

ENANTIOSELECTIVE PHOTOCHEMICAL ORGANOCASCADE CATALYSIS

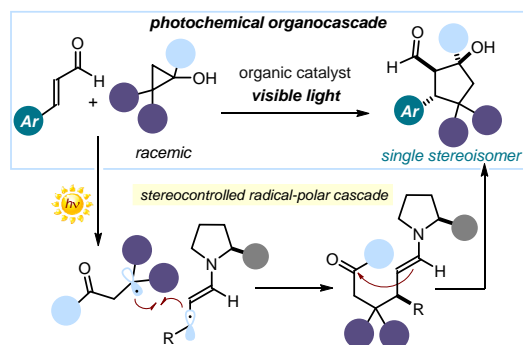
Giandomenico Magagnano,^a Łukasz Woźniak,^a Paolo Melchiorre^{a,b,*}

^a Institute of Chemical Research of Catalonia (ICIQ), Spain

^b ICREA–Catalan Institution for Research and Advanced Studies, Barcelona
gmagagnano@iciq.es

Cascade reactions are valuable tools for streamlining the synthesis of structurally complex chiral molecules in a single operation and from readily available substrates. Their combination with asymmetric aminocatalysis¹ has led to innovative techniques for the one-step enantioselective preparation of stereochemically dense molecules.² Recently, our laboratories found that the synthetic potential of aminocatalytic intermediates is not limited to the ground-state domain but can be expanded by exploiting their photochemical activity. For example, the photoexcitation of iminium ion can switch on novel catalytic functions that are unavailable to the ground-state reactivity. In particular, we demonstrated that excited-state chiral iminium ions act as strong SET oxidants, enabling the enantioselective β -functionalization of enals.³

Reported herein is a photochemical cascade process that combines the excited-state and ground-state reactivity of chiral organocatalytic intermediates. This strategy directly converts racemic cyclopropanols and α,β -unsaturated aldehydes into stereochemically dense cyclopentanols with exquisite stereoselectivity. Mechanistic investigations have enabled elucidating the origin of the stereoconvergence, which is governed by a kinetic resolution process.⁴



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