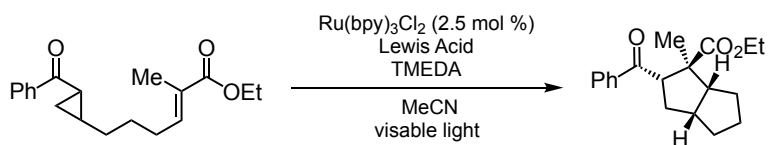


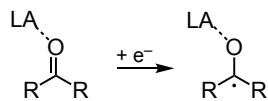
Problem Set #010 (Grosslight)

- (1) Provide a mechanism for the following transformation. The photocatalytic cycle can be disregarded.

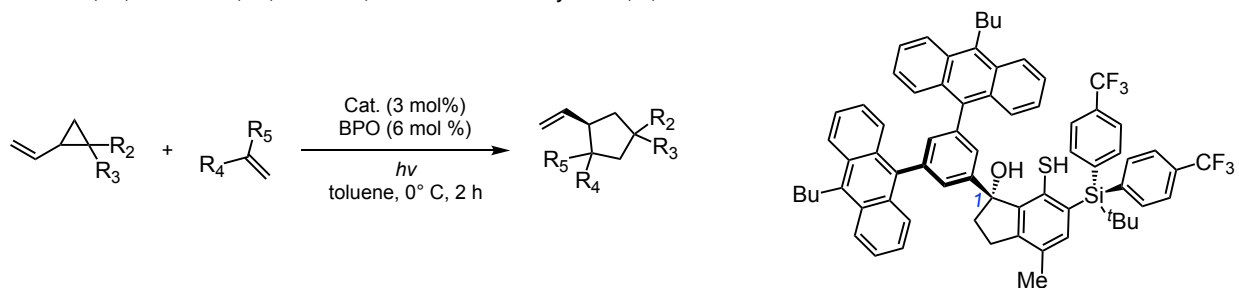
Yoon, T. P. *Acc. Chem. Res.* **2016**, 49, 2307-2315.



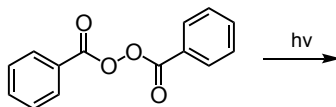
For the oxidation/reduction step, consider drawing as



- (2) In 2014 Hashimoto et al. developed a narley sulfur catalyst for an enantioselective cyclization.
Hashimoto, T.; Kawamata, Y.; Maruoka, K. *Nature Chemistry*. **2014**, 6, 702.



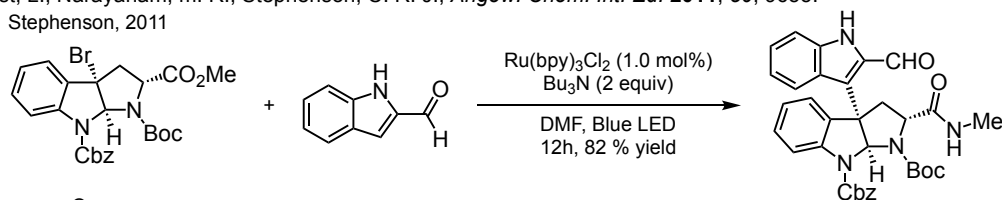
- A) Benzoyl peroxide (BPO) is used to generate/initiate this mechanism by generating the thiol radical. Draw the mechanism for the decomposition of BPO to its reactive radical species.



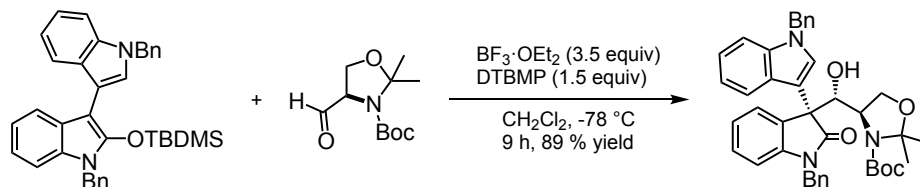
- B) Propose a mechanism for this cyclization.

- (3) Overman reported the enantioselective synthesis of (+)-Gliocladin C in 2007 in 21 steps and a ~4% overall yield (compare to Stephenson's 10 steps and 30% overall yield). Below are the schemes that Overman and Stephenson used to form a quaternary center selectively. Overman, L. E.; et al., *Org. Lett.* **2005**, 7, 2795. Overman, L. E.; Youseungm S. *Org. Lett.* **2007**, 9, 339. Furst, L.; Narayanam, m. R.; Stephenson, C. R. J.; *Angew. Chem. Int. Ed.* **2011**, 50, 9655.

Stephenson, 2011



Overman



Provide a mechanism for Overman's synthesis, what is the name of this reaction?