A Visible-Light-Promoted Metal-Free Strategy towards Arylphosphonates: Organic-Dye-Catalyzed Phosphorylation of Arylhydrazines with Trialkylphosphites

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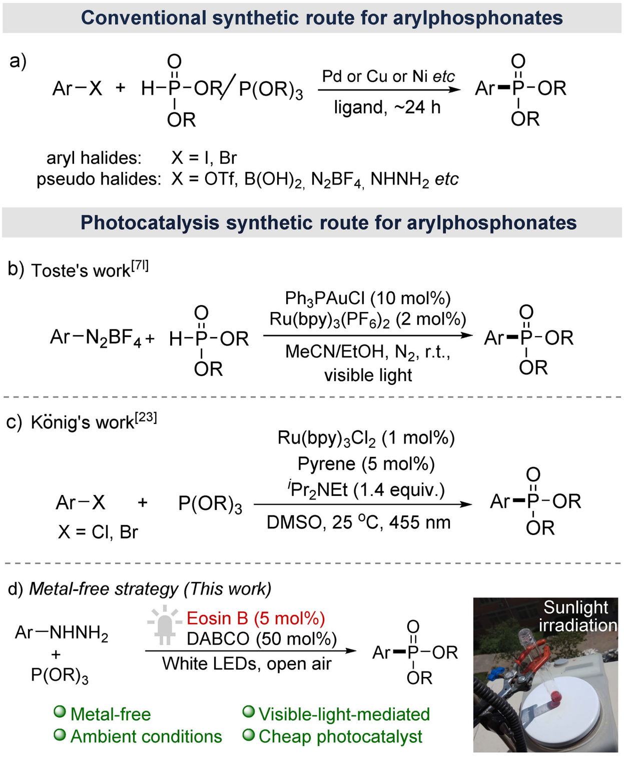
Abstract: A visible-light-induced metal-free catalytic system was developed for the synthesis of arylphosphonates starting from arylhydrazines and trialkylphosphites. By using the inexpensive eosin B as catalyst, substoichiometric amounts of DABCO, and ambient air as oxidant, diverse arylphosphonates were obtained under visible-light irradiation. Notably, this catalytic system is suitable for gram-scale reaction by utilizing sunlight as an illumination source.

Keywords: arylphosphonate; arylhydrazine; visible-light irradiation; metal-free

Introduction

Phosphonates are significant structural motifs existing in a large variety of pharmaceutically active molecules,[1] organic materials[2] and agrochemicals.[3] Phosphonates have also been widely used as ligands[4] and synthetic intermediates.[5] In the past half century, many efforts have been devoted to the preparation of structurally diverse phosphonates. Michaelis-Arbuzov reaction is a well known method used for the preparation of dialkyl alkylphosphonates.[6] In the past few decades, many synthetic methodologies have also been developed for the synthesis of various arylphosphonates. The main conventional methods published from 1981 to 2015 for the synthesis of arylphosphonates were the transition-metal-catalyzed cross-coupling of aryl halides (or pseudo halides) with trialkylphosphites or *H*-phosphonate,[7] pioneered by the work of Hirao et al published in 1981, known as the Hirao cross-coupling (Scheme 1a).[8] Despite significant achievements, from an environmentally friendly point of view, those procedures still suffer from some drawbacks, such as the use of metals even highly toxic noble metals as catalysts, inconveniently long reaction time (usually about 24 h) as well as high reaction temperature.

One of the major research endeavors in modern synthetic chemistry is to find green methods that can work under environmentally friendly conditions.[9] The use of visible-light is an inexpensive and nonpolluting means to initiate organic transformations.[10] Over the last four decades, photoredox catalysts have widely been used in the fields of carbon dioxide reduction,[11] water splitting,[12] and the development of solar cell materials.[13] Only over the past ten years, a blooming development of visible-light photoredox catalysis for organic synthesis has been witnessed.[14] The recently developed visible-light photoredox catalysts include ruthenium and iridium polypyridyl complexes and organic dyes, which efficiently facilitated the conversion of visible-light into chemical energy under extremely mild conditions.[15] In spite of the excellent photocatalytic properties of ruthenium and iridium polypyridyl complexes in organic synthesis, the metal complexes are usually expensive and potentially toxic. In contrast, organic dyes are an attractive alternative to the transition metal complexes as photoredox catalysis in that they are usually less expensive, less



Scheme 1. Synthesis of arylphosphonates.

toxic, and easier to handle.[16] For example, the organic dyes such as methylene blue,[17] eosins,[18] rhodamines,[19] etc. have been proved to be excellent visible-light photocatalysts in a number of synthetic reactions, represented by visible-light induced aerobic oxidative radical addition of aryl hydrazines to alkenes,[17a] cross-dehydrogenative coupling reaction[20] and visible-light photo-Arbuzov reaction[21] etc.

To date, photoredox catalysis has already been extensively used to form C–C and C–X (X=O, N and S) bonds. In contrast, photoredox catalysis is relatively underdeveloped in organophosphorus chemistry to form C–P bonds. Only limited examples concerning using photoredox catalysis to synthesize organophosphorus compounds have been reported over the past five years.[22] Xia *et al* developed a photocatalytic method for the C(sp^2)–P bond formation *via* a denitrogenative coupling of benzotriazoles with phosphites catalyzed by a iridium polypyridyl complex.[22b] Two novel synthetic methodologies, by using ruthenium polypyridyl complexes as visible-light photoredox catalysis for the synthesis of arylphosphonates, were reported successively by Toste *et al* (Scheme 1b)[7l] and König *et al* (Scheme 1c).[23] Nevertheless, the high cost and multi-step synthesis of the noble metal-based photocatalysts, and the transition-metal contamination issue might limit their applications. Very recently, Breugst and Lakhdar group developed an approach to access aryl phosphonates starting from diaryiodonium salts and phosphites under blue-light irradiation.[22c] However, diaryiodonium salts have very limited commercial availability. Therefore, it is highly desirable to exploit inexpensive, metal-free, efficient and environmentally friendly photochemical approaches for the synthesis of arylphosphonates. Based on our continuing study of organophosphorus chemistry and green chemistry,[24] we herein reported a novel visible-light-driven organic-dye-catalyzed photoredox reaction, by which various arylphosphonates were efficiently synthesized from arylhydrazines and trialkylphosphites under mild and metal-free conditions (Scheme 1d). To the best of our knowledge, this is the first example for the construction of arylphosphonates from arylhydrazines by a dye-catalyzed photocatalytic process under irradiation of visible-light and metal-free reaction conditions.

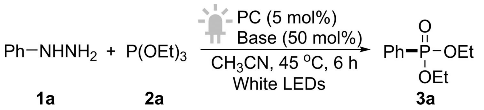
Results and Discussion

We initiated the meaningful study, starting with establishing optimal experimental conditions using the model reaction of phenylhydrazine **1a** with triethylphosphite **2a** under visible-light irradiation in the presence of various organic dyes and bases in CH_3CN at 45 °C for 6 h as shown in Table 1. The solvents and reaction time screening were initially carried out and the yields were determined by ^{31}P NMR with area normalization (for details see Table S1). Then, various organic dyes, such as Rose Bengal, fluorescein, Rhodamine B, eosin Y, Na_2Eosin Y, eosin B and methylene blue, as the photocatalysts were surveyed in the presence of DABCO (50 mol%) in CH_3CN for 6 h in closed tubes, respectively (entries 1–7). Among them, eosin B was the most promising photocatalyst, delivering the desired product **3a** in 27% yield.

By using eosin B as photocatalyst, bases, including $NaHCO_3$, K_2CO_3, Cs_2CO_3, K_3PO_4, 2, 6-lutidine, TBD DBU, TMG, and Et_3N were screened, respectively (entries 8–16). The results indicated that DABCO was superior to the others (entry 6 *vs* entries 8–16). Surprisingly, the yield of **3a** was significantly improved to 70% when the reaction was conducted in open air by using eosin B (5 mol%) and sub-stoichiometric amounts of DABCO (50 mol%) (entry 17). Then the model reaction was evaluated under blue, red and green light in open air, affording the product **3a** in 57%, 22% and 56% yield, respectively. Further investigations on the amounts of DABCO and eosin B were finally carried out (For details, see Table S1). After intensive experimentation, the optimal conditions were established as follows: **1a** (0.5 mmol), **2a** (1.0 mmol), eosin B (5 mol%), DABCO (50 mol%), CH_3CN (1.5 mL) in open air at 45 °C for 6 h with the irradiation of white LEDs.

With the optimized conditions in hand, we further explored the scope of this novel visible-light-induced

Table 1. Optimization of the reaction conditions.[a]



Entry	PC (Photocatalyst)	Base	Yield[b] (%)
1	Rose Bengal	DABCO	15
2	Fluorescein	DABCO	15
3	Rhodamine B	DABCO	14
4	Eosin Y	DABCO	16
5	Na_2Eosin Y	DABCO	16
6	Eosin B	DABCO	27
7	Methylene blue	DABCO	21
8	Eosin B	$NaHCO_3$	11
9	Eosin B	K_2CO_3	9
10	Eosin B	Cs_2CO_3	22
11	Eosin B	K_3PO_4	8
12	Eosin B	2,6-lutidine	7
13	Eosin B	TBD	18
14	Eosin B	DBU	21
15	Eosin B	TMG	19
16	Eosin B	Et_3N	18
17[c]	Eosin B	DABCO	70
18[c,d]	Eosin B	DABCO	57
19[c,e]	Eosin B	DABCO	22
20[c,f]	Eosin B	DABCO	56
21[c,g]	Eosin B	DABCO	60

[a] Reaction conditions unless otherwise specified: To a reaction tube, **1a** (0.5 mmol), **2a** (1.0 mmol), photocatalyst (5 mol%), CH_3CN (1.5 mL), base (50 mol%) were added, then the tube was capped and stirred under the irradiation of white LEDs at 45 °C for 6 h. DABCO = 1,4-diazabicyclo[2.2.2]octane, TBD = 1,5,7-Triazabicyclo[4.4.0]dec-5-ene, DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene, TMG = 1,1,3,3-tetramethylguanidine.

[b] Yields were given by ^{31}P NMR.

[c] Open air.

[d] Blue LEDs.

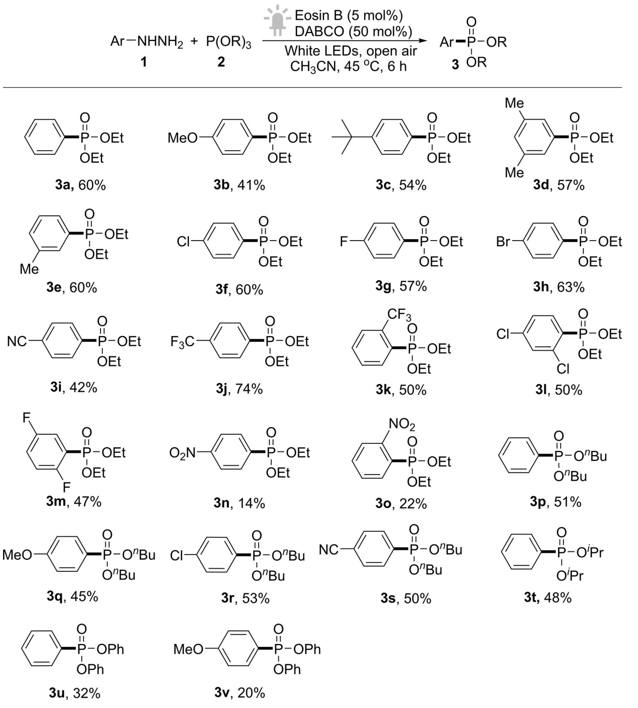
[e] Red LEDs.

[f] Green LEDs

[g] Reaction under sunlight irradiation.

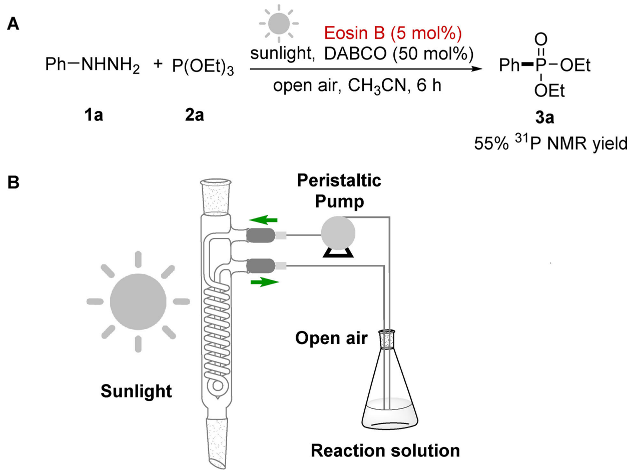
dye-catalyzed reaction *via* the reaction of a variety of commercially available arylhydrazines **1** with various phosphites **2** as shown in Table 2. As it can be seen, diethyl phenylphosphonate **3a** was obtained in 60% isolated yield under the standard conditions. The arylhydrazines bearing electron-rich groups such as MeO-, ^{t}Bu-, Me-groups at different positions of benzene ring showed good reactivities in the catalytic system, giving the corresponding arylphosphonates **3b–e** in moderate to good yields. The mono- or di-substituted arylhydrazines with electron-withdrawing groups at different positions of benzene ring, including F-, Cl-, Br-, CF_3-, and CN-, reacted smoothly with triethylphosphite **2a**, affording the desired arylphosphonates **3f–m** in moderate to good yields. No obvious electronic effects were observed in cases of **3b–m**. However, in contrast, arylhydrazine substrates containing a strong electron-withdrawing nitro group at *para-* or *ortho*-position showed relatively poor reactivities, delivering the corresponding arylphosphonates **3n–o** in 14% and 22% yields, respectively. The reason of low yields was the formation of two by-products confirmed by GC-MS (for details, see the Supporting Information). Furthermore, various phosphites were employed as substrates for this protocol to further examine the reaction scope. As it can be seen, both tributylphosphite and triisopropylphosphite displayed good compatibilities with various arylhydrazines, affording the corresponding arylphosphonates **3p–u** in good yields under the standard reaction conditions. To our delight, triphenylphosphite, a sterically hindered phosphite, was also suitable for the synthesis of arylphosphonates **3v–w** although with diminished yields.

Table 2. Substrate scope of the visible-light-promoted arylphosphonates formation.[a]



[a] Reaction conditions: **1** (0.5 mmol), **2** (1.0 mmol), eosin B (5 mol%), CH_3CN (1.5 mL), DABCO (50 mol%), white LEDs, 6 h, 45 °C, open air. Isolated yields were given.

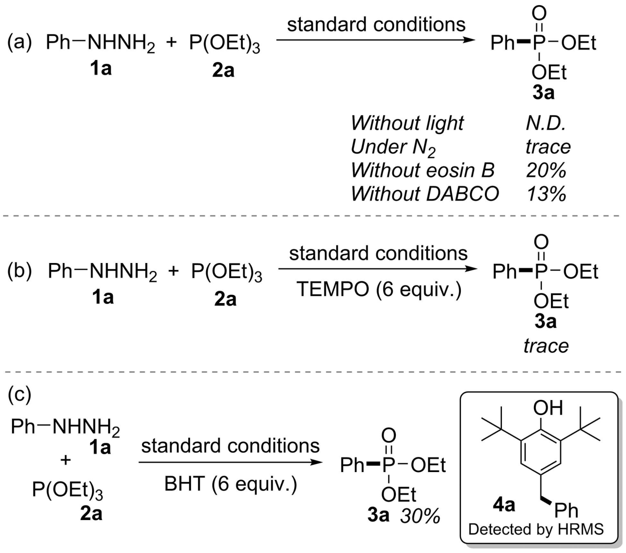
Given the fact that this photocatalysis system works well for the synthesis of arylphosphonates under irradiation of white LEDs, we conducted the reaction to access **3a** with solar irradiation (Table 1, entry 17). As it can be seen, 60% ^{31}P NMR yield of **3a** was obtained when the reaction was irradiated by sunlight for 6 h in the open air. Following that, a gram-scale experiment was carried out under solar irradiation for 6 h in the open air in our specially designed reactor as illustrated in Scheme 2. We were delighted to find that the arylphosphonate **3a** was obtained in 55% ^{31}P NMR yield. The results indicate sunlight, as a renewable and clean energy source, is suitable for being employed as our energy source for synthesizing arylphosphonates as well (For details, see the Supporting Information).



Scheme 2. A: Gram-scale synthesis of **3a** with sunlight irradiation: phenylhydrazine **1a** (13.8 mmol, 1.5 g), triethylphosphites **2a** (27.6 mmol, 4.59 g), eosin B (5 mol%), CH_3CN (25 mL), DABCO (50 mol%), 6 h, 45 °C; **B**: A specially designed apparatus for gram-scale synthesis of **3a**.

To gain a deeper insight into the mechanism of this photocatalysis reaction, we carried out a series of control experiments. As shown in Scheme 3a, when the reaction was conducted in the absence of visible-light, or air, or photocatalyst, or base, none or trace amounts of product **3a** were observed. When the reaction was treated with 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), a radical scavenger, only a trace of **3a** was detected based on ^{31}P NMR analysis (Scheme 3b). Additionally, when the reaction was treated with 2,6-di-*tert*-butyl-4-methyl-phenol (BHT), another radical scavenger, the reaction was seriously inhibited with only 30% product of **3a** being detected. Meanwhile, a radical coupling adduct **4a** was detected in the reaction solution using HRMS (see Figure S1), reminding that phenyl radical was produced and trapped by BHT (Scheme 3c).

One more experiment was carried out for further demonstrating the important role of visible-light irradiation in the synthesis as depicted in Figure 1. The model reaction of **1a** with **2a** was designed to be conducted under successive on/off LED irradiation conditions at every 30 min interval for a total of 150 min. The yield of **3a** was determined by ^{31}P NMR every 30 min. As it can be seen, rapid increases in yields were always observed in those situations as the reaction being carried out under irradiation conditions. However, in contrast, slow increases in yields were always observed in those situations as the reaction being done in the absence of irradiation conditions, demonstrating an essential role of the visible-light irradiation in the reaction transformation.



Scheme 3. Control experiments.

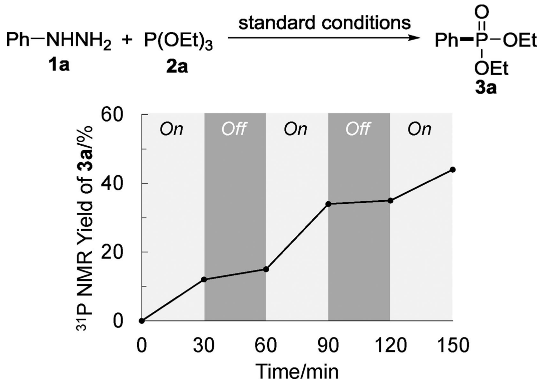


Figure 1. "On/off" LED irradiation experiment for the synthesis of phenylphosphonate **3a**.

We subsequently conducted a series of luminescence quenching studies to gain further insight into the related photocatalytic mechanism. We carried out the luminescence quenching studies (Stern-Volmer quenching experiments) by mixing eosin B (**EB**) with **1a**, **2a**, and DABCO, respectively. The significant luminescence quenching effect of DABCO was observed. However, in contrast, the luminescence quenching effects from the other reactants like **1a** and **2a** were not obvious (Figure 2a). As delineated in Figure 2b–c, a linear relationship between I_0/I (I_0 and I are the fluorescence intensities before and after the increasing the concentration of DABCO, respectively) and the concentration of DABCO was observed, indicating the DABCO was an effective quencher of **EB**.

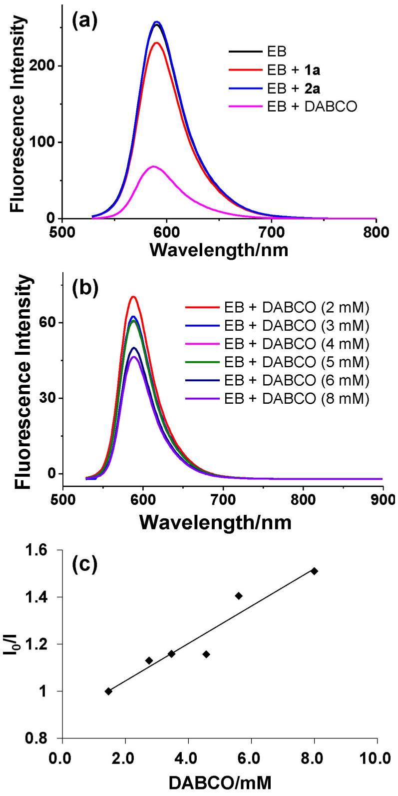
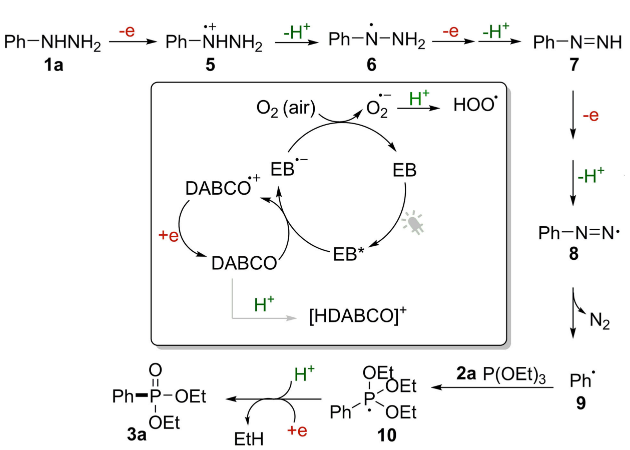


Figure 2. Luminescence quenching study: (a) the emission spectra of a 5×10^{-5} M solution of eosin B with reactants in degassed anhydrous CH_3CN excited at 508 nm; (b) the emission spectra of a 5×10^{-5} M solution of eosin B with various concentrations of DABCO in degassed anhydrous CH_3CN excited at 508 nm; (c) The linear relationship between I_0/I and the increasing concentration of DABCO.

Based on the above-mentioned results and literature reports,[17a,21] a plausible mechanism for this visible-light-mediated reaction was proposed (Scheme 4). First, **EB** is excited to form **EB*** in the presence of white LEDs light. Then *via* a single electron transfer (SET) process from DABCO to **EB***, the excited state of **EB** (**EB***) is reductively quenched by DABCO with generation of the radical cation $DABCO^{\bullet+}$ and anion $\mathbf{EB}^{\bullet-}$. The oxidation of $\mathbf{EB}^{\bullet-}$ by dioxygen (air) in the following step affords the ground state **EB** and $O_2^{\bullet-}$. In those process, DABCO is also partially consumed by protonation. Meanwhile, hydrazine **1a** is oxidized by $DABCO^{\bullet+}$, affording hydrazine radical ion **5** together with DABCO. Then the deprotonation of radical ion **5** by $O_2^{\bullet-}$ or DABCO results the formation of radical **6** and hydroperoxyl radical ($HOO^\bullet$) or $[HDABCO]^+$. Afterwards, a single-electron oxidation of radical **6** by $DABCO^{\bullet+}$, followed with deprotonation, leads to the formation of phenyldiazene **7**. Then another single-electron oxidation followed by deprotonation realizes the transformation of **7** to radical **8**. The subsequent release of a molecule of nitrogen from **8** generates the phenyl radical **9**. Finally, an addition of phenyl radical **9** to trialkylphosphites is followed, generating an unstable phosphoranyl radical **10**, which is then quickly transformed into the target phosphonate (**3a**) and ethane (EtH) with participation of a proton and an electron generated in the process of the photocatalytic reaction.



Scheme 4. The proposed mechanism.

A measurement on quantum yield of the photoreaction was further conducted. The result of the quantum yield of the photoreaction showed that 4 equivalents of product were formed for every photon absorbed (for details, see the Supporting Information), which was a result that could be consistent with the chain mechanism shown in Scheme 4.[25]

Conclusions

In summary, we have developed a metal-free photocatalysis system for the construction of arylphosphonates from easily available arylhydrazines and trialkylphosphites under visible-light irradiation. By using the organic dye eosin B as catalyst, sub-stoichiometric amounts of DABCO, and ambient air as oxidant, a variety of arylphosphonates were successfully synthesized. Notably, this catalytic system is also possible for gram-scale reaction by utilizing sunlight as an illumination source. The eminent merits of the synthetic method include an inexpensive and non-toxic photocatalyst (eosin B), a simple one-pot operation, metal-free and mild reaction conditions as well as eco-friendly energy source (solar light) and oxidant (oxygen in air). This strategy demonstrates that visible-light-mediated organic dye-catalyzed photocatalysis as an eco-friendly method has high potential for the synthesis of various arylphosphonates.

Experimental Section

To a 25 mL reaction tube, arylhydrazines (0.5 mmol), trialkylphosphite (1.0 mmol), eosin B (5 mol%), DABCO (50 mol%) were dissolved in CH_3CN (1.5 mL), and then the tube was stirred under the irradiation of white LEDs in open air at 45 °C for 6 h. After reaction, the mixture was diluted with water and extracted with ethyl acetate (25 mL × 3). The combined organic layers were collected and dried by anhydrous Na_2SO_4. The residue was purified by column chromatography on silica gel to afford the desired products.

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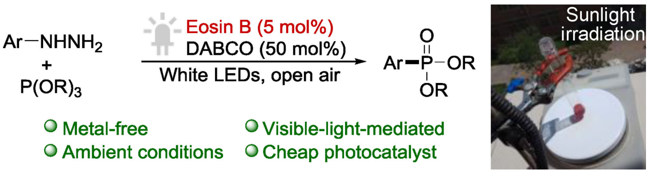

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