

Enlightening an atom-economical route to molecular complexity

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The use of visible light to promote complex chemical events under ambient conditions is both an elegant research strategy and a key tool to devise sustainable synthetic methods. As part of an ongoing interest towards atom-economical cascades,¹ the presentation will focus on the fundamental investigation of new activation modes, which is applied to the ordered assembly of complex molecular architectures (Figure 1).

We recently discovered that acyl-allenamides could undergo photosensitization affording the corresponding biradical triplet. This original activation can trigger unusual reactivities, such as the formal 1,3-sigmatropic shift of sulfonyl fragments² and the elaborate intermolecular dimerization of enallenes.³ The latter is among the longest visible-light-promoted cascade reported to date, and could be tuned to afford bridged taxane-like tricycles through the assembly of a cyclooctane ring. By taking advantage of the highly reactive vinyl radical site of an allenyl triplet, it has been possible to solve a longstanding synthetic challenge,⁴ devising the first general Himbert-type dearomative *para*-cycloaddition methods on electronically unbiased simple arenes.⁵ Ongoing developments are focused on the preparation of relevant, and yet synthetically tricky, *N*-heterocycles, including azetidines, β -lactams and [2.2.0] bicyclic architectures that are pyridine bioisosters.

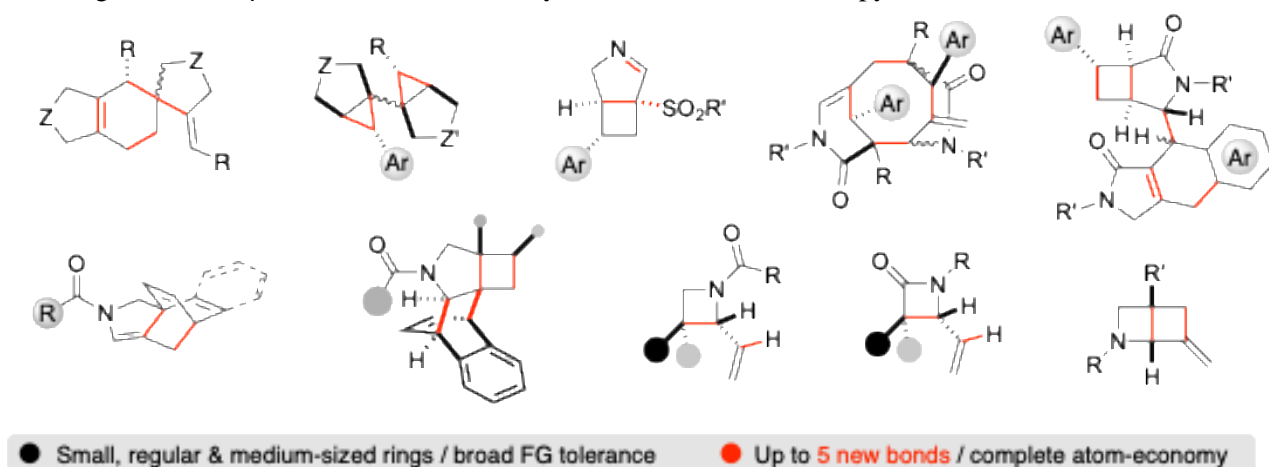


Figure 1: Complex molecular architectures achieved through atom-economical cascades.

References:

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