Visible-Light-Driven C–H Functionalization of N-Heterocycles and C–C Activation of 1,3-Dicarbonyl Compounds

Xi Chen

Under the supervision of Professor Dian Wang

at Marquette University

Abstract

For the past decade, photochemistry, especially visible light photocatalysis, has drawn wide attention in synthetic organic chemistry. In organic synthesis, photocatalysis has been considered as an important and powerful strategy as a photoactive species absorbs visible light to reach to its excited state and then generate reactive radical intermediates via single-electron transfer or energy-transfer events, followed by subsequent transformations to form C–C or C–heteroatom bonds. As such, visible-light driven photocatalysis has become a valuable tool in organic chemistry for structural modification and late-stage functionalization.

This dissertation presents three different research projects on the development of visible-light-driven reactions. In the first project, various types of C–H functionalized 2,2′-bipyridine derivatives were synthesized via light-driven, cobalt-mediated method, and were characterized by different techniques. The proposed mechanism demonstrated the roles of zinc in the reaction and indicated that the reaction proceeds via a radical pathway. In the second project, we successfully synthesized and characterized different palladium-N-heteroarene complexes. Individual C–H halogenation and thiolation of palladium-N-heteroarene complex occurred under the light, which provided a solid foundation for the development of light-driven C–H difunctionalization in the future. Lastly, we investigated light-driven, metal-free C–C bond cleavage of 1,3-dicarbonyl compounds. C–C bond of β-keto esters was cleaved under the light and a new C–N bond was formed by reacting with amine to afford structurally remodeled products. This study provided us with deeper understanding of how compounds can be edited and modified via bond cleavage and subsequent new bond formation, highlighting the significance of C–C cleavage in organic chemistry.