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Note	

Organophotoredox-Catalyzed C–H Functionalizations of Benzophospholes

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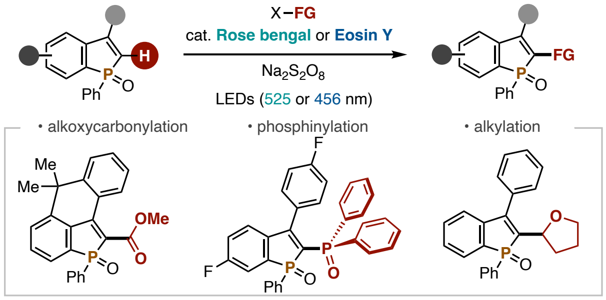
Supporting Information Placeholder



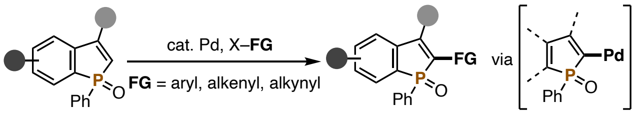
ABSTRACT: An organophotoredox-catalyzed oxidative C–H functionalization of benzophospholes has been developed. The C–H alkoxycarbonylation with methyl carbazate occurs in the presence of Rose bengal, whereas Eosin Y enables the dehydrogenative coupling with secondary phosphine oxides and ethers, delivering the C–H phosphinylated and alkylated products. The scope of coupling partners is complementary to that of conventional metal-promoted C–H activation, thus successfully expanding the chemical space of substituted phospholes accessed by C–H functionalization protocols.

Organophosphorus compounds are indispensable in modern organic chemistry. In particular, the phosphole derivatives have unique optical and physical properties and thus deserve significant attention in the field of material science.[1] Accordingly, the methodology development for creation and decoration of the phosphole ring is one of the most active research subjects in synthetic community.[2] Among them, the C–H functionalization protocol of relatively easily available simple phosphole nuclei can provide a modular approach to highly substituted phosphole derivatives. To date, the metal-based strategy, particularly with palladium catalysts via phosphole-Pd intermediate, has been mainly developed (Scheme 1a).[3,4] However, under metal-promoted conditions, only $C(sp^2)$- and $C(sp)$-functional groups such as aryl, alkenyl, and alkynyl substituents could be introduced. Therefore, further development of new catalyst systems for the introduction of more versatile functional groups into the phosphole core is greatly appealing.

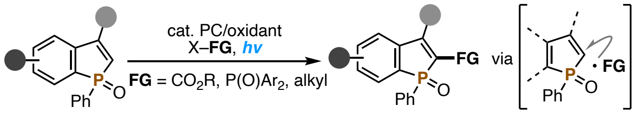
Here, we report C–H alkoxycarbonylation, phosphinylation, and alkylation reactions of benzophosphole oxides under visible-light-promoted organophotoredox catalysis[5] (Scheme 1b): by using the suitable organic photosensitizers and external oxidants, carbazate ester, secondary phosphine oxides, and ethers are successfully coupled with the phosphole ring, via radical species, to form the corresponding C–H functionalized products. The scope of coupling partners is complementary to the aforementioned palladium catalysts, thus increasing the synthetic utility of the C–H functionalization protocol in the synthesis of substituted phosphole derivatives.

Scheme 1. C–H Functionalization Approaches to Substituted Benzophospholes

(a) Pd catalysis via phosphole-Pd intermediates (previous work)

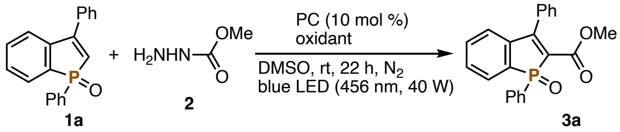


(b) Organophotoredox catalysis via radical intermediates (**this work**)



Optimization studies commenced with 3-pheynlbenzophosphole oxide **1a** (0.050 mmol), which was readily prepared from 1,1-diphenylethene and phenylphosphinic acid in a one-step and scalable manner,[3d,6] and methyl carbazate (**2**; 0.20 mmol) to identify the suitable photocatalyst (PC) and external oxidant (Table 1). In an initial trial, treatment of **1a** with **2** in the presence of Eosin Y (10 mol %, Figure 1) and $Na_2S_2O_8$ (3.0 equiv) in DMSO solvent (1.0 mL) under blue LED irradiation (456 nm, 40 W) afforded the desired C2-alkoxycarbonylation product **3a** in 45% yield (entry 1). Notably, exclusive site selectivity was observed: only C2–H was selectively functionalized over other potentially reactive C–H bonds such as ortho C–Hs of the Ph group on phosphorus. This is probably attributed to the nonaromatic, alkene-like character of phosphole oxide.[7] A trace amount of **3a** was observed even in the absence of PC (entry 2),[8] but no conversion occurred without light (entry 3), confirming that the photopromoted process is a major reaction pathway. Encouraged by the intriguing results, we next investigated several organic PCs (entries 4–7), with Rose bengal proving to be the most performant (entry 4). The choice of external oxidant was also critical: other persulfate-based oxidants, $K_2S_2O_8$ and $(NH_4)_2S_2O_8$, promoted the reaction to some extent (entries 8 and 9), while TBHP and PIDA dramatically decreased the reaction efficiency (entries 10 and 11). Finally, replacement of blue LED with green LED (525 nm) and a slightly higher reaction concentration (0.50 mL of DMSO) further improved the yield to 79% (73% after isolation; entry 13). The reaction could also be conducted on a preparative 1.0 mmol scale (77% isolated yield). The conversion of **1a** was 80%. The prolonged reaction durations increased the conversion but decreased the yield of **3a** because of its gradual decomposition under the reaction conditions (entry 14). We also noticed the following: the corresponding benzophosphole sulfide **1a-S** instead of oxide **1a** also afforded the product **3a-S** but albeit in lower 31% yield (entry 15), possibly suggesting acceleration effects by the stronger electron-withdrawing nature of P=O than P=S;[9] Ru- and Ir-based photocatalysts were also tested, but they gave more complicated mixtures containing **3a** (less than 35%) and unidentified compounds. Other solvents, such as MeCN, DMF, and acetone, resulted in much lower yields (see the Supporting Information for more details).

Table 1. Condition Optimization for the Alkoxycarbonylation of Benzophosphole Oxide 1a with 2 under Photoredox Catalysis[a]



entry	PC	oxidant	yield (%)[b]
1	Eosin Y	$Na_2S_2O_8$	(45)
2[c]	none	$Na_2S_2O_8$	<5
3[d]	Eosin Y	$Na_2S_2O_8$	0
4	Rose bengal	$Na_2S_2O_8$	75
5	Fluorescein	$Na_2S_2O_8$	71
6	Rhodamine B	$Na_2S_2O_8$	51
7	4CzIPN	$Na_2S_2O_8$	0
8	Rose bengal	$K_2S_2O_8$	52
9	Rose bengal	$(NH_4)_2S_2O_8$	69
10	Rose bengal	TBHP	12
11	Rose bengal	PIDA	0
12[e]	Rose bengal	$Na_2S_2O_8$	78
13[e,f]	Rose bengal	$Na_2S_2O_8$	79 (73, 77[g])
14[e,h]	Rose bengal	$Na_2S_2O_8$	60
15[e,f,i]	Rose bengal	$Na_2S_2O_8$	31

[a] Conditions: **1a** (0.050 mmol), **2** (0.20 mmol), PC (0.0050 mmol), oxidant (0.15 mmol), DMSO (1.0 mL), blue LED (456 nm, 40 W), rt, 22 h, N_2. [b] $^{31}P\{^1H\}$ NMR yields with $P(O)(OEt)_3$ as the internal standard. Isolated yields are in parentheses. [c] No PC. [d] In dark. [e] With green LED (525 nm, 40 W). [f] In DMSO (0.50 mL). [g] On a 1.0 mmol scale with two green LEDs. [h] For 48 h. [i] With the phosphole sulfide **1a-S** instead of oxide **1a**. The product was the corresponding sulfide **3a-S**.

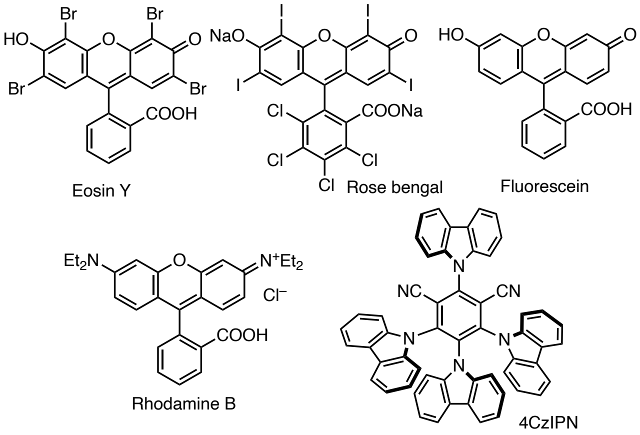
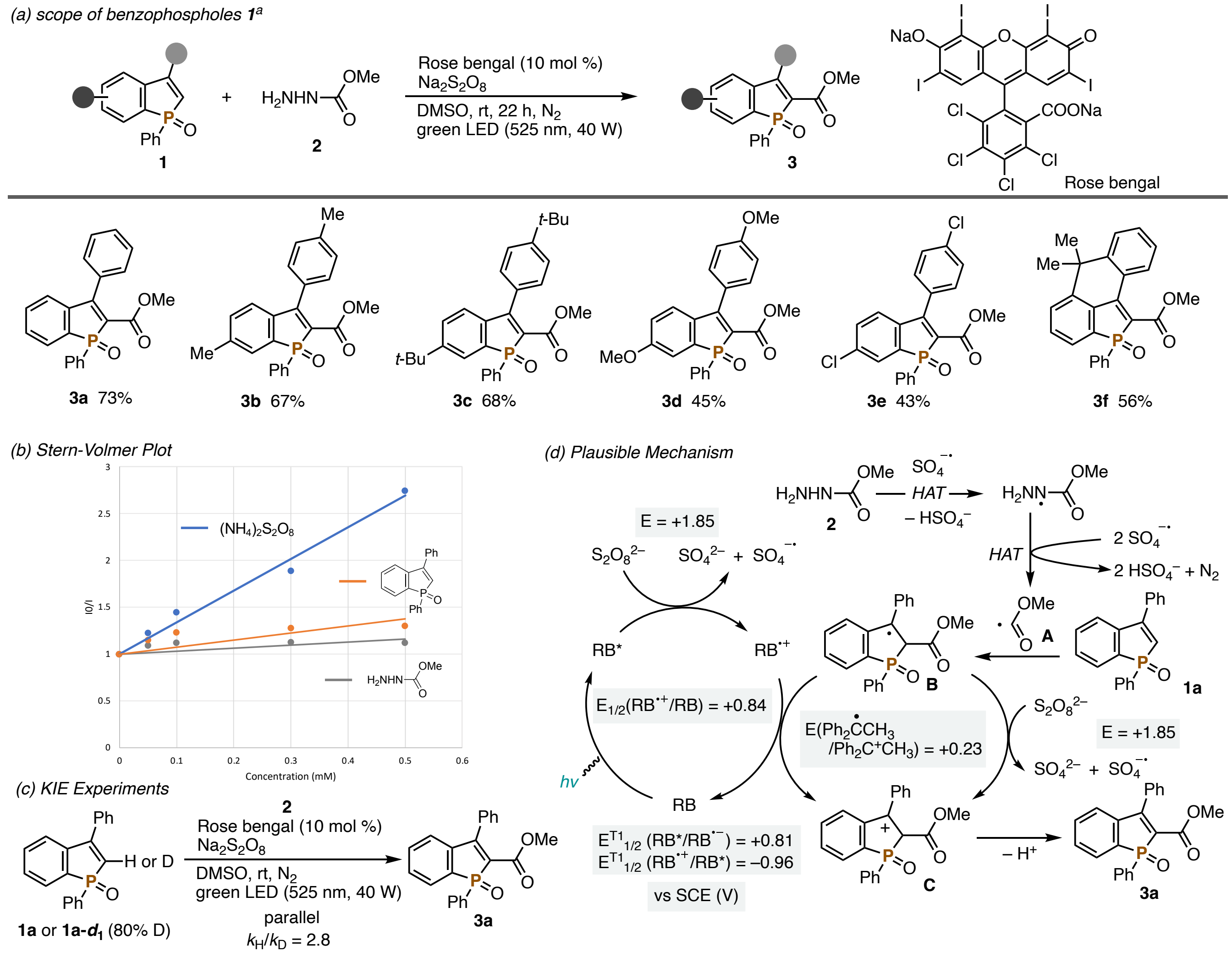


Figure 1. Structures of photocatalysts used in Table 1.

The conditions of entry 13 in Table 1 were applicable to several substituted benzophosphole oxides **1** (Scheme 2a). The electron-neutral (Me, *t*-Bu), -donating (OMe), and -withdrawing (Cl) substituents were tolerated, and the corresponding C2–alkoxycarbonylated benzophospholes **3b**–**e** were obtained in 43–68% yields. The methylene-bridged unique tricyclic system **3f** was also formed in an acceptable yield. We next performed several experiments to gain a mechanistic insight. The Stern-Volmer plot revealed that the effective photoluminescence quenching occurred by the addition of persulfate $(NH_4)_2S_2O_8$,[10] while phosphole **1a** or carbazate **2** gave the negligible impact on the luminescence intensity (Scheme 2b). On the other hand, the deuterium-labeling experiments with **1a** and **1a-*d*1** (80% D) in two different reaction vessels provided a 2.8 value of kinetic isotope effect (KIE), thus suggesting the rate-limiting C–H cleavage of phosphole **1a** (Scheme 2c). On the basis of the above outcomes and literature knowledge, we propose the reaction mechanism of **1a** with **2** as follows (Scheme 2d). First, Rose bengal (RB) is excited by green light and then oxidatively quenched with $Na_2S_2O_8$ to form the $RB^{\bullet+}$ and $SO_4^{-\bullet}$ species.[5b] A subsequent hydrogen-atom-transfer (HAT) sequence between $SO_4^{-\bullet}$ and **2** delivers the methoxycarbonyl radical **A** with the concomitant evolution of N_2 gas.[11] The site-selective radical addition to **1a** is followed by the back electron transfer to $RB^{\bullet+}$ to generate the cation **C**[12] along with completion of the photocatalytic cycle. Final deprotonation afforded observed **3a**. The KIE value observed in Scheme 2c is suggestive of rate-determining deprotonation (**C** to **3a**). From the viewpoint of redox potential, each electron transfer step would be thermodynamically favored. In addition, given its strong oxidation aptitude,[13] the direct

Scheme 2. C–H Alkoxycarbonylation of Benzophospholes 1 with Methyl Carbazate 2



[a] Reaction conditions: **1** (0.050 mmol), **2** (0.20 mmol), Rose bengal (0.0050 mmol), $Na_2S_2O_8$ (0.15 mmol), DMSO (0.50 mL), green LED (525 nm, 40 W), rt, 22 h, N_2. Isolated yields are shown.

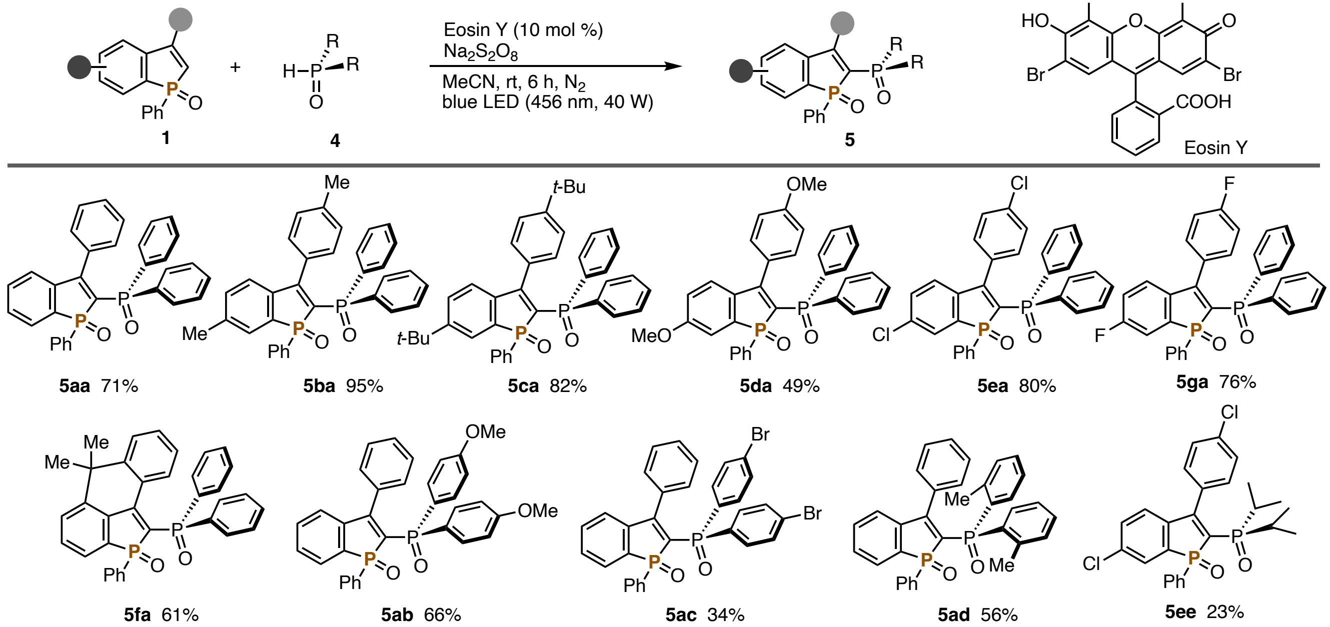
oxidation of **B** with persulfate $S_2O_4^{2-}$ to **C** and $SO_4^{-\bullet}$, namely, radical chain process should also be involved.[14]

As mentioned in Scheme 2d, the in situ generated $SO_4^{-\bullet}$ is considered to be a HAT reagent, thus suggesting its capability of homolytically cleaving other C–H or heteroatom–H bonds with bond dissociation energies (BDEs) similar to carbazate N–H (~83 kcal/mol).[15] After additional optimization studies, pleasingly, we also found secondary phosphine oxides (BDE of P–H ≃ 79 kcal/mol)[16] and alkyl ethers (BDE of αC–H ≃ 92 kcal/mol)[17] to serve as the effective coupling partners under slightly modified conditions using Eosin Y and blue LED in place of Rose bengal and green LED (Scheme 3). For example, the dehydrogenative C2-phosphinylation of **1a** with **4a** proceeded smoothly to afford **5aa** in 71% yield (Scheme 3a). Also in this case, a variety of substituted benzophospholes **1** bearing Me, *t*-Bu, OMe, Cl, and F were tolerated under visible-light-promoted conditions (**5ba–ea** and **5ga**). Particularly noteworthy is the high regioselectivity: in the previous protocols with phosphinylated alkynes as the starting substrates, all attempts to synthesize the related substituted C2-phosphinylated benzophospholes formed a mixture of regioisomers because of the noncontrollable radical rearrangement.[18] In addition, methylene-bridged **5fa** was also successfully prepared. Several substituted diarylphosphine oxides participated in the reaction. The electron-rich, electron-deficient, and sterically demanding diarylphosphinyl groups were also successfully introduced at the C2-position to deliver the corresponding **5ab–ad** in synthetically acceptable yields. The dialkylphosphine oxide could also be used albeit with moderate yield (**5ee**). The αC–Hs of THF, 1,4-dioxane, and diethyl ether were cleaved under similar conditions and coupled with **1a** to form the C–H alkylated **7aa–ac, 7bc**, and **7ec** in good yields (Scheme 3b).[19] Similar to the C–H alkoxylation (Scheme 2a), ca. 80–90% conversion of the phosphole substrate **1** was generally observed in the C–H phosphinylation and alkylation reactions, except for formation of **5ee** (60% conversion).

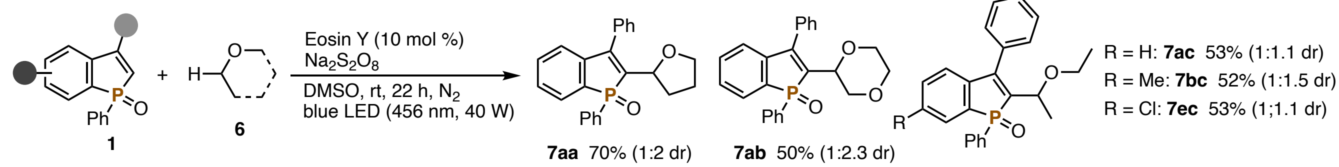
In summary, we have developed organophotoredox-catalyzed oxidative C–H alkoxycarbonylation, phosphinylation, and alkylation reactions of benzophospholes with high regioselectivity. Under the visible-light-promoted photoredox catalysis, the scope of coupling reagents can compensate for the conventional meta-catalyzed C–H activation protocols,

Scheme 3. C–H Phosphinylation and Alkylation of Benzophospholes 1 with Secondary Phosphine Oxides 4 and Ethers 6

*(a) C–H phosphinylation with secondary phophine oxides **4**[a]*



*(b) C–H alkylation with ethers **6**[b]*



[a] Reaction conditions: **1** (0.10 mmol), **4** (0.40 mmol), Eosin Y (0.010 mmol), $Na_2S_2O_8$ (0.30 mmol), MeCN (0.50 mL), blue LED (456 nm, 40 W), rt, 6 h, N_2. Isolated yields are shown. [b] Reaction conditions: **1** (0.050 mmol), **6** (1.0 mL), Eosin Y (0.0050 mmol), $Na_2S_2O_8$ (0.15 mmol), DMSO (0.50 mL), blue LED (456 nm, 40 W), rt, 22 h, N_2. Isolated yields are shown.

thus increasing the synthetic potential of C–H functionalization strategy in the synthesis of highly functionalized and substituted phosphole derivatives of great potential in fields of material chemistry. To the best of our knowledge, this is the first successful example of photoredox-catalyzed C–H functionalizations of phosphole nuclei. Additional mechanistic studies and further development of related photopromoted synthetic methodologies for highly substituted and π-extended phosphole derivatives are ongoing in our laboratory.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are openly available in the published article and its Supporting Information.

Supporting Information

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

^1H, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra, detailed optimization studies, substrate limitation, light ON/OFF experiments, and deuterium-labeling studies (PDF)

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Author Contributions

[§]Y.T. and S.X. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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