Copper-catalyzed Synthesis of Diversely Functionalized Allyl Boranes, Starting from Nitro Allyl and Allyl Sulfone Derivatives

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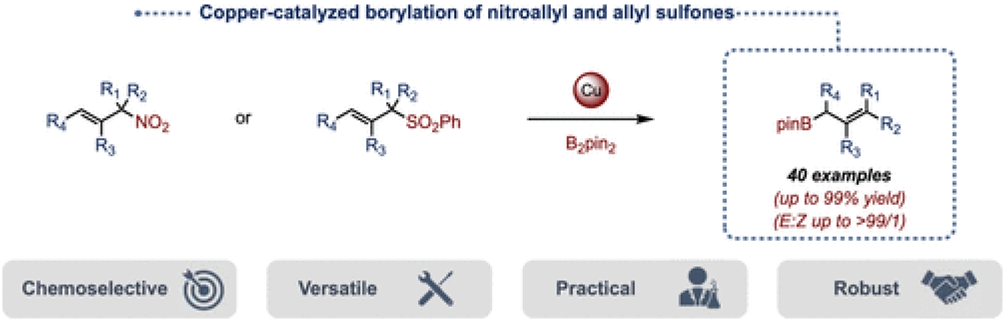
We report[1] a new transition-metal-catalyzed borylation of allyl derivatives using nitroallyls and allylsulfones for the first time. The pioneering work of Miyaura[2] and Ito[3] prompted the study of numerous catalysts and allyl derivatives, however the scope of accessible functions remains limited. The precursors described provide straightforward access to a wide variety of functional groups (esters, cyanides, sulfones, silyl-protected alcohols) due to the acidic α-position of the nitro or sulfone group. The allylboranes are obtained in excellent yields regardless of the functional group. For example, the method enables the synthesis of γ-fluoroallyl boronic esters, which are useful building blocks, as well as tri- and tetrasubstituted allylboranes. Moreover, copper represents one of the most environmentally friendly alternatives to palladium. The synthetic utility of allylboranes was demonstrated through various post-functionalizations. The results were rationalized through DFT calculations, which reveal a mechanism different from what observed with conventional leaving groups.



References

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