

Photoinduced Copper-Catalyzed Asymmetric Acylation of Allylic Phosphates with Acylsilanes

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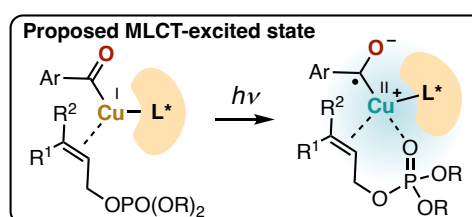
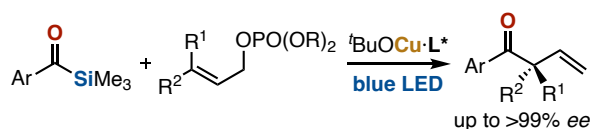
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Photoinduced catalysis enables novel molecular transformations for organic synthesis complementary to thermal catalytic reactions. In particular, photoinduced transition-metal-catalyzed reactions in which the metal plays a dual role as a photoabsorbent and a center for chemical bond cleavage/formation are distinct from the more broadly investigated reactions with external photoredox catalysts, offering advantages of simplicity of the reaction system and cost-effectiveness by avoiding the use of expensive external substances.¹ In addition, the better reaction control by metal-bound ligands is an attractive feature of this methodology as evidenced by the growing number of reports in this regard, some of which detail highly enantioselective reactions by the use of chiral ligands.²

Here, we report a visible-light-induced copper-catalyzed highly enantioselective umpolung allylic acylation reaction with acylsilanes as acyl anion equivalents.³ Triplet-quenching experiments and DFT calculations suggested the reaction mechanism involving copper-to-acyl metal-to-ligand charge transfer (MLCT) photoexcitation that generates a charge-separated triplet state as a highly reactive intermediate. According to the calculations, the allylic phosphate substrate in the excited state undergoes novel molecular activation into an allylic radical weakly bound to the copper complex. The allyl radical fragment undergoes copper mediated regio- and stereocontrolled coupling with the acyl group under the influence of the chiral N-heterocyclic carbene ligand.

Photoinduced Cu-Catalyzed Asymmetric Allylic Acylation



- 1) (a) Parasram, M.; Gevorgyan, V. *Chem. Soc. Rev.* **2017**, *46*, 6227–6240. (b) Hossain, A.; Bhattacharyya, A.; Reiser, O. *Science* **2019**, *364*, eaav9713. (c) Cheng, W.-M.; Shang, R. *ACS Catal.* **2020**, *10*, 9170–9196.
- 2) (a) Lipp, A.; Badir, S. O.; Molander, G. A. *Angew. Chem., Int. Ed.* **2021**, *60*, 1714–1726. (b) Genzink, M. J.; Kidd, J. B.; Swords, W. B.; Yoon, T. P. *Chem. Rev.* **2021**, DOI: 10.1021/acs.chemrev.1c00467.
- 3) Ueda, Y.; Masuda, Y.; Iwai, T.; Imaeda, K.; Takeuchi, H.; Ueno, K.; Gao, M.; Hasegawa, J.; Sawamura, M. *J. Am. Chem. Soc.* **2022**, *in press*. DOI: 10.1021/jacs.1c11526