DIRECT CROSS-COUPLING OF ALLYLIC C(sp³)-H BONDS WITH ARYL- AND VINYLBROMIDES

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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 vinylbromides via nickel and visible light photocatalysis.[3] The method allows the C(sp³)-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]

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