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ARTICLE

Using Blue-Light Driven Iron-Catalysis to Afford Molecular Diversity in Phosphindole Oxide Derivatives

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We have developed original blue-light promoted iron-catalyzed reactions of activated alkynes with secondary phosphine oxides in the presence of tert-butylhydroperoxide under argon at room temperature. Depending the nature of the iron precursors, benzo[*b*]phosphole oxides were obtained using $Fe(NO_3)_3$ in methanol and 9-phenyltribenzo[*b,e,g*]phosphindole 9-oxide derivatives utilizing $Fe(OTf)_2$ in acetic acid. Control experiments revealed that radical processes are involved, permitting the proposal of a reasonable mechanism.

Introduction

Phosphorus-containing heterocycles showed wide applications in organic synthesis, medicinal chemistry, and materials science.[1-4] Among these compounds, phosphole-based conjugated systems, and in particular benzo[*b*]phosphole derivatives have attracted significant interest from synthetic chemists in the last few years due to their intrinsic physical and optical properties, which have enabled the development of novel organic semiconductors for OLEDs (organic light-emitting diodes), OPVs (organic photovoltaics), cell imaging dyes or phototherapy.[5-8] (Figure 1)

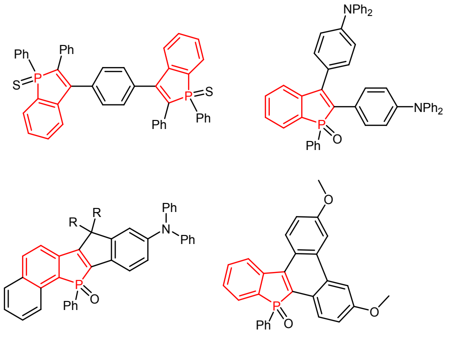
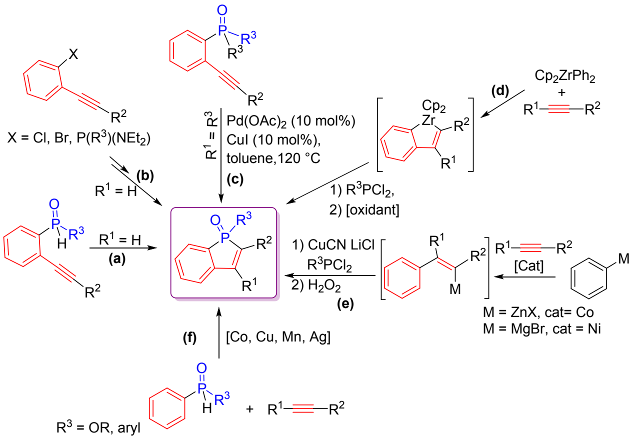


Figure 1. Representative examples of benzo[*b*]phosphole for optoelectronics or biophotonics.

Most of the conventional preparations of benzo[*b*]phosphole derivatives[9] were performed starting from alkynes bearing *ortho*-phosphorus substituents involving one intramolecular cyclization step,[10-15] the main limitation of such pathways being the preparation of the starting materials. (Scheme 1a-b) Transition metal catalysis has also shown its advantages for the preparation of benzo[*b*]phosphole oxides starting from *o*-diarylphosphinophenylalkynes using $Pd(OAc)_2$/CuI cocatalysts.[16] (Scheme 1c) Benzophospholes synthesis can be also done through electrophilic trapping with $PhPCl_2$ of a zirconaindene, obtained from Cp_2ZrPh_2 and an alkyne.[17] (Scheme 1d)



Scheme 1. Classical methodologies to prepare benzo[*b*]phosphole derivatives.

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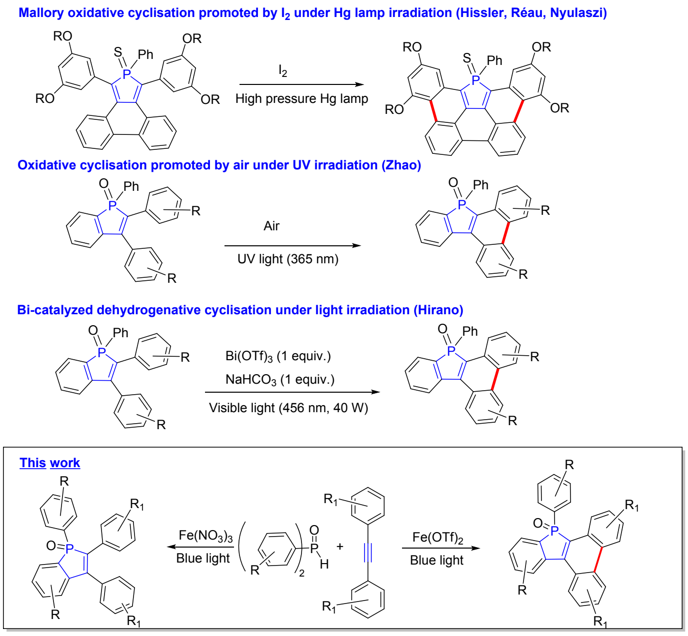
Starting from metallated arenes (M = ZnX, MgBr), benzo[*b*]-phosphole oxides can be obtained *via* the insertion of the alkyne catalyzed by nickel or cobalt species, then electrophilic trapping reaction with R^3PCl_2, Friedel-Crafts type cyclisation and oxidation (Scheme 1e).[18,19] On one hand, during the past decade, transition metal-catalyzed C-H bond functionalization reactions have been extensively studied to afford a wide variety of heterocyclic compounds, notably for the synthesis of P-containing heterocyclic compounds. Indeed, catalyzed oxidative C-H/P-H functionalization reactions starting from internal alkynes and secondary phosphine oxides or H-phosphonates were reported using metal salts under oxidative conditions, such as copper,[20-21] manganese,[22] and silver (Scheme 1f).[23] Additionally, using a well-defined cobaloxime based catalyst $Co(dmgH_2)_2PyCl$ (15 mol%) in the presence of HCO_2Na at 60 °C for 20 h under blue LED irradiation, internal alkynes reacted with diarylphosphine oxides to lead to benzo[*b*]phosphole oxides in 43-90% yields.[24] Noticeably, metal-free promoted preparation can be conducted such as using Eosin Y as a photocatalyst and *N*-ethoxy-2-methylpyridinium tetrafluoroborate as the oxidant under green light.[25]

On the other hand, highly condensed heteroaromatics based on phosphole motifs have received significant attention thanks to their physical and optoelectronic properties and were applied for the design and synthesis of organic semi-conductors or fluorescent bioprobes.[5,8] In terms of preparation, one efficient approach deals with the Mallory photo-promoted oxidative cyclization.[26-28] Indeed, as a representative example, the synthesis of highly condensed dibenzophosphapentaphenes bearing peripherally electron-donating dialkoxyphenyl or thienyl groups was reported by Bouit, Hissler, Réau, Nyulászi, *et al.* (Scheme 2).[29] In 2023, Zhao described the oxidative cyclisation of 2,3-diarylbenzo-phospholes under aerobic conditions under UV light irradiation (365 nm) (Scheme 1).[30] Noticeably, when starting from 1-phenyl-2,3-di(*p*-substituted-aryl)phosphindole oxides, the corresponding tribenzophosphindole oxides were obtained in 72-91% yields, whereas conducting the cyclisation with1-phenyl-2,3-di(*m*-substituted-aryl)phosphindole oxides, low to moderate yields were observed (1-36% yields). Recently, Hirano reported a $Bi(OTf)_3$-mediated oxidative cyclization of 2,3-diarylbenzophopholes under blue visible light irradiation (456 nm) in the presence of 1 equiv. of $NaHCO_3$ as the base, but without any additional oxidants.[31] Alternative preparations can be done starting from *o*-arylalkynylanilines with $R_2HP(=O)$ in the presence of 2 equiv. of DTBP and 2 equiv. of $Mg(NO_3)_2·6H_2O$ in 1,4-dioxane under air at 100 °C.[32]

Additionally, since the beginning of this millennium, iron has emerged as a powerful substitute to noble metals in homogeneous catalysis, more particularly in hydroelementation areas,[33] including in regioselective hydrophosphination. Following our continuous contribution in iron catalyzed transformations, notably involving organophosphorous derivatives such as α-alkylation reaction of methyldiarylphosphine oxides,[34] or oxophosphinylation of activated alkenes by secondary phosphine oxides leading to β-ketophosphine oxides,[35] we report hereafter a blue-light driven iron-controlled oxidative C-H/P-H functionalization method for benzo[*b*]phosphole oxide and tribenzophosphindole oxide synthesis using secondary phosphine oxides with alkynes, conducting the reaction at ambient conditions.

To the best of our knowledge, there are no reports addressing such transformations using only iron as a catalyst.[36]



Scheme 2. Methodologies to prepare 9-phenyltribenzo[*b,e,g*]-phosphindole 9-oxide derivatives.

Results and discussions

First of all, in order to evaluate the ability of iron salts to lead to the annulation of secondary phosphine oxides **1** with internal alkynes **2** leading to benzo[*b*]phosphole oxide derivatives **3**, the reaction of diphenylphosphine oxide **1a** with diphenylacetylene **2a** was selected as the benchmark reaction. Thus, in the presence of 10 mol% $Fe(NO_3)_3$, and 2 equiv. of *tert*-butylhydroperoxide (TBHP) as the oxidant, **1a** reacted with 2 equiv. of **2a** in acetonitrile upon blue light irradiation (using two 24-watt LED lamps, 450-460 nm) at room temperature (rt) for 12 h, and the corresponding benzo[*b*]phosphole oxide **3a** was obtained in 40% isolated yield. (Table 1, entry 1)
We then evaluated the effect of the iron salt nature on the transformation. Among the tested salts (10 mol%), $FeBr_3$ and FeF_3 exhibited no or very low activity. Noticeably, when conducting the reaction with $Fe(OTf)_3$ or $FeCl_3$, no benzo[*b*]phosphole oxide **3a** was detected, but a by-product identified as 9-phenyltribenzo-[*b,e,g*]phosphindole 9-oxide **4a** was obtained in a in 40% and 22% yields, respectively. (Entries 4 and 5) With $FeSO_4$, the reaction led to a mixture of 12% of **3a** and <5% of **4a**. (Entry 6)

The nature of the solvent was then evaluated, and among the solvents tested (acetonitrile, 1,4-dioxane, toluene, 1-pentanol), methanol exhibited the best efficiency with 73% of **3a** obtained. (Entries 1, 7-9 *vs* 10)

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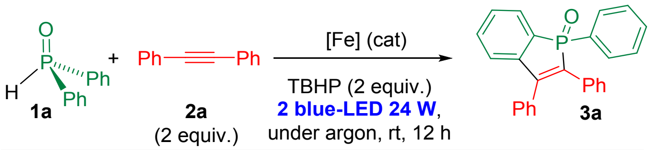
Table 1. Optimization of the light driven iron-catalyzed annulation reaction of diphenylacetylene **2a** with diphenylphosphine oxide **1a**.[a]



Entry	[Fe] (10 mol%)	light	Solvent	**3a** Yield (%)
1	$Fe(NO_3)_3$	Blue-LED	CH_3CN	40
2	$FeBr_3$	Blue-LED	CH_3CN	-
3	FeF_3	Blue-LED	CH_3CN	6
4	$Fe(OTf)_2$	Blue-LED	CH_3CN	-[b]
5	$FeCl_3$	Blue-LED	CH_3CN	-[c]
6	$FeSO_4$	Blue-LED	CH_3CN	12[d]
7	$Fe(NO_3)_3$	Blue-LED	toluene	30
8	$Fe(NO_3)_3$	Blue-LED	1,4-dioxane	54
9	$Fe(NO_3)_3$	Blue-LED	1-Pentanol	50
10	**$Fe(NO_3)_3$**	**Blue-LED**	**MeOH**	**73**
11	$Fe(NO_3)_3$	White light	MeOH	53
12	$Fe(NO_3)_3$	No light	MeOH	2
13[e]	$Fe(NO_3)_3$	Blue-LED	MeOH	-
14	-	Blue-LED	MeOH	-
15[e]	-	Blue-LED	MeOH	-

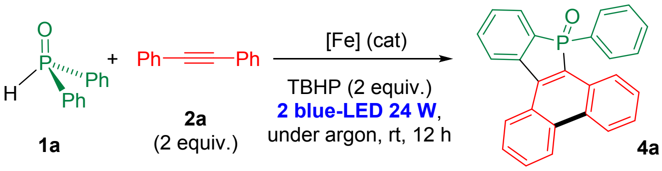
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), [Fe] (10 mol%), TBHP (2 equiv.), solvent (1 mL), 2 blue-LEDs 24 W (450-460 nm), rt, 12 h under argon. Isolated yields after purification by flash chromatography on silica. [b] A by-product was observed in 40% yield and was identified as 9-phenyltribenzo[*b,e,g*]phosphindole 9-oxide **4a**. [c] **4a** was obtained in 22% yield. [d] > 5% of **4a** was observed as a by-product. [e] no TBHP was used.

The nature of the light had also a great influence on the efficiency of the transformation. Indeed, using white light (two 24-watt compact fluorescent lamps) reduced the yield but did not inhibit the reactivity by contrast with the reaction conducted in dark. (53% vs 73%, Entries 11 *vs* 10 and 12) Control experiments showed that in the absence of catalyst, and of TBHP oxidant, no reaction took place. (Entries 13-15) Additionally, when the reaction was performed under air instead of under argon, only trace amount of product **3a** was detected.

As mentioned, when using $Fe(OTf)_2$, $FeCl_3$ and $Fe(SO_4)$, a by-product, named 9-phenyltribenzo[*b,e,g*]phosphindole 9-oxide **4a** was isolated in >5-40% yields and fully characterized, including by X-ray analysis (see SI, Figure S1 for the molecular structure of **4a**). This specific reaction is highly attractive as it allows obtaining tribenzo[*b,e,g*]phosphindole 9-oxide in a single step at rt from commercially available precursors, which appear as an interesting alternative to Hirano's 2-steps P-cyclization/Mallory reaction.[31]

Based on these promising results, the parameters of the reaction were evaluated to determine their effect on switching the chemoselectivity toward the formation of 9-phenyltribenzo-[*b,e,g*]phosphindole 9-oxide **4a**. (Table 2). As already shown in Table 1, among the 3 tested salts, $Fe(OTf)_2$, $FeCl_3$ and $FeSO_4$ (10 mol%), for the reaction of **1a** with 2 equiv. of **2a** in the presence of 2 equiv. of TBHP in acetonitrile upon blue light irradiation at rt for 12 h, $Fe(OTf)_2$ exhibited the highest performance, **4a** being obtained in 40% yield. (Table 2, entries 1-3).

Table 2. Optimization of the light driven iron-catalyzed reaction of diphenylacetylene **2a** with diphenylphosphine oxide **1a** leading to 9-phenyltribenzo[*b,e,g*]phosphindole 9-oxide **4a**.[a]



Entry	[Fe] (10 mol%)	light	Solvent	**4a** Yield (%)
1	$Fe(OTf)_2$	Blue-LED	CH_3CN	40
2	$FeCl_3$	Blue-LED	CH_3CN	22
3	$FeSO_4$	Blue-LED	CH_3CN	>5[b]
4	$Fe(OTf)_2$	Blue-LED	CH_2Cl_2	26
5	$Fe(OTf)_2$	Blue-LED	1,2-DCE	-
6	$Fe(OTf)_2$	Blue-LED	Dioxane	54
7	$Fe(OTf)_2$	Blue-LED	TFE	61
8	**$Fe(OTf)_2$**	**Blue-LED**	**AcOH**	**70**
9[c]	$Fe(OTf)_2$	Blue-LED	AcOH	trace
10[d]	$Fe(OTf)_2$	Blue-LED	AcOH	27
11[e]	$Fe(OTf)_2$	Blue-LED	AcOH	20
12	$Fe(OTf)_2$	White light	AcOH	trace
13	$Fe(OTf)_2$	No light	AcOH	-

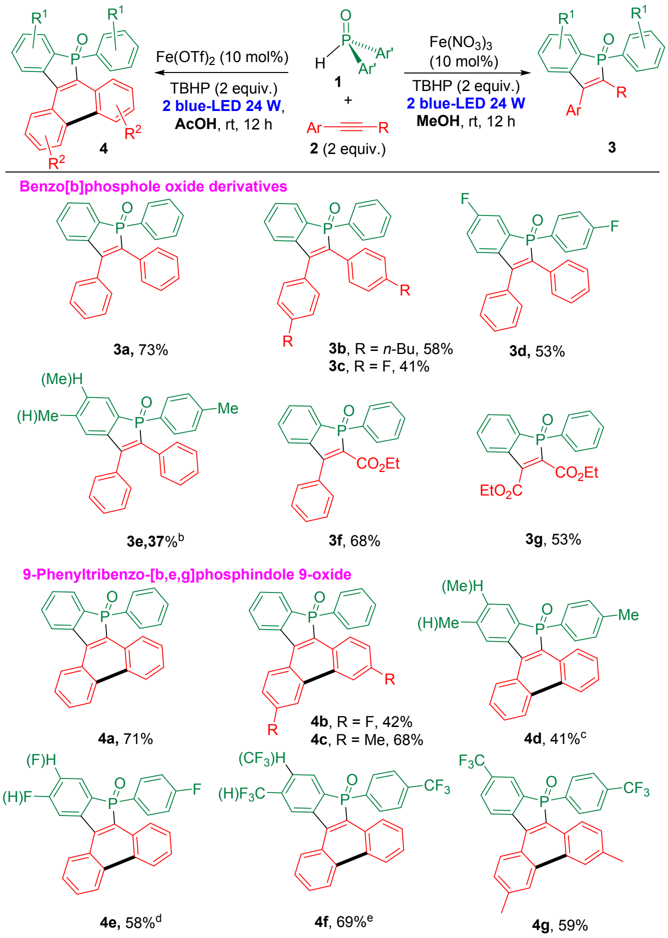
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), [Fe] (10 mol%), TBHP (2 equiv.), solvent (1 mL), 2 blue-LEDs 24 W (450-460 nm), rt, 12 h under argon. Isolated yields after purification by flash chromatography on silica. [b] **3a** was obtained in 22% yield. [c] Dicumylperoxide was used instead of TBHP. [d] Cumylhydroperoxide was used instead of TBHP. [e] DTBP was used instead of TBHP.

The nature of the solvents on the activity was then evaluated. In non-protonic chlorinated solvents such as dichloromethane and 1,2-dichloroethane (1,2-DCE), the formation of **4a** was not favored with a maximum of 26% yield in CH_2Cl_2. (Entries 4 and 5) Conducting the reaction in 1,4-dioxane led to a better efficiency and 54% of **4a**. (Entry 6) However, protic solvents such as 2,2,2-trifluoromethanol (TFE) and acetic acid were found to favor the reaction. (Entries 7 and 8) Especially when acetic acid was used as the solvent, the product **4a** can be isolated in 70% yield. Noticeably, replacing *tert*-butyl hydroperoxide (TBHP) to other peroxides such as dicumyl peroxide, cumyl hydroperoxide and di-*tert*-butyl peroxide (DTBP) didn't favor the efficiency of the reaction (up to 27% yield, entries 9-11).

The nature of the light again played a crucial role. When activating the reaction with white light (24 W bulk lamp) in acetic acid, only trace amount of **4a** was detected. Noticeably, in dark, no reaction took place. (Entries 12 and 13)

With these optimized reaction conditions in hands, the substrate scope for the preparation of benzo[*b*]phosphole oxide **3** derivatives was evaluated [$Fe(NO_3)_3$ (10 mol%), 2 equiv. of alkyne, 1 equiv. of secondary phosphine oxide and 2 equiv. of TBHP in methanol for 12h at rt under blue light activation (2×24W-blue LED) under argon]. (Scheme 3) The reaction of diphenylphosphine oxide **1a** was successfully performed with substituted diarylacetylenes bearing *para*-electron donating group such as *n*-butyl, leading to the corresponding benzo[*b*]phosphole oxide **3b** in 58% isolated yield. By contrast, when starting from bis(4-nitrophenyl)acetylene or bis(4-dimethylaminophenyl)-acetylene, no reaction took place. Diarylacetylene with a *p*-substituted fluoro can be also used and was selectively converted in the benzo[*b*]phosphole oxide **3c** in 41% yield. When conducting the reaction with di(*p*-tolyl)phosphine oxide and diphenylacetylene, benzo[*b*]phosphole oxide **3e** was obtained in 37% yield with the methyl located at the *para* and *meta* position of the phosphorus of the benzophosphole moiety. Additionally, the reaction can be conducted successfully with ethyl 3-phenylprop-2-ynoate and diethyl but-2-yndioate yielding the corresponding benzo[*b*]phosphole oxide **3f** and **3g** in 68% and 53%, respectively.

Then, the substrate scope and limitation of the formation of 9-phenyltribenzo[*b,e,g*]phosphindole 9-oxide derivatives **4** were evaluated using the optimized conditions [$Fe(OTf)_2$ (10 mol%), 2 equiv. of alkyne, 1 equiv. of secondary phosphine oxide and 2 equiv. of TBHP in acetic acid for 12 h at rt under blue light activation (2×24W-blue LED) under argon]. (Scheme 3) The reaction of diphenylphosphine oxide **1a** can be conducted with bis(4-fluorophenyl)acetylene or bis(4-methylphenyl)-acetylene giving the corresponding compunds **4b** and **4c** in 42% and 68% yields, respectively. The nature of the diarylphosphine oxides can be also modulated and the reaction of di(*p*-tolyl)phosphine oxide, di(4-fluorophenyl)phosphine oxide and (4-trifluoromethylphenyl)-phosphine oxide with diphenyl-acetylene and di-*p*-tolylacetylene led to the derivatives **4d-f** in 41-69% yields. In our hands, with diisopropylphosphite and diphenylphosphite, no reaction occurred. Noticeably, crystals suitable for X-ray analysis were grown by diffusion of cyclohexane into a solution of **4g** in EtOAc. The molecular structure of **4g** is depicted in Figure 2. First of all, it demonstrated the formation of benzo[*b*]phosphindole motif, with the formation of the additional C-C bond (herein C19-C20, 1.455(3) Å). Importantly, the *meta* relationship between the trifluoromethyl substituent on the aromatic ring of the benzo[*b*]phosphindole motif and the phosphorus atom was unambiguously confirmed. In the phosphole ring, the bond lengths and angles are classical for such P-cycle.[8] Similarly, *meta* relationships were also observed with fluoro substituants when starting with di(4-fluorophenyl)phosphine oxide and diphenylacetylene leading to the benzo[*b*]phosphole oxide derivative **3d** and the 9-aryltribenzo[*b,e,g*]phosphindole 9-oxide **4e**. Noticeably, in the X-ray structure of **4e**, it was shown shown two structures in which the fluorine was located at the *para* position (**4e-1**) and at the *meta* position (**4e-2**) (see SI, Figure S3). Noticeably, no expected 9-phenyltribenzo[*b,e,g*]phosphindole 9-oxide product was obtained by reaction of **1a** with di(2-naphthyl)acetylene.



Scheme 3. Scope of iron-catalyzed annulation reaction of internal alkynes **2** with diarylphosphine oxide **1** leading to benzo[*b*]phosphole oxides **3** and 9-phenyltribenzo-[*b,e,g*]phosphindole 9-oxide derivatives **4**. [a] For the preparation of benzo[*b*]phosphole oxides **3**: $Fe(NO_3)_3$ (10 mol%), alkyne (2 equiv.), secondary phosphine oxide (1 equiv.), TBHP (2 equiv.) in methanol, 12 h at rt under blue light activation (2×24W-blue LED) and argon. Isolated yields. [b] ~ 1:1 ratio based on ^{31}P-NMR. For the preparation of 9-phenyltribenzo- [*b,e,g*]phosphindole 9-oxide derivatives **4**: $Fe(OTf)_2$ (10 mol%), alkyne (2 equiv.), secondary phosphine oxide (1 equiv.), TBHP (2 equiv.) in acetic acid, 12 h at rt under blue light activation (2×24W-blue LED) and argon. Isolated yields. [c] ~ 1:1 ratio based on ^{31}P-NMR; Purity ~ 80%. [d] 85% of *p*-subtituted F, 15% of *m*-substituted F on the benzo[*b*]phosphindole motif, based on X-Ray analysis. [e] Undefined ratio *p*-subtituted CF_3 and *m*-substituted CF_3 on the benzo[*b*]phosphindole motif.

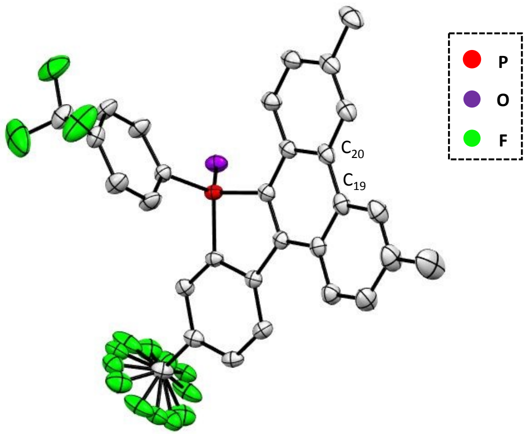
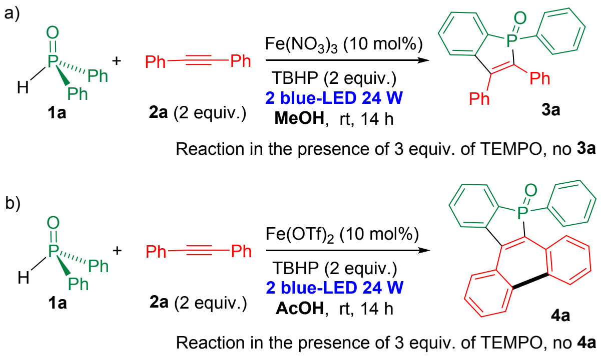


Figure 2. Molecular structure of **4g**.

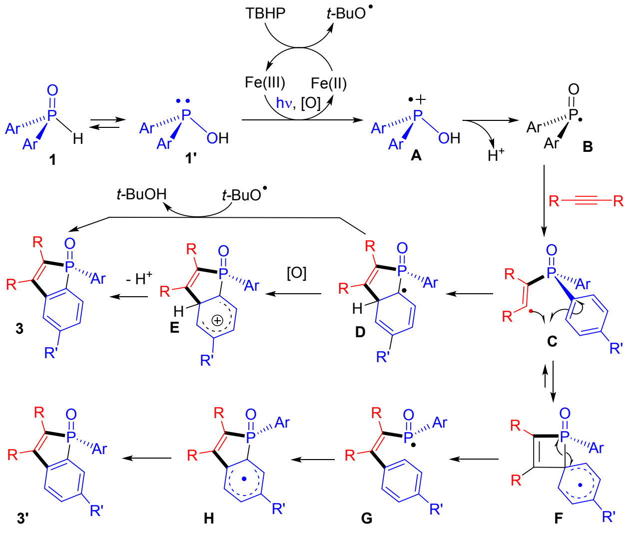
In order to gain insights into those two transformations, we then conducted preliminary mechanistic studies. First, in order to check if a radical process was involved, 3 equiv. of TEMPO (2,2,6,6-tetramethyl-1-piperi-dinyloxy) was added to the reaction mixture (1 equiv. of diphenylphosphine oxide **1a**, 2 equiv. of diphenylacetylene **2a**, 2 equiv. of TBHP in the presence of 10 mol% of Fe(NO_3)$_3$ at rt under blue light activation for 14 h). Under such conditions, no product **3a** was detected. Noticeably, TEMPO-**B** adduct was detected by LR-MS at m/z = 357.[34] (Scheme 3) Similarly, when conducted the reaction with 3 equiv. of TEMPO and 10 mol% of Fe(OTf)$_2$ catalyst, no product **4a** was observed. These experimental evidences support a radical pathway.



Scheme 4. Control experiments.

Based on our previous work[35b] demonstrating that the reaction of diphenylphosphine oxide **1a** with 1 equiv. of TEMPO under blue light activation and oxidative conditions allowed for the detection of the TEMPO-**1a** adduct in HR-MS, thus highlighting the formation of a P-centered phosphinoyl radical **B**, and supported by the literature, a plausible mechanism is described in Scheme 4. In an initial step, the secondary phosphine oxide **1** is oxidized to phosphorus radical **B** via a blue light promoted oxidative process catalyzed by iron[28a,35b,37] species.[38] This P-centered radical **B** then underwent an intermolecular addition to the alkyne to afford the corresponding alkenyl radical **C**[23b,25,39] which thus reacted with the phenyl ring of the phosphine oxide via a *5-exo-trig* cyclisation leading the cyclohexadienyl radical **D**. Two pathways can then be considered: (i) the oxidation of **D** in the arenium cation **E** either by Fe(III)[40] and/or TBHP[20] through a single electron transfer process followed by the elimination of a proton to generate the expected benzo[*b*]phosphole oxide;(ii), the production of **3** by the reaction of **D** with the tert-butoxyl radical generated during the formation of the phosphinoyl radical **B**, via the abstraction of one radical H$^\cdot$. At this point, the *para/meta* relationship of fluoro and trifluoromethyl groups on the benzo[*b*]phosphindole motif can be rationalized starting from the intermediate **C**. Indeed, an alternative pathway can be conducted via a 4-*exo-trig* cyclisation at the *ipso*-carbon leading the spiro-cyclohexadienyl radical species **F**. Thus, via a ring expansion, the intermediate **H** was obtained and similarly to **D** finally gave the isomer **3'**.[23a-b] The variable regioselectivity of the transformation may be due to the equilibrium between the alkenyl radical **C** and the spiro-cyclohexadienyl radical **F** and their relative stability and reactivity.

The formation of compound **4a** from **3a** was then studied. It was shown that all the reactant (AcOH, TBHP, Fe(OTf)$_2$ catalyst) and blue light are crucial to be able to observe the transformation of **3a** to **4a**. (see SI, Table S7) Noticeably, when the reaction was performed with **3a** in the reaction conditions [Fe(OTf)$_2$ (10 mol%), 2 equiv. of TBHP in acetic acid at rt under blue light activation (2×24W-blue LED) under argon], 20% of **4a** was detected after 7 h. Thus, the formation of the 9-phenyltribenzo[*b,e,g*]-phosphindole 9-oxide derivatives **4** from benzo[*b*]phosphole oxides **3** can be described a Mallory type reaction promoted by blue light with assitance of iron catalyst, even if its nature is not fully rationalized.[29b,41]



Scheme 5. Proposed reaction mechanism for the benzo[*b*]phosphole oxide **3** and 9-phenyltribenzo- [*b,e,g*]phosphindole 9-oxide **4** preparation.

Spectroscopic analyses of obtained tribenzophosphindole oxides showed, as expected, absorption bands in the visible range associated with intense blue luminescence (Fig. S73-75 and Table

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S8).[30,31] In addition, they also display easily accessible reduction (Fig. S67) which is an advantage in the context of organic batteries.[43]

Conclusions

In summary, we have developed a straightforward protocol for the synthesis of benzo[*b*]phosphole oxides **3** and 9-phenyltribenzo[*b,e,g*]phosphindole 9-oxides **4** starting from secondary diarylphosphine oxides and internal alkynes catalyzed by $Fe(NO_3)_3$ and $Fe(OTf)_2$, respectively, in the presence of TBHP as the oxidant and promoted by blue light activation at ambient temperature. Control experiments revealed that radical processes are involved which permitted to propose a reasonable mechanism. This innovative synthetic approach will open new perspectives for the synthesis of phosphindoles which are strategic compounds in the fields of optoelectronics, biophotonics or energy.

Experimental section

General procedure for blue-light driven iron-catalyzed synthesis of benzo[*b*]phosphole oxide 3. In a Schlenk tube, under argon atmosphere, secondary phosphine oxide **1** (0.2 mmol), alkyne **2** (0.4 mmol), $Fe(NO_3)_3$ (10 mol%), TBHP (2.0 equiv.), were dissolved in 1.0 mL of MeOH and the resulting mixture was stirred at rt under blue light irradiation (2 × 24 W LED; **λ**= 450-460 nm) for 12 h. Thus, the crude reaction mixture was diluted with EtOAc (5 mL), filtered through a Celite pad which was then washed with 10 mL of CH_2Cl_2. The volatiles were then removed under reduced pressure, and the residue was subjected to silica gel column chromatography [eluting with petroleum ether (PE)/ethyl acetate (EA)] to afford the corresponding product **3**.

General procedure for the one pot synthesis of 9-phenyltribenzo[*b,e,g*]-phosphindole 9-oxide 4. In a Schlenk tube, under argon atmosphere, secondary phosphine oxide **1** (0.2 mmol), alkyne **2** (0.4 mmol), $Fe(OTf)_2$ (10 mol%), TBHP (2.0 equiv.), were dissolved in 1.0 mL of AcOH and the resulting mixture was stirred at rt under blue light irradiation (2 × 24 W LED; **λ**= 450-460 nm) for 12 h. Thus, the crude reaction mixture was diluted with EtOAc (5 mL), filtered through a Celite pad which was then washed with 10 mL of CH_2Cl_2. The volatiles were then removed under reduced pressure, and the residue was subjected to silica gel column chromatography [eluting with petroleum ether (PE)/ethyl acetate (EA)] to afford the corresponding product **4**.

Conflicts of interest

There are no conflicts to declare.

Data availability

A data supporting this article have been included as part of the ESI. Crystallographic data for compound **4e** and **4g** have been deposited at the CCDC under deposition numbers 2448333 and 2448328, respectively, and can be obtained from https://www.ccdc.cam.ac.uk. All other data including NMR supporting this article have been included as part of the ESI.

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Using Blue-Light Driven Iron-Catalysis to Afford Molecular Diversity in Phosphindole Oxide Derivatives

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Data Availability Statement

A data supporting this article have been included as part of the ESI.
Crystallographic data for compound 4e and 4g have been deposited at the CCDC under deposition numbers 2448333 and 2448328, respectively, and can be obtained from https://www.ccdc.cam.ac.uk. All other data including NMR supporting this article have been included as part of the ESI.