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Merging organic photoredox catalysis and hypervalent iodine reagents for efficient alkynylation and cyanation

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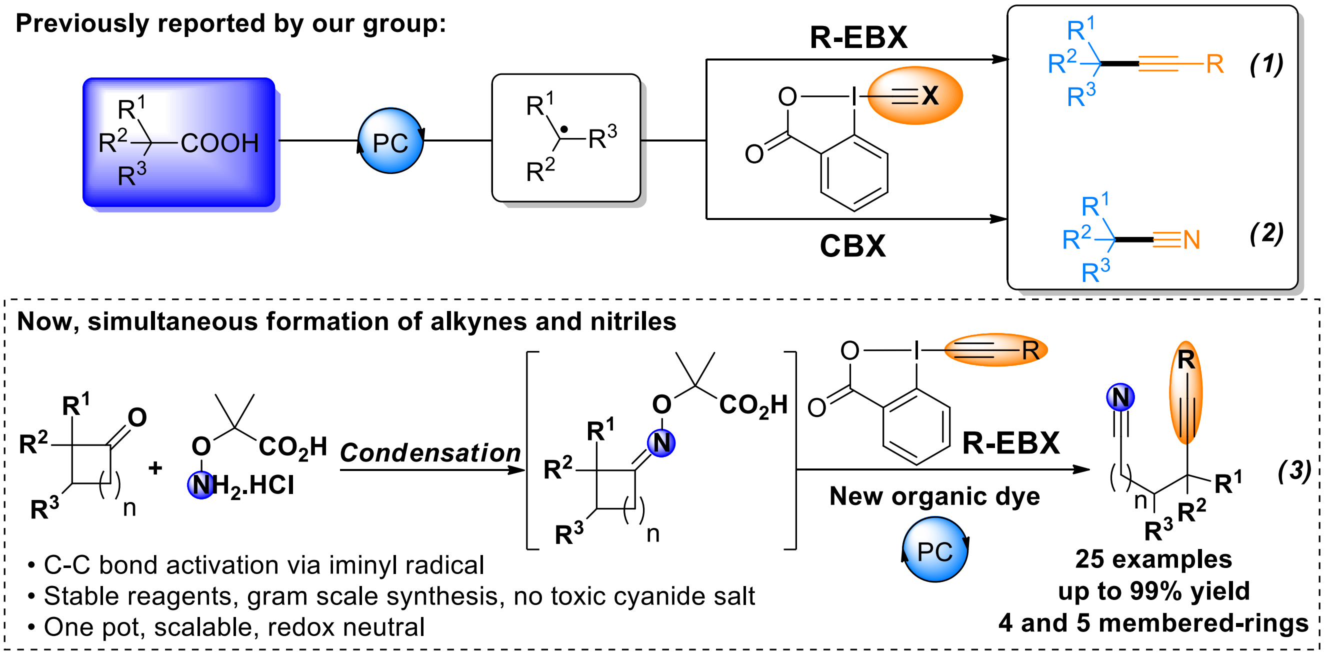
Aliphatic alkynes and nitriles are functional groups of great significance, naturally occurring and broadly used as versatile building blocks in organic synthesis. We developed a unified strategy to access both classes of compounds from carboxylic acids, using photoredox catalysis and hypervalent iodine reagents.[1,2] According to computational and experimental studies, two different mechanisms can be proposed: via radical intermediates for alkynylation, and carbocation intermediates for cyanation. Herein, we describe the remote alkynylation cyanation of cyclic alkylketone oxime ethers via a photoredox catalyzed radical cascade.[3] The reaction is redox neutral and avoid toxic cyanide salts. Fine-tuned organic dyes and one-pot procedure are also reported. Further ongoing applications of the photoredox-catalyzed decarboxylative alkynylation will be presented during the poster session.[4,5,6]



- C-C bond activation via iminyl radical
- Stable reagents, gram scale synthesis, no toxic cyanide salt
- One pot, scalable, redox neutral

[1] F. Le Vaillant, T. Courant, J. Waser, *Angew. Chem. Int. Ed.* **2015**, *54*, 11200-1204.
[2] a) F. Le Vaillant, M. Wodrich, J. Waser, *Chem. Sci.* **2017**, *8*, 1790-1800.; b) F. Le Vaillant, J. Waser, *Chimia* **2017**, *71*, 4, 226-230.
[3] F. Le Vaillant, M. Garreau, S. Nicolai, G. Gryn'ova, C. Corminboeuf, J. Waser, *Chem. Sci.* ***2018**, 9,* 5883-5889.
[4] F. Le Vaillant, S. Amos, J. Waser, *Manuscript in preparation.*
[5] M. Garreau, J. Waser, *Manuscript in preparation.*
[6] F. Le Vaillant, N. Declas, J. Waser, *Submitted.*