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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 on the nature of the iron precursors, benzo[*b*]phosphole oxides were obtained using Fe(NO₃)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 have shown 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} (Fig. 1).

Most of the conventional preparations of benzo[*b*]phosphole derivatives⁹ 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 and b). Transition metal catalysis has also shown its advantages for the preparation of benzo[*b*]phosphole oxides starting from *o*-diaryl-phosphino-phenylalkynes using Pd(OAc)₂/CuI cocatalysts¹⁶ (Scheme 1c). Benzophosphole synthesis can be also done through electrophilic trapping with PhPCl₂ of a zirconaindene, obtained from Cp₂ZrPh₂ and an alkyne¹⁷ (Scheme 1d).

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 R³PCl₂, 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-phosponates 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(dmgh₂)₂PyCl (15 mol%) in the presence of HCO₂Na 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

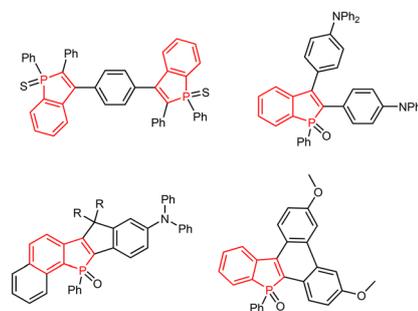


Fig. 1 Representative examples of benzo[*b*]phosphole for optoelectronics or biophotonics.

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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 ₃ CN	40
2	FeBr ₃	Blue-LED	CH ₃ CN	—
3	FeF ₃	Blue-LED	CH ₃ CN	6
4	Fe(OTf) ₂	Blue-LED	CH ₃ CN	— ^b
5	FeCl ₃	Blue-LED	CH ₃ CN	— ^c
6	FeSO ₄	Blue-LED	CH ₃ CN	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	—

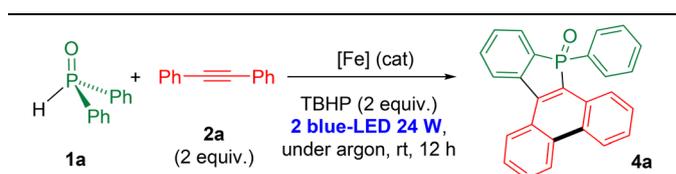
^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), [Fe] (10 mol%), TBHP (2 equiv.), solvent (1 mL), 2 blue-LEDs 24 W (450–460 nm), rt, 12 h under argon. Isolated yields after purification by flash chromatography on silica. ^b A by-product was observed in 40% yield and was identified as 9-phenyltribenzo[*b,e,g*]phosphindole 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.

ducted 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, FeCl₃ and Fe(SO₄), 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 Fig. 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, FeCl₃ and Fe(SO₄) (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).

The nature of the solvents on the activity was then evaluated. In non-protonic chlorinated solvents such as dichloro-

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 ₃ CN	40
2	FeCl ₃	Blue-LED	CH ₃ CN	22
3	FeSO ₄	Blue-LED	CH ₃ CN	>5 ^b
4	Fe(OTf) ₂	Blue-LED	CH ₂ Cl 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	—

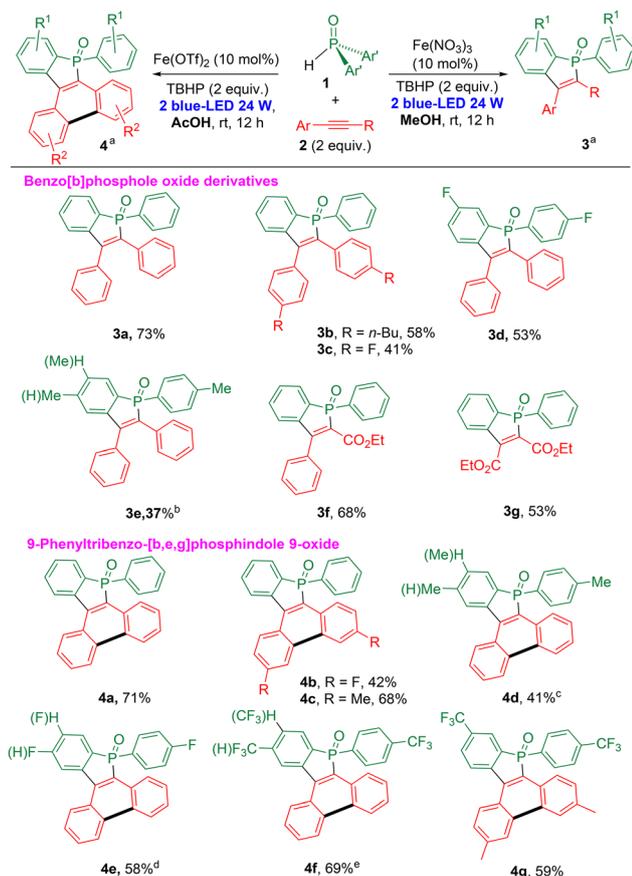
^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), [Fe] (10 mol%), TBHP (2 equiv.), solvent (1 mL), 2 blue-LEDs 24 W (450–460 nm), rt, 12 h under argon. Isolated yields after purification by flash chromatography on silica. ^b **3a** was obtained in 22% yield. ^c Dicumylperoxide was used instead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

methane and 1,2-dichloroethane (1,2-DCE), the formation of **4a** was not favored with a maximum of 26% yield in CH₂Cl₂ (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(NO₃)₃ (10 mol%), 2 equiv. of alkyne, 1 equiv. of secondary phosphine oxide and 2 equiv. of TBHP in methanol for 12 h at rt under blue light activation (2 × 24 W-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-





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**: $\text{Fe}(\text{NO}_3)_3$ (10 mol%), alkyne (2 equiv.), secondary phosphine oxide (1 equiv.), TBHP (2 equiv.) in methanol, 12 h at rt under blue light activation (2×24 W-blue LED) and argon. Isolated yields. ^b ~1:1 ratio based on ³¹P-NMR. For the preparation of 9-phenyltribenzo-[*b,e,g*]phosphindole 9-oxide derivatives **4**: $\text{Fe}(\text{OTf})_2$ (10 mol%), alkyne (2 equiv.), secondary phosphine oxide (1 equiv.), TBHP (2 equiv.) in acetic acid, 12 h at rt under blue light activation (2×24 W-blue LED) and argon. Isolated yields. ^c ~1:1 ratio based on ³¹P-NMR; purity ~ 80%. ^d 85% of *p*-substituted F, 15% of *m*-substituted F on the benzo[*b*]phosphindole motif, based on X-ray analysis. ^e Undefined ratio *p*-substituted CF_3 and *m*-substituted CF_3 on the benzo[*b*]phosphindole motif.

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-ynoate 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 [$\text{Fe}(\text{OTf})_2$ (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 (2×24 W-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 compounds **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 diphenylacetylene 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 Fig. 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 substituents 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 two structures in which the fluorine was located at the *para* position (**4e-1**) and at the *meta* position (**4e-2**) (see Fig. S3). Noticeably, no expected 9-phenyltribenzo[*b,e,g*]phosphindole 9-oxide product was obtained by reaction of **1a** with di(2-naphthyl)acetylene.

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

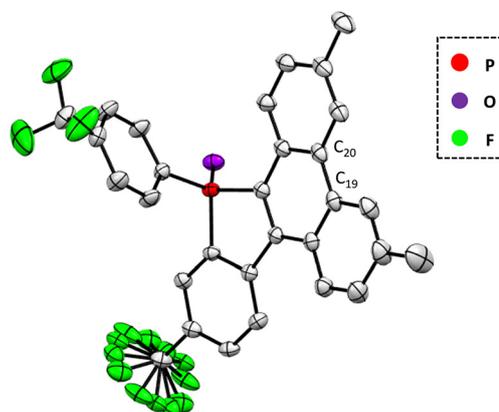
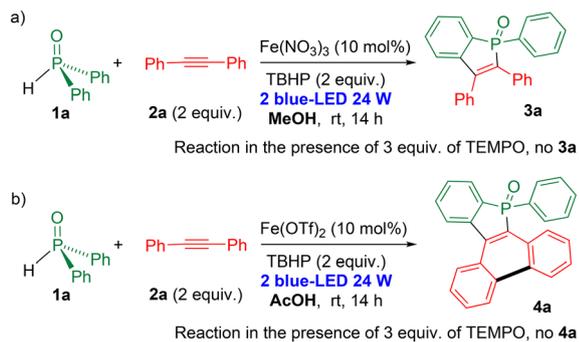


Fig. 2 Molecular structure of **4g**.

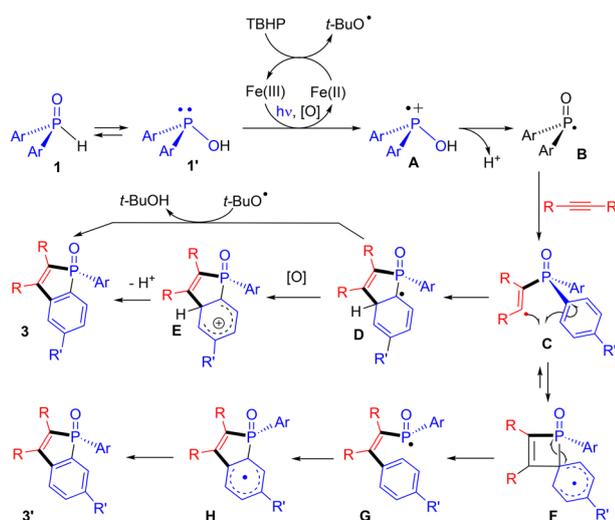




Scheme 4 Control experiments.

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 $\text{Fe}(\text{NO}_3)_3$ 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 4a). Similarly, when conducted the reaction with 3 equiv. of TEMPO and 10 mol% of $\text{Fe}(\text{OTf})_2$ catalyst, no product **4a** was observed (Scheme 4b). These experimental evidences support a radical pathway.

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 5. 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^{28,35b,37}



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

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 $\text{Fe}(\text{III})$ ⁴⁰ and/or TBHP²⁰ 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, $\text{Fe}(\text{OTf})_2$ catalyst) and blue light are crucial to be able to observe the transformation of **3a** to **4a** (see Table S7). Noticeably, when the reaction was performed with **3a** in the reaction conditions [$\text{Fe}(\text{OTf})_2$ (10 mol%), 2 equiv. of TBHP in acetic acid at rt under blue light activation (2×24 W-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 assistance of iron catalyst, even if its nature is not fully rationalized.^{29b,41}

Spectroscopic analyses of obtained tribenzophosphindole oxides showed, as expected, absorption bands in the visible range associated with intense blue luminescence (Fig. S73–S75 and Table S8).^{30,31} In addition, they also display easily accessible reduction (Fig. S67) which is an advantage in the context of organic batteries.^{42,43}

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 $\text{Fe}(\text{NO}_3)_3$ and $\text{Fe}(\text{OTf})_2$, 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(NO₃)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 CH₂Cl₂. 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 CH₂Cl₂. 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 SI.

Experimental details and analytical data, NMR data and X-ray crystallographic data. See DOI: <https://doi.org/10.1039/d5dt01551k>.

CCDC 2448328 and 2448333 contains the supplementary crystallographic data for this paper.^{44a,b}

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and diethyl but-2-ynedioate, the expected benzo[*b*]phosphindole was the major compound ($\delta = 32.5$ ppm) associated to 5 by products ($\delta = 47.2, 44.1, 43.9, 30.0,$ and 25.1 ppm), in ratio 1/0.08/0.03/0.04/0.08/0.05 (purity $\sim 75\%$).

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