INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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Thesis Title: Photo and Electrochemical Strategies to C-N Bond Formation

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SHORT ABSTRACT

The contents of this thesis have been divided into six chapters based on the experimental works performed and results obtained during the research period. The introductory chapter of the thesis represents a summary of '**Photo and Electrochemical Strategies to C–N Bond Formation**'. For simplicity and brevity, **Chapter I** is divided into two parts. **Chapter IA** includes a photochemical C–N bond formation *via* difunctionalization of alkenes and indoles, whereas, **Chapter IB** deals with electrochemical approach for the C–N bond construction. The subsections of **Chapter IA** and **IB** are based on the mode of reactivity of difunctionalization and cross-coupling reactions.

Chapter II demonstrates a visible-light-induced synthesis of *N*-hydroxybenzimidoyl cyanides from aromatic terminal alkenes using Eosin Y as an organic photoredox catalyst. The process goes via a radical pathway with successive incorporation of two nitrogen atoms, one each from *tert*-butyl nitrite and ammonium acetate. The final product is achieved by the concomitant installation of an oxime and a nitrile group. DFT calculation supports a bi-radical pathway and

all the proposed steps. A few useful synthetic transformations of *N*-hydroxybenzimidoyl cyanide have also been illustrated.

Chapter III describes a visible-light-mediated concomitant C3 oxidation and C2 amination of indoles at room temperature using Ir (III) photocatalyst. This reaction proceeds without any isatin intermediate via the attack of singlet oxygen at the C3 position followed by C2 amination leading to difunctionalization of indoles.

Chapter IV describes an electrochemical amidation of benzoyl hydrazine/carbazate and primary/secondary amine as coupling partners via concomitant cleavage and formation of $C(sp^2)–N$ bonds. This methodology proceeds under metal and exogenous oxidant-free conditions producing N_2 and H_2 as by-products. Mechanistic studies reveal the *in situ* generations of both acyl and *N*-centered radicals from benzoyl hydrazines and amines respectively. The utility of this protocol is demonstrated in the large-scale, and synthesis of bezafibrate, a hyperlipidemic drug.

Chapter V delineates a robust electrochemical cross-coupling between aroyl hydrazine and *NH*-sulfoximine via concomitant cleavage and formation of $C(sp^2)–N$ bond with the evolution of H_2 and N_2 as innocuous by-products. This sustainable protocol avoids the use of toxic reagents and occurs at room temperature. The reaction proceeds via the generation of an aroyl and a sulfoximidoyl radical via anodic oxidation under constant current electrolysis (CCE), affording *N*-aroylated sulfoximine. The strategy is applied to late-stage sulfoximidation of L-menthol, (−)-borneol, D-glucose, vitamin-E derivatives, and marketed drugs such as probenecid, ibuprofen, flurbiprofen, ciprofibrate, and sulindac. In addition, the present methodology is mild, high functional group tolerance with broad substrate scope and scalable.

Chapter VI describes a robust electrochemical cross-coupling between α-keto acids and *NH*-sulfoximines is established. This process cleaves the C–C bond and forms a $C(sp^2)–N$ bond with the evolution of by-products H_2 and CO_2. This sustainable approach eliminates the need for hazardous reagents and operates at room temperature. In this process, *N*-aroylated sulfoximines are produced through the generation of aroyl and sulfoximidoyl radicals by anodic oxidation in constant current electrolysis (CCE). This approach is successfully employed for the late-stage

sulfoximidation of various compounds, including L-menthol, (-)-borneol, D-glucose, derivatives, and commercial drugs such as probenecid, ibuprofen, and flurbiprofen. This methodology features good functional group compatibility, a broad scope, and a detailed mechanistic investigation