

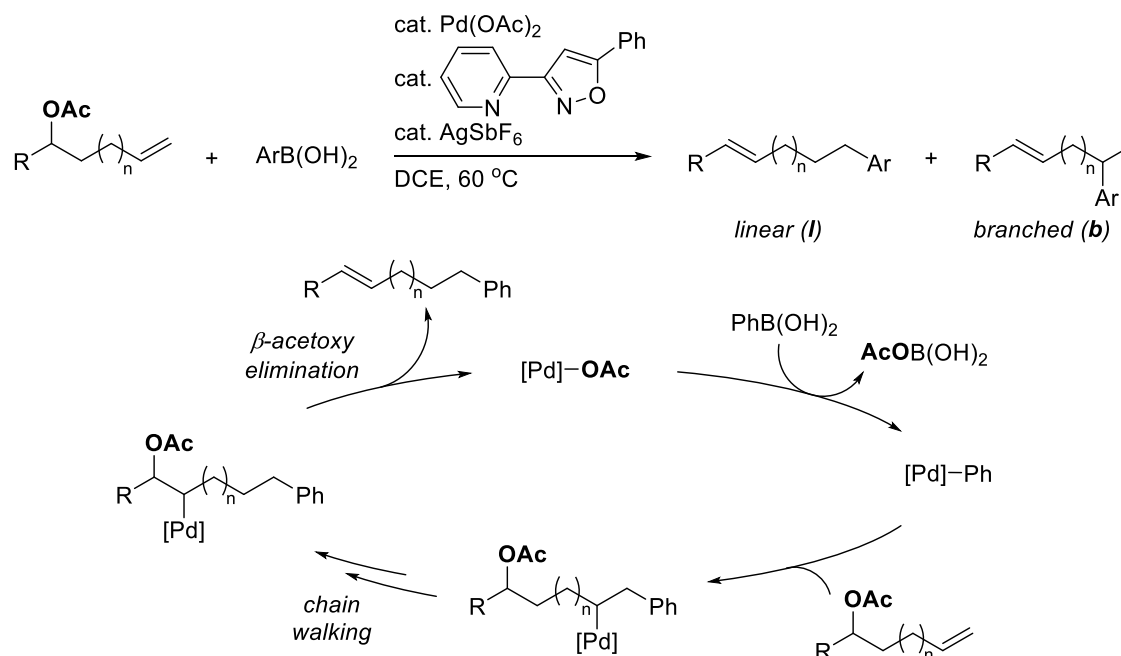
## Palladium-Catalyzed Remote Arylative Substitution of Various Terminal Alkenes

(Faculty of Science and Technology, Keio University) ○Kazuma Muto, Fumitoshi Kakiuchi, Takuya Kochi

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While catalytic allylic substitution has become one of the most powerful classes of transition-metal-catalyzed reactions, the corresponding remote substitution has rarely been explored. In this context, we envisioned that the incorporation of a chain-walking process into catalytic cycles of allylic substitution reactions would realize the remote substitution reactions.<sup>1</sup> Here we report a palladium-catalyzed remote arylative substitution of alkenes bearing a distant acetoxy group via chain walking and  $\beta$ -acetoxy elimination.<sup>2</sup>

The reaction of a terminal alkene having a remote acetoxy group with phenylboronic acid using a 1,10-phenanthroline palladium catalyst provided the remote arylation product with ca. 2:1 regioselectivity. Ligand screening was then conducted to improve the linear/branched regioisomer ratio, and a pyridine-isoxazole ligand was found to give the product with ca. 4:1 regioselectivity. The reaction is applicable to various terminal alkenes having a distant acetoxy group containing 1 to 7 methylenes and arylboronic acids possessing a variety of functional groups. The remote arylative substitution is considered to proceed via transmetalation between an acetoxypalladium species with arylboronic acid, alkene insertion, chain walking, and  $\beta$ -acetoxy elimination.



(1) Ohmiya, H.; Makida, Y.; Tanaka, T.; Sawamura, M. *J. Am. Chem. Soc.* **2008**, *130*, 17276-17277.

(2) Muto, K.; Kumagai, T.; Kakiuchi, F.; Kochi, T. *Angew. Chem., Int. Ed.* **2021**, *60*, 24500-24504.