

## Site-selective $\alpha$ -C( $sp^3$ )-H Alkylation of Alcohols and Primary Amines Promoted by Photoredox, HAT, and Bond-Weakening Hybrid Catalysis

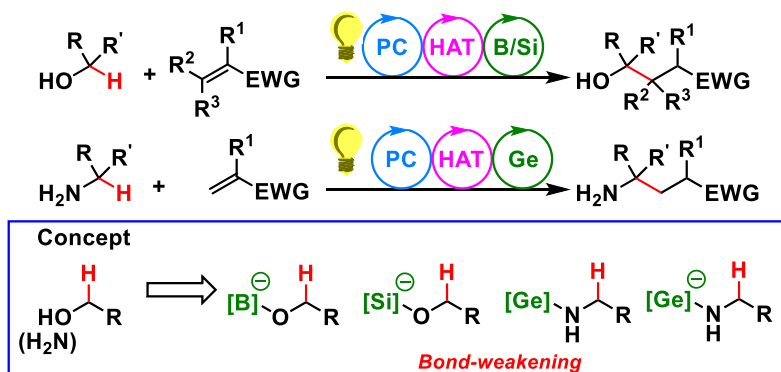
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The development of catalytic C( $sp^3$ )-H functionalization reactions can explore various applications, such as the discovery of functional materials and drugs. To realize functionalization of unreactive C( $sp^3$ )-H bonds, hydrogen atom transfer (HAT) catalysts have been attracting much attention because of their mild reaction conditions.<sup>1</sup> However, most of reported HAT catalysis have limited substrate scopes, which can only target the weakest or highly hydridic C( $sp^3$ )-H bonds in the substrate. Targeting other C( $sp^3$ )-H bonds in high regioselectivity under catalyst-control remains challenging.

We would like to report ternary hybrid catalyst systems consisting of photoredox (PC), HAT, and bond-weakening catalysts.<sup>2</sup> The bond-weakening catalyst design is based on DFT calculations uncovering that  $\alpha$ -C( $sp^3$ )-H bonds of alcohol<sup>3a,3b</sup> and primary amine<sup>3c</sup> substrates were effectively weakened by complexation as silicates, borates, and germane/germate species. These bond-weakening phenomena accelerates the HAT process of specific C( $sp^3$ )-H bonds, leading to catalyst-controlled site-selectivity of C( $sp^3$ )-H functionalization.

In this talk, we would like to focus mainly on the  $\alpha$ -C( $sp^3$ )-H alkylation of primary amines promoted by the PC-HAT-Ge hybrid system.



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