Photochemistry and Photocatalysis for the Generation of Triplet Carbene Intermediates

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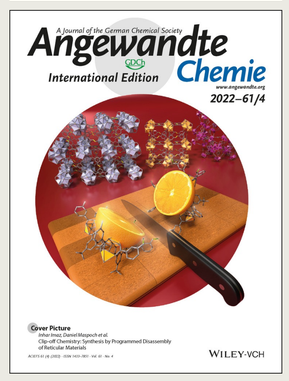
Introduction

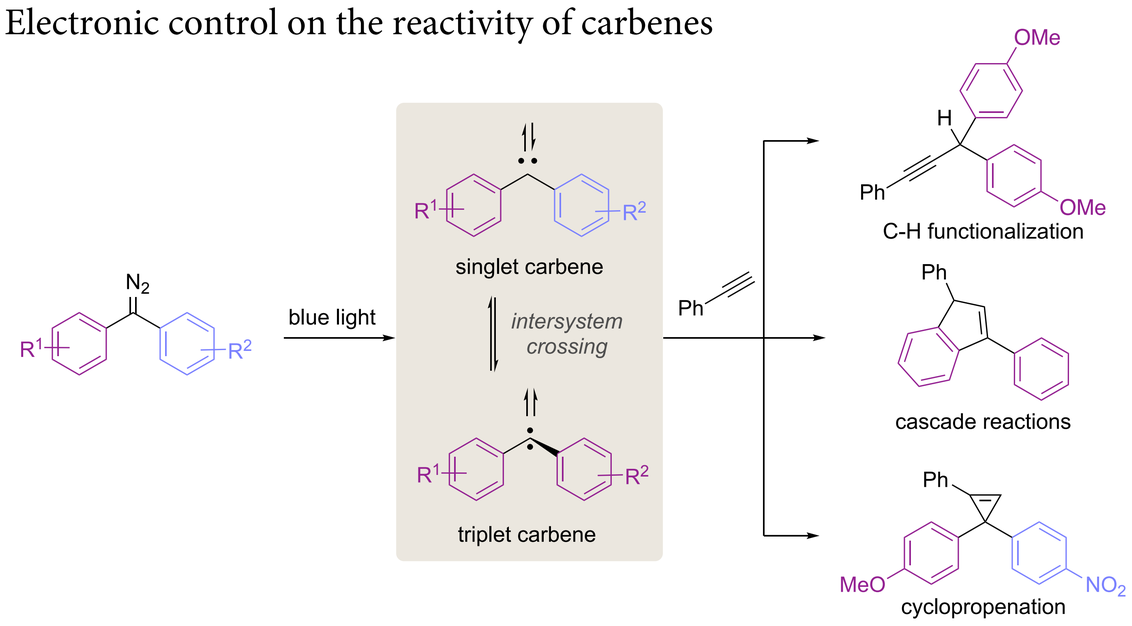
Photochemistry Aryl/aryl diazoalkanes undergo distinct, chemoselective reactions with alkynes upon blue light photolysis. The introduction of electron-donating and -withdrawing groups results in a significant perturbation of singlet triplet energy splitting of the diaryl carbene intermediate and of activation energies of consecutive carbene transfer reactions. We could show that free diaryl carbenes can be readily accessed via photolysis of the corresponding diazo compounds and that these carbenes can undergo highly chemoselective cyclopropenation, cascade, or C−H functionalization reactions. Experimental and theoretical mechanistic analyses confirm the participation of different carbene spin states and rationalize for the observed reactivity.

Photocatalysis Herein, we describe a photocatalytic approach that allows the access of triplet carbene intermediates via energy transfer to conduct highly efficient gem-difluoroolefination reactions with α-trifluoromethyl styrenes. The use of a tertiary amine proved pivotal to unlock this unusual reaction pathway and to prevent undesired cyclopropanation pathways. The amine further facilitates the ultimate abstraction of fluoride to yield gem-difluoroolefins, which is supported by experimental and theoretical mechanistic studies.

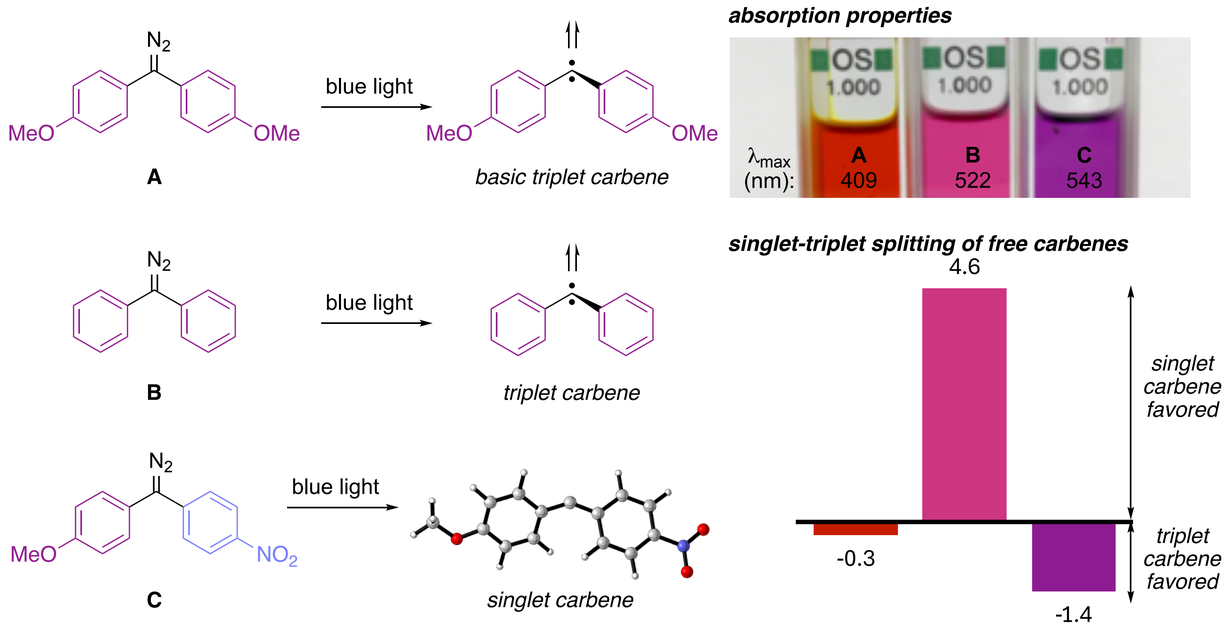


Photochemistry

Electronic control on the reactivity of carbenes

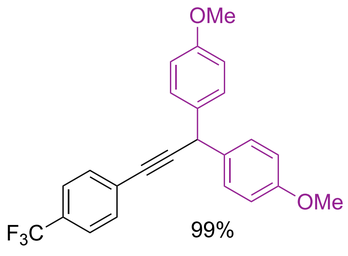


From diazoalkane to carbene

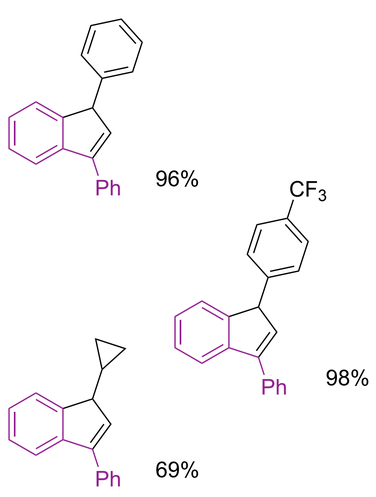


Application in synthesis

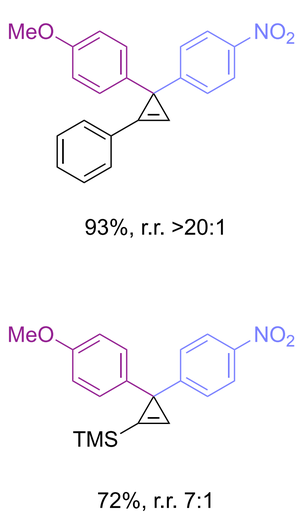
*from diazoalkane **A** via C-H functionalization*



*from diazoalkane **B** via cascade reaction*

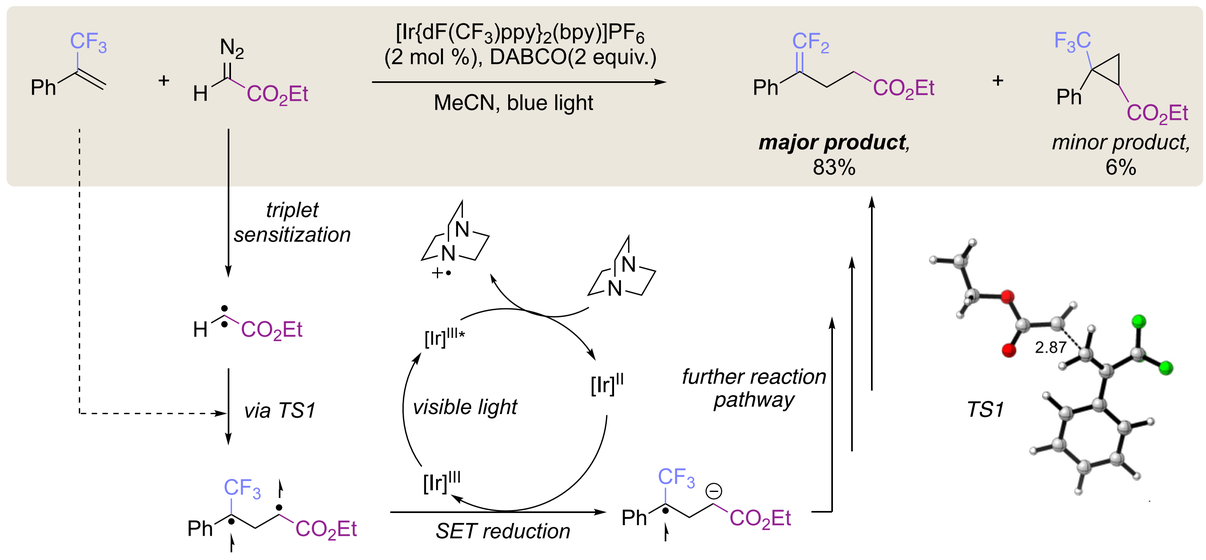


*from diazoalkane **C** via cyclopropenation*



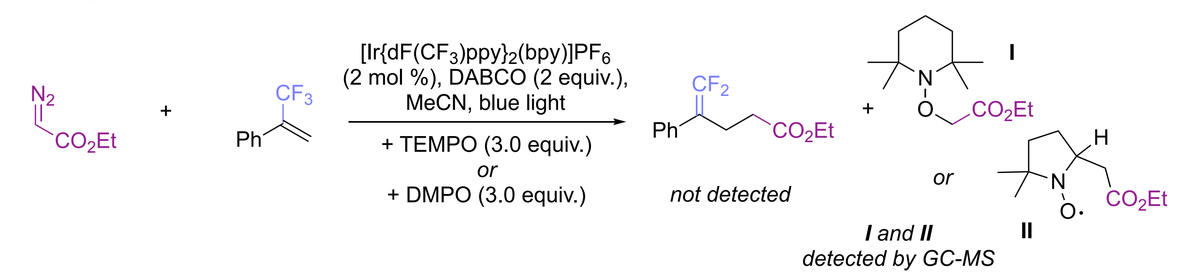
Photocatalysis

Synthesis of gem-difluoroolefins

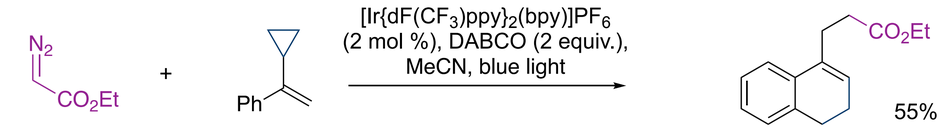


Control experiments

Trapping experiment with TEMPO and DMPO



Radical clock experiment



Application in synthesis