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Review

Visible light-mediated C—P bond formation reactions

Bao-Gui Cai [a], Jun Xuan [a,*], Wen-Jing Xiao [b,*]

[a] Anhui Province Key Laboratory of Chemistry for Inorganic/Organic Hybrid Functionalized Materials, College of Chemistry & Chemical Engineering, Anhui University, Hefei 230601, China
[b] Key Laboratory of Pesticide & Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, China

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ABSTRACT

Organophosphorus compounds have attracted continuous attention in materials science, agrochemical and pharmaceutical fields due to their unique bioactivities. Thus, the development of novel and robust manners for the construction new C—P bond has therefore gained great interests in synthetic organic chemistry. Because of their intrinsic sustainability and green chemistry character, visible light-induced photoredox catalysis has been widely applied in the construction of new chemical bonds, including the formation of C—P bond. In this review, we summarized recent achievements in C—P bond formation reactions initiated by visible light-induced photoredox catalysis, which mainly focusing on the discussion of reaction design and the mechanism.

1. Introduction

Organophosphorus compounds are one of the most important class of organic products, because of their broad applications in the field of materials science [1–3], medicinal chemistry [4], and organic synthesis [5,6]. Consequently, there is no doubt that the development of efficient method towards the construction of new C—P bond has received continuing research interests from the synthetic community. Generally, classical synthetic strategies for the formation of C—P bond are largely rely on the use of transition-metal-catalyzed cross-coupling processes [7–9]. In the past few years, the addition of P-centered radicals to arenes or other unsaturated functionalities opened a new avenue for the construction of C—P bond [10,11]. However, the formation of P-centered radicals in those processes generally needs to use transition-metal salts or oxidants at high reaction temperature. Consequently, it is still highly desirable to develop alternative and complementary synthetic strategy for C—P bond construction, especially under eco-benign and sustainable reaction conditions.

Since 2008, visible light-mediated photoredox catalysis has emerged as a powerful method for creating new chemical bonds under low-energy irradiation and very mild reaction conditions [12–20]. Generally, those photo-induced reactions were performed at room temperature with simple house light-bulb or direct sunlight irradiation by using metal-based complexes or organic dyes as the photoredox catalyst. In 2011, Rueping et al. [21] realized the first example of C—P bond formation reaction promoted by visible light-induced photoredox catalysis. Since this elegant discovery, significant achievements were made in this fast-developing research filed. To the best of our knowledge, there is only one review paper documented on this topic which was published at the end of 2016 [22]. In last two years, a variety of new C—P bond formation reactions mediated by visible-light induced photoredox catalysis were elegantly reported. Recent advances in this area convincingly document that visible light-induced photoredox catalyzed C—P bond formation strategy can be applied not only to the simple functionalization reactions, but also to the synthesis of valuable phosphorus-containing heterocyclic ring systems. In this review, we summarized recent achievements in C—P bond formation reactions initiated by visible light-induced photoredox catalysis, which mainly focusing on the discussion of reactions which appeared in the past two years.

2. Visible light-mediated C(sp^3)P bond formation reactions

Photoredox functionalization of C—H bonds adjacent to a tertiary amine N-atom is one of the most attractive research fields at the early stage of visible light-mediated photoredox catalysis, especially utilization of *N*-aryl tetrahydroisoquinoline as starting material [23,24]. The strategy has been successfully applied to create new C—C, C—N, C—O, and C—P bonds. As shown in Scheme 1, photo-generated iminium ion was considered as the key intermediate for those C—H functionalization process, which was subject to further nucleophilic addition with different nucleophiles to

* Corresponding authors.
E-mail addresses: xuanjun@ahu.edu.cn (J. Xuan), wxiao@mail.ccnu.edu.cn (W.-J. Xiao).

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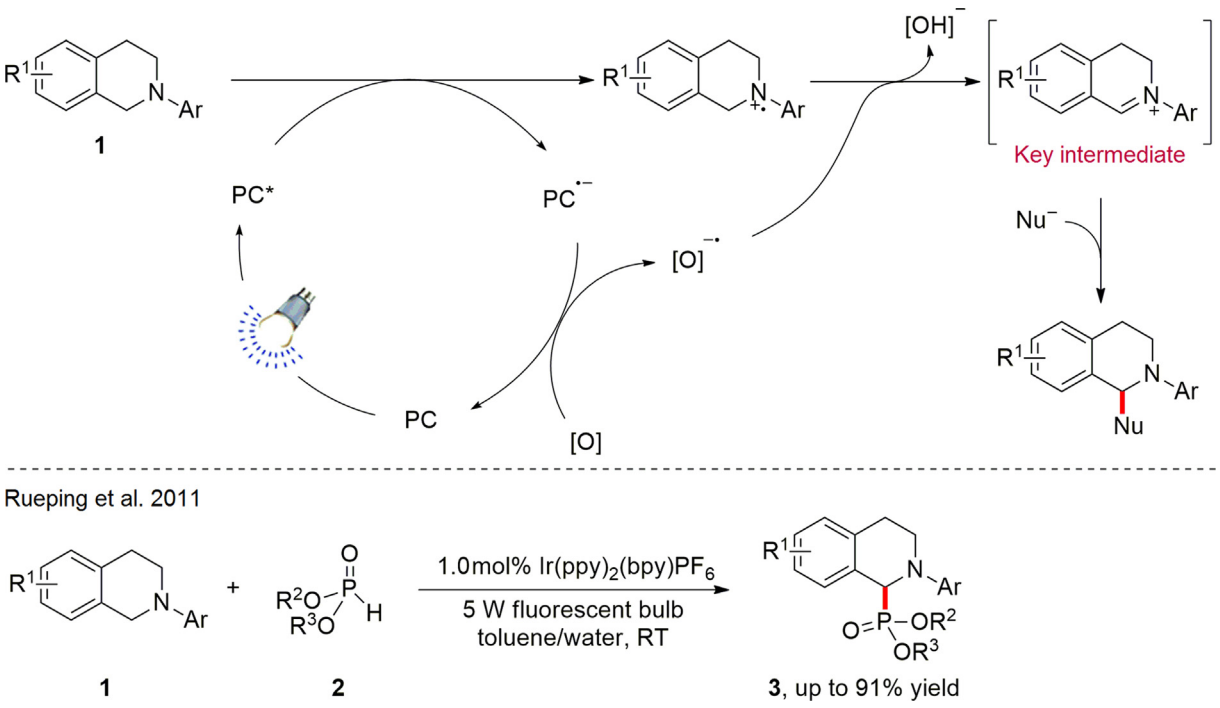


Scheme 1. (Color online) Visible-light-mediated oxidative phosphonylation of *N*-aryl-tetrahydroisoquinolines. ppy = 2-phenylpyridine; bpy = 2,2′-bipyridine.

create new chemical bonds. In 2011, Rueping et al. [21] firstly realized the photo-catalytic oxidative phosphonylation of *N*-aryl-tetrahydroisoquinolines by using phosphite ester as the iminium ion trapping reagent, which providing an efficient route to various α-amino phosphonates in moderate to excellent yields. Following this elegant pioneering work, oxidative phosphonylation of *N*-aryl-tetrahydroisoquinoline derivatives under other photocatalytic conditions were sequentially investigated by other research groups [25–31]. All of those reactions have been well documented in the previous review paper [22].

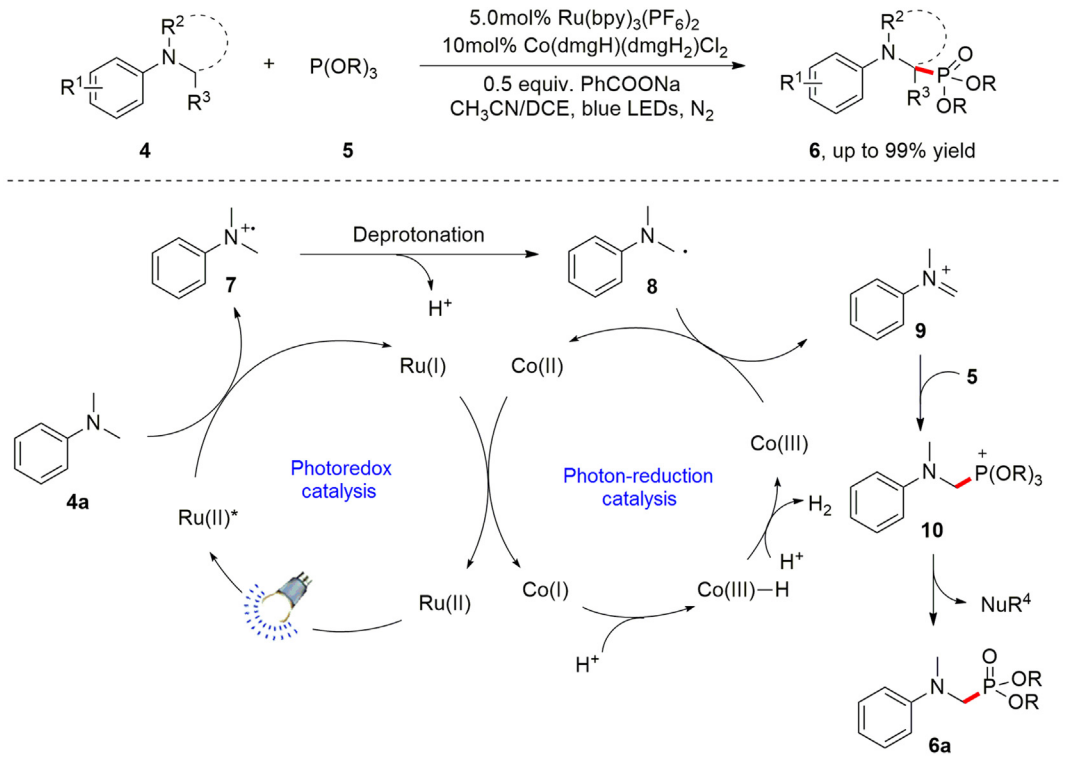
Comparing with well investigated *N*-aryl tetrahydroisoquinoline derivatives, a photocatalytic strategy for the phosphonylation of C(sp^3)—H bond adjacent to nitrogen atom of *N,N*-dialkylanilines is quite limited. In 2018, Lei and co-workers [32] realized the breakthrough of oxidative C(sp^3)—H phosphonylation of *N,N*-dialkylaniline derivatives by synergistically combining visible light-induced photoredox catalysis with proton-reduction catalysis (Scheme 2). Note that, this process is performed under external oxidant free conditions and the oxidative breakage of C—N bond side reactions can be successfully avoided [33,34]. Under optimal reaction condition, a variety of *N*-alkyl substituted anilines, such as *N,N*-dialkylanilines, cyclic amines can be phosphonylated in good to high yields.

Based on the results of a series of mechanistic experiments, a plausible reaction mechanism is proposed in Scheme 2. The formation of α-amino carbon radical intermediate **8** is same as the previously reported process [23,24]. Then single-electron oxidation of **8** with Co(III) oxime complex provides the key iminium ion intermediate **9**. The formed Co(II) species can oxidize the low-valent Ru(I) to regenerate the Ru(II) species to complete the photocatalytic cycle and form Co(I). Nucleophilic trapping of **9** by trialkyl phosphite **5** provides P-cation adduct **10**, which subsequently rearranges to the final phosphonylation product **6** with the assistance of PhCOONa [35]. Meanwhile, protonation of Co(I) provides Co(III)-H species, which further capture another proton to achieve the release of hydrogen gas and the regeneration of Co(III).

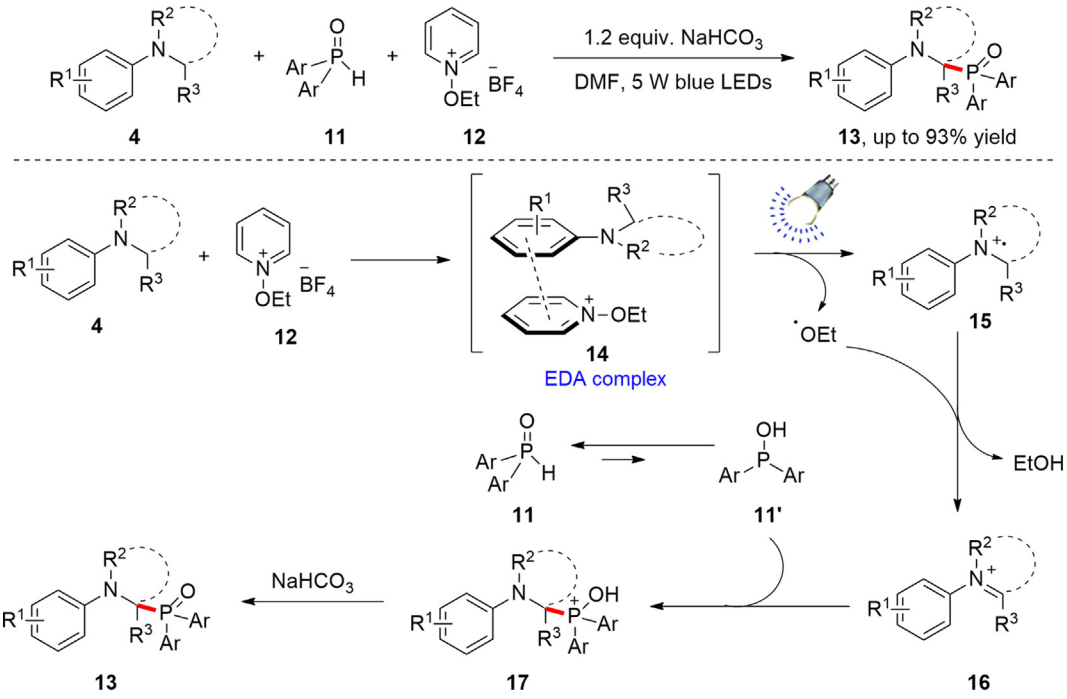
Very recently, Lakhdar and co-workers [36] reported a visible-light promoted α-phosphorylation reaction of *N*-aryl tertiary amines via the formation of electron-donor-acceptor (EDA) complexes (Scheme 3). Comparing with Lei group [32] dual catalytic strategy, transition-metal photoredox catalyst is not required to run the reaction. Secondary phosphine oxide, a bench-stable phosphorus nucleophile under oxidative conditions, can be well tolerated in this metal-free C(sp^3)—P bond formation process. As the reaction mechanism revealed in Scheme 3, key to this success is the formation of EDA complex **14** between the *N,N*-dialkylanilines **4** and the electron-deficient pyridinium **12** [37,38]. Note that, the existence of **14** is also proved by a series of physical organic investigations.

P-centered radical triggered functionalization of C=C bond is another represented strategy for C(sp^3)—P bond formation [39]. In 2013, Kobayashi group [40] reported a hydrophosphinylation reaction of unactivated alkenes with secondary phosphine oxides (SPOs) by visible light-mediated photoredox catalysis (Scheme 4a). The reaction is performed under very mild conditions by using cheap organic dye (Rhodamine B) as the photoredox catalyst. One of the major limitations of the process is the electron-rich SPOs, which exists nearly exclusively in their pentavalent tautomeric form, can not participate in this hydrophosphinylation process. Four years later, Lakhdar and co-workers realized the first example of hydrophosphinylation of unactivated alkenes by using ethyl and butyl phosphinates as the phosphinoyl radical precursors (Scheme 4b) [41]. The strategically combination of Fukuzumi organic dye photoredox catalyst (9-mesityl-10-methylacridinium perchlorate) with diphenyliodonium triflate as oxidant is the key point for this success.

β-Ketophosphine oxides are one of the most significant phosphorus-containing organic compounds which have been widely applied as potential ligands or metal extractants because of their coordination ability [42–44]. In 2016, Cai and co-workers [45] reported the first example of *β*-ketophosphine oxides synthesis via visible light-promoted oxidative phosphinylation of aryl alkynes. Two years later, Zou and co-workers [46] demonstrated an alternative photocatalytic method for *β*-ketophosphine oxides



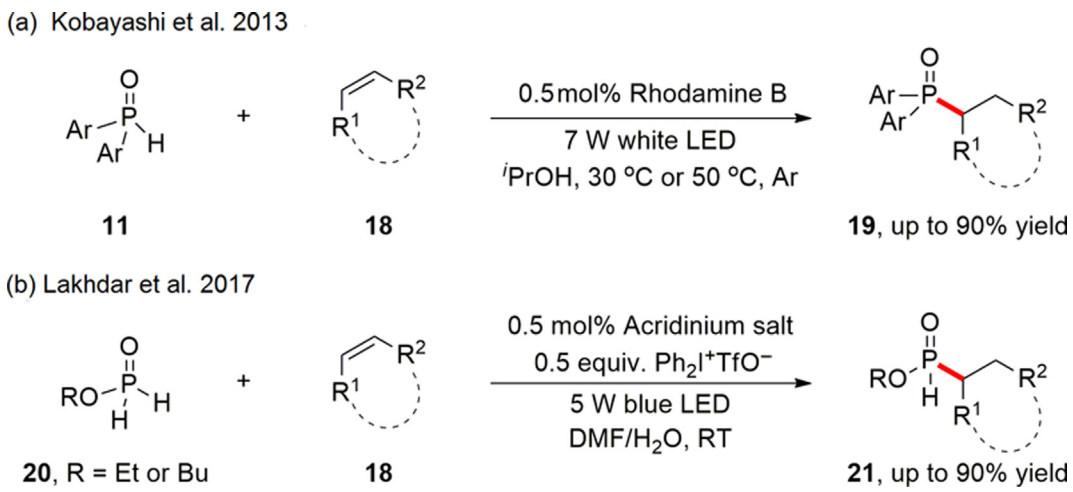
Scheme 2. (Color online) Visible-light-mediated α- phosphonylation of *N,N*-dialkylanilines via dual catalysis. dmgH = dimethylglyoximate monoanion; $dmgH_2$ = dimethylglyoxime.



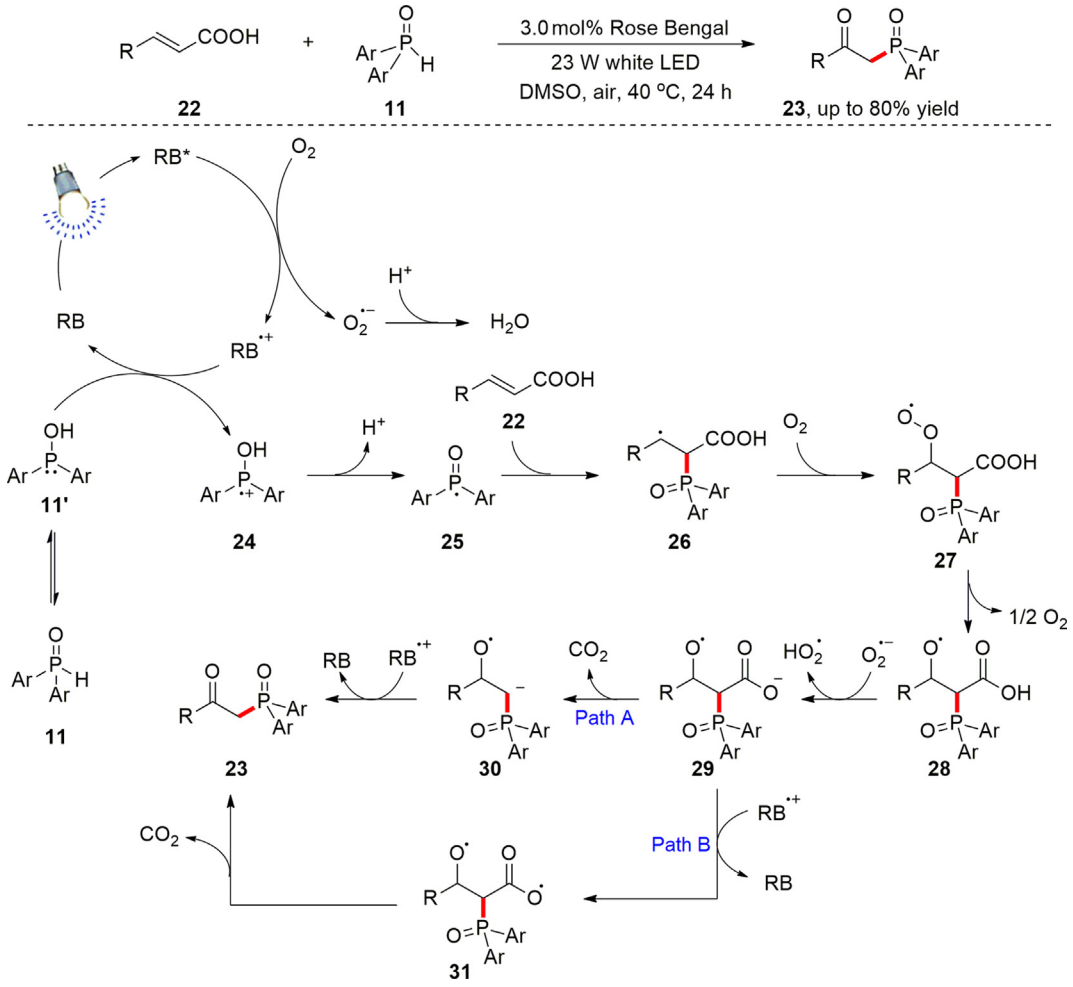
Scheme 3. (Color online) Visible-light-mediated α-phosphorylation of *N,N*-dialkylanilines via the formation of EDA complexes.

synthesis (Scheme 5). In this contribution, the cheap Rose Bengal (RB) is used as photoredox catalyst and a variety of cinnamic acids were applied as the phosphorus-centered radical acceptors. Under the optimal reaction conditions, the corresponding β-ketophosphine oxide products can be isolated in moderated to good yields. Note that, aliphatic acrylic acids and electron rich secondary phosphine oxides are inert to this transformation.

A plausible reaction mechanism is proposed based on the results of control experiments and EPR study (Scheme 5). Initially, photoredox catalyst RB transferred to its excited state (RB*) upon visible light irradiation. Then, a single electron transfers from RB* to molecular oxygen delivered superoxide radical anion ($O_2^{\cdot-}$) and RB radical cation ($RB^{\cdot+}$). In the reaction system, diarylphosphine oxide **11** could exist in equilibrium with its trivalent tautomer



Scheme 4. (Color online) Visible-light-mediated hydrophosphinylation of unactivated alkenes.



Scheme 5. (Color online) Visible-light-mediated decarboxylative oxyphosphorylation of cinnamic acids with diarylphosphine oxides.

phosphinous acid **11′**. Single electron oxidation of **11′** with RB radical cation gives the p-centered radical cation **24** and regenerated RB to complete the photocatalytic cycle. Deprotonation of **24** provides the key phosphorus-centered radical **25**, which subsequently adds to the α-position of cinnamic acid **22** to give the carbon-centered radical intermediate **26**. Radical **26** reacts with O_2, followed by peroxo bond cleavage affording oxygen-centered radical species **28**. A superoxide anion radical promoted deprotonation of **28** gives the intermediate **30**, which further underwent decarboxylation and single electron oxidation to provide the final

β-ketophosphine oxide **23**. Another reaction pathway involving the SET oxidation/decarboxylation sequence via a biradical intermediate **31** is also plausible (Scheme 5, path B).

Recently, visible light-mediated radical migration reactions have been recognized as a powerful method to trigger C—C and C—H bond functionalization [47–49]. Along these lines, Zhang group [50] developed an elegant method for the synthesis of β-aryl-γ-ketophosphine oxides by using visible light-promoted 1,2-aryl migration as the key step (Scheme 6). The reaction proceeds under very mild conditions with excellent functional group tolerance. Apart from commonly used diarylphosphine oxides, the unsymmetric phosphine oxides including butyl(phenyl)phosphine oxide and ethyl phenylphosphinate, even the electron rich dialkylphosphine oxides can also be well tolerated under the optimal reaction conditions, albeit with relative low yield in some cases.

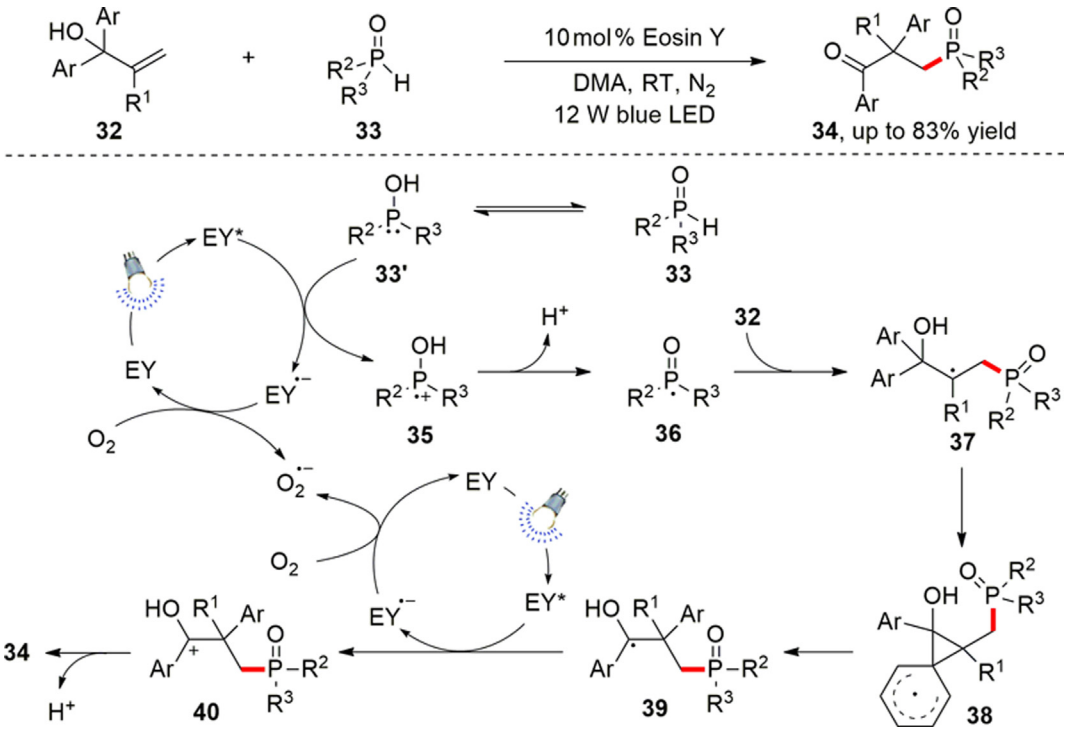
The possible reaction mechanism is depicted in Scheme 6 starting with the addition of the P-centered radical, which is generated from photocatalytic cycle, to the C=C bond of allylic alcohol **32** to give the carbon-centered radical species **37**. Then a 1,2-aryl migration via a spiro [2,5] octadienyl radical intermediate **38** generates radical **39**, which subsequently be oxidized by excited photoredox catalyst (EY*) to give the carbon cation **40**. Deprotonation of **40** affords the final β-aryl-γ-ketophosphine oxide **34**. The trace amounts of molecular oxygen in the reaction system may act as the oxidant to regenerate the EY photoredox catalyst.

Radical cascade cyclization is one of the most efficient strategies for the synthesis of biologically important carbon- and heterocycles, since the core structures can be built up in a single operation comprising multiple bond forming steps [51–53]. Attracted by the rich bioactivities of phosphorus-containing cyclic compounds, there is no doubt that significant improvements have been achieved in the utilization of P-centered radical species to trigger radical cascade cyclization reactions. In 2016, Yan, Lu and co-workers [54] reported a visible light-promoted radical cascade cyclization of *N*-arylacrylamides with diphenylphosphine, leading to a variety of phosphorus-containing indolin-2-ones in average good yields. By choosing different radical acceptors, the method can be further extended to the construction of phosphorylated phenanthridines and isoquinoline derivatives.

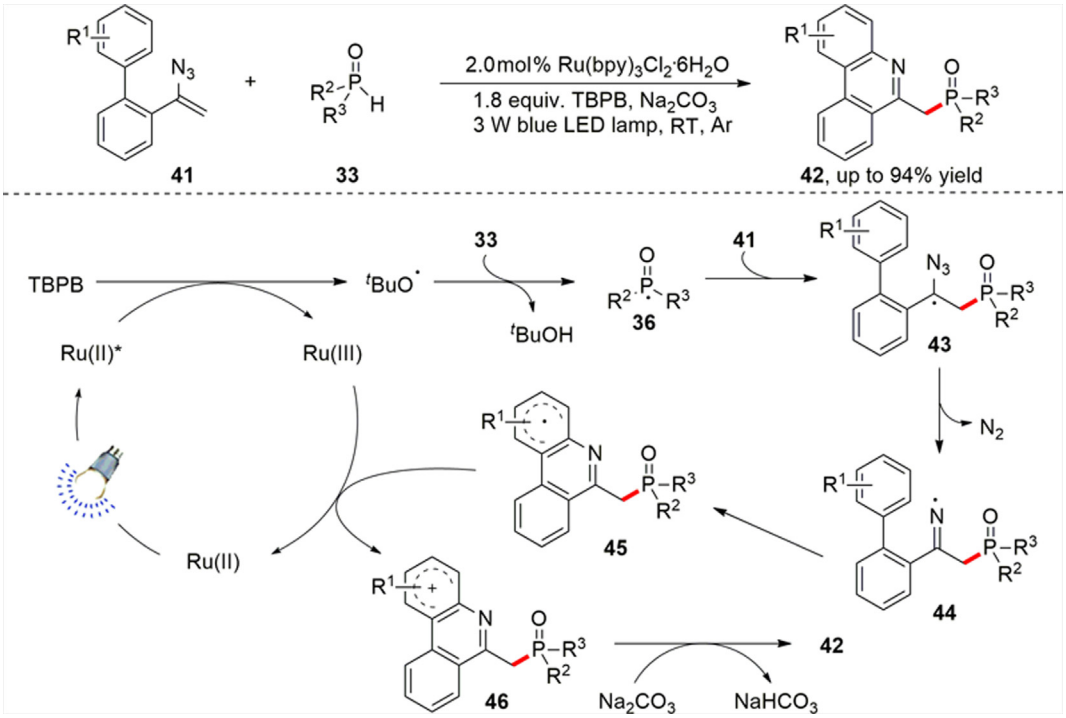
Shortly after this disclosure, Yang group [55] demonstrated an alternative photocatalytic radical cascade strategy for phosphorus-containing phenanthridines synthesis involving the use of biphenylvinyl azides as the P-centered radical acceptors (Scheme 7). For this cascade, 2.0 mol% $Ru(bpy)_3Cl_2·6H_2O$ photoredox catalyst in combination with 1.8 equiv. *tert*-butylperoxybenzoate (TBPB) as the oxidant is found to be the most effective catalyst system. Moreover, another important heterocycle 6-phosphorylated phenanthridine derivatives can also be easily accessed through replacing the radical acceptors from biphenylvinyl azides to biaryl cyanides or isocyanides.

The proposed reaction mechanism of this radical cascade cyclization is based on the oxidative quenching cycle (Scheme 7). Under 3 W blue LED irradiation, the Ru(II) photoredox catalyst is converted to its photo-excited state Ru(II)*. Single electron reduction of TBPB with Ru(II)* generates high valent Ru(III) species and *tert*-butoxyl radical, which subsequently undergoes a hydrogen atom abstraction from **33** to give the key P-centered radical **36**. Radical addition of **36** to the C=C bond of biphenylvinyl azide **41** provides carbon-centered radical **43**. The radical **43** can transfer to the iminyl radical **44** through release of molecular nitrogen. Intramolecular addition of iminyl radical to aryl ring leads to **45** which upon oxidation by the Ru(III) species provides the cation **46** thereby regenerating the initial Ru(II) complex to complete the photocatalytic cycle. Finally, base promoted deprotonation of **46** affords phenanthridine product **42**.

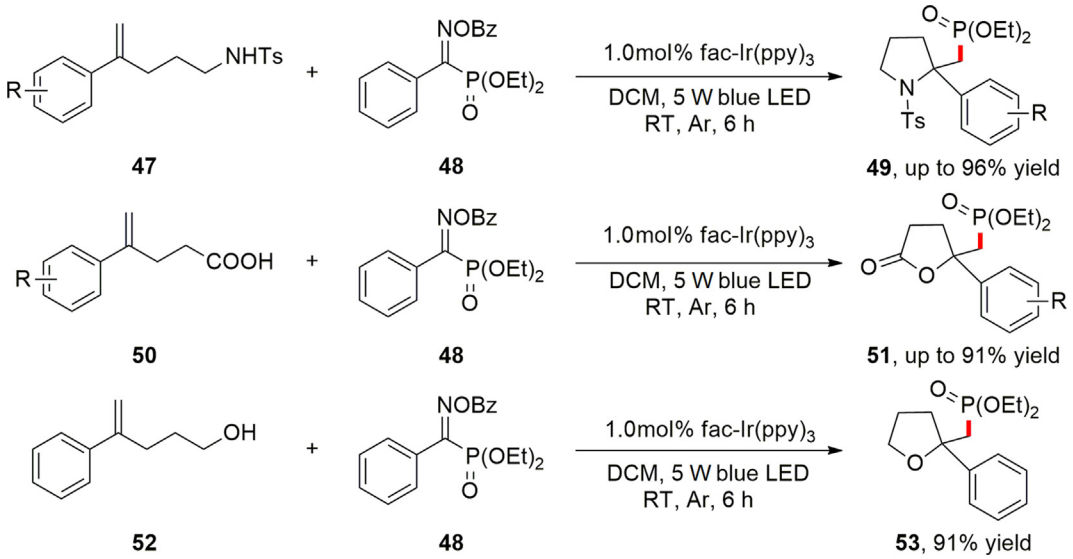
Shortly after this discovery, photocatalytic synthesis of β-phosphonopyrrolidines **49**, β-phosphonolactones **51** and β-phosphonotetrahydrofuran **53** was sequentially realized by the same group (Scheme 8) [56]. In comparison to previous works, reagent **48** was employed as a new type of phosphine radical precursor with high efficiency.



Scheme 6. (Color online) Visible-light-promoted carbophosphinylation of allylic alcohols via 1,2-aryl migration. DMA = *N*,*N*'-dimethylacetamide.



Scheme 7. (Color online) Visible-light-promoted cascade radical cyclization of biphenylvinyl azides with P-centered radicals.

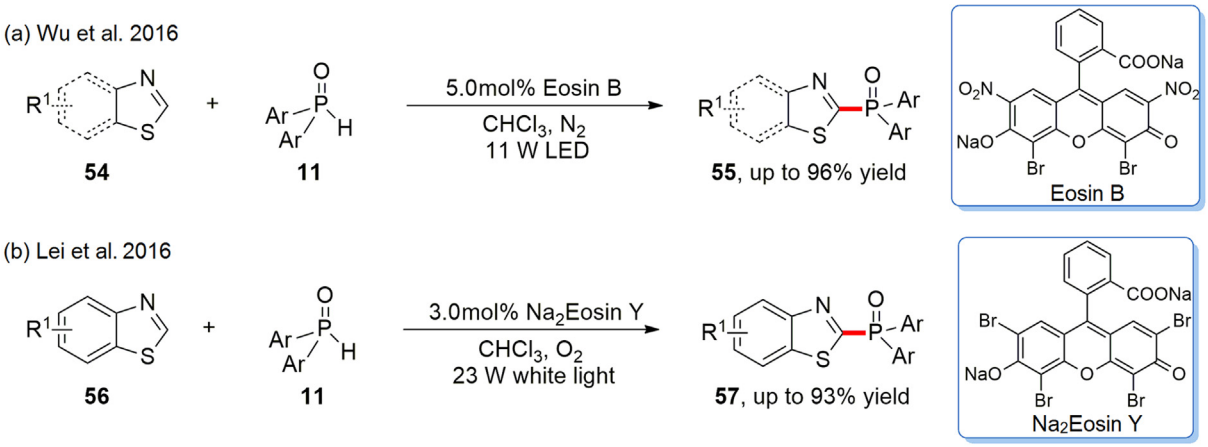


Scheme 8. (Color online) Photocatalytic synthesis of phosphorus-containing pyrrolidine **49**, lactone **51** and tetrahydrofuran **53**.

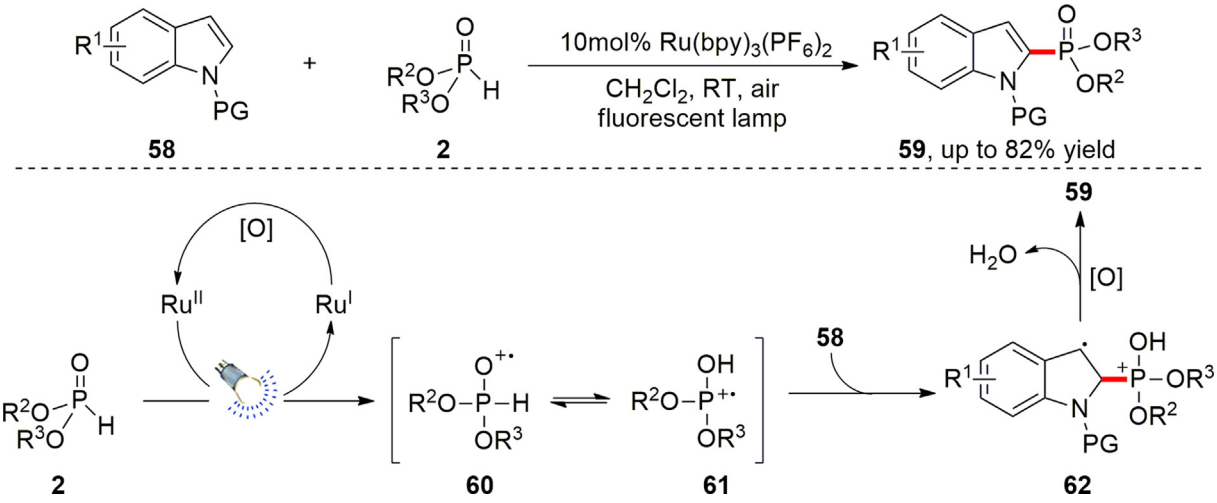
3. Visible light-mediated C(Sp^2)P bond formation reactions

The direct C—H phosphorylation of arenes and heteroarenes is one of the most important methods to create new C(sp^2)—P bond. In 2016, Wu and co-workers [57] developed the first example of C—H phosphorylation of thiazole derivatives with diarylphosphine oxides promoted by visible light-induced photoredox catalysis (Scheme 9). In this process, 5 mol% Eosin B is used as photoredox catalyst and the reaction shows high functional group tolerance with respect to the both thiazole and diarylphosphine oxide components. Shortly after this report, a similar visible light-promoted C—H phosphorization of benzothiazoles towards the construction of arylphosphonates was also realized by Lei group (Scheme 9) [58]. One of the most attractive features is that oxygen is used as the sole green oxidant. The results of EPR study clearly revealed the formation of phosphonyl radical intermediate during the process.

In 2016, An, Dong and co-workers [59] disclosed a visible light promoted regioselective hetero-cross-dehydrogenative-coupling (hetero-CDC) of N-protected indoles with dialkylphosphites, affording a variety of 2-indolyphosphites in good yields with high functional group tolerance (Scheme 10). The dialkylphosphites, which are generally known as insuperable substrates in photocatalytic C—P bond formation reactions, proceeded well for this hetero-CDC process. In proposed mechanism, the photogenerated radical cation **60** and **61** are recognized as the key intermediates.



Scheme 9. (Color online) Visible light-induced C—H phosphorylation of thiazole derivatives with diarylphosphine oxides.



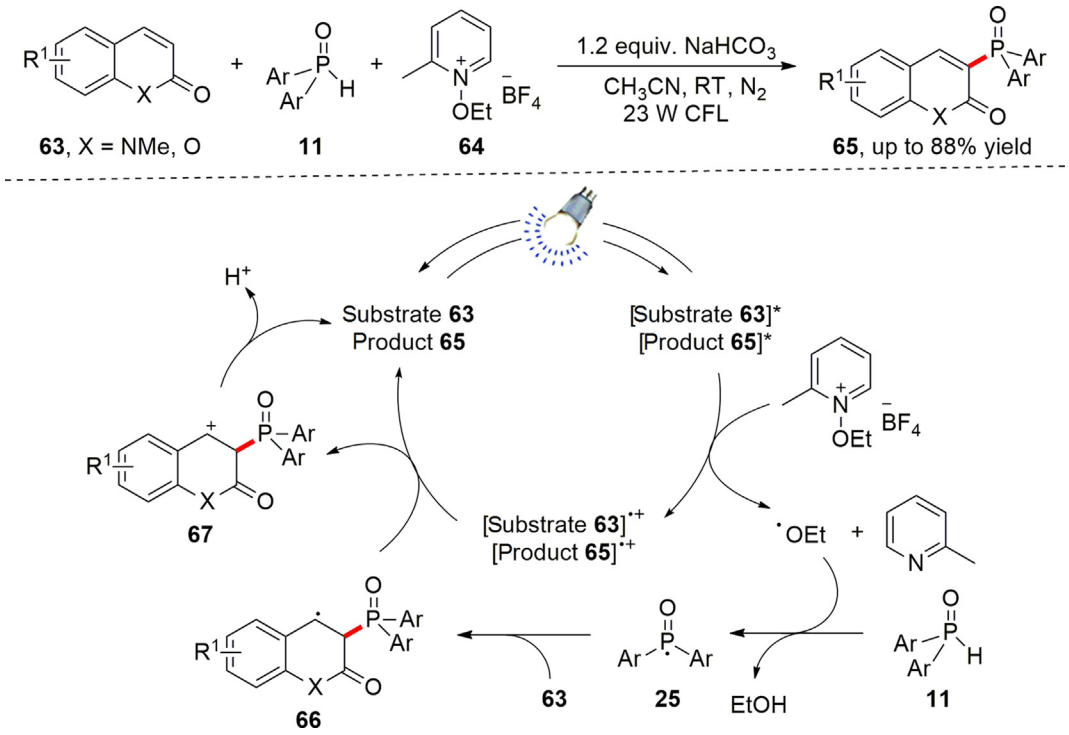
Scheme 10. (Color online) Visible light-induced C—H phosphonylation of indoles with dialkylphosphites.

Since the above elegant discoveries, visible light-promoted C(sp^2)—H phosphorylation of other heterocyclic ring structures, including coumarins [60], quinoxalin-2(1*H*)-ones [61] and 2*H*-indazoles [62] was sequentially disclosed by different research groups.

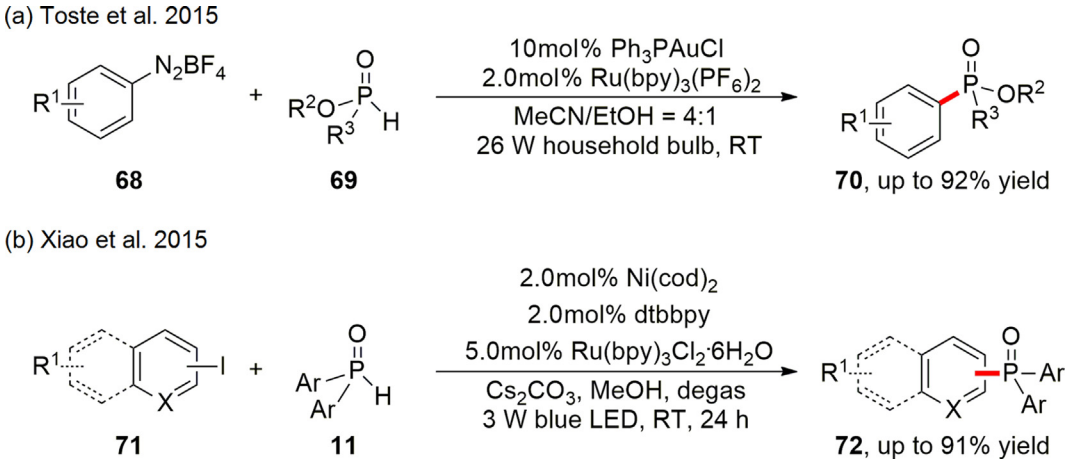
In 2017, Hong and co-workers [63] described a light-promoted direct phosphonation reaction of quinolinones and coumarins without the addition of an external photoreodx catalyst (Scheme 11). Mechanistic investigation revealed that the substrates and the final C—H phosphonylation products both can serve as effective photosensitizers up on the irradiation with 23 W compact fluorescent light bulb, and the entire set of C—H phosphonation reactions are self-sustaining in an autocatalytic manner. Initially, substrate **63** serves as the photoredox catalyst to reach its excited state under the irradiation of visible light. Then, dissociation of the N—O bond in pyridinium salt **64** by a single electron transfer pathway affords ethoxy radical intermediate and the 2-methylpyridine by-product. Hydrogen transfer from diarylphosphine oxide to ethoxy radical intermediate provides the key phosphinoyl radical **25** with the release of EtOH. Radical addition of **25** to substrate **63** gives the carbon-centered radical **66**, which is subsequently oxidized to the carbon cation intermediate **67** and complete the photocatalytic cycle. Under the basic reaction conditions, deprotonation of **67** delivers the final C—H phosphonation product. It is observed that the reaction rate can be dramatically accelerated once the product **65** formed, indicating that **65** also can act as the photoredox catalyst in the rest catalytic process.

Another impressive method for the construction of C(sp^2)—P bond is the utilization of dual catalytic strategy by merging visible light-induced photoredox catalysis with other catalytic manners [64,65]. Early example from Toste group reported the carbon-phosphorus cross-coupling of *H*-phosphonates with aryl diazonium salts by photoredox/gold dual catalysis (Scheme 12a) [66]. Besides a variety of *H*-phosphonate diesters, phenyl phosphinic acid is also a competent nucleophile for this transformation. In the same year, Xiao group [67] realized another example of C(sp^2)—P bond formation reaction of diarylphosphine oxides with aryl or heteroaryl iodides by merging nickel catalysis and visible-light-induced photoredox catalysis (Scheme 12b). Note that, this is the first reported example of the formation of C-heteroatom bonds by using photoredox/nickel dual catalytic system. The transition metal-free process of this reaction was recently realized by Yu, Che and co-workers [68].

In 2017, Yu and co-workers [69] developed an efficient phosphorylation reaction of enol sulfonates with phosphonate via photoredox/nickel dual catalysis (Scheme 13). Comparing with the Toste and Xiao's dual catalytic strategies for creating aryl C(sp^2)—P bond, this method provides a facile manner to various structurally complicated alkenyl phosphonates in moderate to excellent yields. More significantly, the mild reaction conditions, high selec-



Scheme 11. (Color online) Visible light-promoted phosphonation of quinolinones and coumarins via autocatalysis.

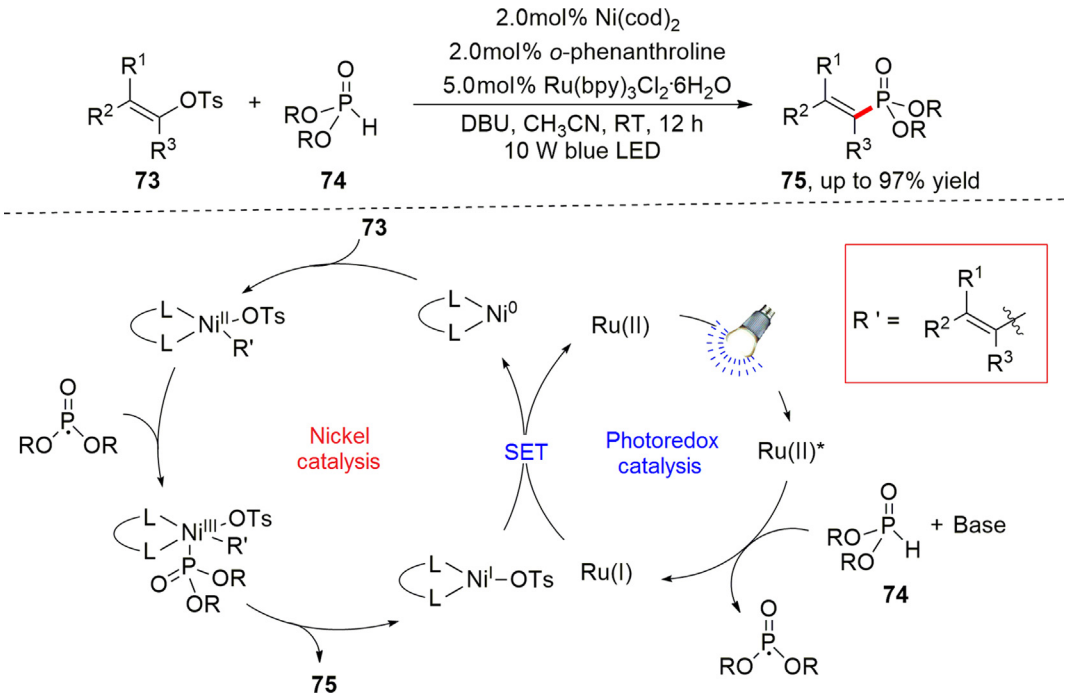


Scheme 12. (Color online) Visible light-promoted phosphonation of quinolinones and coumarins via autocatalysis. cod = 1,5-cyclooctadiene; dtb-bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine.

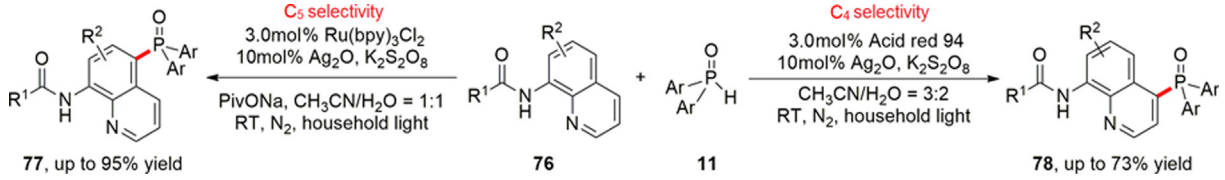
tivity and excellent functional group tolerance further render the approach valuable. In the proposed mechanism, the photocatalytic cycle begins with the reductive quenching of Ru(II)* with phosphonate **74** to give the P-centered radical species and low-valence Ru (I) complex. Meanwhile, oxidative addition of Ni(0) to the C—O bond in tosylate **73** affords Ni(II) species, which rapidly intercepts the P-centered radical to provide the Ni(III) complex. Reductive elimination of Ni(III) complex affords the final C(sp^2)—P bond formation product **75**. Finally, a single electron reduction of Ni(I) species by low-valence Ru(I) complex completes both of the catalytic cycles

In same year, Wu and co-workers [70] reported a mild and simple site-selective C_4—H or C_5—H phosphonation of 8-aminoquinoline amides with diarylphosphine oxides by merging visible light-induced photoredox catalysis with silver catalysis (Scheme 14). It is found that the reaction occurs smoothly at C_5 position of 8-aminoquinoline amides by using $Ru(bpy)_3Cl_2$ as photoredox catalyst, Ag_2O as co-catalyst and PivONa as the additive. While the C_4—H phosphonation product **78** is observed as the major product when the reaction is performed in the presence of Acid red 94 photoredox catalyst and Ag_2O. Mechanistic investigations revealed that the reactive site might be caused by the stronger X → M coordination bond in the bidentate chelated intermediates. Shortly after this study, the direct C_4—H phosphonation of 8-hydroxyquinoline derivatives by using visible light promoted dual-catalytic strategy was realized by the same research group [71].

Recently, Xie et al. [72] reported a C(sp^2)—P bond formation reaction of alcohols with various P-H species by merging Bronsted acid catalysis and organic photoredox catalysis (Scheme 15). This mild protocol is compatible with a wide range of 1,1-diarylenthanols and phosphine oxidants, providing the



Scheme 13. (Color online) Visible light-promoted phosphonation of alkenyl C—O bonds via photoredox/nickel dual catalysis.



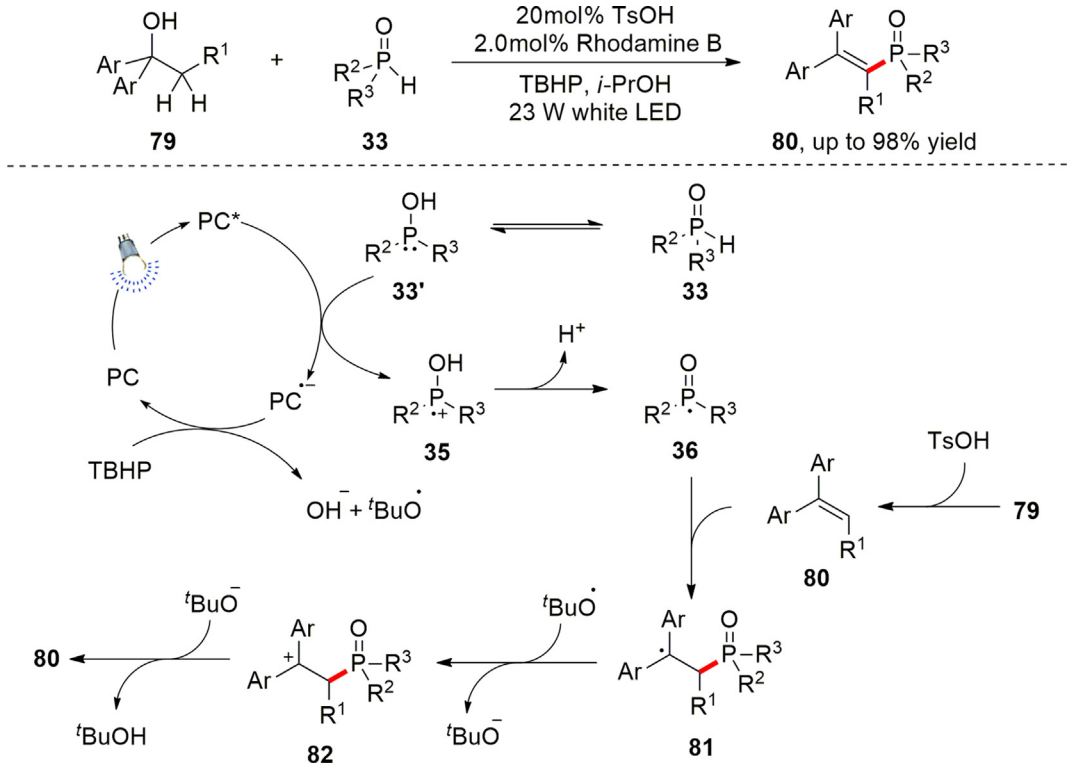
Scheme 14. (Color online) Visible light-promoted site-selective C_4 or C_5-H phosphonation of 8-aminoquinoline amides.

corresponding tri- and the challenging tetrasubstituted alkenylphosphine oxides in average good yields and selectivities. However, 1-alkyl-1-arylethanols are not suitable for this dual-catalytic transformation. Control experiments revealed that both of the TsOH and Rhodamine B are crucial for this reaction. Only water and *tert*-butyl alcohol are generated as by-products, further documenting the green chemistry features of the process. In the proposed reaction mechanism, 1,1-diarylenthanol **79** is transferred to alkene **80** with the assistance of TsOH. Then, P-centered radical species **36**, generated from photocatalytic cycle, undergoes an anti-Markovnikov radical addition to alkenes **80** to give radical species **81**. TBHP serves as the final oxidant to complete the photocatalytic cycle and generates *t*-BuO·. Single electron-transfer from radical species **81** to *t*-BuO· delivers the carbon cation intermediate **82**, which subsequently deprotonation to afford the final alkenylphosphine oxides.

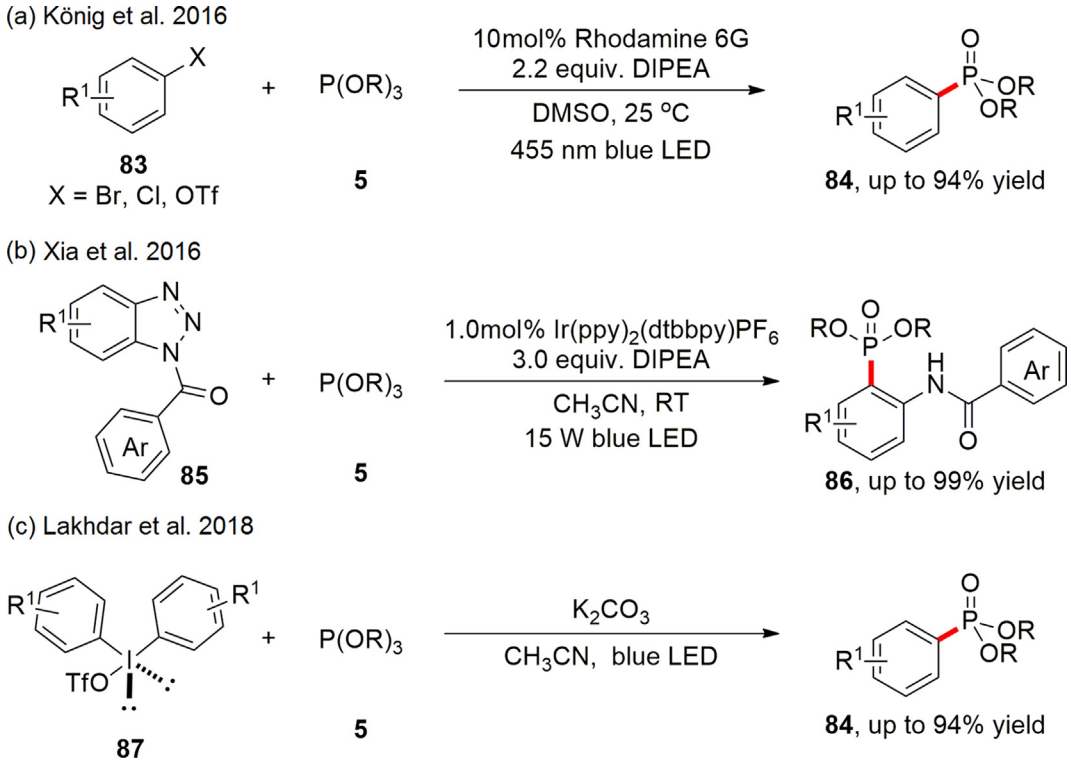
The first visible light-induced Arbuzov reaction was disclosed by König and co-workers [73] in 2016 (Scheme 16a). The reaction uses cheap organic dye Rhodamine 6G as the photoredox catalyst and aryl bromides as the aryl radical precursors, which providing a variety of phosphonates in consistent yields. Apart from aryl bromides, aryl chlorides and aryl triflates are suitable for the transformation. A similar elegant work was also realized by Xia and co-workers [74] by using benzotriazoles as aryl radical precursors (Scheme 16b). Very recently, Lakhdar group [75] reported a visible light-promoted synthesis of aryl phosphonates from diaryliodonium salts with phosphites under photoredox catalyst free conditions (Scheme 16c). Mechanistic investigation revealed that a weak EDA complex was formed between diaryliodonium salt **87** with phosphite **5**. And this thermodynamically unstable EDA complex decomposed under the irradiation with blue LED lamp to form the key aryl radical species.

In 2016, Lakhdar group [76] realized the photo-catalytic synthesis of biologically important benzo[*b*]phosphole oxides by using Eosin Y as the catalyst and *N*-ethoxy-2-methylpyridinium tetrafluoroborate as the oxidant. In this reaction, the photo-generated P-centered radicals can efficiently add to the carbon-carbon triple bond of alkynes, thus providing an alternative manner to forge new C(sp^2)—P bond. Two years later, the addition of P-centered radical species to alkynes under visible light irradiation was strategically applied to the synthesis of previously inaccessible *Z*-alkenes by Lei and his co-workers [77] (Scheme 17). This protocol is effective with both terminal and internal alkynes, affording the corresponding alkenylphosphine oxides with excellent *Z*-stereoselectivity. It is found that water is the optimal reaction media for the transformation. The results of deuterium labeling experiments clearly show that the α-proton in the vinyl group of **89** comes from water (**91** to **89** in Scheme 17). Moreover, the formation of P-centered radical intermediate **25** is confirmed by EPR studies and radical trapping experiments. The high *Z*-selectivity of the product can be attributed to the π−π stacking interaction of the aromatic ring of the phenylacetylene and diarylphosphine oxide.

Coumarin derivatives are important classes of heterocycles which can be frequently found in many natural isolates and bioactive molecules [78,79]. In 2017, Xu group [80] demonstrated an

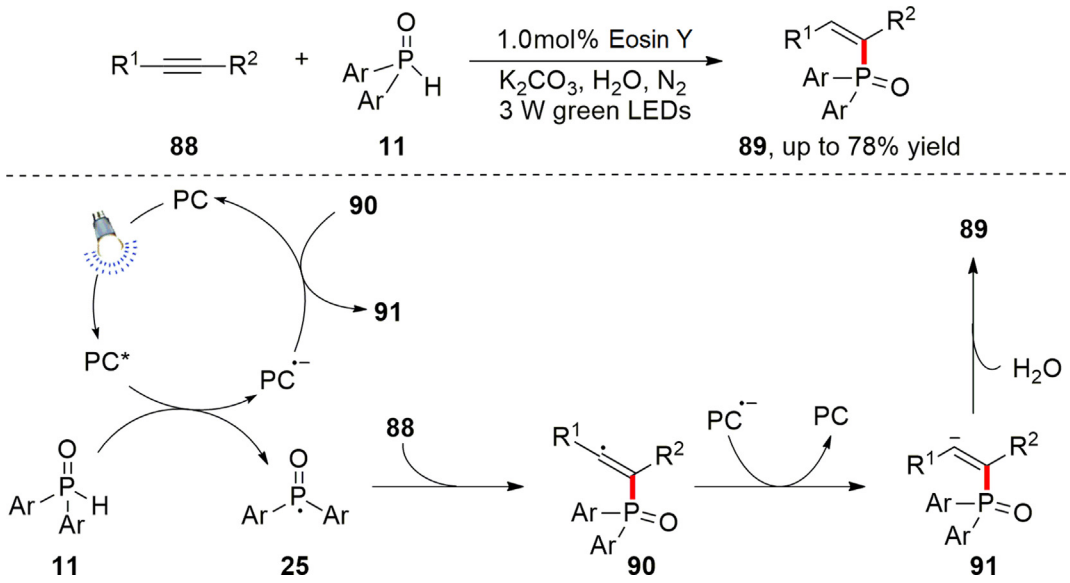


Scheme 15. (Color online) Alkenyl phosphorus compounds synthesis via Bronsted acid/photoredox dual catalysis. TBHP = *tert*-butyl hydroperoxide.



Scheme 16. (Color online) Visible light-induced Arbuzov type reactions with different aryl radical precursors. DIPEA = *N*,*N*-diisopropylethylamine.

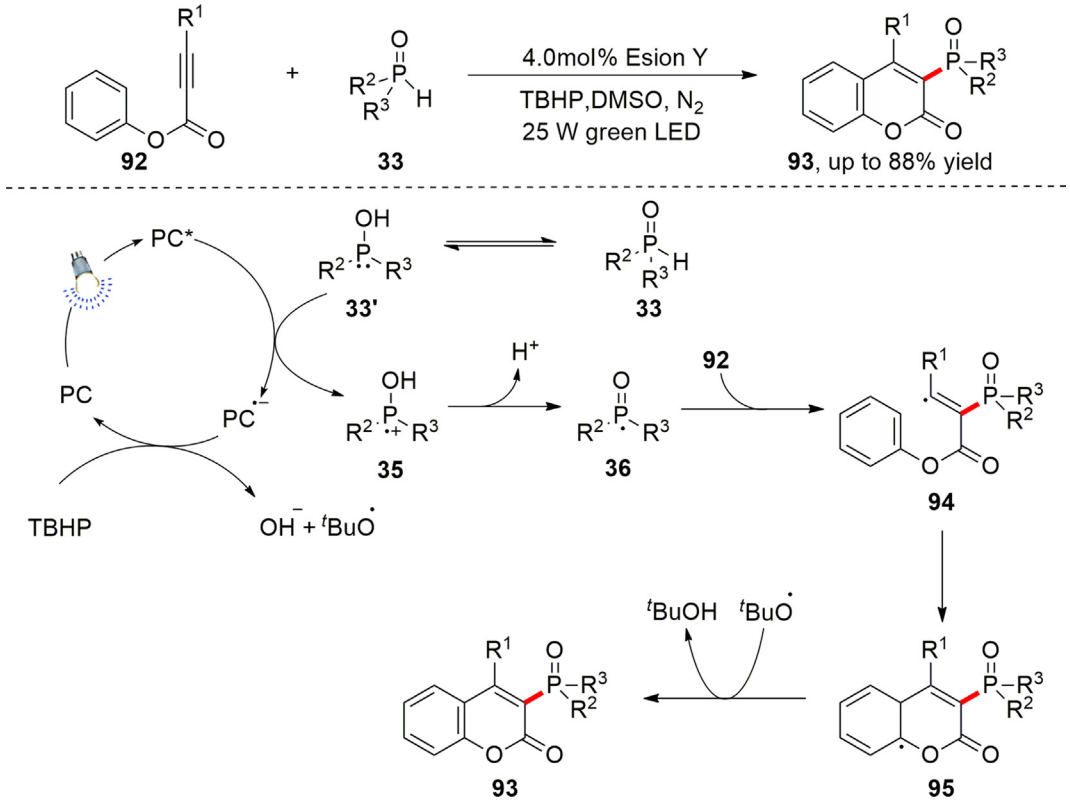
elegant strategy for the synthesis of 3-phosphorylated coumarin derivatives via a visible light-promoted cascade radical cyclization of alkynoates (Scheme 18). The catalytic system, consisting of 4.0 mol% Eosin Y as the photoredox catalyst and 2.0 equiv. TBHP as oxidants, worked well for a broad substrate scope, and showed high functional group tolerance with respect to both alkynoates and phosphoryl radical precursors. Remarkably, direct sun-light irradiation of the reaction system still gives 3-phosphorylated



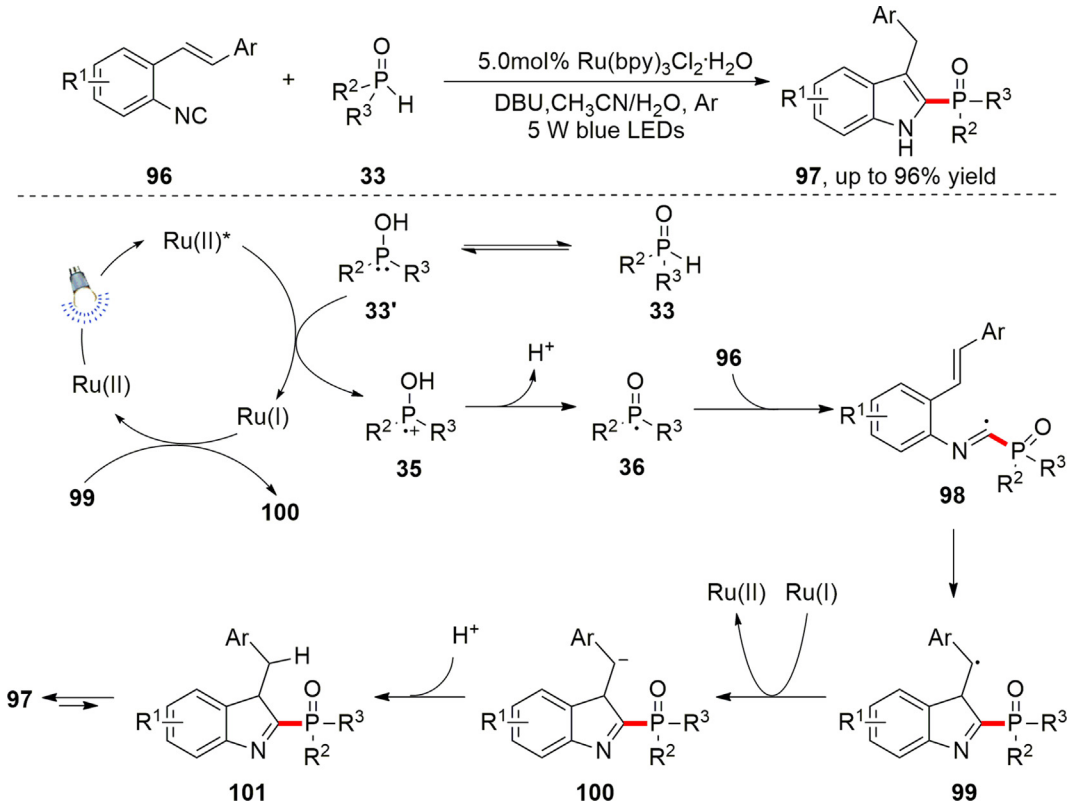
Scheme 17. (Color online) Visible light-promoted *Z*-selective addition of diaryl phosphine oxides to alkynes.

coumarin product in high yield. In the proposed mechanism showing in Scheme 18, the photo-generated P-centered radical species **36** regioselectively adds to the triple bond of alkynoate **92** to afford vinyl radical **94**, which subsequently undergoes intramolecular radical cyclization to produce radical intermediate **95**. TBHP acts as the final oxidant to complete the photocatalytic cycle and generates *tert*-butoxyl radical. Hydrogen transfer from **95** to *tert*-butoxyl radical provides the final 3-phosphorylated coumarin **93**. The strategy recently was further extended to the radical cascade cyclization of 1,6-diyne by the same research group [81].

In a recent publication, Yang group [82] reported a visible light-promoted radical cascade cyclization of P-centered radical species with arene isonitriles, leading to a wide range of 2-phosphinoylindoles in good yields (Scheme 19). No external oxidants are needed for the process documenting the redox neutral character of the reaction. Furthermore, the synthetic value of the method is highlighted by the formal synthesis of Zafirlukast derivative, an oral leukotriene receptor antagonist for the maintenance treatment of asthma [83]. A series of control experiments suggested a reductive quenching process of this process. Initially,



Scheme 18. (Color online) Visible light-promoted synthesis of 3-phosphorylated coumarins.



Scheme 19. (Color online) Visible light-promoted synthesis of 2-phosphinoylindoles.

the P-centered radical intermediate **36**, generated from reductive quenching of Ru(II)* species with phosphine oxide **33**, is trapped by arene isonitriles **96** to form alkene radical **98**, which further undergoes an intramolecular cyclization to deliver carbon-centered radical species **99**. Then, reductive of **99** with low-valent Ru(I) species to provide carbon anion **100** and regenerate the photoredox catalyst to complete the photo-catalytic cycle. Finally, carbon anion **100** undergoes a protonation/isomerization sequence to afford the final 2-phosphinoylindole product.

4. Conclusions

This review is focused on the recent advances of C—P bond formation reactions promoted by visible-light induced photoredox catalysis. Generally, visible light-induced C—P bond formation reactions can be divided into the following two types: (1) the trapping of the photo-generated iminium ions with P-centered nucleophiles; (2) the addition of photo-generated P-centered radical species to unsaturated chemical bonds, such as arenes, heteroarenes, alkenes and alkynes. Recent advances in this area clearly revealed that visible light-induced C—P bond formation reaction can be applied not only to the simple functionalization of unsaturated chemical bonds, but also to the construction of more complex P-centered carbo- and heterocycles. There is no doubt that C—P bond formation reactions initiated by visible-light photoredox catalysis will further attract the attention of chemists in future.

Despite some significant progress has been made in this fast-developing research area, some challenges and opportunities still remain: firstly, most of the photo-promoted C—P bond formation reactions are needed the photoredox catalysts, including organic dyes and metal-pyridine complex. Thus, one future goal is to develop the catalyst free C—P bond process, especially the formation of EDA complex. Secondly, the design of new types of P-radical triggered cascade radical cyclization processes represents another important direction for future investigations which would further enlarge the structural space of the accessible organophosphorus compounds. Thirdly, the development of visible light-promoted catalytic asymmetric C—P bond formation reactions would be another interesting research area.

Conflict of interest

The authors declare that they have no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scib.2019.02.002.

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Bao-Gui Cai received his B.S. degree in chemistry at Anhui Science and Technology University in 2018. He is currently conducting studies in organic chemistry under the direction of Prof. Jun Xuan at Anhui University. His research interests are heterocyclic compound synthesis via visible light-induced photoredox catalysis.

Jun Xuan received his Ph.D. degree at Central China Normal University (CCNU) under the supervision of Prof. Wen-Jing Xiao in 2015. During 2015−2017, he worked as a Humboldt postdoctoral fellow with Professor Armido Studer at Westfälische Wilhems-University (Germany). In 2017, he joined at the Department of Chemistry at Anhui University to start his independent career. His current research interests are focused on the development of efficient synthetic methodologies for the synthesis of biologically important heterocycles.

Wen-Jing Xiao completed his M.Sc in 1990 under the supervision of Prof. Wen-Fang Huang at Central China Normal University. In 2000, he received his Ph.D. degree under the direction of Prof. Howard Alper at the University of Ottawa, Canada. After post-doctoral studies with Prof. David W. C. MacMillan (2001–2002) at the California Institute of Technology, USA, he became a full professor at the College of Chemistry at the Central China Normal University in 2003. His research interests include the development of new synthetic methods and the synthesis of biologically active compounds.