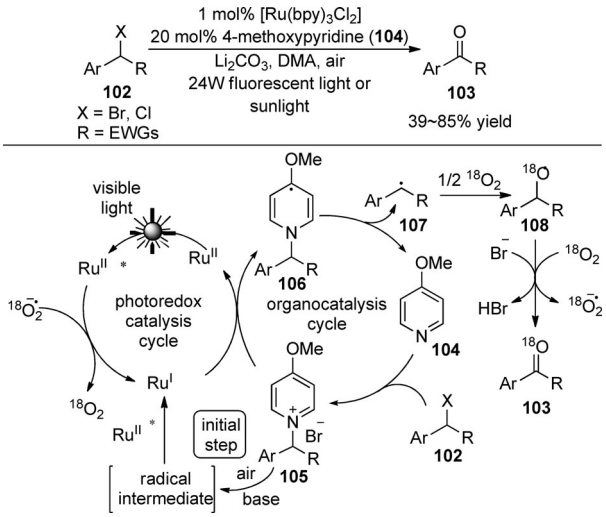
4. Merger of Photoredox Catalysis with Other Catalytic Systems

In 2008, MacMillan and co-workers were the first to combine SOMO-type aminocatalysis with $[Ru(bpy)_3]^{2+}$-mediated visible-light photoredox catalysis in a process leading to the direct asymmetric alkylation of aldehydes (Scheme 24).[19a] Inspired by the earlier observations, this group applied the dual-catalysis strategy to α-trifluoromethylation, α-perfluoroalkylation, and α-benzylation reactions of aldehydes.[20]

Another impressive example showing the utilization of a combination of photocatalysis and organocatalysis was uncovered by Jiao and co-workers. The process, which promotes aerobic oxidation of benzyl halides (Scheme 25),[40] not only employs a combination of photocatalysis and



Scheme 24. Asymmetric α-alkylation of aldehydes through photoredox catalysis and organocatalysis.



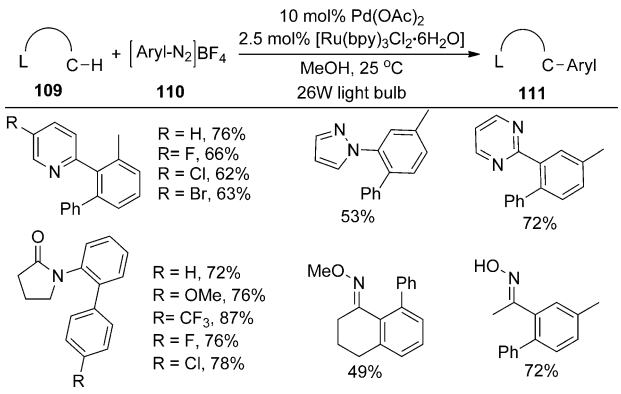
Scheme 25. The aerobic oxidation of benzyl halides through photocatalysis and organocatalysis.

organocatalysis, but also relies on a novel pyridine radical intermediate. This effort has shown that a variety of α-aryl chlorides and α-aryl bromides can be oxidized to form the corresponding α-aryl carbonyl compounds in moderate to excellent yields. Moreover, sunlight can be used as the light source. The results of ^{18}O-labeling experiments reveal that the oxygen in the newly formed carbonyl group derives from molecular oxygen.

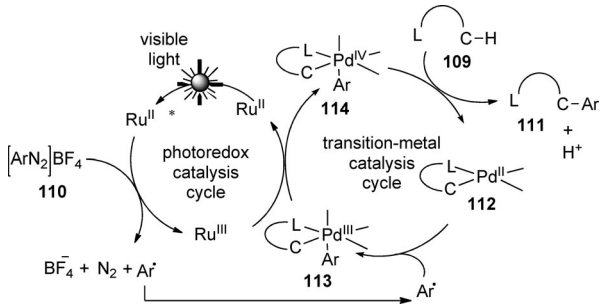
Jiao and his co-workers proposed that the mechanistic pathway for this process involves the sacrificial pyridinium salt **105**, which is generated by reaction of 4-methoxypyridine (**104**) with halide **102** in the organocatalysis cycle (Scheme 25). It is believed that reaction of **105**, O_2, and base with the photoexited Ru^{II}* forms Ru^{I} in the initial step of this dual-catalysis reaction. Then, SET from Ru^{I} to the pyridinium salt **105** generates the dihydropyridyl radical **106**, which undergoes homolysis of the C–N bond to give the benzyl radical **107** and regenerates **104** to complete the organocatalysis cycle. Aerobic oxidation of the benzyl radical with O_2 then produces the carbonyl product. It should be noted that the generated $O_2^{-\bullet}$ acts as the final reductant to reduce the Ru^{II}* to form Ru^{I} in the photoredox catalysis cycle.

Recently, Sanford and co-workers uncovered the first example in which heterocycle-directed photoredox catalysis is merged with transition-metal catalysis to achieve a room-temperature C–H arylation reaction (Scheme 26).[41] This dual-catalysis reaction displays substantial generality with respect to both arene and aryldiazonium salt components. Moreover, along with pyridine other directing groups, such as amides, pyrazoles, pyrimidines, and oximes effectively promote the process. Compared with most current C–H arylation reactions, this transformation features mild reaction conditions, common solvents, and the generation of simple by-products (N_2 and HBF_4).

A plausible mechanism for this process starts with SET from Ru^{II}* to the aryldiazonium salt, thus forming Ru^{III} and the aryl radical, which sequentially reacts with the palladacycle **112** to give the Pd^{III} intermediate **113** (Scheme 27). One-



Scheme 26. Room temperature C-H arylation via photocatalysis and transition-metal catalysis.



Scheme 27. Possible mechanism for room temperature C–H arylation through photocatalysis and transition-metal catalysis.

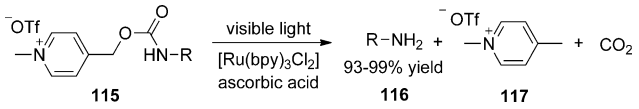
electron oxidation of **113** by Ru^{III} affords the Pd^{IV} intermediate **114** and the regenerated photoredox catalyst. Reductive elimination of **114** provides the arylation product and regenerates the Pd^{II} to accomplish the palladium catalysis cycle.

5. Other Reactions

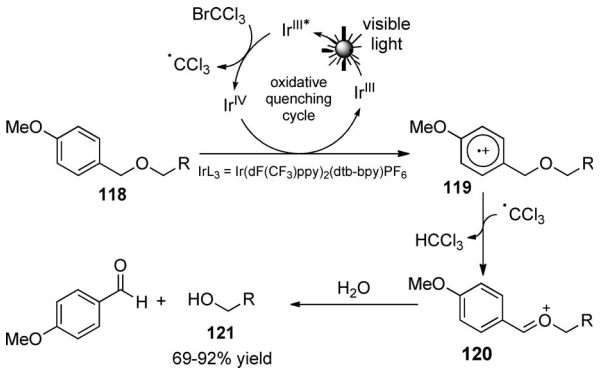
Photoremoval of protecting groups (PRPGs) constitutes another aspect of visible-light-induced organic transformations.[42] Expanding earlier work on the photocatalytic reductive cleavage reaction of decanoic acid picolinium esters,[31c] Boncella et al. recently demonstrated that photoinduced electron transfer to *N*-methylpicolinium (NMP) carbamates results in reductive cleavage of the C–O bond followed by spontaneous CO_2 release to generate free amines (Scheme 28).[43] In this process, ascorbic acid serves as both an electron donor to reduce the Ru^{II}* to Ru^{I} and a hydrogen donor to trap NMP methylene radicals.

In 2011, Stephenson and co-workers developed the selective removal of *para*-methoxybenzyl (PMB) ethers by visible-light-mediated oxidation of electron-rich arenes (Scheme 29).[44] This methodology shows great functional-group tolerance under very mild reaction conditions and gives the $CHCl_3$ as the only stoichiometric oxidation by-product.

Phthalimide derivatives are well-known substrates to undergo various UV-light irradiated photoreactions.[45] How-

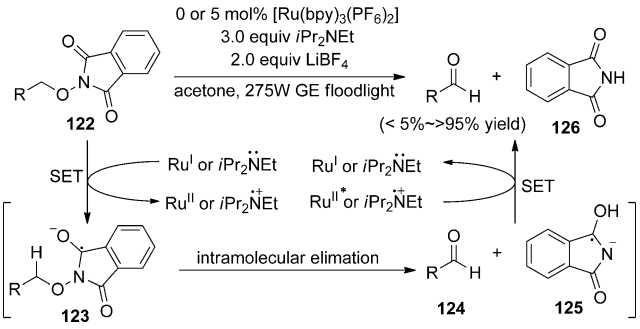


Scheme 28. Photorelease of NMP carbamates.



Scheme 29. Visible-light-mediated oxidative cleavage of PMB ethers.

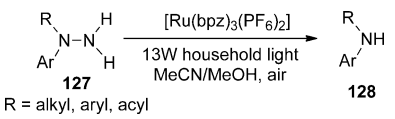
ever, only *N*-acyloxyphthalimide has been employed in visible-light-mediated photoinduced electron transfer (PET).[46] Recently, Sammis et al. developed a mild method for the redox fragmentation of *N*-alkoxyphthalimides, thus leading to a variety of carbonyl compounds in good yields (Scheme 30).[47] Mechanistic studies revealed that this unique transformation proceeded through a visible-light-induced single-electron transfer either from a ruthenium catalyst or directly from the iPr$_2$NEt to the carbonyl of the phthalimide, and an intramolecular elimination process.



Scheme 30. PET-promoted redox fragmentation of *N*-alkoxyphthalimides.

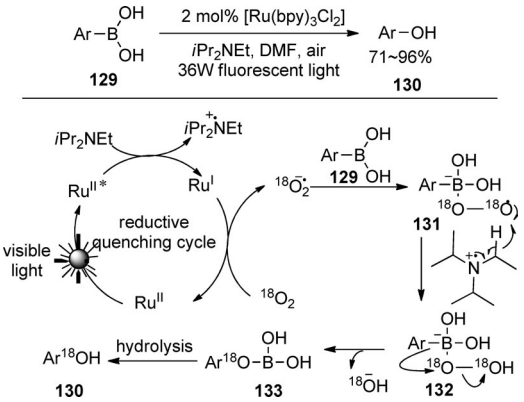
Another impressive example of visible-light-mediated cleavage of the heteroatom–heteroatom bonds was reported by Zheng and co-workers (Scheme 31).[48] In this report, photoinduced cleavage of the N–N bonds of aromatic hydrazines and hydrazides was successfully realized.

On the basis of the proposed mechanism in their previous reports Xiao and co-workers[37] and Jørgensen and co-workers[49] anticipated that the superoxide radical anion generated from molecular oxygen under photoredox conditions might have some Lewis basicity and could react with the appropriate



Scheme 31. Photoinduced clevaged of N–N bonds of aromatic hydrazines and hydrazides.

acidic components, such as arylboronic acids to provide aryl alcohols (Scheme 32). Indeed, visible-light-initiated aerobic oxidative hydroxylations of arylboronic acids works very well in DMF using [Ru(bpy)$_3$Cl$_2$] in combination with iPr$_2$NEt as



Scheme 32. Visible-light-induced aerobic oxidative hydroxylation of arylboronic acids.

the electron donor. Both of the electron-deficient and electron-rich arylboronic acids can be effectively converted into the corresponding phenols in good to excellent yields. It was found that phenboronic esters are also suitable substrates.

Based on the results of ^{18}O-labelling experiments and computational studies, a possible mechanism was proposed. As shown in Scheme 32, a superoxide radical anion, generated by a reductive quenching cycle, reacts with boronic acid to give the intermediate **131**. Proton abstraction from amine radical cation by the radical anion **131** affords the boron peroxo complex **132**, which rearranges to form the borate monoester **133**. Subsequent hydrolysis of **133** gives the phenol product. Computational studies show that the aryl group in **132** is transferred to a peroxygen atom in a concerted manner.

6. Conclusions

As discussed above, visible-light photoredox catalysis has quickly become a powerful and efficient tool in synthetic organic chemistry. Some recent observations made in this area strongly demonstrate that these processes not only serve as viable methods to carry out simple organic transformations, but they can also be employed in sequences to prepare various bioactive natural products. There is no doubt that future explorations of visible-light photoredox catalysis will lead to the discovery of fascinating and useful chemistry. Although progress has been made in this area, many

questions and challenges remain. A deeper understanding of the mechanisms of the processes uncovered together with the development of more robust and efficient photoredox catalysts constitute two important directions for future investigations of visible-light photoredox catalysis.

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