

C(sp³)-H ACETOXYLATION OF FREE CARBOXYLIC ACIDS

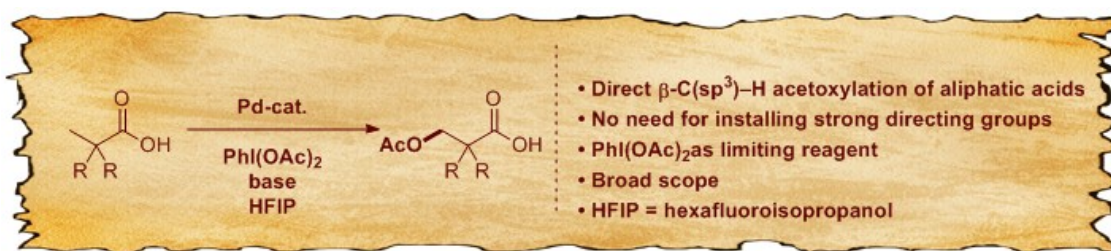
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Transition metal-catalyzed sp³ C–H bond activations remain as one of the most challenging transformations for the last few years. Aliphatic carboxylic acids are one of the cheap sources for the synthesis of interesting building blocks in organic synthesis. Until now multiple directing groups have been utilized in order to achieve higher reactivity for the sp³ C–H bond functionalizations.^[1] Directing groups have its inherent disadvantage of the installation and removal from the acids. Eventually, keeping in mind about the step and atom economy researchers are now highly interested to solve this problem with the free carboxylic acids. Recently several sp³ C–H bond arylations of free carboxylic acids have been reported.^[2] So we focused to form β-sp³ C–O bond of the free carboxylic acids.

Here, we developed a catalytic system for the acetoxylation of aliphatic carboxylic acids by using phenyliododiacetate as the limiting reagent. We could clearly depict the role of the additive in this system. We have tried several commercially available sodium bases (NaHCO₃, Na₂CO₃, Na₂HPO₄, NaOMe) which gave less yield than sodium hexafluoroisopropanolate (NaHFIP). This gives a clear understanding of the detrimental effect of the anionic counterpart of the additives. Overall this reaction is widely applicable to the substituted long chain α-quaternary acids but limited to the electron-deficient arene substituents.



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