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ケトイミンの触媒的不斉アルキニル化反応

◯殷　亮[1], 大塚　安成[1], 高田　久嗣[1], 毛利　伸介[1], 矢崎　亮[1,2], 熊谷　直哉[1], 柴崎　正勝[1]（[1]微化研, [2]東大院薬）

The direct catalytic addition of terminal alkynes to ketoimines is in its infancy and has suffered from low yield and low catalytic efficiency. Furthermore, there is no report on the catalytic asymmetric variant that proceeds in perfect atom economy. Here we report a general method for the addition of terminal alkynes to ketoimines and the first example of catalytic asymmetric version. The racemic reaction conditions showed broad substrate generality. High conversion was observed with 5 mol % of catalyst loading irrespective of the electronic nature of the aromatic group or steric factors of alkyl group adjacent to the ketoimine carbon. Moreover, both aromatic alkynes and aliphatic alkynes served as suitable substrates. In particular, the current conditions were successfully applied to the alkyne bearing a free hydroxyl group. This efficient catalytic protocol was then extended to asymmetric version by using (*S*,*S*)-Ph-BPE as a chiral ligand. The propargylamines were obtained in good yield and with 50-80% ee. The simultaneous activation of pronucleophiles and electrophiles by copper complex catalyst is the key to achieving this unprecedented reaction.