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**Preprint Title** Metal-free synthesis of biarenes via photoextrusion in di(tri)arylphosphates

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**Publication Date** 28 Sep. 2020

**Article Type** Full Research Paper

**Supporting Information File 1** Fagnoni\_Metal-free synthesis of biarenes\_SI.pdf; 3.6 MB

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# Metal-free synthesis of biarenes via photoextrusion in di(tri)arylphosphates

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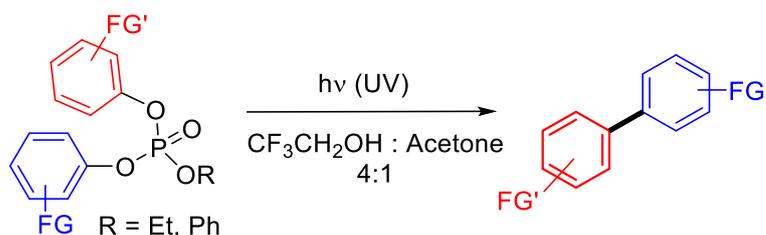
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Keywords: aryl phosphates, biarenes, metal-free synthesis, photochemistry, photoextrusion.

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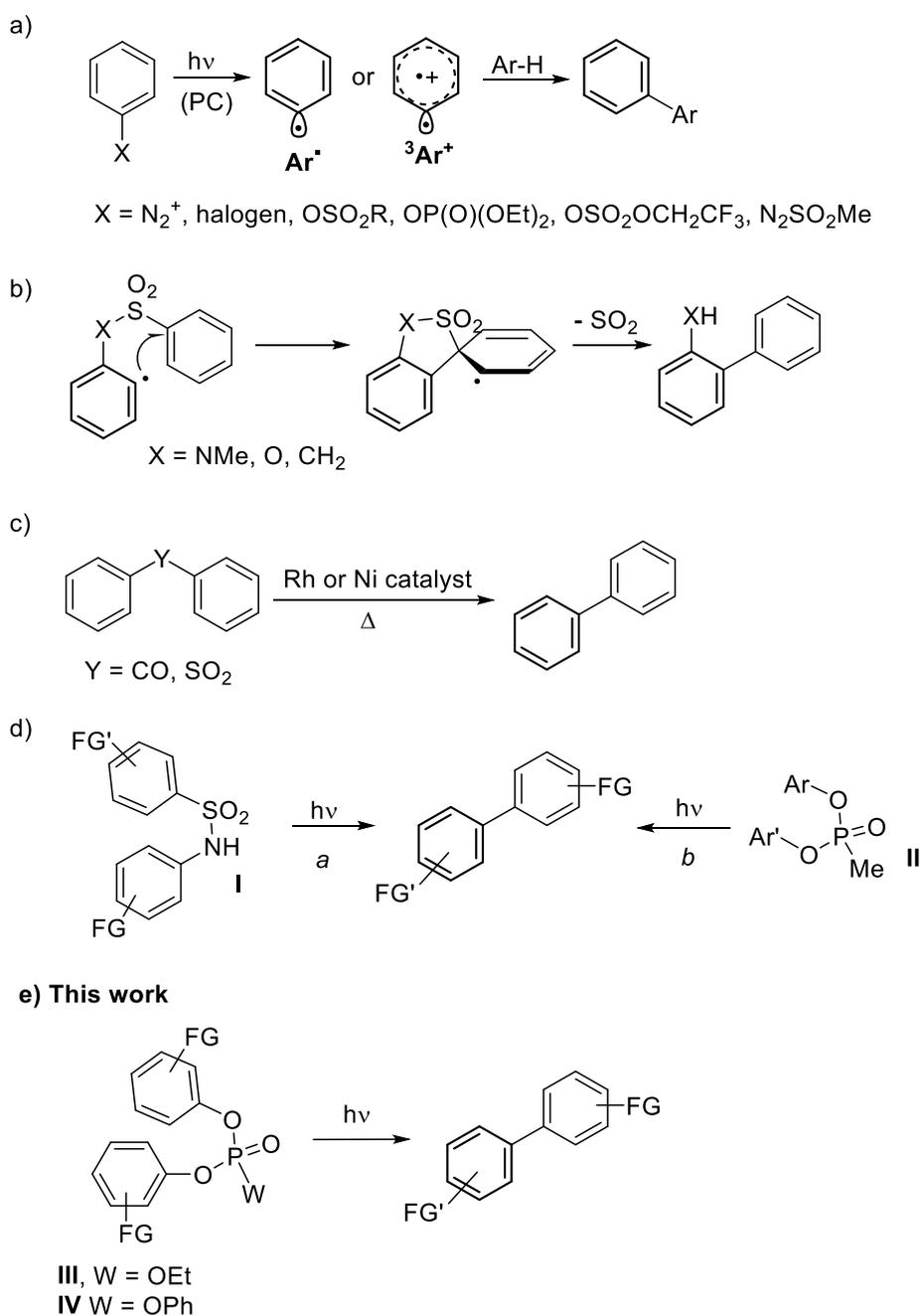


**Abstract:** A metal-free route for the synthesis of biarenes has been developed. This approach is based on the photoextrusion of a phosphate moiety occurring upon irradiation of biaryl- and triarylphosphates. The reaction involved an exciplex as the intermediate and it is especially suitable for the preparation of electron-rich biarenes.

## Introduction

It is difficult to overestimate the importance of aromatics in drug development. Indeed, introducing an aromatic or a heteroaromatic ring, most often a (substituted) phenyl ring, into a biologically active compound is a common practice in medicinal chemistry [1]. In particular, the biaryl moiety is a privileged structure largely present in the skeleton of natural substances [2] and in useful chiral ligands [3]. The synthesis of biaryl derivatives remains, however, a considerable challenge [4]. Common methods, such as the Ullmann and Gomberg synthesis [5] have been nowadays supplanted by the much more versatile metal catalyzed cross-coupling reactions [6]. This excellent approach still encounters some limitation in the scope and in the practical application, due to the use of labile and expensive reagents. Moreover, elimination of metal trace residues and wastes is of some concern particularly for products destined to pharmaceutical applications as it is imperative operating under 'green' conditions. As for the last issue, there is nowadays a growing interest in the forging of Ar-Ar bonds under transition metal-free conditions [7]. Apart the most common pathways e.g. Friedel-Crafts functionalization [8] or nucleophilic aromatic substitution [9], different approaches are emerging that made use of photogenerated intermediates (triplet aryl cations [10] or aryl radicals [11]). As for the former case, the intermolecular formation of a biaryl arose from the photoheterolysis of an Ar-N bond (in arene diazonium salts or their derivatives [12a,b], of an Ar-Cl bond [12c,d], of an Ar-O bond (in aryl phosphates [12e], aryl sulfonates [12e] and in aryl trifluoroethyl sulfate [12f], (Scheme 1a) followed by the reaction of the thus formed aryl cation with an aromatic. In alternative, aryl radicals may be generated under photoredox catalysis (mostly from arene diazonium salt or aryl iodides) [11] or by direct photolysis of arylazo sulfones [13] and employed for the desired arylations. These reactions have the advantage of being applied to non-functionalized arenes but have the drawback to require a large excess of the nucleophilic reagent (the arene Ar-H) in up to 10-20 fold amount. Furthermore, the aryl radical/cation addition onto the aromatic may lead to a mixture of regioisomers when using non-symmetrical Ar-H. A possible solution is having recourse to an intramolecular free radical ipso substitution reaction where a XSO<sub>2</sub> tether is placed between two aromatic rings to direct the selective Ar-Ar bond formation (Scheme 1b) [14]). In this case, *N*-methylsulphonamides were the elective substrates albeit part of the tether is maintained in the final structure. This is common even for other related metal-free biaryl synthesis exploiting the Truce-Smiles rearrangement in aryl sulfonamides and aryl phenylsulfonates [15] or the [3,3]-sigmatropic rearrangement of sulfonium salts arising from the reaction of aryl sulfoxides and phenols [16]. To overcome this problem the use of a metal-catalyst (mainly Ni) was mandatory as reported for the real extrusion of CO in diaryl

ketones [17] or of SO<sub>2</sub> in diaryl sulfones (Scheme 1c) [18]. Nevertheless, a recent publication demonstrated that a metal-free photoextrusion was feasible when starting from benzenesulfonamides **I** (Scheme 1d, path a) [19]. Following the same approach, sparse reports described that in some cases biaryls may be obtained in variable yields starting from biaryl phosphates [20], biaryl phosphonates **II** [21] and triaryl phosphates [22] (Scheme 1d, path b). In search for alternative ways for the preparation of biaryls under photoinduced metal-free eco-sustainable conditions we reinvestigated the photochemistry of di- and triarylphosphates **III** and **IV** (Scheme 1e), compounds that can be easily achieved from the corresponding phenols [23].



**Scheme 1.** Synthesis of biarenes via a) photogenerated triplet aryl cations and aryl radicals (PC = photocatalyst) b) intramolecular free radical ipso substitution c) thermal catalyzed extrusion of CO and SO<sub>2</sub>, d) photoinduced photoextrusion from benzenesulfonamides **I** and phosphonates **II** e) photoextrusion from diaryl- and triarylphosphates.

## Results and Discussion

At the onset of our investigation, we tested a triaryl phosphate such as 4-chlorophenyl diphenyl phosphate (**1a**) as the model compound in different solvents under 310 nm irradiation. The obtained results are depicted in Table 1. Compound **1a** (0.02 M) was quite photostable in dichloromethane, acetonitrile and acetone (entries 1-3), whereas 4,4'-dichlorobiphenyl **2a** was observed in traces as the only product in neat methanol (30% of **1a** consumption, entry 4). Interestingly, the addition of water (a methanol/water 2:1 mixture) increased the overall yield of **2a** (up to 16 %) along with negligible amounts of biphenyl **2b**. Decreasing of **1a** concentration (down to 10<sup>-2</sup> M) in the examined conditions was found noxious for the reaction course (entry 6) but shifting to 254 nm led to significant amounts of the desired biphenyl (entry 7). The yields started to be satisfactory, however, at 310 nm when using 2,2,2-trifluoroethanol (TFE) as the solvent (45% yield, entry 8). We thus decided to replace part of such rather expensive and toxic solvent with acetone (entries 9-12) and the best results were obtained when using a TFE/Acetone 4:1 mixture (entry 10) with an isolated yield of **2a** of 67% along with **2b** (4% yield) as the byproduct. A further increase in the concentration of the substrate (entries 13,14) resulted in a lowering of the selectivity (the undesired **2b** detected in up to 12% yield). Finally, no reaction took place when the solution was covered by an aluminum foil and stored in the photochemical apparatus for 24 h (entry 15).

**Table 1.** Optimization of the reaction conditions.

$\text{1a} \xrightarrow[\text{Conditions}]{h\nu (310 \text{ nm})} \text{2a} + \text{Ph-Ph (2b)}$

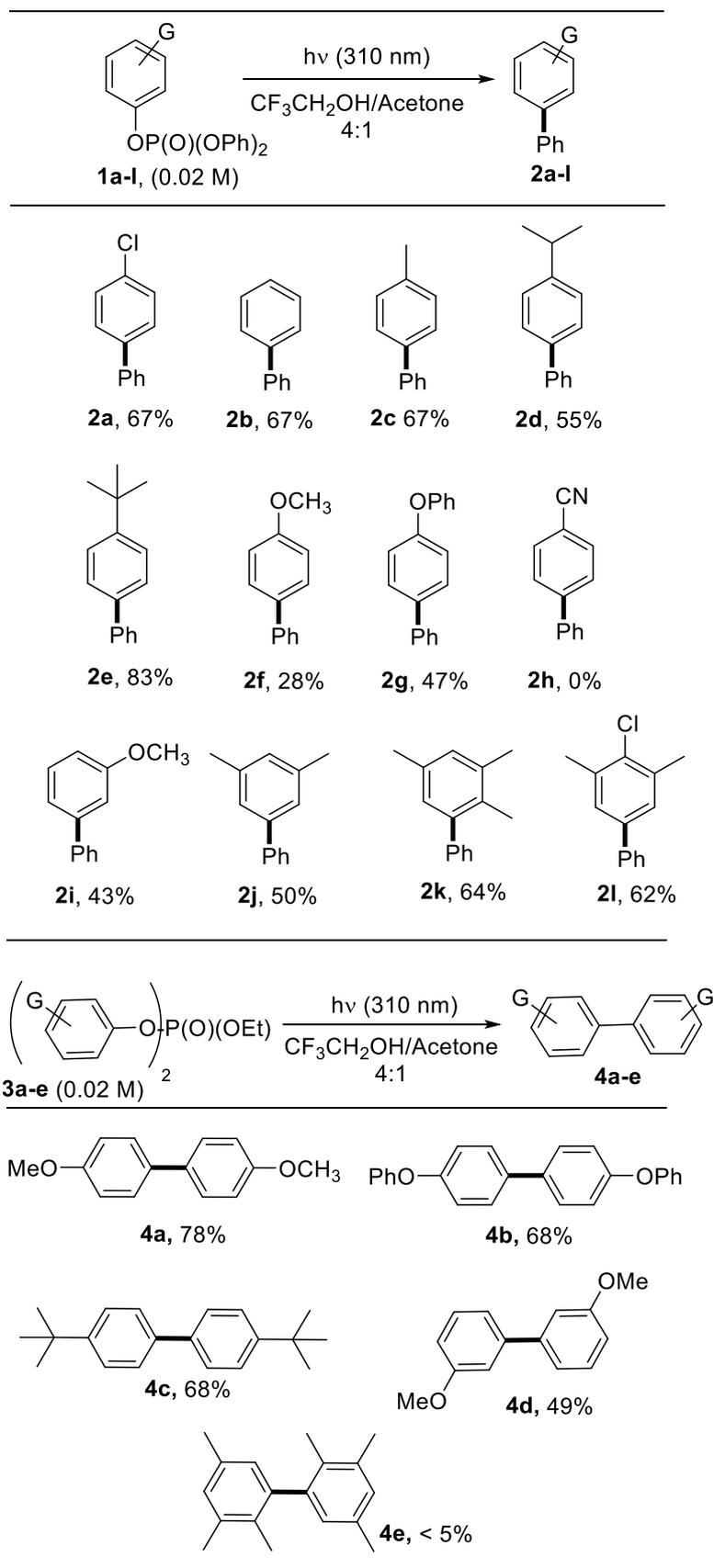
Entry	Reaction conditions	$\lambda_{\text{irr}}$ (nm)	Products, % yield
1	<b>1a</b> (0.02 M), CH <sub>2</sub> Cl <sub>2</sub>	310	- <sup>a</sup>
2	<b>1a</b> (0.02 M), CH <sub>3</sub> CN	310	- <sup>a</sup>
3	<b>1a</b> (0.02 M), Acetone	310	- <sup>a</sup>
4	<b>1a</b> (0.02 M), CH <sub>3</sub> OH	310	<b>2a</b> , 3 <sup>b</sup>
5	<b>1a</b> (0.02 M), CH <sub>3</sub> OH/H <sub>2</sub> O 2:1	310	<b>2a</b> , 16; <b>2b</b> , 1
6	<b>1a</b> (0.01 M), CH <sub>3</sub> OH/H <sub>2</sub> O 2:1	310	<b>2a</b> , 6
7	<b>1a</b> (0.01 M), CH <sub>3</sub> OH/H <sub>2</sub> O 2:1	254	<b>2a</b> , 44
8	<b>1a</b> (0.02 M), CF <sub>3</sub> CH <sub>2</sub> OH	310	<b>2a</b> , 45; <b>2b</b> , 2
9	<b>1a</b> (0.02 M), CF <sub>3</sub> CH <sub>2</sub> OH/Acetone 9:1	310	<b>2a</b> , 38; <b>2b</b> , 2
<b>10</b>	<b>1a</b> (0.02 M), CF <sub>3</sub> CH <sub>2</sub> OH/Acetone 4:1	<b>310</b>	<b>2a</b> , 67; <b>2b</b> , 4
11	<b>1a</b> (0.02 M), CF <sub>3</sub> CH <sub>2</sub> OH/Acetone 7:3	310	<b>2a</b> , 48; <b>2b</b> , 3
12	<b>1a</b> (0.02 M), CF <sub>3</sub> CH <sub>2</sub> OH/Acetone 1:1	310	<b>2a</b> , 14; <b>2b</b> , 2
13	<b>1a</b> (0.04 M), CF <sub>3</sub> CH <sub>2</sub> OH/Acetone 4:1	310	<b>2a</b> , 57; <b>2b</b> , 2
14	<b>1a</b> (0.06 M), CF <sub>3</sub> CH <sub>2</sub> OH/Acetone 4:1	310	<b>2a</b> , 67; <b>2b</b> , 12
15	<b>1a</b> (0.02 M), CF <sub>3</sub> CH <sub>2</sub> OH/Acetone 4:1 <sup>c</sup>	310	- <sup>a</sup>

<sup>a</sup> No consumption of **1a** observed <sup>b</sup> 30% consumption of **1a** measured. <sup>c</sup> the reaction mixture was stored in the dark for 24 h.

Encouraged by the results of Table 1, in particular with the fact that byproduct **2b** was formed in such a small amount, we used the conditions described in entry 10 to explore the scope of the process investigating other n-substituted phenyl diphenyl phosphates (**1a-l**, see Table 2). Thus, irradiation of triphenylphosphate **1b** gave the corresponding biphenyl **2b** in 67% yield. Similar results were obtained with 4-alkylphenyl diphenyl phosphates, that afforded the 4-substituted biaryls **2c-e** in up to 83% yield. However, when examining substrates bearing strong electron-donating substituent (G = 4-OMe, 4-OPh, 3-OMe), the efficiency of the process decreased (see the yields of **2f,g** and **2i**). On the other hand, the presence of an electron-withdrawing group (e.g. 4-CN, compound **1h**) completely inhibited the reaction and **1h** was recovered unaltered after the irradiation. Better results have been however obtained with polysubstituted derivatives **1j-1l**. In this case, the expected phenylated arenes **2j-2l** have been isolated in the 50-64% range.

We were then intrigued to extend the scope of the reaction by focusing on a few ethyl diarylphosphates **3a-e**. Gratifyingly, the formation of symmetric biaryls **4** took place efficiently with substrates bearing strong electron-donating substituents, especially when present in para-position (see the case of **4a-c**). Unfortunately, the unsymmetric biaryl **4e** was detected in a very poor amount.

**Table 2.** Metal-free photochemical synthesis of biaryls **2**, **4**.



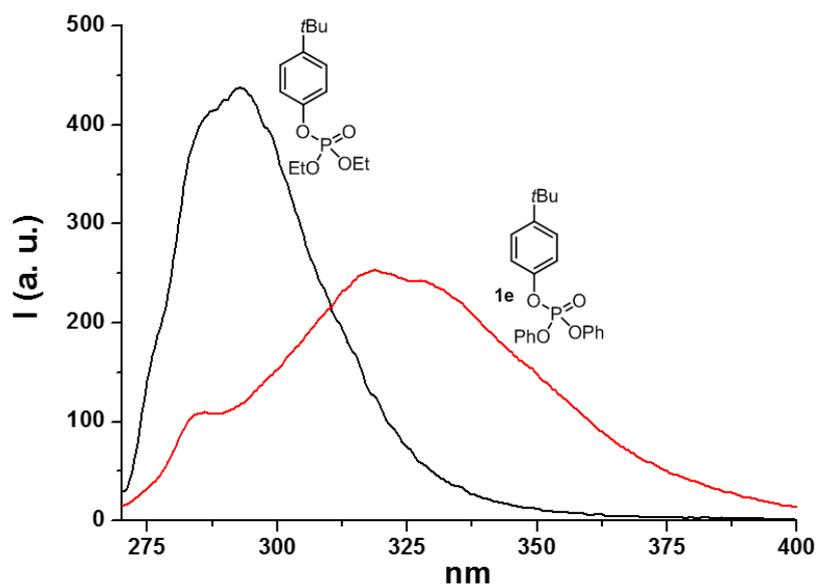
To investigate the reaction mechanism, some photophysical parameters of compounds **1** and **3** have been determined. All the phosphates examined were barely fluorescent in methanol, with an emission quantum yield ( $\Phi_{em}$ ) in the 0.005-0.06 range (see Table 3 and the Supporting Information for further details).

**Table 3.** Emission data of selected diaryl and triarylphosphates **1, 3**

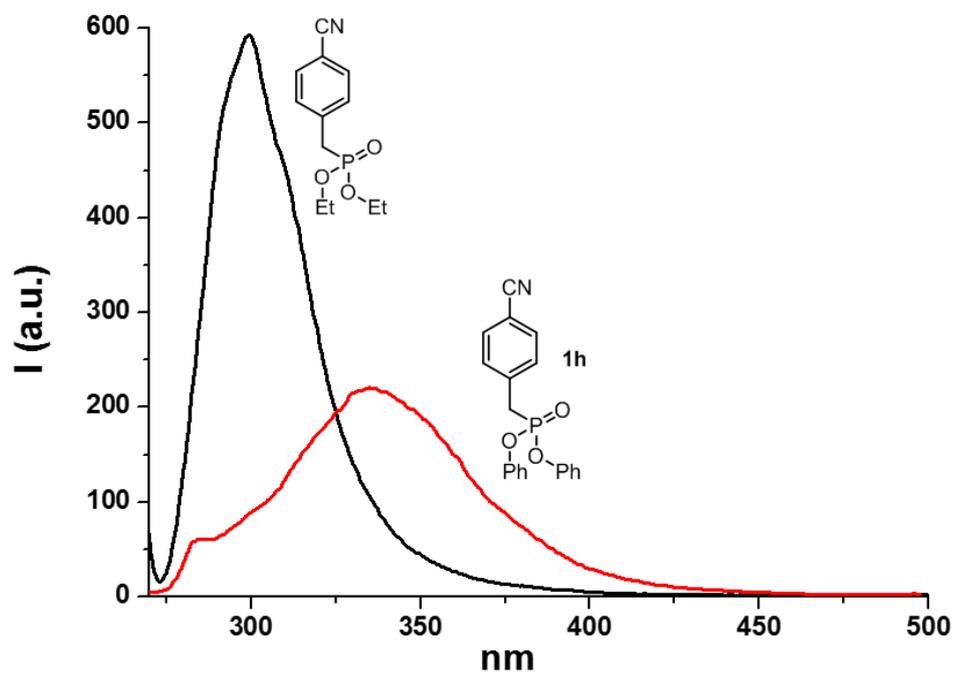
Compound	$\lambda_{em}$ (nm)	$\Phi_{em}^a$
<b>1a</b>	300	0.005
<b>1b</b>	315	0.017
<b>1e</b>	319	0.025
<b>1f</b>	312	0.059
<b>1h</b>	335	0.023
<b>3a</b>	307, 360	0.030
<b>3c</b>	294	0.062

<sup>a</sup> Measured by comparison with 4-chloroanisole ( $\Phi_F = 0.019$  in MeOH) [24]

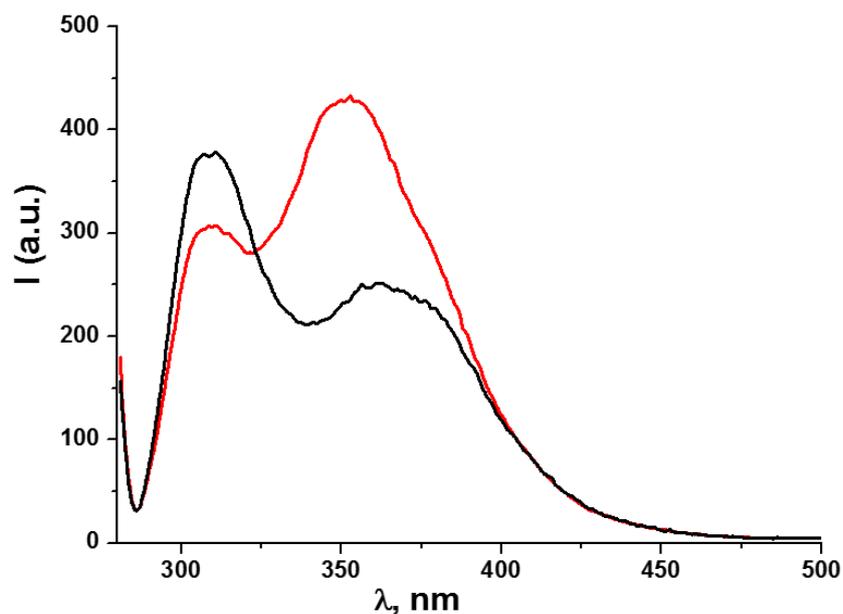
We thus focused on compounds **1e**, **1h**, **3a** and **3c** as the model substrates. In the case of compounds **1e** and **1h**, we observed that the fluorescence is significantly red shifted (about 30 nm) with respect to that of the corresponding diethyl aryl phosphates (see Figures 1, 2). On the other hand, when focusing on compound **3a**, we noticed the presence of two emission bands, located at 307 and 360 nm, respectively (see Figure 3) and their relative intensity is solvent dependent. Indeed, the band at 360 nm is favored when increasing the proticity of the medium (see the comparison of the fluorescence spectra obtained in methanol and in methanol/TFE 4:1 mixture, Figure 3). A similar behavior was observed in the case of **3c**, where a single emission band located at ca. 290 nm is observable in neat methanol, whereas the presence of TFE causes a lowering of that emission, in favor of a second band in the 330-350 nm region (Figure 4).



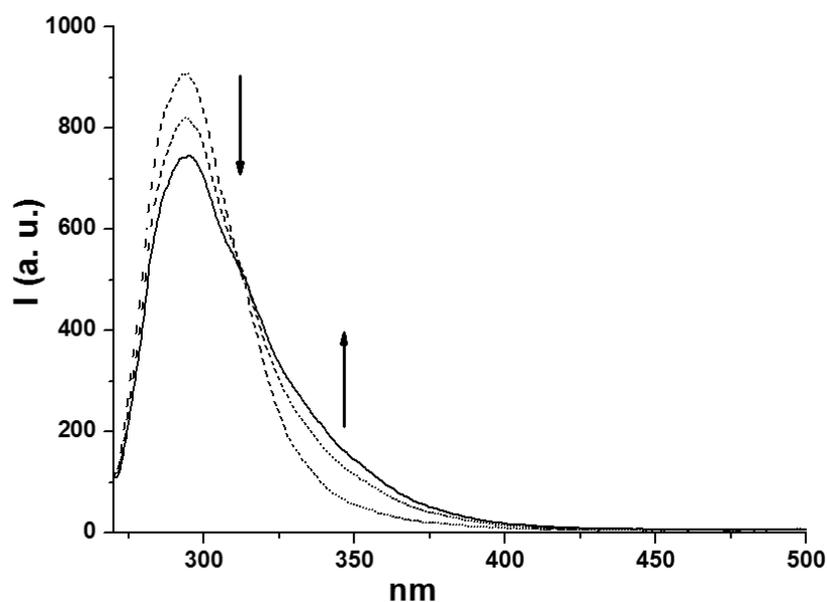
**Figure 1.** a) Emission spectrum of compound **1e** (red) and of diethyl *p*-tertbutylphenyl phosphate (black) in methanol.



**Figure 2.** a) Emission spectrum of compound **1h** (red) and of diethyl *p*-cyanophenyl phosphate (black) in methanol.



**Figure 3.** b) Emission spectrum of compound **3a** in methanol (black) and in methanol/2,2,2-trifluoroethanol (TFE) 4:1 mixture (red).

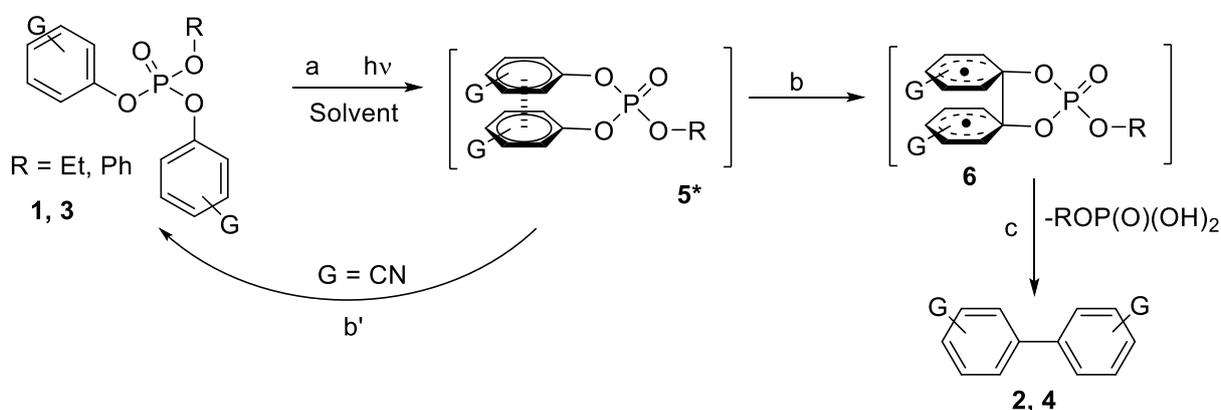


**Figure 4.** Emission spectrum of **3c** in MeOH (continuous line) and in the presence of increasing amounts of 2,2,2-trifluoroethanol (up to 20% v/v, dotted line)

While aryl phosphates have been only sparsely used as substrates in thermal cross-coupling reactions [25], their photochemical behavior has been the subject of various investigations in the last decades [10, 24, 26a]. Simple (electron-rich) monoaryl phosphates are known to undergo the photolysis of the Ar-O bond to form aryl cations. [10, 12e] The presence of electron-withdrawing group (e.g.

NO<sub>2</sub>) may however divert the reactivity since a photosolvolysis occurred as demonstrated by Havinga more than 70 years ago [26b]. In alternative, irradiation of monoaryl phosphates in the presence of a strong nucleophile (e.g. a tin anion) led to an ipso-substitution reaction via an ArS<sub>RN1</sub> process [27]. The situation dramatically changes when a further aryl group is present in the phosphates since none of the above-mentioned processes took place. In fact, our investigations, in according with early works [20, 28] suggested that both diaryl and triaryl phosphates are prone to generate an intramolecular exciplex **5\*** under irradiation (Scheme 2, path a), on the route to the extrusion of the phosphate moiety. This is demonstrated by the formation of a new emission band when more than one aryl group is present in the aryl phosphate (see Figure 1). In our investigation, we likewise discovered that the formation of **5\*** (from **1** and **3**) is highly favored in highly protic solvents such as TFE, as well evidenced, among the others, in the cases of **1e** and **4c**.

The so-generated exciplex apparently plays a key role in the formation of biaryls **2**, **4** probably via the formation of biradical intermediate **6** preceding the loss of ROP(O)(OH)<sub>2</sub> (paths b, c). However, a dependence on the nature of the aromatic substituents G was apparent since arylation took place (in variable yields) with electron-rich aromatic substituents, while is completely inhibited in the presence of electron-withdrawing groups (path b'). In the case of triarylphosphates, biphenyl **1b** is formed as the byproduct in < 5% yield.



**Scheme 2.** Photoreactivity of arylphosphates **1**, **3** in protic media.

## Conclusion

In conclusion, we demonstrated that biaryls can be smoothly prepared via photoextrusion in diaryl- and triaryl phosphates in protic media, with the concomitant release of a molecule of phosphoric acid monoester. The reaction takes place in moderate yields but under very mild conditions with no need

of any (photo)catalyst or additive, despite the scope of the process is in part limited since the presence of at least one electron-withdrawing group on an aromatic ring completely suppressed the reaction.

## Funding

H. Q. thanks the Arab American University- Palestine (AAUP) for financial support, and the University of Pavia (Italy) for hosting.

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