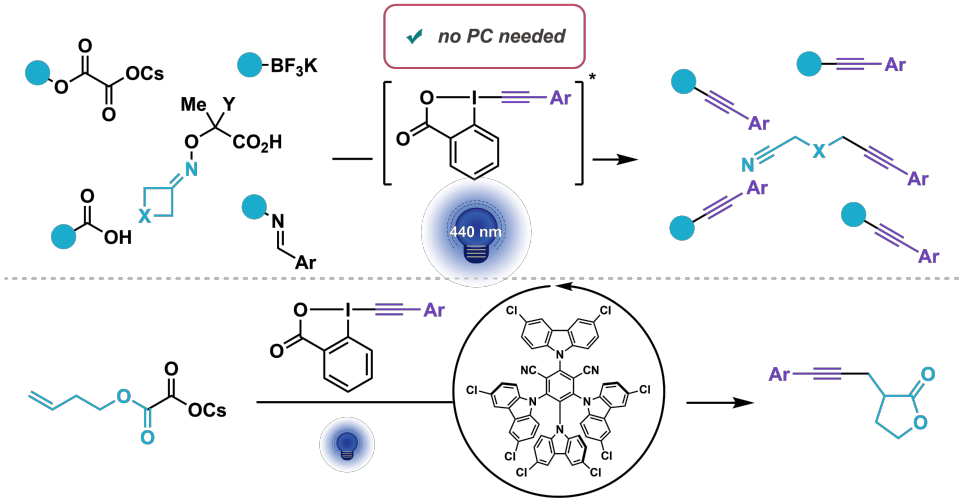
Ethynylbenziodoxolones and Cesium Oxalates under Blue Light: from Deoxyalkynylation to Lactonization

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Alkynes are important moieties for synthetic chemists, and have many applications in biochemistry, medicinal chemistry and material science. Developing new alkynylation strategies is therefore of high importance. A possible method is to combine photoredox catalysis with ethynylbenziodoxolones (EBXs), which have been proved to act as efficient SOMOphiles.[1] Because the alcohol functionality is ubiquitous in nature, the development of new strategies for their re-functionalization is highly appealing. In photochemistry, in order to generate a radical via C-O bond cleavage, the alcohol functionality has to be converted into a redox-active group first. One example of active group is the oxalate moiety developed by MacMillan and Overman.[2] Herein, we describe the development of two different strategies that combine radicals generated from cesium oxalates and EBXs. In our first strategy, we demonstrated how aryl-substituted EBXs can undergo direct photoexcitation and act as photooxidant themselves, alleviating the need for a photocatalyst.[3] The developed reaction conditions were further applied to the deoxyalkynylation of tertiary cesium oxalates. The scope was then extended to previously reported photocatalyzed alkynylation reactions to demonstrate the generality. In the second strategy, we combined homoallylic cesium oxalates and EBXs in a photocatalytic lactonization reaction.[4] A weaker irradiation combined with a sustainable organic photocatalyst was necessary to inhibit competing polymerization



[1] Franck Le Vaillant, *Chemical Science*, **2019**, 10, 8909-8923.
[2] Christopher C. Nawrat, Christopher R. Jamison, Yuriy Slutskyy, David W. C. MacMillan, Larry E. Overman, *Journal of the American Chemical Society*, **2015**, 137, 11270-11273.
[3] Stephanie G. E. Amos‡, Diana Cavalli‡, Franck Le Vaillant, Jerome Waser, *Angewandte Chemie International Edition*, **2021**, 60, 23827-23834. ‡These authors contributed equally to this work.
[4] Manuscript in Preparation.