

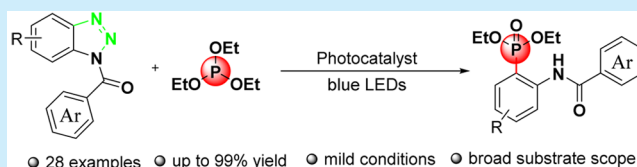
# Visible-Light-Induced C(sp<sup>2</sup>)–P Bond Formation by Denitrogenative Coupling of Benzotriazoles with Phosphites

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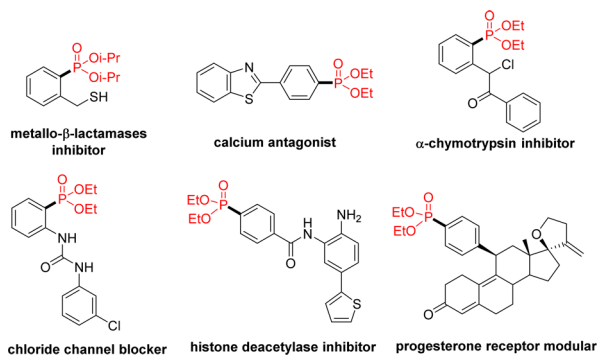
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**S** Supporting Information

**ABSTRACT:** A visible-light-induced denitrogenative phosphorylation of benzotriazoles is presented, in which diverse substituted aryl phosphonates could be obtained in good to excellent yields. This efficient protocol exhibits good tolerance with various functional groups. Furthermore, the utility of this photochemical protocol is demonstrated by a gram-scale reaction, and a reasonable mechanism is proposed.



Organophosphorus compounds have attracted continuous attention in pharmaceutical and agrochemical fields because of their unique bioactivities. Due to their high solubility, many aryl phosphonates are applied as prodrugs or even drugs in medicinal chemistry (Figure 1).<sup>1</sup> Besides, as an important ligand, they have been widely applied in a wide range of organic synthetic methodologies.<sup>2,3</sup>

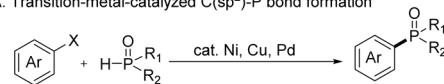


**Figure 1.** Representative bioactive molecules containing aryl phosphonates.

The Hirao cross-coupling reaction, which was first reported in 1981, is one of the most powerful tools in constructing C(sp<sup>2</sup>)–P bonds,<sup>4</sup> in which transition-metal complexes such as Ni,<sup>5</sup> Cu,<sup>6</sup> and Pd<sup>7</sup> are employed to promote this transformation. The cross-coupling partners have been extended from aryl halides to aryl esters,<sup>8</sup> aryl sulfides,<sup>9</sup> aryl boronic acids,<sup>6a,10</sup> aryl silanes,<sup>7c</sup> and aryl amides<sup>11</sup> over the past decades (Scheme 1A). Alternatively, Arbuzov reaction provides another choice to access arylphosphonates.<sup>12</sup> However, the harsh reaction conditions and limited substrate scopes obstructed the wide range of application of the above techniques. Therefore, developing an efficient method with benign conditions to access aryl phosphonates is in high demand. In recent years, photoredox catalysis has become one of the most convenient methods in building new chemical

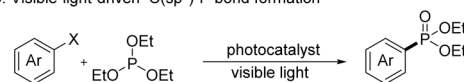
## Scheme 1. Context and This Work

A. Transition-metal-catalyzed C(sp<sup>2</sup>)–P bond formation



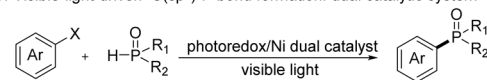
X = Br, I, OR, SR, B(OH)<sub>2</sub>, Si(OEt)<sub>3</sub>, C(O)NRR'

B. Visible-light-driven C(sp<sup>2</sup>)–P bond formation



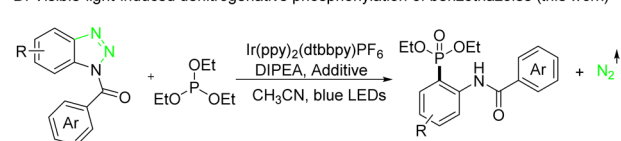
X = H, Br, Cl, OTf

C. Visible-light-driven C(sp<sup>2</sup>)–P bond formation: dual catalytic system



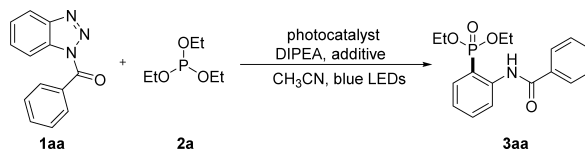
X = I, OTs, OMs, OSO<sub>2</sub>NMe<sub>2</sub>

D. Visible-light-induced denitrogenative phosphorylation of benzotriazoles (*this work*)



bonds,<sup>13</sup> and notably, it exhibits great superiority in the construction of C(sp<sup>2</sup>)–P bonds.<sup>14</sup> For example, Wu<sup>15</sup> and Lei<sup>16</sup> simultaneously reported the direct C–H phosphorylation of heteroaromatic compounds catalyzed by organic dyes (Scheme 1B). Then, König and co-workers disclosed a rhodamine 6G-catalyzed phosphorylation of aryl halides, and soon after, they realized the phosphorylation of arenes and heteroarenes (Scheme 1C).<sup>17</sup> Recently, Xiao and co-worker developed the first C(sp<sup>2</sup>)–P bond formation from aryl iodide combination of Ir(ppy)<sub>2</sub>(dtbbpy)PF<sub>6</sub> with Ni(cod)<sub>2</sub> as catalysts.<sup>18</sup> A similar dual catalytic system could facilitate the phosphorylation of alkenyl and aryl C–O bonds.<sup>19</sup> Never-

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Table 1. Optimization of Reaction Conditions<sup>a</sup>


entry	solvent	photocatalyst	additive	yield (%) <sup>b</sup>
1	CH <sub>3</sub> CN	[Ir(dF(CF <sub>3</sub> )ppy) <sub>2</sub> (dtbbpy)]PF <sub>6</sub>	--	33
2	CH <sub>3</sub> CN	[Ir(ppy) <sub>2</sub> (dtbbpy)]PF <sub>6</sub>	--	66
3	CH <sub>3</sub> CN	<i>fac</i> -Ir(ppy) <sub>3</sub>	--	48
4	DMF	[Ir(ppy) <sub>2</sub> (dtbbpy)]PF <sub>6</sub>	--	39
5	DCE	[Ir(ppy) <sub>2</sub> (dtbbpy)]PF <sub>6</sub>	--	36
6	DMSO	[Ir(ppy) <sub>2</sub> (dtbbpy)]PF <sub>6</sub>	--	57
7	CH <sub>3</sub> CN	[Ir(ppy) <sub>2</sub> (dtbbpy)]PF <sub>6</sub>	(PhCO) <sub>2</sub> O	99
8 <sup>c</sup>	CH <sub>3</sub> CN	[Ir(ppy) <sub>2</sub> (dtbbpy)]PF <sub>6</sub>	(PhCO) <sub>2</sub> O	n.d.
9 <sup>d</sup>	CH <sub>3</sub> CN	[Ir(ppy) <sub>2</sub> (dtbbpy)]PF <sub>6</sub>	(PhCO) <sub>2</sub> O	n.d.
10 <sup>e</sup>	CH <sub>3</sub> CN	--	(PhCO) <sub>2</sub> O	23

<sup>a</sup>Reaction conditions: **1aa** (0.1 mmol), **2a** (0.3 mmol), photocatalyst (1.0 mol %), DIPEA (0.3 mmol), (PhCO)<sub>2</sub>O (0.2 mmol), CH<sub>3</sub>CN (1.0 mL), 15 W blue LEDs, rt, 8 h. ppy = 2-phenylpyridine, dtbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine. <sup>b</sup>Isolated yield. <sup>c</sup>In the dark. <sup>d</sup>No DIPEA. <sup>e</sup>Irradiated time prolonged to 30 h.

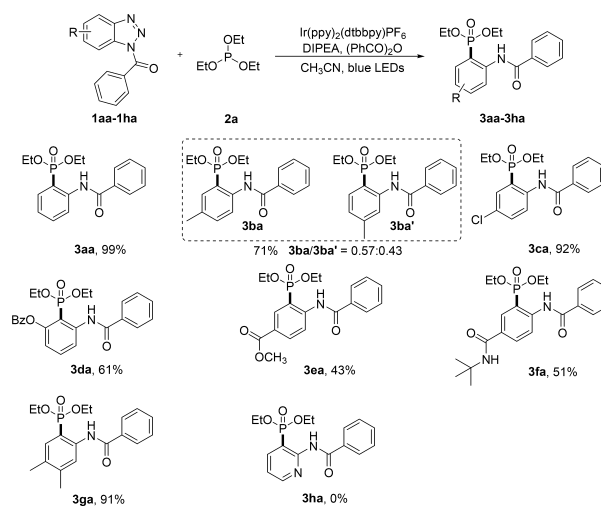
theless, compared with C(sp<sup>2</sup>)-P bond construction catalyzed by transition metals that has been well developed in past decades, reactions conducted under mild conditions, such as organic photocatalysis, are still in their infancy.

Benzotriazoles, the unique structural motif which tends to denitrogenate for construction of new bonds, have been developed as useful synthons in metal-catalyzed reactions. For example, very recently, Tang et al. reported a palladium-catalyzed Suzuki coupling and carbonylative Suzuki coupling by employing benzotriazoles and boronic acids as reactants.<sup>20</sup> Moreover, Glorius and co-workers disclosed that benzotriazoles could serve as precursors of aryl radicals in photochemical reactions.<sup>21</sup> Therefore, we were intrigued to choose benzotriazoles as masked diazoniums to build C(sp<sup>2</sup>)-P bonds through a photoredox catalytic process. Herein, we report a visible-light-induced denitrogenative phosphorylation reaction of benzotriazoles, and this protocol provides an efficient approach for preparation of diverse substituted aryl phosphonates under mild conditions (Scheme 1D).

The initial experiment was carried out using 1-(benzoyl)-benzotriazole (**1aa**) as the model substrate, triethyl phosphite as the phosphorylation agent, and Ir(ppy)<sub>2</sub>(dtbbpy)PF<sub>6</sub> as catalyst at room temperature in DMSO. To our delight, after irradiating with 15 W blue LEDs for 10 h, the product **3aa**, an important intermediate in the synthesis of benzoxaphospholenes,<sup>22</sup> was obtained in 61% yield (for details, see Supporting Information (SI), Table S1). After a series of condition screenings, we found CH<sub>3</sub>CN to be the optimal solvent, Ir(ppy)<sub>2</sub>(dtbbpy)PF<sub>6</sub> to be the most efficient catalyst, and P(OEt)<sub>3</sub> (3.0 equiv) to be the best phosphorylation agent, respectively (SI, Tables S2 and S3). Besides, addition of (PhCO)<sub>2</sub>O could improve the yield from 66% to 99%, probably due to its protective effect for benzotriazoles in the reductive quenching (Table 1, entry 2 vs entry 7).<sup>21c</sup>

With the optimized conditions in hand, we then investigated the scope of benzotriazoles. As shown in Scheme 2, benzotriazoles bearing electron-withdrawing or electron-donating groups could smoothly undergo the phosphorylation with P(OEt)<sub>3</sub>. Methyl- and Cl-substituted benzotriazoles afforded corresponding products **3ba** (**3ba'**) and **3ca** in 71% and 92% yields, respectively. Other functional groups, such as

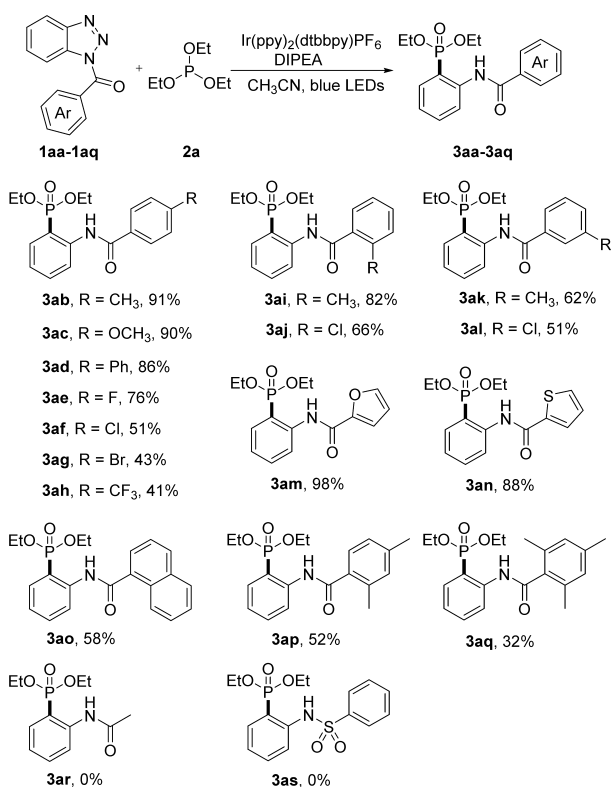
## Scheme 2. Visible-Light-Induced C-P Bond Formation: Scope of Benzotriazoles<sup>a,b</sup>



<sup>a</sup>Reaction conditions: **1aa-1ha** (0.1 mmol), **2a** (0.3 mmol), Ir(ppy)<sub>2</sub>(dtbbpy)PF<sub>6</sub> (1.0 mol %), DIPEA (0.3 mmol), (PhCO)<sub>2</sub>O (0.2 mmol), CH<sub>3</sub>CN (1.0 mL), 15 W blue LEDs, rt, 10 h. <sup>b</sup>Isolated yield.

ester (**3da**, **3ea**) and amide groups (**3fa**), were also compatible with the standard conditions. Notably, multisubstituted phosphonate **3ga** was obtained in 91% yield by employing 5,6-dimethyl benzotriazole as a substrate. Further investigation showed that the heterotriazole compound was not suitable for the reaction conditions; for example, no desired product **3ha** was detected when the phenyl group was switched to the pyridine ring.

We next investigated the substituent effect on the nitrogen atom of benzotriazoles, and the results are listed in Scheme 3. It was found that substrates with different substituents on *para*-, *ortho*-, and *meta*-position of the aryl group were applicable to the standard conditions. For example, benzotriazoles with a *para*-methyl or methoxyl group gave **3ab** and **3ac** in relatively high yields (91% and 90%, respectively). It seems that the electronic effect has influenced the result; e.g.,

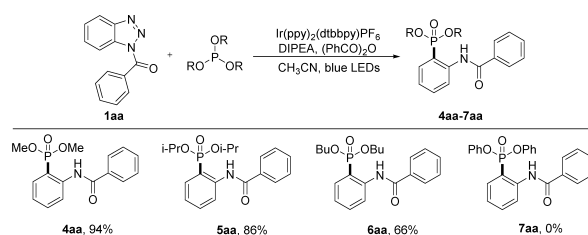
**Scheme 3. Visible-Light-Induced C–P Bond Formation: Scope of Aryl Groups<sup>a,b</sup>**


<sup>a</sup>Reaction conditions: **1aa–1aq** (0.1 mmol), **2a** (0.3 mmol),  $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$  (1.0 mol %), DIPEA (0.3 mmol),  $\text{CH}_3\text{CN}$  (1.0 mL), 15 W blue LEDs, rt, 10 h. <sup>b</sup>Isolated yield.

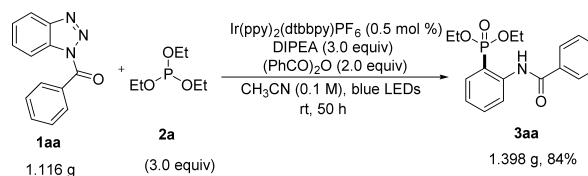
substrates bearing electron-withdrawing groups at *para*-position of the aryl fragment yielded the desired products in lower yields (**3ad–3ah**). Substrates bearing a methyl or chlorine on the *ortho*-position of the carbonyl group delivered phosphorylation products in yields of 82% and 66%, respectively (**3ai**, **3aj**). In addition, the yields decreased slightly when the groups were on the *meta*-position (**3ak**, **3al**). Interestingly, the reaction protocol could also be applied to substrates with heterocyclic or fused aryl groups; e.g., **3am** and **3an** were obtained in excellent yields. Further investigation showed that substrates with multisubstituents on the aryl group also could yield the corresponding products, e.g., **3ap** and **3aq**. Unfortunately, no desired products were obtained when acetyl or benzenesulfonyl was substituted on the nitrogen of benzotriazoles (**3ar** and **3as**).

We also examined the scope of phosphite coupling partners by subjection of various trialkyl phosphites to the standard reaction conditions which delivered the corresponding products in good to excellent yields (Scheme 4). The results indicate that the steric hindrance of phosphites has a negative effect on the yield of product. For example, **4aa** was obtained in 94% yield, while no desired product was obtained when  $\text{P}(\text{OPh})_3$  was used as phosphorylation agent (**7aa**).

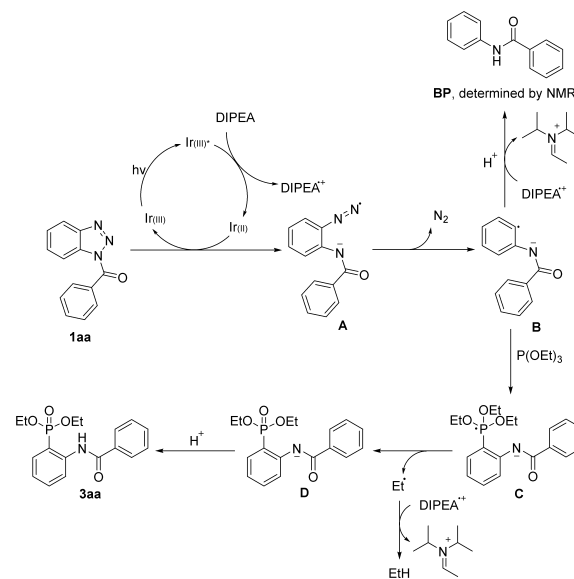
In order to demonstrate the utility of this protocol, we performed a gram-scale reaction of **1aa** with **2a**, in which the loading of  $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$  was decreased to 0.5 mol %. Finally, the corresponding product **3aa** was obtained in 84% yield when the irradiation time was prolonged to 50 h (Scheme 5).

**Scheme 4. Visible-Light-Induced C–P Bond Formation: Scope of Phosphites<sup>a,b</sup>**


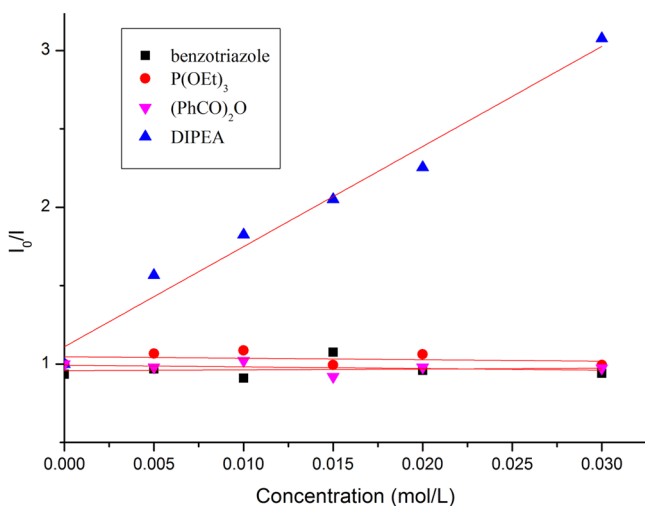
<sup>a</sup>Reaction conditions: **1aa** (0.1 mmol),  $\text{P}(\text{OR})_3$  (0.3 mmol),  $\text{Ir}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$  (1.0 mol %), DIPEA (0.3 mmol),  $(\text{PhCO})_2\text{O}$  (0.2 mmol),  $\text{CH}_3\text{CN}$  (1.0 mL), 15 W blue LEDs, rt, 10 h. <sup>b</sup>Isolated yield.

**Scheme 5. Gram-Scale Reaction**


Based on the previous literature<sup>17a,21c</sup> and the experimental results, we propose the reaction mechanism in Scheme 6. After

**Scheme 6. Proposed Reaction Mechanism**


irradiation with visible light, the excited state of the photocatalyst  $\text{Ir}^{\text{III}}(\text{ppy})_2(\text{dtbbpy})\text{PF}_6$  ( $E_{1/2}^{*\text{III}/\text{II}} = +0.66$  V vs SCE)<sup>23</sup> was formed which was quenched by DIPEA ( $E_{1/2}^{\text{red}} = +0.65$  V vs SCE in  $\text{CH}_3\text{CN}$ ),<sup>24</sup> to afford the reduced photocatalyst  $\text{Ir}^{\text{II}}(\text{ppy})_2(\text{dtbbpy})$ . The above case is in accordance with the result of the fluorescence quenching experiment, in which only DIPEA could quench the excited catalyst (Figure 2). Then benzotriazole is reduced by  $\text{Ir}^{\text{II}}(\text{ppy})_2(\text{dtbbpy})$  to give a ring-opened radical anion (A) through a single-electron-transfer process, regenerating the photocatalyst. The denitrogenation of radical anion (A) led to the aryl radical anion (B), which could abstract a hydrogen atom from DIPEA<sup>•+</sup> to yield the NMR-detectable byproduct N-phenylbenzamide (BP). When the aryl radical anion B was



**Figure 2.** Stern–Volmer luminescence quenching experiments. The quenching experiments were carried out in a CH<sub>3</sub>CN solution of [Ir(ppy)<sub>2</sub>(dtbbpy)](PF<sub>6</sub>) (10<sup>−4</sup> M), and variable concentrations of benzotriazole, P(OEt)<sub>3</sub>, (PhCO)<sub>2</sub>O, and DIPEA (diisopropylethylamine) were added, respectively, λ<sub>ex</sub> = 420 nm, λ<sub>em</sub> = 570 nm.

reacted with P(OEt)<sub>3</sub>, the unstable phosphoranyl radical anion (C) containing a C(sp<sup>2</sup>)–P bond<sup>12b</sup> was formed, which tended to release an ethyl radical to yield the intermediate D. The final aryl phosphonate product **3aa** was produced by abstraction of a proton.

In summary, we have developed a mild and efficient photocatalytic method for the C(sp<sup>2</sup>)–P bond formation via a denitrogenative coupling of benzotriazoles with phosphites. The substrate scope indicates that this protocol is compatible with various functional groups. Additionally, we demonstrated the synthetic application of the photochemical reaction by a scaled-up experiment. Mechanistic study discloses that the aryl radical is generated through a reductive denitrogenation of benzotriazole.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02288.

Experimental procedures and <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra for new compounds (PDF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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