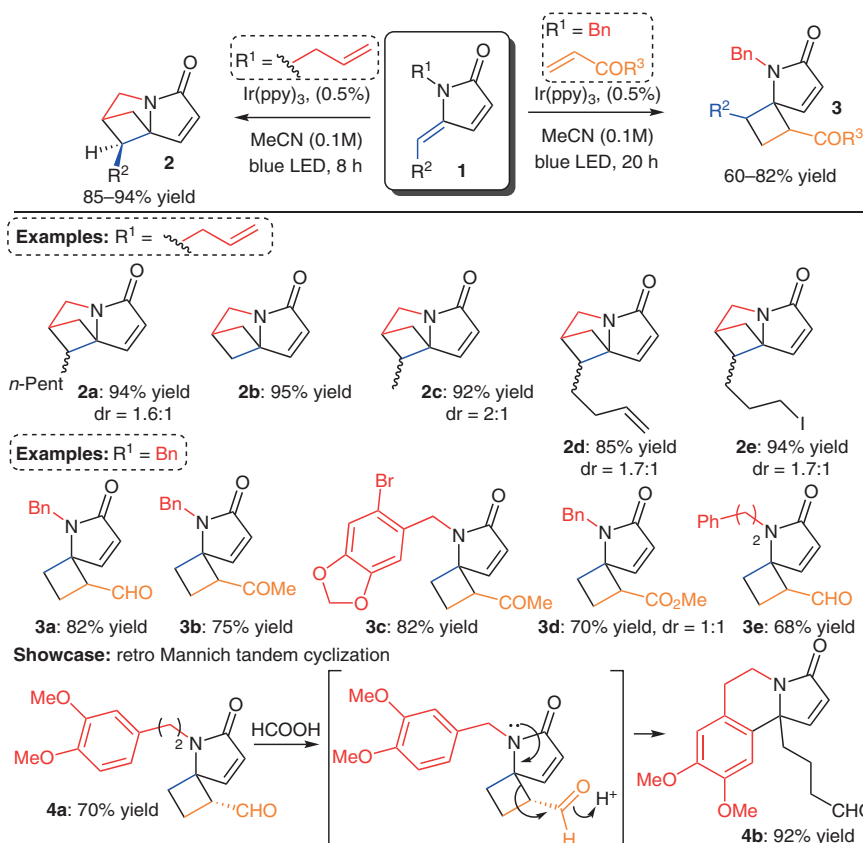


D. KALAITZAKIS, I. KAMPOUROPOULOS, M. SOFIADIS, T. MONTAGNON, G. VASSILIKOGIANNAKIS* (UNIVERSITY OF CRETE, GREECE)
Access to High Value sp³-Rich Frameworks Using Photocatalyzed [2 + 2] Cycloadditions of γ -Alkylidene- γ -Lactams
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[2+2] Cycloadditions to Access sp³-Rich Spirocycles



Significance: sp³-Rich chemotypes are becoming of greater importance in developing new molecular entities, improving structural novelty and physico-chemical properties of the molecule. The Vassiliko-giannakis group has developed a series of elegant photocatalyzed mediated cyclizations to obtain complex cyclobutane, spirocyclic lactams systems. These molecular frameworks are accessed through intramolecular [2+2] photocycloaddition to give compounds **1**, or alternatively, intermolecular [2+2] delivers compound class **2**. The latter series can be further elaborated, as showcased by a formic acid induced retro-Mannich reaction followed by intramolecular regiospecific Friedel–Crafts cyclization to form aromatic compounds such as **3b**.

Comment: Inspired by previous findings that γ -lactams could isomerize substantially when irradiated with blue light in the presence of Ru(bpy)₃Cl, this energy transfer reaction (EnT) was harnessed to facilitate [2+2] cycloadditions. An optimal catalyst Ir(ppy)₃ was identified and used throughout. When R¹ = allyl, irradiation with blue light in MeCN (0.1 M) gave intermolecularly derived compounds **2a–e** in high yields. Compounds **3** were obtained by first benzylating the lactam nitrogen, followed by intermolecular reaction with α,β -unsaturated esters, ketones, and aldehydes to give **3a–e** in high yields. Although examples regarding the reaction scope are limited, this methodology is highly effective to deliver complex and unique sp³-rich molecules.