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A scenic view of the Alhambra in Granada, Spain, with the city's orange-tinted buildings and walls set against a backdrop of lush green trees and blue mountains. A red glow is visible on the mountain peaks in the background.

ABSTRACTS BOOK

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NEW FORMING C(sp²)-P(B) BONDS DRIVEN BY VISIBLE LIGHT

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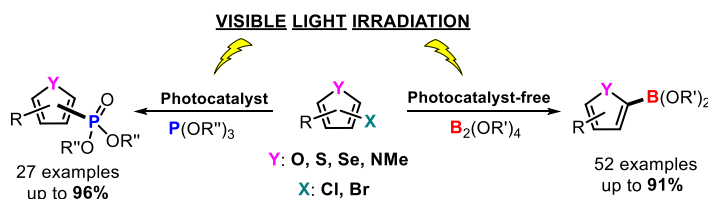
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We have witnessed during the last decade the great evolution that visible-light photoredox catalysis has experienced as a powerful tool in organic synthesis and formation of new compounds can be now tackle. In this context, generation of radical intermediates such as aryl radicals and their subsequent trapping by the appropriate nucleophile is nowadays one of the main strategies to obtain added-value products.^[1] The use of milder conditions and “sometimes” metal-free photocatalysts encompasses this methodology into the green principles from an economical and environmental point of view.

Aryl phosphonates and their derivatives are fascinating moieties which present a widespread applicability in scientific fields such as life science, materials or as ligand in catalysis.^[2] On the other hand, organoboron compounds, environmentally benign scaffolds, attract considerable interest not only in organic synthesis (they can be easily transformed into any other functional group) but also in other scientific areas of research, for example, as conjugated materials such as organic electronic applications and LEDs manufacturing or antimicrobial agents in medicinal chemistry.^[3]

Therefore, exploration of new procedures for their construction under milder conditions appears to be a challenge task. The question then arises whether production of new forming C(sp²)-heteroatom (B, P) bonds can be achieved by visible light as energy source. Herein, we wish to show our recent results on the phosphorylation and borylation of five-membered heteroarene halides (Figure).^[4] Regarding heteroarene phosphonates, a consecutive photoinduced electron transfer mechanism has been employed whereas new boronic esters have synthesized following a photocatalyst-free protocol. Interestingly, an easy-to-use gel nanoreactor has been used in both strategies which has permitted to enhance the production rate and to protect against oxygen poisoning.



Formation of heteroarene phosphonates and boronic esters by visible light irradiation.

References

- [1] (a) J. Twilton, C. Le, et. al. *Nat. Rev. Chem.* **2017**, 1, 0052. (b) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, 113, 5322.
- [2] (a) X. Chen, D. J., et. al. *J. Med. Chem.* **2012**, 55, 3837. (b) Gagnon, K. J.; Perry, H. P.; Clearfield, A. *Chem. Rev.* **2012**, 112, 1034.
- [3] (a) E. C. Neeve, S. J. Geier, et. al. *Chem. Rev.* **2016**, 116, 9091. (b) T. Noda, Y. J. Shirota, J. *Am. Chem. Soc.* **1998**, 120, 9714.
- [4] (a) J. C. Herrera-Luna, et. al. *ACS App. Mater. Interfaces* **2021**, 13, 48784. (b) J. C. Herrera-Luna, et. al. *Org. Lett.* **2021**, 23, 2320. (c) J. C. Herrera-Luna, et. al. *Org. Lett.* **2020**, 22, 3273.