

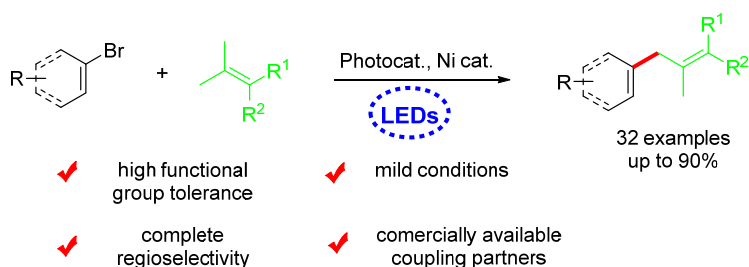
DIRECT CROSS-COUPPLING OF ALLYLIC C(sp³)-H BONDS WITH ARYL- AND VINYL BROMIDES

Long Huang, and Magnus Rueping*

Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1,
D-52074 Aachen, Germany
magnus.rueping@rwth-aachen.de

To date, the construction of C(sp²)-C(sp³) bonds *via* direct functionalization of C-H bonds is a powerful tool for the synthesis of highly functionalized and complex alkenes. However, compared with the significant progress in direct oxidation and amination of allylic C-H bonds, routes toward direct arylation are narrowly explored.^[1] Visible light photoredox and metal dual catalysis has emerged as an effective strategy for diverse C-C and C-X (X = N, O, S, P) bond formations in a redox-, atom-, and step-economical fashion. Key to this success is the capacity of photocatalysts to act as both strong oxidants and reductants via single electron transfer (SET) upon irradiation with visible light.^[2]

Herein, we present a protocol for the direct allylic C(sp³)-H bond activation in unactivated tri- and tetrasubstituted alkenes and their reaction with aryl- and vinyl bromides *via* nickel and visible light photocatalysis.^[3] The method allows the C(sp²)-C(sp³) formation under mild reaction conditions, with good functional group tolerance and excellent regioselectivity. The exclusive preference for primary allylic C(sp³)-H bonds can be rationalized by a hydrogen atom abstraction process with photocatalytically generated bromine radical.^[4]



[1] a) M. Sekine, L. Ilies, E. Nakamura, *Org. Lett.* **2013**, *15*, 714-717; b) R. M. Borg, D. R. Arnold, T. S. Cameron, *Can. J. Chem.* **1984**, *62*, 1785-1802; c) J. D. Cuthbertson, D. W. C. MacMillan, *Nature* **2015**, *519*, 74-77.

[2] Twilton, J., Le, C. Zhang, P., Shaw, M. H., Evans, R. W., MacMillan, D. W. C. *Nat. Rev. Chem.* **2017**, *1*, 0052.

[3] L. Huang, M. Rueping, *Angew. Chem. Int. Ed.* **2018**, *57*, 10333.

[4] a) D. R. Heitz, J. C. Tellis, G. A. Molander, *J. Am. Chem. Soc.* **2016**, *138*, 12715-12718; b) B. J. Shields, A. G. Doyle, *J. Am. Chem. Soc.* **2016**, *138*, 12719-12722.