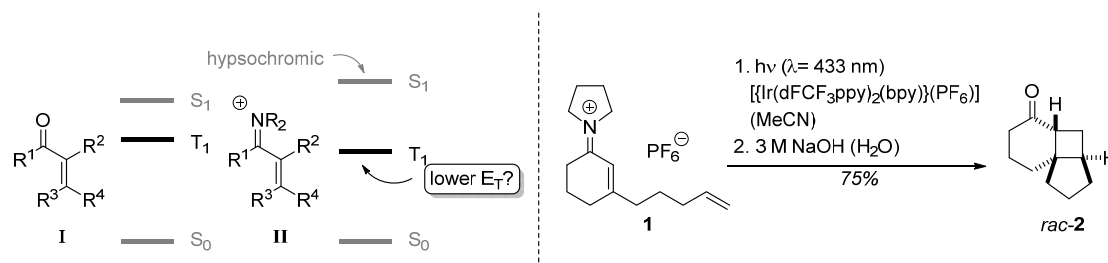


# EVIDENCE FOR TRIPLET SENSITIZATION IN THE VISIBLE-LIGHT-INDUCED [2+2]-PHOTOCYCLOADDITION OF ENIMINIUM IONS

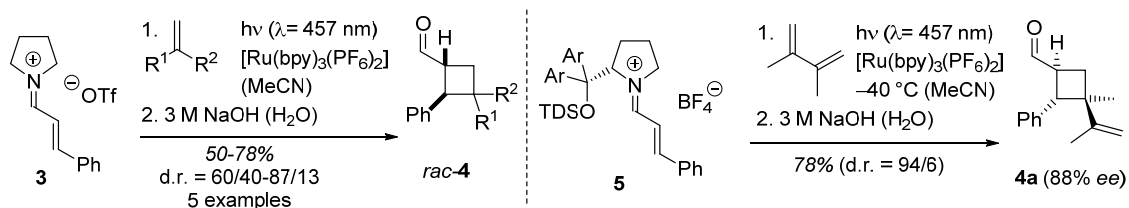
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In stark contrast to  $\alpha,\beta$ -unsaturated carbonyl compounds (enones, and enals), in which the [2+2] photocycloaddition chemistry has been extensively explored, the related  $\alpha,\beta$ -unsaturated iminium ions (eniminium ions) have received little attention. The  $S_1$  state of eniminium ions is of  $\pi\pi^*$  character and the absorption occurs hypsochromically relative to the  $n\pi^*$  transition of the enone. Since intersystem crossing to  $T_1$  is notoriously slow for the eniminium ion, subsequent reactions occur exclusively from the  $S_1$  state.<sup>[1]</sup> We speculated that  $T_1$  would be accessible by carefully choosing a suitable triplet sensitizer and we expected it to be lower in energy than the one of the respective carbonyl compound.



In order to investigate our hypothesis, we synthesized eniminium ion **1** and found that the intramolecular [2+2] photocycloaddition followed by hydrolysis gave product *rac*-**2** in 75% yield by employing an iridium-catalyst as the sensitizer, whereas the corresponding carbonyl compound did not react under these reaction conditions.



In a second set of experiments we studied the intermolecular [2+2] photocycloaddition of eniminium ion **3** with dienes and enynes. The cyclobutanes *rac*-**4** were obtained in good yields (50-78%) with modest to high d.r. (60/40-87/13) with  $Ru(bpy)_3(PF_6)_2$  as the sensitizer. Employing the reaction conditions to the chiral eniminium ion **5**, the cyclobutane **4a** could be isolated in 78% yield and 88% ee.<sup>[2]</sup>

[1] a) P. S. Mariano, *Acc. Chem. Res.* **1983**, *16*, 130-137; b) P. S. Mariano, *Tetrahedron* **1983**, *39*, 3845-3879; c) Y.-Q. Zou, F. M. Hörmann, T. Bach *Chem. Soc. Rev.* **2018**, *47*, 278-290.

[2] F. M. Hörmann, T. S. Chung, E. Rodriguez, M. Jakob, T. Bach, *Angew. Chem. Int. Ed.* **2018**, *57*, 827-831; *Angew. Chem.* **2018**, *130*, 835-839.