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Metal-Free, Visible Light-Photocatalyzed Synthesis of Benzo[*b*]phosphole Oxides: Synthetic and Mechanistic Investigations

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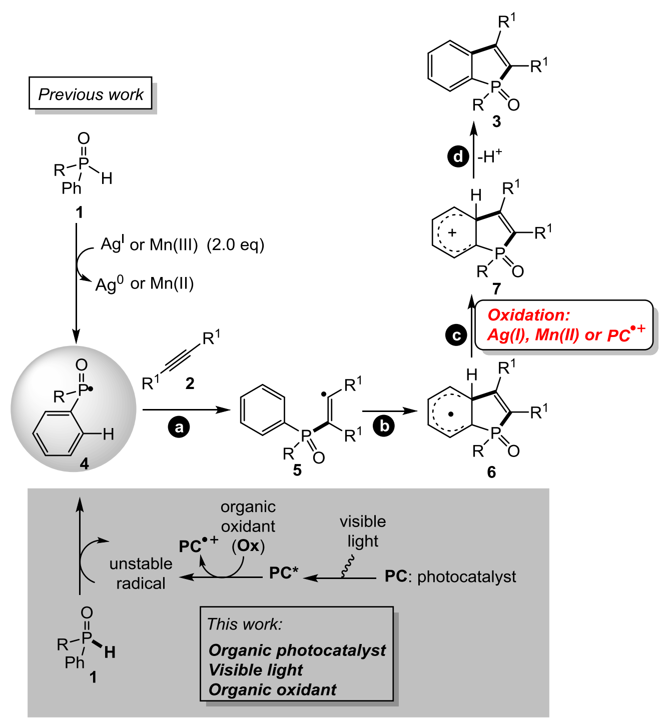
ABSTRACT: Highly functionalized benzo[*b*]phosphole oxides were synthesized from reactions of arylphosphine oxides with alkynes under photocatalytic conditions by using eosin Y as the catalyst and *N*-ethoxy-2-methylpyridinium tetrafluoroborate as the oxidant. The reaction works under mild conditions and has a broad substrate scope. Mechanistic investigations have been undertaken and revealed the formation of a ground state electron donor acceptor complex (EDA) between eosin (the photocatalyst) and the pyridinium salt (the oxidation agent). This complex, which has been fully characterized both in the solid state and in solution, turned out to exhibit a dual role *i.e.* the oxidation of the photocatalyst and the formation of the initiating radicals, which undergoes an intramolecular reaction avoiding the classical diffusion between the two reactants. The involvement of ethoxy and phosphinoyl radicals in the photoreaction has unequivocally been evidenced by EPR spectroscopy.

INTRODUCTION

Due to their unique photophysical and electronic properties, π-conjugated phosphole molecules have become of substantial importance in the burgeoning fields of organic light-emitting diodes (OLEDs) and photovoltaic cells.[1] While synthesis and electronic characterization of these molecules have previously been reported,[1] little is known about benzo[*b*]phosphole oxides, which have recently emerged as promising scaffolds for organic electronics and bioimaging probes.[2] Common synthetic approaches to this type of molecules include treatment of prefunctionalized substrates with strong bases[3] or use of expensive transition metal catalysts.[4] Recently, the groups of Duan, Satoh and Miura simultaneously showed that benzo[*b*]phosphole oxides **3** are accessible through combination of secondary phosphine oxides **1** with alkynes **2** in the presence of a stoichiometric amount of AgOAc (2 equiv) or Mn salts at typically 100°C (Scheme 1).[5] The reaction is depicted as proceeding through a radical pathway, where the phosphinoyl radical **4** is generated upon oxidation of the secondary phosphine oxide **1** with Ag(I) or Mn(III). Subsequent reaction of **4** with the alkyne **2** affords the alkenyl radical **5**. Then, this radical undergoes intramolecular addition to the aryl ring at the *ortho* position of the phosphorus atom. This gives the cyclohexadienyl intermediate **6**, which yields the phosphorus heterocycle **3** upon oxidation and deprotonation. While this approach has proven valuable for the synthesis of numerous benzo[*b*]phosphole oxides **3**, it suffers from disadvantages of requiring high temperature and stoichiometric amounts of metal oxidants.



Scheme 1. Synthesis of benzo[*b*]phosphole oxides **3** through silver or manganese-mediated processes (previous work) and visible photoredox approach (this work).

Based on previous kinetic studies by Turro *et al.*, who measured several bimolecular rate constants of the reactions of phosphinoyl radicals with different substrates, typically ranging from 10^6 to 10^9 M^{-1} s^{-1},[6] one can hypothesize that the addition of **4** to the alkyne **2** (step a in Scheme 1) and the subsequent steps can occur at room temperature. It is therefore likely that the high temperature required in the silver-mediated approach is only required for the formation of the phosphinoyl radical **4**.[7] Thus, it should be possible to develop an approach for generating phosphinoyl radicals under mild reaction conditions at room temperature without requiring expensive transition-metal catalysts or toxic reagents.

Because of the relatively low bond dissociation energies of P–H bonds of phosphine oxides (BDE = 317 kJ/mol for diphenylphosphine oxide),[8] we anticipated that the use of a visible-light photocatalyst (PC)[9] in the presence of a well-selected organic oxidant would, after a photon absorption, reduce the oxidant to generate a radical along with the oxidized form of the photocatalyst ($PC^{\bullet+}$). Two parameters are crucial for the success of the photoredox process: *i*) the formed radical should be able to abstract the P–H hydrogen to form the corresponding radical, and *ii*) the redox potential of ($PC^{\bullet+}$) should be high enough to oxidize the cyclohexadienyl intermediate **6** (step c in Scheme 1) to the corresponding arenium ion **7** and to regenerate ground-state photocatalyst.

RESULTS AND DISCUSSION

To test this hypothesis, we examined the reaction of diphenylphosphine oxide **1a** with diphenylacetylene **2a** in the presence of organic oxidants, bases, and photocatalysts under visible light irradiation. To keep the process as green as possible, only organic photocatalysts, which are known to be inexpensive, environmentally friendly and easy to handle, have been tested.[9j,k] The choice of external oxidant was based on their low redox potentials compared to those of the excited forms of the photocatalysts.

Being recognized as efficient oxidants in photopolymerization reactions, the onium salts **8a-c** were good candidates for our photoreaction.[10] Indeed, apart from their inertness to absorb in the visible region, **8a-c** can easily be reduced by common visible-light excited photocatalysts to generate very energetic radicals thermodynamically capable to abstract hydrogen from phosphine oxides (Figure 1).

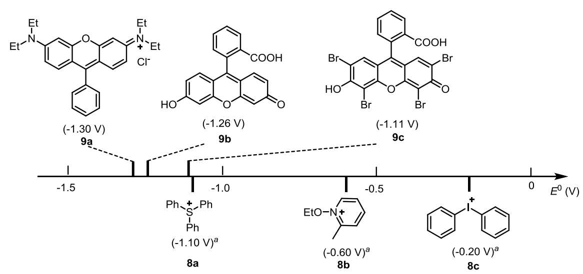
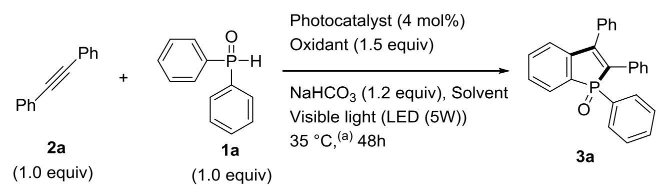


Figure 1. Redox potentials of onium salts **8a–c** and organic dyes **9a–c**. a) Taken from Ref. [10].

In line with our working hypothesis, we were pleased to find that all organic dyes **9a–c** catalyzed the reaction of **1a** with **2a** in the presence of any of the three external oxidants **8a–c** (Entries 1–3). In particular, combination of eosin Y **9c** as a photocatalyst and *N*-ethoxy-2-methylpyridinium **8b** as an external oxidant delivered the desired product in very high yield (95%) under visible light (green LED, λ_{max} = 525 nm, 5 W) irradiation (Entry 8). From the solvents tested, dimethylformamide (DMF) was confirmed to be the solvent of choice (Supporting Information). Moreover, the use of a base was found to be crucial for the reaction, not only to deprotonate the arenium intermediate **7** (Scheme 1), but also to deprotonate the two acidic protons of **9c**, affording the photophysically more active dianionic eosin form, as in the absence of base only 24% of the product was formed (Entry 11).[9j,11] Bromotrichloromethane ($BrCCl_3$), which has previously been employed by Stephenson, König and others as an efficient oxidant for photoredox functionalizations of α–amino carbons,[12] has failed to deliver the desired product (entry 6). This can be rationalized on the basis of previous kinetic investigation by Turro *et al.*, who showed that phosphinoyl radical can react with $BrCCl_3$ with rate constants close to the diffusion limit ($k \approx 10^9$ $M^{-1}s^{-1}$),[12] to give the corresponding halogenated phosphine oxides, which was identified by ^{31}P NMR. Furthermore, changing the base from $NaHCO_3$ to NaOAc resulted in dropping the conversion to about 40% (entry 9, Table 1).

Table 1. Identification of the Optimal Reaction Conditions



Entry	PC	Oxidant	Solvent	Conversion (%)^b
1	**9b**	**8b**^{c}	DMF	37
2	**9a**	**8b**^{c}	DMF	25^c
3	**9c**	**8c**^{c}	DMF	43
4	**9c**	**8a**^{c}	DMF	62
5	**9a**	**8b**^{c}	DMSO	70
6	**9c**	$BrCCl_3$	DMF	0
7	**9c**	**8b**^{c}	DMF	75
8	**9c**	**8b**	DMF	95^d
9	**9c**	**8b**^{c}	DMF	52^e
10	–	**8b**^{c}	DMF	4^f
11	**9c**	**8b**^{c}	DMF	24^g
12	**9c**	–	DMF	0

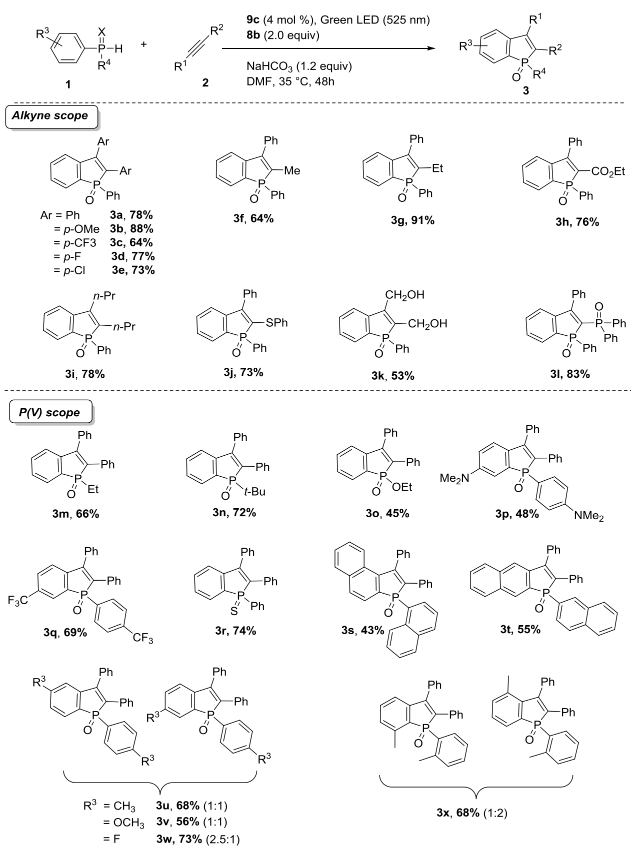
[a] Heating caused by the LED lamp. [b] Determined from ^{31}P NMR spectroscopy using trioctylphosphine oxide as internal standard. [c] Counterion: tetrafluoroborate. [d] Conditions used: **1a** (2 equiv), **2a** (1 equiv), **8b** (2 equiv), $NaHCO_3$ (1.2 equiv). [e] NaOAc was used as a base. [f] Reaction time: 72h. [g] Without a base.

Control experiments highlighted the essential role of the photocatalyst, oxidant, and light in this photoreaction (entries 10 and 11). While less than 4% of background reaction was observed in the absence of **9c** even after a long time irradiation (72h); no product was detected in the absence of **8b** after 24 h.

With the optimized conditions in hand, we applied our protocol for the synthesis of a large variety of benzophosphole oxides derived from different alkynes and phosphine oxides. As depicted in Table 2, diphenylphosphine oxide **1a** reacts smoothly with various alkynes **2** under standard conditions, affording **3** in good to excellent yields (43 to 91%). Remarkably, apart from the tolerance of alcohol and ester groups, complete control of selectivity has been obtained with the tested unsymmetrical alkynes. This regioselectivity can be attributed to the ability of aryl groups to stabilize the formed alkenyl radical (**5**).

Good to excellent yields were also obtained when different pentavalent phosphorus derivatives P(V) were combined with diphenylacetylene **2a**. Notably, in contrast to silver-mediated dehydrogenative annulation, where the reaction of diphenylphosphine sulfide **1r** with diphenylacetylene **2a** does not proceed at all,[5b] presumably due to the high thiophilicity of silver, the same reaction proceeds smoothly under the current protocol (**3r**, 74% yield).

Table 2. Substrate Scope.



Reaction conditions: secondary phosphine oxide (1.0 mmol), alkyne (0.5 mmol), *N*-ethoxy-2-methylpyridinium tetrafluoroborate (1.0 mmol), $NaHCO_3$ (0.6 mmol), eosin Y (0.02 mmol) in 8 mL of DMF and under green light irradiation.

Remarkably, phosphine oxides bearing either dimethylamino (**1p**) or trifluoromethyl (**1q**) groups at the *para* positions of the aromatic ring react with **2a** to afford exclusively the expected regioisomers **3p** and **3q**, respectively in fairly good yields.

Similar to the report of Duan, Satoh and Miura,[5] the desired benzophospholes were formed, along with their regioisomers, resulting from the aryl migration, were formed for the reaction of the diphenylphosphine oxides bearing electron donor or electron acceptor groups at the aromatic rings (**1u**–**x**).[13]

Next, to evaluate the scalability of the reaction, we carried out the reaction of **1a** with **2a** on a gram scale under standard conditions. To our delight, 1.5 g of benzophosphole oxide **3a** was isolated (81% yield), thus proving the effectiveness of our protocol.

In order to gain insights into the mechanism of this new photoredox coupling, we have first recorded the electron paramagnetic resonance (EPR) spectra of the reaction of eosin Y (**9c**) and diphenylphosphine oxide **1a** in the presence of the onium salt **8b** and phenylbenzonitroxide (PBN) **10** as a radical trap in toluene. Under irradiation with LED@530 nm of a mixture of eosin Y **9c** (5×10^{-5} M) and *N*-ethoxy-2-methylpyridinium **8b** (5×10^{-2} M) in *tert*-butylbenzene, a radical characterized by the hyperfine coupling constants hfc (a_N = 13.6 G, a_H = 1.9 G) for the PBN adduct **11** is directly observed (Figure 2a); this radical has been ascribed to $EtO^\bullet$ in agreement with literature data.[14]

Remarkably, when diphenylphosphine oxide **1a** is added in this solution, the phosphinoyl radical **4a** is unequivocally identified along with remaining ethoxy radical (Figure 2b). The hyperfine coupling constants hfc of the phosphinoyl/PBN adduct **12** (a_N = 14.18 G, a_H = 3.03 G, and a_P = 18.76 G) are in perfect agreement with those reported in the literature,[15] thus leaving no doubt as to the role of this intermediate in this photoreaction

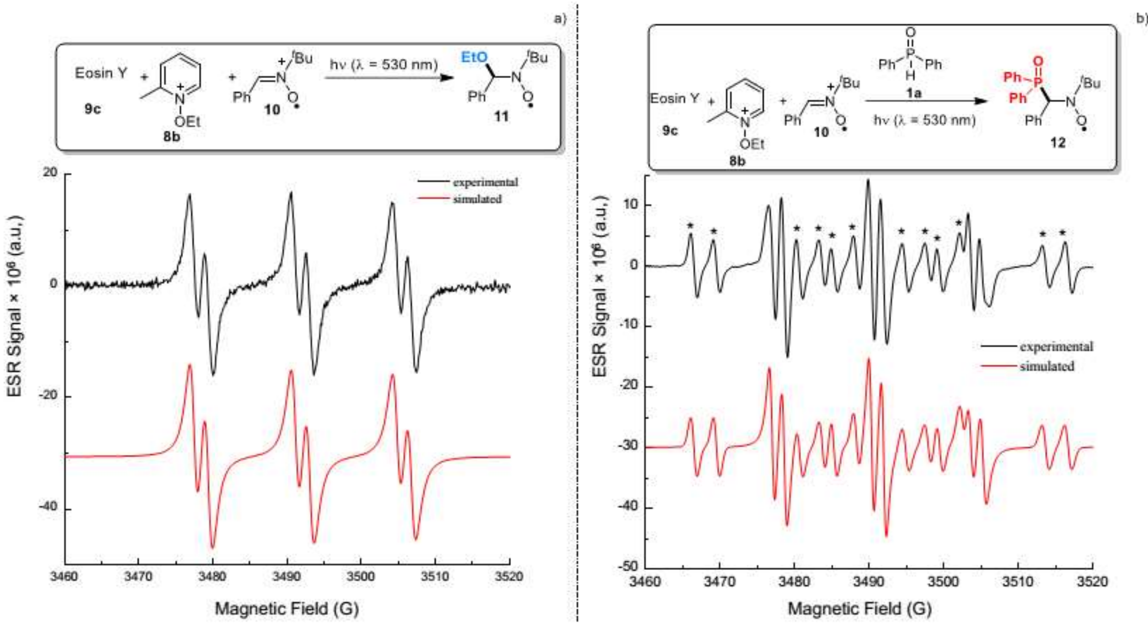


Figure 2. (a) EPR spectra of spin adduct **11** generated in toluene in the presence of eosin Y **9c** (5×10^{-5} M), *N*-ethoxy-2-methylpyridinium **8b** (5×10^{-2} M) and PBN **10** (2×10^{-2} M) at room temperature. (b) EPR spectra of spin adduct **12** generated in toluene in the presence of eosin Y **9c** (5×10^{-5} M), *N*-ethoxy-2-methylpyridinium **8b** (5×10^{-2} M), diphenylphosphine oxide (2×10^{-2}M) and PBN **10** (5×10^{-2} M) at room temperature; the stars are related to the phosphinoyl radical.

Furthermore, UV-vis spectroscopy showed that the addition of different concentrations of *N*-ethoxy-2-methylpyridinium **8b** to a DMF solution of eosin gave rise to the appearance of a red-shifted band (Figure 3). This can be attributed to the formation of a ground state electron donor acceptor (EDA) complex between eosin and the pyridinium salt **8b**. Similar complexes have previously been isolated and characterized by Willner *et al.*, who showed that eosin and derivatives are good donor partners for the formation of EDA complexes.[16]

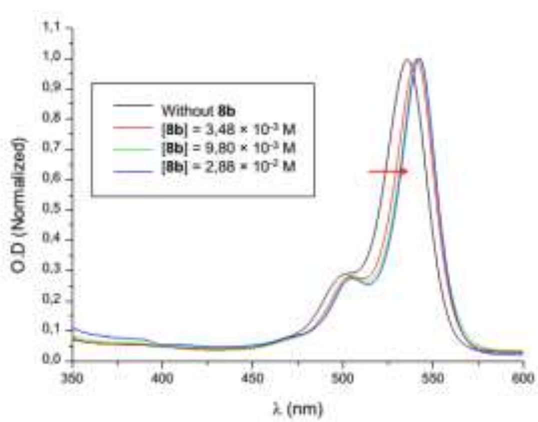


Figure 3. UV-visible spectra of eosin Y (**9c** = 1.0×10^{-5} M) after addition of different concentration of pyridinium **8b** in DMF at 20 °C.

Further evidence for the formation of an EDA complex came from fluorescence spectroscopy, which showed a Stokes shift of the emission peak of the eosin (**9c**) when increasing concentration of the pyridium ion **8b** are added in DMF (Figure S7, Supporting Information).

More importantly, a higher quenching constant ($k_q = 1.8 \times 10^{10}$ M^{-1} s^{-1}) was derived from the Stern Volmer plot, thus attesting of the efficiency of the excited state of the EDA complex to reduce the pyridinium salt **8b** (Figure S8, Supporting Information). In line with this, when the EDA complex (**EY-8b**) is exposed to a green irradiation at 530 nm, a fast and strong photobleaching reaction is observed (Figure 4). This suggests the occurrence of an electron transfer within the EDA complex giving rise to a very fast diffusionless generation of the ethoxy radical.

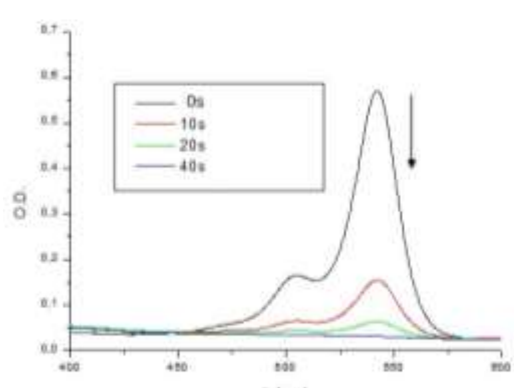


Figure 4. Changes in the UV-visible absorption spectrum of a DMF solution of **EY-8b** (5.9×10^{-6} M) under light irradiation (λ_{max} = 530 nm)–aerated solution.

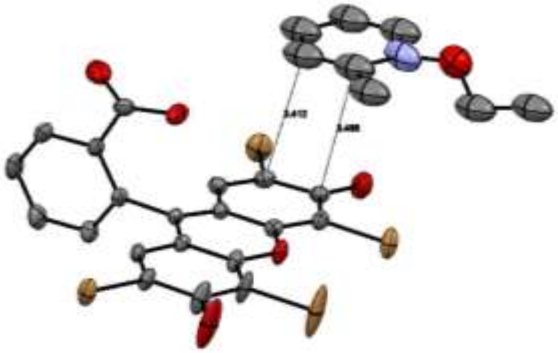


Figure 5. Asymmetric unit of **EY-8b** complex. Displacement ellipsoids are drawn at the 50% probability level. For the sake of clarity, H atoms and disordered pyridinium moiety have been omitted.

The most informative result has however been derived from the isolation of stable dark-red crystals, suitable for an X-ray diffraction analysis, grown by slow evaporation of the solvent from a solution of eosin **9c** and pyridinum **8b** in methanol at room temperature. As shown in Figure 5, the X–ray structure confirms the formation of an eosin-pyridinium complex (**EY-8b**) as a π–π complex with a 1:1 donor-acceptor ratio (Figure 5). The molecules adopt a slipped stacking motif and π–π interactions between the pyridinium ring and an aromatic ring of an adjacent eosin molecule (short C–C distances of 3.412(13) and 3.495(13) Å). With a centroid-centroid separation of 4.366(9) Å, this interaction is characteristic of an electron donor-acceptor complex of this type.[17]

Insights into the structure of the eosin-pyridinium assembly in solution are obtained by NMR spectroscopy. Indeed, when isolated crystals of **EY-8b** are dissolved in deuterated methanol, only small changes have been detected compared to the individual spectra. However, ROESY NMR spectroscopy revealed through-space interactions between H_1 of the eosin and H_e, H_f and H_g of the pyridinium, which indicates that the two components are in close proximity one to another (Figure 6).

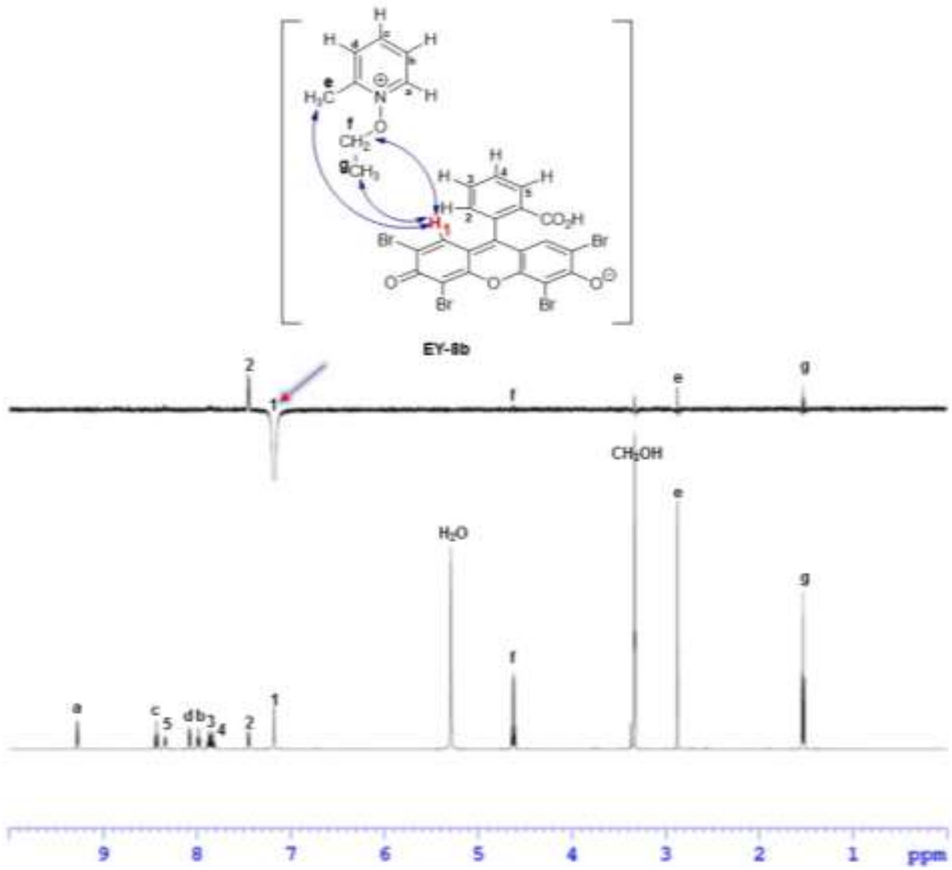


Figure 6. ^{1}H NMR and ^{1}D-ROESY spectra of the complex (**EY-8b**) in CD_3OD at −15 °C, showing the irradiation of H_1 and subsequent correlations.

Based on these investigations, a plausible mechanism for the formation of the heterocycle **3**, is given in Figure 7. The reaction begins with the formation of the EDA complex between the eosin **9c** and the onium salt **8b**. Upon absorption of a green photon, the **EY-8b** complex exhibits a single electron transfer event to generate the unstable ethoxy radical, which undergoes a hydrogen abstraction from the secondary phosphine oxide **1a** to give rise to the corresponding phosphinoyl radical **4a**. This radical then reacts with the alkyne **2a** to generate the alkenyl radical **5a**, which subsequently attacks the phenyl ring of the phosphine oxide to give the cyclohexadienyl radical **6a**. With a redox potential of about –0.1 V,[18] **6a** is readily oxidized by **EY**$^{\bullet+}$ (E^{o}(EY$^{\bullet+}$/EY)= 0.70 V/SCE)[9c] to release the photocatalyst **9c** and generate the Wheland intermediate **7a**. This species is immediately rearomatized after deprotonation with $NaHCO_3$ to yield the desired benzophosphole oxide **3a**.

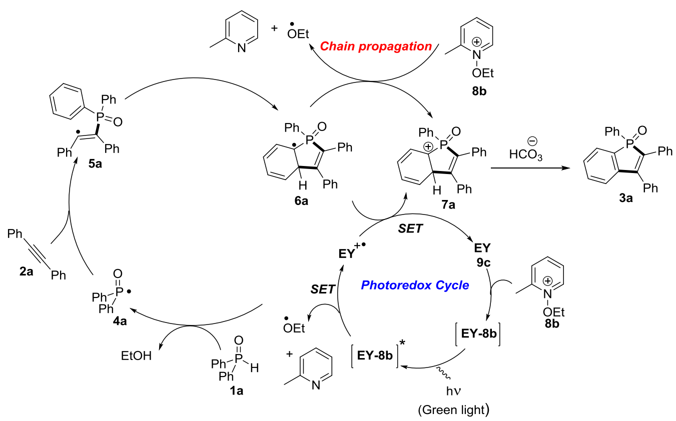


Figure 7. Postulated mechanism for the synthesis of the benzo[*b*]phosphole oxides **3a** *via* photoredox catalysis. EY: eosin Y.

Taking into account the fact that many photoredox processes can involve radical chains,[19] one can hypothesize that the external oxidant 8**b** can be reduced by **6a** to form **7a** inducing a chain propagation (Figure 7). Although this scenario can thermodynamically be excluded on the basis of redox potentials of **6a** and **8b**, we proceeded with the measurement of the quantum yield (QY) of the reaction of **1a** with **2a** under the optimized photocatalytic conditions to confirm this hypothesis. By employing a protocol previously described by Jacobi von Wangelin *et al.*,[11c] we measured a QY of 0.27, which implies that a chain propagation is unlikely and that the photocatalytic pathway is populated.

CONCLUSIONS

In conclusion, we have described the first photocatalytic method for the synthesis of benzo[*b*]phosphole oxides through an oxidative *C-H*/*P-H* functionalization reaction of secondary phosphine oxides with alkynes. The reaction proceeds smoothly under metal-free conditions and has a broad substrate scope. The efficiency of the process relies on the formation of a donor-acceptor ground state complex **EY-8b** between the photocatalyst and the oxidant, which turned out to be highly reactive. The sustainable generation of the phosphinoyl radical **4**,[20] which has unambiguously been confirmed by EPR spectroscopy, opens a new avenue for the synthesis of various phosphorus-heterocycles under very mild conditions. Extension of this methodology toward the synthesis of new phosphorus-based molecules is currently under investigation in our laboratory and will be reported in due course.

ASSOCIATED CONTENT

Supporting Information.

Supporting information is available free of charge via the Internet at http://pubs.acs.org.

NMR spectra, experimental procedures, and mechanistic studies.

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Author Contributions

The manuscript was written through contributions of all authors.

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REFERENCES

[1] For selected reviews on synthesis and reactivity of phospholes and derivatives, see: a) Mathey, F. *Angew. Chem. Int. Ed.* **2003**, *42*, 1578–1604; *Angew. Chem.* **2003**, *115*, 1616–1643; b) Baumgartner, T.; Réau, R. *Chem. Rev.* **2006**, *106*, 4681–4727; c) Crassous, J.; Réau, R. *Dalton Trans*. **2008**, 6865–6876; d) Matano, Y.; Imahori, H. *Org. Biomol. Chem*. **2009**, *7*, 1258–1271; e) Baumgartner, T. *Acc. Chem. Res*. **2014**, *47*, 1613–1622; f) Stolar, M.; Baumgartner, T. *Chem. Asian J*. **2014**, *9*, 1212–1225.

[2] a) Tsuji, H.; Sato, K.; Sato, Y.; Nakamura, E. *J. Mater. Chem.* **2009**, *19*, 3364–3366; b) Tsuji, H.; Sato, K.; Sato, Y.; Nakamura, E. *Chem. Asian J*. **2010**, *5*, 1294– 1297; c) Yamaguchi, E.; Wang, C. G.; Fukazawa, A.; Taki, M.; Sato, Y.; Sasaki, T.; Ueda, M.; Sasaki, N.; Higashiyama, T.; Yamaguchi, S. *Angew. Chem. Int. Ed*. **2015**, *54*, 4539–4543; *Angew. Chem*. **2015**, *127*, 4622–4626.

[3] a) Tsuji, H.; Sato, K.; Ilies, L.; Itoh, Y.; Sato, Y.; Nakamura, E. *Org. Lett*. **2008**, *10*, 2263–2265; b) Sanji, T.; Shiraishi, K.; Kashiwabara, T.; Tanaka, M. *Org. Lett*. **2008**, *10*, 2689–2692; c) Fukazawa, A.; Hara, M.; Okamoto, T.; Son, E.-C.; Xu, C.; Tamao, K.; Yamaguchi, S. *Org. Lett*. **2008**, *10*, 913–916; d) Fukazawa, A.; Yamada, H.; Yamaguchi, S. *Angew. Chem*. **2008**, *120*, 5664–5667; *Angew. Chem.*

Int. Ed. **2008**, *47*, 5582– 5585; e) Fukazawa, A.; Ichihashi, Y.; Kosaka, Y.; Yamaguchi, S. *Chem. Asian. J*. **2009,** *4*, 1729– 1740.

[4] For seminal contributions, see: a) Baba, K.; Tobisu, M.; Chatani, N. *Angew. Chem*. **2013**, *125*, 12108–12111; *Angew. Chem. Int. Ed*. **2013**, *52*, 11892–11895; b) Berger, O.; Petit, C.; Deal, E. L.; Montchamp, J. -L. *Adv. Synth. Catal*. **2013**, *355*, 1361–1373; c) Wu, B.; Santra, M.; Yoshikai, N. *Angew. Chem. Int. Ed*. **2014**, *53*, 7543–7546; *Angew. Chem*. **2014**, *126*, 7673– 7676; d) Wu, B.; Chopra, R.; Yoshikai, N. *Org. Lett*., **2015**, *17*, 5666– 5669; e) Zhou, Y.; Gan, Z.; Su, B.; Li, J.; Duan, Z.; Mathey, F. *Org. Lett*. **2015**, *17*, 5722–5724.

[5] a) Chen, Y. R.; Duan, W. L. *J. Am. Chem. Soc*. **2013**, *135*, 16754 – 16757; b) Unoh, Y.; Hirano, K.; Satoh, T.; Miura, M. *Angew. Chem. Int. Ed*. **2013**, *52*, 12975 – 12979; *Angew. Chem*. **2013**, *125*, 13213–13217; c) Ma, W.; Ackermann, L. *Synthesis* **2014**, *46*, 2297–2304; d) Fisher, H. C.; Berger, O.; Gelat, F.; Montchamp, J. -L. *Adv. Synth. Catal*. **2014**, *356*, 1199–1204; e) during the preparation of this manuscript, Tang *et al.* reported on the synthesis of benzophospholes by using a copper (2 mol%)/tert-butyl hydroperoxide (2 equiv.) catalyst system; see: Zhang, P.; Gao, Y.; Zhang, L.; Li, Z.; Liu, Y.; Tang, G.; Zhao, Y. *Adv.Synth. Catal*. **2016**, *358*,138 –142

[6] Sluggett, G. W.; Tuorro, C.; George, M. W.; Koptyug, I. V.; Turro, N. J. *J. Am. Chem. Soc*. **1995**, *117*, 5148–5153.

[7] Liu *et al*. have shown that diphenylphosphinoyl radical can be formed at 110 °C, when diphenyl phosphine oxide is combined with AgF in the presence of 5,5-dimethyl-1-1-pyrroline *N*-oxide as a radical spin trap see: Li, Z.; Fan, F.; Zhang, Z.; Xia, Y.; Liu, D.; Liu, Z-Q. *RSC. Adv*. **2015**, *5*, 27853–27856.

[8] For a recent comprehensive review on phosphorus–centered radical reactions; see: Pan, X.-Q.; Zou, J.-P.; Yi, W.-B.; Zhang, W. *Tetrahedron* **2015**, 71, 7481-7529, and references therein.

[9] For selected reviews on visible-light photoredox catalysis; see: a) Zeitler, K. *Angew. Chem. Int. Ed*. **2009**, *48*, 9785–9789; *Angew. Chem*. **2009**, *121*, 9969–9974; b) Narayanam, J. M.; Stephenson, C. R. J.; *Chem. Soc. Rev*. **2011**,*40*, 102–113; c) Xuan, J.; Xiao, W.-J. *Angew. Chem. Int. Ed*. **2012**, *51*, 6828– 6838; *Angew. Chem*. **2012**, *124*, 6934–6944; d) Shi, L.; Xia, W. *Chem. Soc. Rev*. **2012**, *41*, 7687–7697; e) Reckenthaeler, M.; Griesbeck, A. G. *Adv. Synth. Catal*. **2013**, *355*, 2727–2744; f) Ravelli, D.; Fagnoni, M.; Albini, A. *Chem. Soc. Rev*. **2013**, *42*, 97–113; g) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev*. **2013**, *113*, 5322–5363; h) Schultz, D. M.; Yoon, T. P. *Science* **2014**, *343*, 985; i) Koike, T.; Akita, M. *Inorg. Chem. Front*. **2014**, *1*, 562–576; j) Hari, D. P.; König, B. *Chem. Commun*. **2014**, *50*, 6688–6699; k) Nicewicz, D. A.; Nguyen, T. M. *ACS Catal*. **2014**, *4*, 355–360; l) Pitre, S. P.; McTiernan, Ch. D.; Scaiano, J. C. *Acc. Chem. Res*. **2016**, 10.1021/acs.accounts.6b00012.

[10] Fouassier, J. P.; Lalevée, J. *Photoinitiators for Polymer Synthesis: Scope, Reactivity and Efficiency*, Wiley-VCH, Weinheim, **2012**.

[11] a) Neumann, M.; Fuldner, S.; König, B.; Zeitler, K. *Angew. Chem. Int. Ed*. **2011**, *50*, 951–954; *Angew. Chem*. **2011**, *123*, 981–985; b) Hari, D. P.; Schroll, P.; König, B. *J. Am. Chem. Soc*. **2012**, *134*, 2958–2961; c) Majek, M.; Filace, F.; Jacobi von Wangelin, A. *Beilstein J. Org. Chem*. **2014**, *10*, 981–989.

[12] Sluggett, G. W.; Macgary, P. F.; Koptyug, I. V.; Turro, N. J. *J. Am. Chem. Soc.* **1996,** *118,* 7367-7372.

[13] For a review on radical aryl migration reactions, see: Chen, Z. -M.; Zhang, X. -M.; Tu, Y. -Q. *Chem. Soc. Rev*. **2015**, *44*, 5220–5245.

[14] Jenkins, C. A.; Murphy, D. M.; Rowlands, C. C.; Egerton, T. A. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2479–2485.

[15] a) Morlet-Savary, F. ; Klee, J. E. ; Pfefferkon, F. ; Fouassier, J. P. ; Lalevée, J. *Macromol. Chem. Phys*. **2015**, *216*, 2161–2170; b) Lalevée, J. ; Morlet-Savary, F. ; Tehfe, M. A. ; Graff, B. ; Fouassier, J. P. *Macromolecules* **2012**, *45*, 5032–5039.

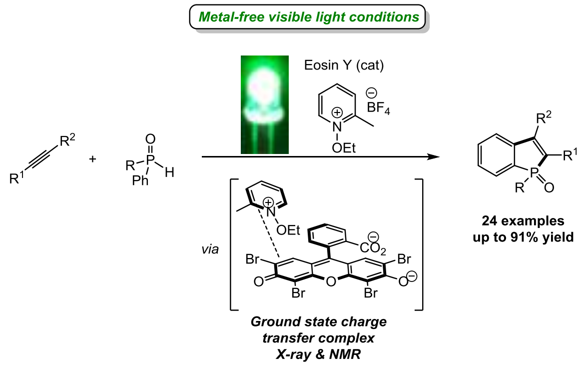
[16] a) Willner, I.; Eichen, Y.; Rabinovitz, M.; Hoffman, R.; Cohen, S. *J. Am. Chem. Soc.* **1992**, *114*, 637–644; b) Willner , I.; Marx , S.; Eichen, Y. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1243–1244 *Angew. Chem.* **1992**, *104*, 1255–1256.

[17] for selectd examples on the use of electron donor–acceptor complexes in organic synthesis; see: a) Lima, C. G. S.; Lima, T. de M.; Duarte, M.; Jurberg, I. D.; Paixão, M. W. *ACS Catal*. **2016**, *6*, 1389–1407; b) Arceo, E.; Jurberg, I. D.; Álvarez-Fernández, A.; Melchiorre, P. *Nat. Chem*. **2013**, *5*, 750–756; c) Nappi, M.; Bergonzini, G.; Melchiorre, P. *Angew. Chem., Int. Ed*. **2014**, *53*, 4921–4925; *Angew. Chem*. **2014**, *126*, 5021–5025; d) for the elucidation of the structure of an electron donor-acceptor complex in the solid state; see: Kandukuri, S. R.; Bahamonde, A.; Chatterjee, I.; Jurberg, I. D.; Escudero-Adan, E. C.; Melchiorre, P. *Angew. Chem., Int. Ed*. **2015**, *54*, 1485–1489; *Angew. Chem*. **2015**, *127*, 1505 –1509.

[18] Bahtia, K.; Schuler, R. H. *J. Phys. Chem*. **1974**, *78*, 2335–2338.

[19] a) Cismesia, M. A.; Yoon, T. P. *Chem. Sci*. **2015**, *6*, 5426–5434; b) Kärkäs, M. D.; Matsuura, B. S.; Stephenson, C. R. J. *Science* **2015**, *349*, 1285–1286; c) Studer, A.; Curran, D. P. *Angew. Chem. Int. Ed*. **2016**, 55, 58–102; *Angew. Chem*. **2016**, *128*, 58–102.

[20] For recent contributions on the generation of phosphorus centered radical under photoredox conditions, see: He, Y.; Wu, H.; Toste, F. D. *Chem. Sci*. **2015**, *6*, 1194– 1198, (b) Xuan, J.; Zeng, T.-T.; Chen, J.-R.; Lu, L.-Q.; Xiao, W.-J. *Chem. - Eur. J*. **2015**, *21*, 4962–4965.


Metal-free visible light conditions
Eosin Y (cat)
via
Ground state charge
transfer complex
X-ray & NMR
24 examples
up to 91% yield