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

F. Le Vaillant¹, M. Garreau¹, S. Nicolai¹, S. Amos¹, N. Declas¹, J. Waser¹

¹EPF Lausanne, Laboratory of Catalysis and Organic Synthesis
EPFL SB ISIC LCSO, BCH 4306, 1015 Lausanne, CH, Switzerland
dranck.levaillant@epfl.ch

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 alkyynylation, and carbocation intermediates for cyanation. Herein, we describe the remote alkyynylation 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 alkyynylation will be presented during the poster session.[4,5,6]

Previously reported by our group:

\[ \text{R-EBX} \]

![Diagram](image_url)

Now, simultaneous formation of alkynes and nitriles

\[ \text{R}^1 \text{R}^2 \text{R}^3 \text{COOH} + \text{O} \text{O} \text{CO}_2 \text{H} \text{NH}_2 \text{HCl} \xrightarrow{\text{Condensation}} \text{R}^1 \text{R}^2 \text{R}^3 \text{O} \text{CO}_2 \text{H} \]

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

New organic dye

R-EBX

25 examples up to 99% yield
4 and 5 membered-rings