## **Uncovering New Excited State Reactivity Through Rationale Design of Molecules**

Jayaraman Sivaguru\*

Center for Photochemical Sciences and Department of Chemistry, Bowling Green State University, Bowling Green OH, 43403. United States. E-mail: sivagj@bgsu.edu

Uncovering new excited state reactivity provides opportunities to build complex molecular architectures often with unique stereochemistry. A fundamental challenge in such a process involves controlling excited state reactivity of organic molecules due to the short lifetimes of the reactive species leading to stereo-enriched products. We have been interested in developing strategies for controlling the stereochemistry of products where the reactants reach the excited state(s) upon UV

and/or visible light irradiations. This presentation will highlight our methodology of employing UV and/or visible light for performing photoreactions with excellent control over reactivity and selectivity. Based on photochemical and photophysical investigations, the presentation will highlight novel excited state reactivity of organic molecules, how to influence their excited state behavior towards productive reaction pathways and provide a mechanistic rationale for the observed reactivity in different systems.<sup>1-6</sup>



## References

- Kandappa, S. K.; Valloli, L. K.; Jockusch, S.; Sivaguru, J.\* "Uncovering new excited state photochemical reactivity by altering the course of the De Mayo reaction" *J. Am. Chem. Soc.*, **2021**, 143, 3677–3681. (DOI: <u>https://doi.org/10.1021/jacs.0c12099</u>).
- (2) Kandappa, S.; Kumarasamy, E.; Singhati, R.; Valloli, L. K.; Ugrinov, A.; Sivaguru, J.\* Chemoselective Photoreaction of Enamides – Divergent reactivity towards [3+2]photocycloaddition vs Paternò-Büchi reaction. *Photochem. Photobiol.*, **2021**, *97(6)*, 1391-1396. (Edward Clennan Special issue).
- (3) Ahuja, S.; Raghunathan, R.; Kumarasamy, E.; Jockusch, S.; Sivaguru, J. Realizing the Photoene Reaction with Alkenes under Visible Light Irradiation and Bypassing the Favored [2 + 2]-Photocycloaddition *J. Am. Chem. Soc.*, **2018**, *140*, 13185–13189.
- (4) Kumarasamy, E.; Kandappa, S.; Raghunathan, R.; Jockusch, S.; Sivaguru, J.\* Realizing Aza Paternò-Büchi reaction" *Angew. Chem. Int. Ed.* **2017**, 56, 7056–7061.
- (5) Kumarasamy, E; Raghunathan, R.; Jockusch, S.; Sivaguru, J.\* Transposed Paternò-Büchi Reaction *J. Am. Chem. Soc.*, **2017**, *139*, 655–662.
- (6) Kandappa, S. K.; Ahuja, S.; Singathi, R.; Valloli, L. K.; Baburaj, S.; Parthiban, J.; Sivaguru, J. Using Restricted Bond Rotations to Enforce Excited-State Behavior of Organic Molecules. *Synlett* **2022**, 33, 1123-1134. (invited feature article)

Dr. Jayaraman Sivaguru