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# Visible-light-induced denitrogenative phosphorylation of benzotriazinones: a metal- and additive-free method for accessing *ortho*-phosphorylated benzamide derivatives

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Metal-free, visible-light-induced denitrogenative phosphorylation of 1,2,3-benzotriazinones was achieved. With the use of eosin Y as a photoredox catalyst, *N*,*N*-diisopropylethylamine as a base, CH<sub>3</sub>CN-H<sub>2</sub>O as a solvent and sunlight or blue LED as a light source, a variety of aryl-phosphonates, -phosphinates, and -phosphine oxides were efficiently prepared. In addition, B<sub>2</sub>pin<sub>2</sub> instead of P-nucleophiles as a radical acceptor was also demonstrated. The key advantages of this newly developed method are the clean reaction profile, use of low-cost organic-dye catalyst, energy-efficiency, broad substrate scope, good to excellent yields and large-scale synthetic applicability. The gram-scale synthesised compounds could be isolated pure just upon extraction, followed by re-crystallisation; no tedious chromatographic purification was required.

# Introduction

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Organophosphorus compounds are widely utilised in the fields of pharmaceutical<sup>1</sup>, functional material<sup>2</sup> and agricultural chemistry,<sup>3</sup> particularly aromatic phosphorus compounds act as useful ligands in transition-metal-catalysed reactions.<sup>4</sup> Consequently considerable attention has been paid to the study of aryl-P bonds formation and various strategies for the synthesis of these scaffolds have been established over the past few decades. Pioneered by Hirao,<sup>5</sup> the transition-metal-catalysed phosphorylation of different aryl precursors such as arylhalides, aryl boronic acids, aryl mesylates, triarylbismuths, arylnitriles, aryl sulfides, arylsilanes and aroylhydrazides with phosphorus-based nucleophiles has seen an explosion of interest.<sup>6</sup> Although remarkable achievements have been made in this field, high reaction temperature as well as long reaction time are still needed.

Over the past several years, transition-metal-triggered denitrogenative annulation of 1,2,3-benzotriazin-4(3*H*)-ones with various  $\pi$ -compounds provided an applicable route to heterocyclic skeletons (Scheme 1A).<sup>7</sup> This synthetic strategy has aroused great attention due to the use of benzotriazinones as a versatile and important building block, which can be easily prepared from commercially available methyl anthranilate. Besides, nitrogen is the only byproduct in the reactions. Recently, Yu *et al.* discovered an iridium-polypyridyl complex catalysed denitrogenative alkyne insertion of 1,2,3-benzotriazinones for the preparation of isoquinolones via a radical mechanism (Scheme 1B).<sup>8</sup> Apart from

A. Ni(0)-catalyzed denitrogenative transannulation  $O = \frac{Ni(cod)_2/L}{N} = \frac{N^2}{N}$ 



C. Ni(0)-catalyzed denitrogenative ortho-functionalization





E. Organic-dye-catalyzed denitrogenative *ortho*-phosphorylation (this work)



Scheme 1. Denitrogenative reactions of benzotriazinones.

cyclisation products, nickel-catalysed *ortho*-alkenylated, -arylated and -alkylketoned benzamides were successfully synthesised from benzotriazinones by the research groups of Mannathan,<sup>9a</sup> Cheng<sup>9b</sup> and Li (Scheme 1C).<sup>9c</sup> The Mannathan group also reported an efficient palladium-catalyzed *ortho*-alkynylation reaction of 1,2,3-

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benzotriazinones with aromatic terminal alkynes (Scheme 1D).<sup>7g</sup> Although the use of transition-metal catalysts in the synthesis of fine chemicals and pharmaceutical intermediates has become common in the last few decades, the use of transition metals often entails additional procedures to reduce the content of the residual metals and improve the quality of pharmaceutical ingredients.<sup>10</sup>

Photoredox catalysis has emerged as a powerful and reliable tool for the construction of C-C and C-heteroatom bonds because of its sustainable and economy friendly characteristics. Myriad elegant works of visible-light-induced reaction have been well documented for years.<sup>11</sup> From the environmental and economic points of view, organic-dye is an attractive alternative to expensive and multi-step prepared iridium and ruthenium polypyridyl complexes.<sup>12</sup> Thus, metal-free photocatalytic system has been documented as a promising approach for modern organic synthesis. However, arylation of phosphorus reagents via a single-electron-transfer (SET) process under environment-friendly and metal-free conditions are relatively scarce.<sup>13</sup> Given our ongoing efforts to the exploration of green methods of C-P bond construction,14 herein, we report the convenient and efficient tactic for the synthesis of aromatic phosphorus via organic-dye-catalysed denitrogenative phosphorylation of 1,2,3benzotriazin-4-(3H)-ones under the irradiation of blue light or sunlight without any metal catalysts or additives (Scheme 1E).

# **Results and discussion**

A preliminary optimization of the reaction conditions was carried out with 1,2,3-benzotriazinone 1a and triethyl phosphite 2a as the model substrates (Table 1). A mixture of both compounds, N,Ndiisopropylethylamine (DIPEA) and a photocatalyst was irradiated with LEDs under an argon atmosphere. To our delight, in the presence of fluorescein as a photocatalyst, the reaction in DMSO was irradiated by blue LEDs, affording the desired product **3a** in 48% yield (entry 1). Encouraged by this result, other cheap and readily available organic dyes such as rhodamine B, rhodamine 6G, eosin Y, eosin B and Na<sub>2</sub>eosin Y were next examined (entries 2-6), and eosin Y delivered 3a in a yield of 54% (entry 4). In order to further improve the efficiency of the reaction, many solvents instead of DMSO were investigated, 3a was obtained in a similar yield when the reaction was performed in MeCN or water (entries 7 and 8), and other solvents such as DCE, DMF, THF, acetone and EtOH did not provide satisfactory results (entry 9). Pleasingly, the targeted product 3a was detected in 85% yield in the mixed solvent of MeCN (2 mL) and H<sub>2</sub>O (0.1 mL) at room temperature for 90 min (entry 10). The amount of H<sub>2</sub>O seemed to significantly affect the reaction (entries 7-10). Furthermore, a 93% yield was achieved with the mixed solvent of MeCN (2 mL) and H<sub>2</sub>O (0.3 mL) application (entry 11). Further increasing the amount of H<sub>2</sub>O to 0.5 mL, however, resulted in 3a with a slightly lower yield (entry 12). From an environmental and practical point of view, we were intrigued to use abundant sunlight for activating this chemical transformation. To our delight, the reaction under sunlight could complete within 6 h with a yield of 90% (entry 13). The reaction didn't work without light even at 60 °C (entry 14). Control experiments without DIPEA or catalyst gave no desired product at all (entries 15 and 16).

Table 1	Ontimisation	of the reaction	conditions <sup>a</sup>
I ADIC I.	Optimisation	of the reaction	conuntions

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	N <sup>-Ph</sup>	DIPEA (2 equiv) PC (5 mol %)	P <sup>_0</sup> O ↓ ↓ .Ph		
N	, + P(OEt)₃ − ∠N 1a 2a	Solvent, rt, 90 min Blue LEDs (30 W)	Y N H 3a		
Entry	Photocatalyst	Solvent (mL)	Yield(%) <sup>b</sup>		
1	Fluorescein	DMSO	48		
2	Rhodamine B	DMSO	40		
3	Rhodamine 6G	DMSO	7		
4	Eosin Y	DMSO	54		
5	Eosin B	DMSO	42		
6	Na <sub>2</sub> Eosin Y	DMSO	32		
7	Eosin Y	MeCN	58		
8	Eosin Y	$H_2O$	49		
9	Eosin Y	Solvent <sup>c</sup>	<33		
10	Eosin Y	MeCN/H <sub>2</sub> O(0.1 mL)	85		
11	Eosin Y	MeCN/H <sub>2</sub> O(0.3 mL)	93(91) <sup>d</sup>		
12	Eosin Y	MeCN/H <sub>2</sub> O(0.5 mL)	85		
13 <sup>e</sup>	Eosin Y (sunlight)	MeCN/H <sub>2</sub> O(0.3 mL)	90		
14 <sup>f</sup>	Eosin Y (dark)	MeCN/H <sub>2</sub> O(0.3 mL)	0		
15 <sup>g</sup>	Eosin Y	MeCN/H <sub>2</sub> O(0.3 mL)	0		
16	-	MeCN/H <sub>2</sub> O(0.3 mL)	0		
-D	11.1 A A	e 1 11 1	6 4 (0 9		

<sup>a</sup>Reaction conditions: the reaction were performed with mixtures of **1a** (0.2 mmol), **2a** (0.3 mmol), base (0.4 mmol) and the photocatalyst (5 mol%) in the solvent (2.0 mL) at room temperature under irradiation by blue LEDs (30 W) for 90 min. <sup>b</sup>Yield of **3a**, determined by <sup>31</sup> P NMR analysis of the crude reaction mixture using "C<sub>8</sub>H<sub>17</sub>P(O) ( $\delta$ : 48 ppm) as an internal standard. <sup>c</sup>Solvent: DCE, DMF, THF, acetone, EtOH were used. <sup>d</sup>Value in parentheses indicates the isolated yield. <sup>c</sup>The reaction worked with sunlight (25-30 °C). <sup>f</sup>The reaction was carried out at 60 °C in the darkness. <sup>g</sup>Without DIPEA.

With the optimal reaction conditions identified, the scope of this visible-light-catalysed denitrogenative ring-opening of 1,2,3benzotriazin-4-(3H)-ones for the synthesis of ortho-phosphorylated aryl amide derivatives was investigated (Table 2). It was found that 1,2,3-benzotriazin-4-(3H)-one substrates possessing various functional groups, such as alkyl, halogens, trifluoromethyl, ester, ether and thioether at different positions on the benzene ring 1 could be employed in this reaction, readily affording the respective products in good to excellent yields (74-91%). Besides, substrates with a multisubstituted benzene ring 1 were also well tolerated (3n-3o). Notably, N-napthyl, N-pyridyl and N-styrenyl substrates proceeded smoothly in the system to give corresponding phosphorylated products **3p-3s** in moderate yields (74-82%). Subsequently, we turned our attention to explore the scope of substituents on the benzene ring 2. As expected, both electron-deficient groups (such as -CO<sub>2</sub>Me, -Cl and -Br) and electron-rich groups (such as -Me and -OMe) on the benzene ring 2 did not disturb the efficiency of this transformation and the expected products (3t-3x) were isolated in yields range from 81 to 87%. Significantly, the reaction proceeds well in the presence of a reactive furan ring, leading to the thiophene-derived phosphonate 3y in 87% yield. Unfortunately, substrates bearing an aliphatic chain instead of aryl group at the nitrogen atom were unreactive under standard conditions and can be almost fully recovered probably due to the unstable of radical anion intermediate formed during the reaction (3z and 3aa). Those results clearly revealed that an aryl group at the nitrogen atom was necessary to stabilise the key intermediate and the electronic and steric factor of the aryl groups had a negligible effect on the coupling reactivity. Furthermore, sunlight as a light

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PhO

FtO

Ph

Ph

.Ph

\_Ph

N<sup>Ph</sup>

**4e**. 0%

4f, 89% (83%)

4g, 86% (81%)

Q

source could also effectively promote the reaction. When the reaction tube was put on the window sill under sunlight for 6 hours without stirring, the reaction mixture became turbid, indicating an ongoing reaction and affording corresponding phosphorylated products 3a-3x in satisfied yields.



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phosphine oxides (4g-4i), which are important precursors to triarylphosphine ligands,<sup>4</sup> could be prepared in high wilds under the optimal conditions. Furthermore, the reactions could also be conducted by using sunlight as a light source in MeCN-H<sub>2</sub>O at 25-30 °C and gave corresponding products in good yields. Obviously, this organic-dye-catalysed cleavage of C-N and N-N bonds provides a facile route for the preparation of various valuable aryl-phosphonates and -phosphine oxides.

## Table 3. Scope of P-nucleophiles<sup>a</sup>



Reaction conditions: 1 (0.2 mmol), 2a (0.3 mmol), DIPEA (0.4 mmol), eosin Y (5 mol%), MeCN (2.0 mL), H<sub>2</sub>O (0.3 mL), room temperature, blue LEDs (30 W), stirring under argon for 90 min. Isolated yield. Yields in parentheses determined by <sup>31</sup>P NMR analysis using  ${}^{n}C_{8}H_{17}P(O)$  ( $\delta$ : 48 ppm) as an internal standard and the reaction irradiated by sunlight at 25-30 °C for 6 h.

3aa, trace

The scope of other phosphites was also examined to further demonstrate the generality of this methodology. As depicted in Table 3, apart from 2a, other phosphites such as P(OMe)<sub>3</sub>, P(O<sup>i</sup>Pr)<sub>3</sub> and P(O<sup>n</sup>Bu)<sub>3</sub> were all compatible in this reaction providing 4a, 4b, 4c and 4d in yields of 90%, 87%, 86% and 81%, respectively. It is a pity that the reaction was completely blocked when triphenylphosphite was taken as a substrate. However, benzotriazinones undergo phosphorylation successfully with 2f and 2g to deliver the target products (4f-4i) with excellent reaction efficiency. Triaryl tertiary



Scheme 2. Gram-scale preparation of 3a and 4i.

To examine the synthetic utility of this transformation gram-scale experiments were carried out (Scheme 2). Compound 3a and 4i were

3z. 0%

 $Ar = 4 - C_6 H_4 C I$ 

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obtained with high efficiency in the yields of 82% and 78% after prolonging the blue LED irradiation time to 24 h. The pure gram-scale synthesized compounds were isolated just upon extraction, followed by re-crystallization using a petroleum ether/AcOEt mixture as the solvent; no tedious chromatographic purification was required. Furthermore, sunlight could also effectively promote the reaction, affording compound **3a** in 78% yield.

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Furthermore, the luminescence of eosin Y with excitation at 575 nm could be readily quenched by DIPEA (Figure 1, see ESI). This luminescence quenching is most likely due to photoinduced electron transfer.



Figure 1 Luminescence quenching experiments.



Scheme 3. Investigation of the reaction mechanism.

To understand the mechanism, further experiments were conducted (Scheme 3). Only a trace amount of **3a** was detected when 2,2,6,6-tetramethyl-1-piperidinyloxy(TEMPO) was added

to the reaction system as a radical inhibitor. Recently, significant progress has been made in C-B bond formation though a singleelectron transfer process.<sup>15</sup> Diboron (B<sub>2</sub>pin<sub>2</sub>) as a good radical acceptor could be applied to this system to produce the corresponding borylated products 6a and 6b in good yields. These results suggest that this reaction may involve a radical process. Based on the above results and previous reports,<sup>8,13c,13d,16</sup> a plausible mechanism for the visible-lightpromoted denitrogenative of 1,2,3-benzotriazin-4-(3H)-one was proposed. Initially, the exited-stated eosin Y  $(E_{p/2}^{red} = 0.83 \text{ V})^{17}$ was generated under the irradiation of visible light, which was then reductively quenched by DIPEA ( $E_{p/2}^{ox} = 0.63$  V, see ESI). A single-electron transfer between the anion radical eosin Y<sup>--</sup> and benzotriazinone 1 ( $E_{p/2}^{ox} = 2.04$  V, see ESI) took place to produce the radical anion A with the regeneration of ground-state eosin Y. Intermediate A could undergo an elimination of nitrogen to produce the corresponding aryl radical anion intermediate B, which reacted with phosphite 2 to give the unstable phosphoranyl radical C. The anion species D could be obtained by releasing an alkyl radical from C, followed by the abstraction of a proton from water to give the final desired product 3.

# Conclusions

In summary, we have developed an organic-dye-catalysed denitrogenative phosphorylation of 1,2,3-benzotriazin-4-(3H)-ones for the synthesis of aryl-phosphonates, -phosphinates and -phosphine oxides. This method features low-cost organic-dye catalysis, environmental-friendly reaction conditions, broad substrate scope and excellent functional group compatibility. The radical mechanism was verified by control experiments and employment of B<sub>2</sub>pin<sub>2</sub> as a radical acceptor. Moreover, this method can be easily adapted to large-scale preparation. Further investigation of the mechanism and application of this reaction are currently underway.

# Experimental

# Organic-dye-catalyzed denitrogenative phosphorylation of benzotriazinones

A schlenk tube containing benzotriazinone derivatives (1, 0.2 mmol) and eosin Y (0.01 mmol) were evacuated and purged with argon three times. DIPEA (0.4 mmol), phosphorylation reagent (2, 0.3 mmol),  $H_2O$  (0.3 mL) and  $CH_3CN$  (2.0 mL) were sequentially added to the system at room temperature. Then the system stirred at room temperature under the irradiation of 30 W blue LEDs for 90 min (or irradiated by sunlight at 25-30 °C for 6 h). Afterwards, the solvent was removed in vacuum, and residues were purified by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent (2:1) to afford the desired phosphorylation products.

#### Gram-scale preparation of 3a and 4i.

A round flask containing benzotriazinone derivatives 1a, and eosin Y (5 mol%) were evacuated and purged with argon three times, DIPEA (2.0 equiv), phosphorylation reagent 2a (2g) (1.5 equiv), a mixture of H<sub>2</sub>O and CH<sub>3</sub>CN (0.3:2.0) were sequentially added to the system at

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room temperature. Then the system stirred at room temperature under the irradiation of 30 W blue LEDs for 24 hours (or irradiated by sunlight at 25-30 °C for 36 h). Quenched with addition of potassium carbonate and water (6 mL/1 mmol) to pH = 8.5 and extracted with ethyl acetate (3\*60 mL). The combined organic layer were removed in vacuum, dried over with MgSO<sub>4</sub>. Recrystallization using a petroleum ether/AcOEt mixture as the solvent to afford the desired phosphorylation products.

# **Conflicts of interest**

There are no conflicts to declare.

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