

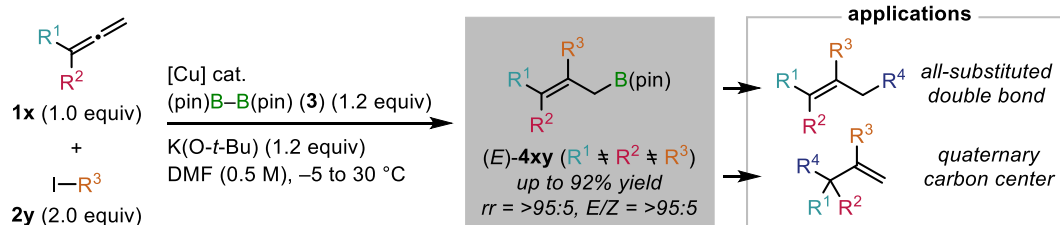
Regio- and Stereoselective Synthesis of Multi-Alkylated Allylic Boronates through Borylative Coupling of 1,1-Disubstituted Allenes and Alkyl Halides

(¹*Division of Applied Chemistry, Graduate School of Engineering, Hokkaido University,*
²*WPI-Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University*) ○Yu Ozawa,¹ Kohei Endo,¹ Hajime Ito^{1,2}

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Allylic boronates are recognized as versatile intermediates because of their high stability under ambient conditions and their reactivity of the α - and γ -position for the stereospecific formation of a new C–C bond. In particular, multi-substituted ones are attractive building blocks for constructing sterically demanding carbon skeletons such as multi-substituted alkenes and quaternary carbon centers.¹ Herein, we describe a new approach to the acyclic allyl boronates bearing three different alkyl groups on its alkene moiety. Inspired by Tsuji's, Hoveyda's, and our previous studies,² we successfully developed a copper(I)-catalyzed three-component coupling between allenes, alkyl halides, and a diboron reagent. The product was obtained in high yield with high regio- and stereoselectivity (up to 92% yield, $rr = >95:5$, $E/Z = >95:5$).

Given the optimized conditions, the substrate scope was investigated with some allenes and alkyl halides. The copper(I) catalyst could differentiate the bulkiness of two substituents of allenes (R^1 and R^2); e.g. methyl and primary alkyl groups, primary and secondary alkyl groups, primary and tertiary alkyl groups, etc. However, we found some limitations of alkyl halides. Although primary alkyl halides could be applied to the reaction, no product was obtained from secondary alkyl halides due to their low reactivity to S_N2 type reaction. Furthermore, stereospecific transformations were performed to obtain all-substituted alkenes and quaternary carbon centers through α - and γ -substitution of the boryl group, respectively.



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