

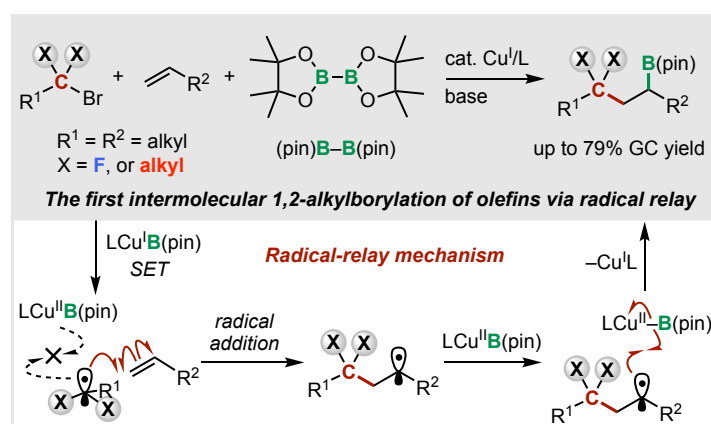
The Intermolecular 1,2-Alkylborylation of Unactivated Olefins through Copper(I)-Catalyzed Radical Relay Reaction

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The transition-metal-catalyzed radical-relay strategy for intermolecular 1,2-carbofunctionalization of widely available unactivated olefins is one of the most useful protocols for rapid construction of complex carbon-based structures with a catalytic amount of a radical-generating reagent.¹ One of the main advantages of this protocol is that it tolerates electronically or sterically demanding alkyl electrophiles that cannot be used in catalytic 1,2-carbofunctionalization reactions that involve S_N2-type nucleophilic substitutions. In this context, the intermolecular 1,2-carboborylation of olefins via a radical relay, a transformation that involves the simultaneous installation of a C–C bond and a transformable C–B bond, would undoubtedly be highly attractive. Despite the significant progress that has been made in radical-relay chemistry, the intermolecular 1,2-carboborylation of olefins via a radical relay remains elusive so far.

Herein, we report the first example of an intermolecular 1,2-alkylborylation of unactivated olefins via a radical-relay strategy. The key to the success of this protocol is the use of electronically or sterically demanding alkyl electrophiles such as α,α -difluoro alkyl bromides or tertiary alkyl bromides to suppress undesired boryl-substitution reactions. Notably, the products of these reactions are difficult to access via any other hitherto reported carboborylation strategies.²



- 1) Huang, H. M.; Gardun˜o-Castro, M. H.; Morrill, C.; Procter, D. J. *Chem. Soc. Rev.* **2019**, 48, 4626. 2) a) Yoshida, H.; Kageyuki, I.; Takaki, K. *Org. Lett.* **2013**, 15, 952. b) Su, W.; Gong, T. J.; Lu, X.; Xu, M. Y.; Yu, C. G.; Xu, Z. Y.; Yu, H. Z.; Xiao, B.; Fu, Y. *Angew. Chem., Int. Ed.* **2015**, 54, 12957.