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Computational study of asymmetric 6π-photoelectrocyclization via visible-light

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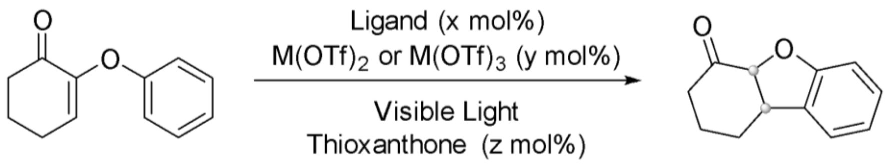
Photocatalyzed reactions are an excellent technique to generate chiral compounds. When combined with Lewis acid ligands, these processes can be driven by visible light, making them more economically viable and environmentally friendly. This work aims investigate the effects operating on a recently published 6***π*** catalyzed electrocyclization [1] under performed photochemical conditions and explore catalysts that promote efficient visible light driven and high enantioselectivity reactions with complementing computational and experimental techniques.

The Lewis acids under consideration are are magnesium, calcium, zinc and scandium. In addition to the metal entity, a quiral ligand was used to induce enantioselectivity in the studied reaction based on chiral complexation with the substrate. For chiral ligands, structures based on bisoxasoline, PyBox and N-Oxide are viable alternatives for a well performed reaction. To achieve the triplet state, a photosensitizer is necessary. Efficient iridium photosensitizers are expensive and not commonly accessible. Instead, thioxanthone-based photosensitizers were utilized.

The structures were optimized with Def-TZVPP/wBX97X-D3BJ//Def2-SVP/wB97X-D3BJ DFT methodology. Current results shows that neutral structures are more stable. Subsequent TDDFT calculations will examine its absorption and overlap with emission spectra photosensitizer. To prevent background reacitons, the complex that results in the strongest bathocromic shift is desired.



$M(OTf)_n = Mg(OTf)_2, Ca(OTf)_2, Zn(OTf)_2$ or $Sc(OTf)_3$

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References

[1] Edtmüller, V., Pöthig, A., Bach, T.: Tetrahedron, **73**(33), 5038–5047 (2017)