

Photoinduced Copper-Catalyzed Asymmetric Allylic Acylation

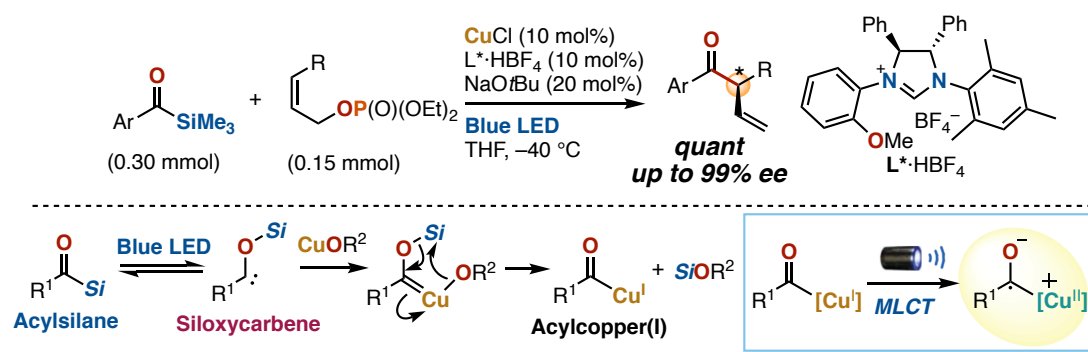
(¹Hokkaido University Department of Chemistry, Faculty of Science. ²Department of Basic Science, Graduate School of Art and Sciences, The University of Tokyo. ³Hokkaido University Institute for Chemical Reaction Design and Discovery)

○Yusuke Ueda,¹ Tomohiro Iwai,² Masaya Sawamura^{1,3}

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The recent decades have seen a surge of interest in the development of photoinduced transition-metal-catalyzed reactions as a rapidly emerging field in the creation of new methodologies for organic synthesis. Here we report a photoinduced copper-catalyzed asymmetric allylic acylation reaction using acylsilanes and allylic phosphates as substrates. The reaction proceeds with complete γ -position selectivity under irradiation by a blue LED lamp (465 nm) at low temperature in the presence of a copper(I) catalyst prepared *in situ* from CuCl, a chiral carbene ligand precursor, and a base.

Photoisomerization of the acylsilane to the corresponding siloxycarbene has been widely studied.¹ We conceived this study by considering the possibility that, after the coordination of the photochemically generated siloxycarbene to the copper(I) complex, an anionic ligand on copper attacks the silicon atom of the siloxycarbene nucleophilically to form a neutral acyl copper complex. The acyl group of this copper(I) complex, however, should be highly electron-deficient. Thus, this group would not have nucleophilicity enough to attack the allylic phosphates. We postulate that photoexcitation of the copper(I) center² would cause a charge transfer from copper to the acyl group (MLCT), forming a nucleophilic radical species and the positively charged highly Lewis acidic copper(II) center.



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