**Enantioselective Amino- and Oxycyanation of Alkenes via Organic Photoredox and Copper Catalysis1**

*β*-Amino nitriles and their derivatives are of synthetic utility in organic/natural product synthesis and drug design.1 They are important moieties in natural products, agrochemicals, biological macromolecules, ligands, and pharmaceuticals.2 Considering that olefins are less expensive or easy to make, the transition metal catalyzed difunctionalization of alkenes has been maximized as a more economical method for the synthesis of *β*-amino nitriles. However, the use of transition metals in alkene difunctionalization affords products of *β*-hydride elimination (Figure 1A).3-4 While product of *β*-hydride elimination is useful, it is undesirable in the synthesis of *β*-amino nitriles. This limits reactivity scope as starting materials may need to be carefully selected.1 Organic photoredox catalysis has recently gained wide recognition for its utility in achieving unique chemical reactivities and for allowing access to a broad range of substrates.5-6 One of such is the highly regioselective anti-Markovnikov difunctionalization of alkenes7. This study explores the enantioselective amino- and oxycyanation of alkenes via regioselective anti-Markovnikov reaction using an acridinium photooxidant and copper catalysis (Figure 1B).1 By employing a dual catalytic system, amino and oxycyanation of various alkene substrates were successful, yielding products with excellent enantiomeric excess. The cation radical intermediate formed expands the substrate scope of amines. Also, the formation of the cation radical intermediate afforded asymmetric oxycyanation of alkyl carboxylic acids.1 These highlights the utility of this method in the synthesis of complex organic molecules in pharmaceuticals and materials science.

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| B. Amino- and Oxycyanation via Olefin Cation Radical (This Work): |
| *A diagram of a cat  Description automatically generated* |
| Figure 1. (A) Transition Metal Catalyzed Difunctionalization of Alkenes. (B) Amino- and oxycyanation via olefin cation radicals. |

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