Development and Scale-up of a Novel Photochemical C-N Oxidative Coupling

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A visible light promoted C-N-coupling of a functionalized pyridazinone with veratrole was developed to forge the central C-N bond of an agrochemical intermediate. Dosing aqueous NaOCl and 4% O_2 in N_2 under blue light irradiation (460 nm) were key to promote the desired transformation while generating benign wastes.[1] Mechanistic studies suggest the formation of a *N*-chloro species which undergoes selective coupling *via* a radical pathway induced by the combination of light and oxygen. Further development led to an optimized semi-batch process, that was successfully scaled up to an initial 20 L and then 1.2 m^3.[2,3]
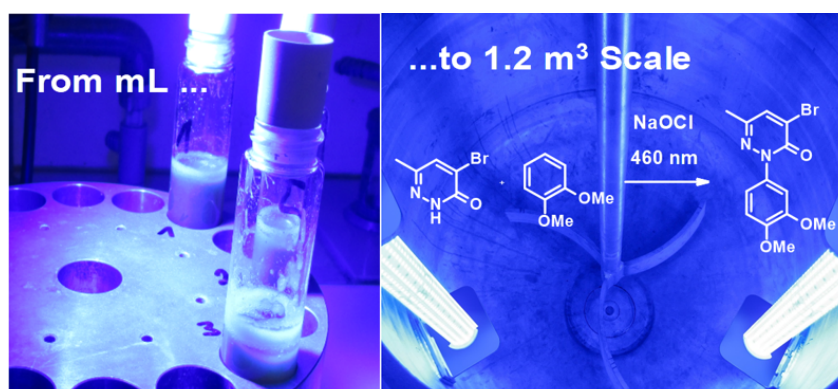
In this presentation we describe the development from conceptualization and screening through to development and technical implementation. Whilst there are several reports on the implementation of continuous photochemistry with homogeneous systems, to the authors' knowledge, this is the first implementation of a heterogenous solid-liquid-liquid-gas photochemical reaction at production scale. The interplay between process chemistry and process engineering, together with the right balance between mechanistic understanding and pragmatism were key factors to success.

[1] WO2019076930 A1 2019-04-25.
[2] A. Robinson, M. Dieckmann, J.-P. Krieger, T. Vent-Schmidt, D. Marantelli, R. Kohlbrenner, D. Gribkov, L. L. Simon, D. Austrup, A. Rod, C. G. Bochet, *Org. Process Res. Dev.* **2021**, *25,* 2205-2220.
[3] L. L. Simon, M. Dieckmann, A. Robinson, T. Vent-Schmidt, D. Marantelli, R. Kohlbrenner, A. Saint-Dizier, D. Gribkov, J.-P. Krieger, *Org. Process Res. Dev.* **2021**, *25,* 2221-2229.