Synthesis Polycycles *via* Photoredox catalyzed Cyclization of Malonate Enol Ethers

Júlia Viñas-Lóbez, Adiran de Aguirre, Guillaume Levitre, Céline Besnard, Amalia I. Poblador-Bahamonde and Jérôme Lacour*

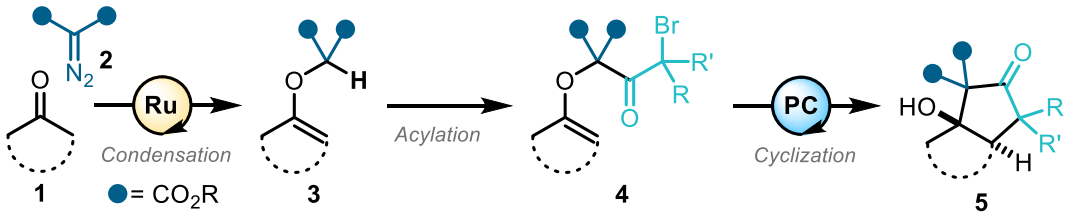
Department of Organic Chemistry, University of Geneva, Geneva.

julia.vinaslobez@unige.ch

Diazo reagents substituted with two electron-withdrawing groups are among the most stable diazo derivatives.[1] Yet, under metal catalysis, they readily decompose to form highly reactive electrophilic carbenes which,[2] upon trapping of various *Lewis* bases, generate subsequent ylide intermediates. Recently, in this context, we reported the condensation of ketones **1** with electrophilic metal carbenes derived from α-diazomalonates **2** and $[CpRu(CH_3CN)_3][BAr_F]$ as catalyst for the effective synthesis of malonate enol ethers **3**.[3]

These 2-vinyloxymalonates **3** are interesting building blocks due to the presence of two different nucleophilic active sites, the enol and malonate groups. They can be exploited separately but also in synergy to promote diverse annulation processes,[3] considerably expanding as a consequence the classical scope of cyclizations derived from carbonyl ylide intermediates.[4]

Herein, capitalizing on the dual reactivity of **3**, we demonstrate that the post-functionalization of the malonate group (**3→4**) paves the way towards the synthesis of complex fused-heterocycles **5**, under visible-light photoredox catalysis.



[1] S.P. Green, K.M. Wheelhouse, A.D. Payne, J.P. Hallett, P.W. Miller, J.A. Bull, J. A., *Org. Process Res. Dev.* **2020**, *24*, 67-84.

[2] a) M.P. Doyle, *Chem. Rev*. **1986**, 86, 919-939 b) D.M. Hodgson, A.H. Labande, S. Muthusa, *Org. React. (Hoboken, NJ, U. S.)* **2013**, *80*, 133-496.

[3] J. Viñas-Lóbez, G. Levitre, A. de Aguirre, C. Besnard, A.I. Poblador-Bahamonde, J. Lacour, *ACS Org. Inorg. Au*, **2021**, *1*, 11-17.

[4] A. Padwa, *ARKIVOC (Gainesville, FL, U. S.)* **2021**, *2021* (5), 24-40.