

USING H₂ AS A HYDRIDE SOURCE – A CHEMO- AND REGIOSELECTIVE REDUCTIVE COUPLING REACTION/ALLYLIC REDUCTION

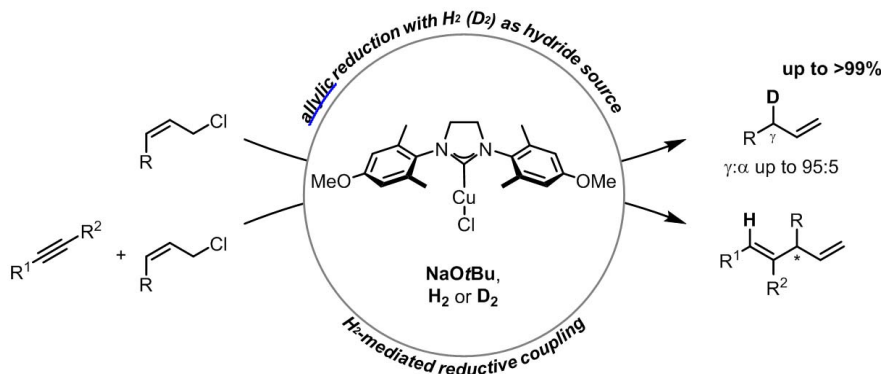
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The transition metal catalyzed allylic substitution is a well-established methodology in organic synthesis.[1] A wide variety of nucleophiles (carbon- and heteroatom-based) can be employed for the generation of functionalized (mostly chiral) α -olefins. However, the use of hydrides as nucleophiles generated from hydrosilanes in a so-called *allylic reduction* has rarely been reported.[2,3]

Replacing the hydrosilane with dihydrogen (H₂) would render this process much more atom economic, but also poses several challenges for catalyst development: Next to regio- and stereoselectivity issues, chemoselectivity is most difficult to obtain, as the catalyst of choice would need to activate H₂, but should not *hydrogenate* the allylic substitution product, namely the terminal alkene.

We now report on a copper(I)-catalyzed allylic reduction with a hydride nucleophile generated from H₂. To further underline the applicability of this approach, we employed D₂ as easy-to-use deuteride source to obtain the desired products with excellent deuterium incorporation.[4] Furthermore, the extension towards a reductive coupling reaction to form skipped dienes as coupling products, which are not further reduced, is also presented.



[1] a) U. Kazmaier, *Transition Metal Catalyzed Enantioselective Allylic Substitution in Organic Synthesis*, Springer, Berlin, **2012**

[2] For examples with Pd catalysts, see: J. Tsuji, T. Mandai, *Synthesis* **1995**, 1.

[3] a) T. N. T. Nguyen, N. O. Thiel, F. Pape, J. F. Teichert, *Org. Lett.* **2016**, *18*, 2455; b) T. N. T. Nguyen, N. O. Thiel, J. F. Teichert, *Chem. Commun.* **2017**, *53*, 11686.

[4] F. Pape, L. T. Brechmann, J. F. Teichert, *Chem. Eur. J.* **2019**, *25*, 985.