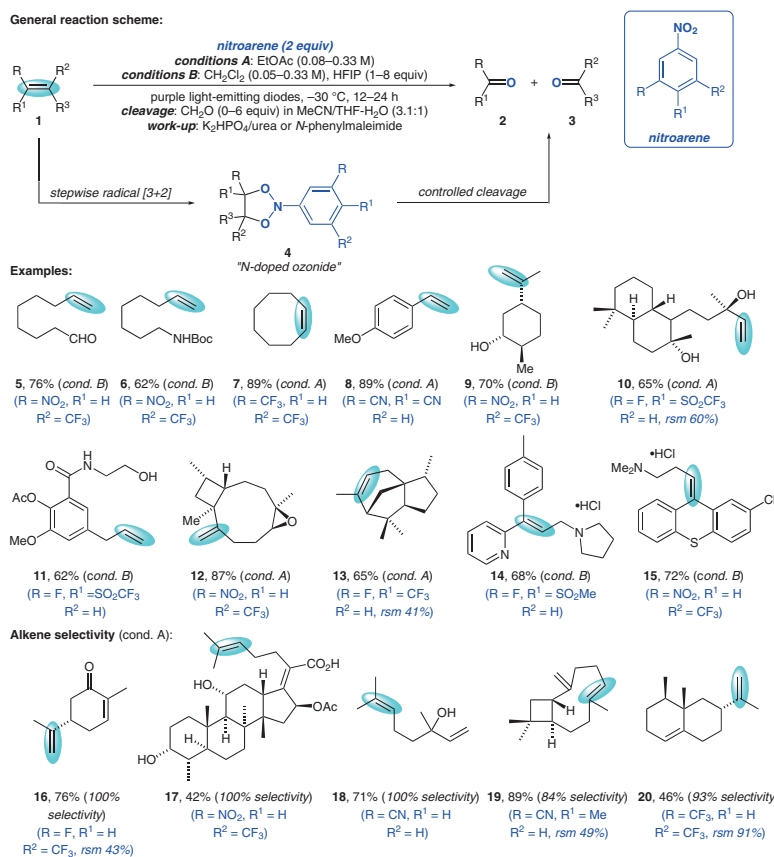


Alternative to Ozonolysis for the Oxidative Cleavage of Olefins



Significance: Ozonolysis is widely utilized as a method to transform feedstock olefins into value-added oxygenated building blocks (alcohols, aldehydes, ketones, or carboxylic acids depending on work-up conditions), though practically the reaction presents significant challenges based on the toxicity of ozone as well as safety concerns around the high-energy intermediates formed. The current report presents an alternative reactive paradigm that accomplishes the same overall transformation as classic ozonolysis though proceeds through an ‘N-doped’ ozonide (formally a 1,3,2-dioxazolidine) that is formed through photo-mediated stepwise radical [3+2] cycloaddition of a nitroarene to the olefin with controlled hydrolytic cleavage leading to the desired carbonyl compounds.

Comment: Kinetic studies on the nature of the nitroarene employed in the photocycloaddition highlighted that tuning of the reagents could be achieved through judicious placement of EWGs on the aromatic core, whilst increased steric hindrance through *ortho*-substitution hindered reactivity. Furthermore, it was demonstrated that it was possible that in contrast to the explosive nature of 1,2,3-ozonides, it was possible to accumulate the ‘N-doped’ ozonides (**4**) in solution and even isolate them as stable solids. A broad range of simple and complex olefins were successful substrates with broad functional group tolerance being observed, while ‘tuning’ of the nitroarene enabled highly selective alkene-cleavage (**16–20**) to be achieved based on electronic, steric, and mediated polar effects in a diverse array of simple/complex systems presenting multiple potential reactive sites.