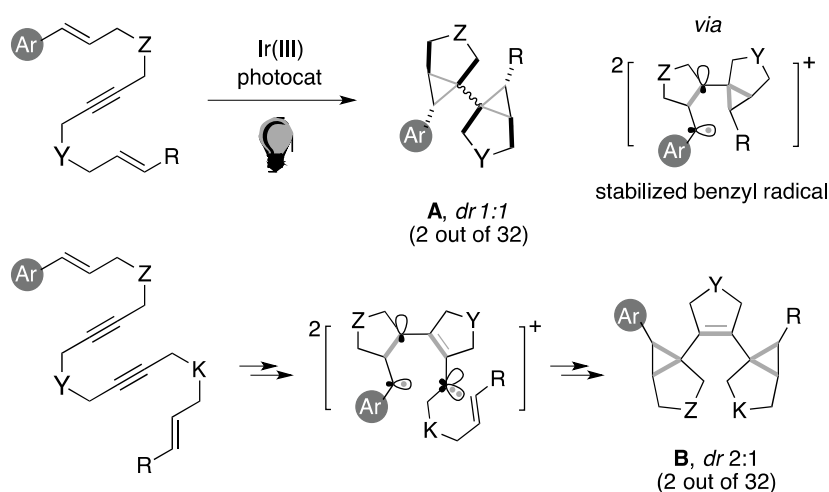


A BIO-INSPIRED POLYCYCLIZATION OF DIEN-N-YNES DRIVEN BY VISIBLE LIGHT

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The work illustrates a radical cationic cascade that parallels a uniquely complex natural tetracyclization reaction, which is the assembly of lanosterol from its linear precursor. Linear dienynes can deliver tetracycles **A** thanks to an Ir(III) photoactive complex and visible-light irradiation.[1] The diastereoselective sequence completely rearranges the π -bonds of the non-conjugated reagent through the assembly of two tethered cyclopropanes presenting six contiguous stereocenters. Alkyne carbons act as carbenoids in the domino reaction, eventually evolving into the two contiguous all-carbon quaternary $C(sp^3)$ centers holding together the [3.1.0] bicyclic units. This reactivity can be extended to the twelve-electron π -bonding network of diendynes, which gave pentacycles **B** through an additional, intermediate carbene dimerization.



The generation of radical cations from these reagents is puzzling because the direct oxidation of their styryl arms should not occur on the basis of redox potential analyses. Alternative rationales based on a two-photon activation, which reminds to natural light up-conversion processes, will be presented.

[1] M. Lanzi, V. Santacroce, D. Balestri, L. Marchiò, F. Bigi, R. Maggi, M. Malacria, G. Maestri *Angew. Chem. Int. Ed.* Accepted article, doi: 10.1002/anie.201902837