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Dual-Catalysis Approach to Stereoselective [2 + 2] Cycloaddition of Erlenmeyer-Plöchl Azlactones

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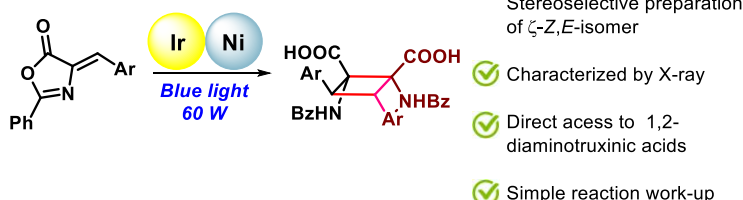
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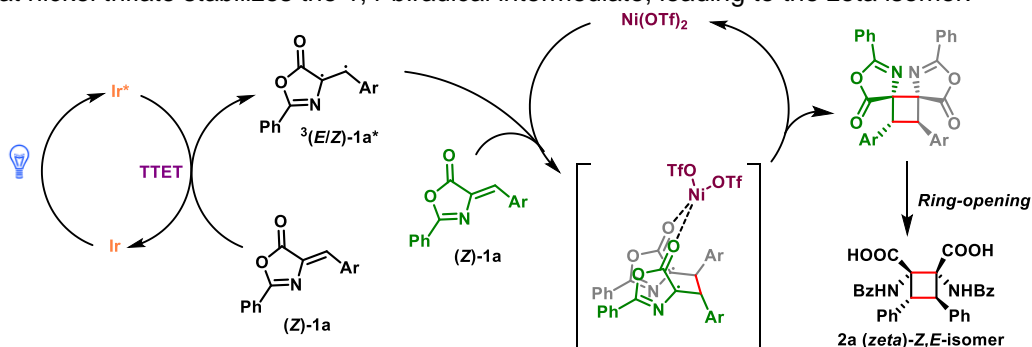
Keywords: Photocatalysis, Dual-catalysis, Azlactone, Cycloaddition, Cyclobutane.

ABSTRACT

Visible-light-driven dual catalysis was employed to stereoselective produce densely substituted cyclobutanes from Erlenmeyer-Plöchl azlactones. The single-step preparation of non-natural amino acid dimers containing the cyclobutane moiety was achieved through a synergy between iridium photocatalysis and catalytic nickel(II) triflate as a Lewis acid. The desired 1,2-(zeta)-Z,E-isomers were isolated in good yields and with high regio- and diastereoselectivity (in all cases, >19:1 d.r.). To the best of our knowledge, this is the first report of direct access to truxinic acid analogues using azlactones.



EPR studies supports proposing an Energy Transfer mechanism. Also, the measurements suggest that the combination of Ir and Ni increases the EPR signal compared to non-irradiated sample. DFT calculations showing that nickel triflate stabilizes the 1,4-biradical intermediate, leading to the zeta isomer.



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REFERENCES

J. Org. Chem. **2022**, *87*, 3529; *J. Org. Chem.* **2018**, *83*, 15144; *Chem. Rev.* **2013**, *113*, 5322; *Chem. Rev.* **2016**, *116*, 10075; *Chem. Soc. Rev.* **2018**, *47*, 7190; *Nat. Commun.* **2022**, *13*, 1313; *Angew. Chem. Int. Ed.* **2009**, *48*, 8716; *Angew. Chem. Int. Ed.* **2008**, *47*, 2283.