

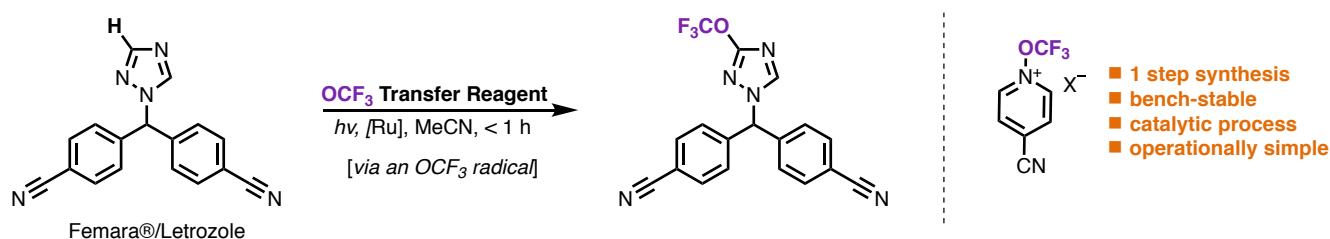
Radical Trifluoromethoxylation of Arenes Triggered by a Visible-Light-Mediated N–O Bond Redox Fragmentation

Benson J. Jelier,^{[a]‡} Pascal F. Tripet,^{[a]‡} Ewa Pietrasiak,^{[a]‡} Ivan Franzoni,^[b] Gunnar Jeschke,^[a] Antonio Togni^{[a]*}

^[a]Department of Chemistry and Biosciences, ETH Zürich,
Vladimir-Prelog-Weg 2, 8093, Zürich, Switzerland

^[b]Department of Chemistry, University of Toronto, Toronto, Canada, M5S 3H6
jelier@inorg.chem.ethz.ch

Although the trifluoromethoxyl substituent is prevalent in a wide range of pharmaceuticals, agrochemicals and materials, methods to introduce this motif into aryl scaffolds are highly underdeveloped and limited. The synthesis of complex aryl trifluoromethyl ethers typically requires building blocks prepared in multistep syntheses with difficult to handle and often harsh reagents and conditions. Furthermore, many of these approaches either suffer from poor substrate scope or require the use of highly reactive, toxic or thermally unstable reagents. Herein, we present a simple trifluoromethoxylation methodology developed in the Togni group that enables non-directed functionalization of C–H bonds on a range of substrates providing direct access to aryl trifluoromethyl ethers. This process is distinctly different than conventional protocols and occurs through an OCF₃ radical mechanism mediated by a photoredox catalyst, triggering a light-driven, neutral N–O bond fragmentation of a bench-stable pyridinium reagent. Furthermore, we will showcase our efforts in developing high-intensity photoreactors suitable for high-throughput screening that may be applicable to the wider community interested in harnessing light driven processes for reaction discovery.



[1] B. J. Jelier, P. F. Tripet, E. Pietrasiak, I. Franzoni, G. Jeschke, A. Togni. *Angew. Chem. Int. Ed.* **2018**, DOI: <https://doi.org/10.1002/anie.201806296>