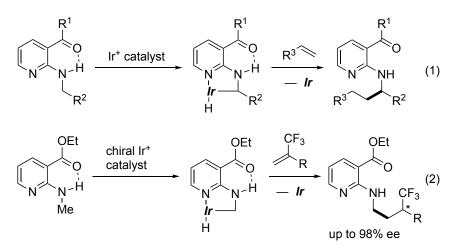
Iridium-Catalyzed Enantioselective sp³ C-H alkylation of a N-Methyl group with α-Trifluoromethyl Styrenes

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Transition-metal-catalyzed sp³ C-H functionalization has been developed as one of the most useful molecular transformations realizing atom economical processes. The sp³ C-H bond adjacent to nitrogen atom is reactive toward transition metal catalysts, and direct alkylation reactions have been achieved by using a variety of early and late transition metal catalysts. In this respect, we have recently developed cationic iridium-catalyzed sp³ C-H alkylation of a methyl group adjacent to nitrogen of 2-(methylamino)pyridines with terminal alkenes (eq 1).¹ In this reaction, the generation of a conformationally rigid intermediate, which is formed by use of a hydrogen bond between the proton of the amino group at the 2-position and a carbonyl group at the 3-position, was required for the effective C–H activation.

Here we reported that a cationic iridium/chiral bisphosphine complex catalyzed the asymmetric hydroalkylation reaction of 1,1-substituted alkenes $via \text{ sp}^3 N$ -methyl C–H bond activation (eq 2).



1) M. Nagai, M. Nagamoto, T. Nishimura, H. Yorimitsu, Chem. Lett. 2017, 46, 1176.