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Transition-Metal-free Hydroboration of Terminal Alkynes Activated by Base

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ABSTRACT

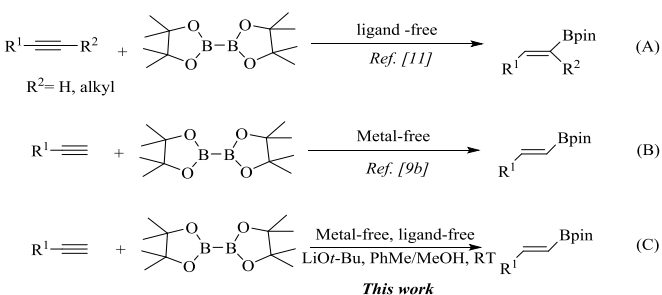
Transition-Metal and ligand-free method for the hydroboration of terminal alkynes with B₂pin₂ was reported in LiOt-Bu/Toluene/MeOH system under room temperature. Alkylalkynes and arylalkynes reacted efficiently with high regioselectivity.

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Organoboron compounds are important subjects in organic chemistry, which play a significant role in organic synthesis, due to highly reactivity, stability under atmospheric conditions and low toxicity.¹ Much attention has been focused on looking for easy and efficient ways to prepare kinds of organoboron reagents, including vinylboronates. Vinylboronates have drawn much attention because of their intrinsic scientific importance and industrial applications.² The traditional C-B formation *via* addition reaction of boranes with alkenes or alkynes, which was conducted under relatively harsh conditions. Recently the synthesis of organoboron compounds by hydroboration of alkene or alkyne derivatives had been disclosed³. Several transition metals have been used to catalyze hydroborations of internal or terminal alkynes over the past few years, including platinum⁴, copper⁵, silver⁶, gold⁷, iridium⁸. Using transition metal and ligand as catalyst system poses challenges in environmental problem

and green chemistry, leading to the limitation in widely application in chemical industry and pharmaceuticals industry.

Recently, transition-metal-free or ligand-free borylation reactions occurred as interesting alterations. Several methods that reactions were catalyzed by ligand without transition-metal have been reported to form C-B bonds and N-B bonds.⁹ Hoveyda also presented transition-metal-free enantioselective method for boron conjugate addition to α,β -unsaturated carbonyls.^{9c} Furthermore, ligand-free hydroboration of alkenes or alkynes successfully catalyzed by transition metals, including platinum and copper.¹⁰ Concerning the hydroboration of alkynes, Li used heterogeneous micro copper powder without ligand as a catalyst for addition of B₂pin₂ to internal and terminal alkynes (Scheme 1A)¹¹. And Sun^{9b} reported a transition-metal-free hydroboration of terminal alkynes under open atmosphere (Scheme 1B). Herein, we firstly report a transition-metal- and ligand-free hydroboration of terminal alkynes directly activated by base at room temperature (Scheme 1C).



Scheme 1. Ligand-free (A) and transition-metal-free (B) hydroboration of alkynes. (C) Our protocol of transition-metal and ligand-free of hydro-boration of termin al alkynes directly was activated by base.

Previously, we reported copper-catalyzed borylation of primary and secondary alkyl halides with bis(pinacolato)diboron (B₂pin₂, **2**).¹² When 6-chloro-1-hexyne (**1a**) and B₂pin₂ were used in an attempt to prepare the alkyne boronate product in the presence of Cu₂O/PPh₃/KOt-Bu. In the solvent of DMF and NMP, the reaction proceeded to conversion of both alkyne and halid group, and produced a mixture of hydroborylated products (**3a+4a**) and alkyne boronate (**5a**) product (Table 1, entry 1, 2). Change solvent to toluene, only compounds of **3a** and **4a** were observed with a low yield of 8%. With MeOH as additive, the yield dramatically increased to 74%. Analysis of the products indicated

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