DEVELOPMENT OF CATALYTIC SYSTEMS FOR C(sp^2)–H BOND FUNCTIONALIZATION OF (HETERO)AROMATICS

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by

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Dedicated to my beloved family
and teachers

CERTIFICATE

This is to certify that the thesis entitled "***Development of Catalytic Systems for C(sp^2)–H Bond Functionalization of (Hetero)aromatics***" being submitted by Ms. **Swati Singh** to the *Indian Institute of Technology Delhi*, for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by her. Ms. **Swati Singh** has worked under my supervision and guidance and has fulfilled all the requirements for the submission of a Ph.D. thesis, which, to my knowledge, has reached the requisite standard and is worthy of consideration for the award of a Ph.D. degree.

The work embodied in this thesis has not been submitted, in part or full, to another university or institute for the award of any degree or diploma.

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ABSTRACT

The thesis entitled "***Development of Catalytic Systems for C(sp^2)–H Bond Functionalization of (Hetero)aromatics***" deals with developing environmentally friendly and sustainable synthetic routes for C-H bond activation of heterocycles and aromatic systems to generate C-C, C-N, and C-S bonds. In this thesis, we have developed an inexpensive and milder catalytic system to demonstrate the C(sp^2)–H bond functionalization from feedstock precursors. We describe the cross-dehydrogenating and decarboxylative coupling approach for synthesizing alkylated heteroaromatics utilizing feedstocks such as unactivated alkanes and carboxylic acids. We have also devised a photoinduced radical-cascade protocol for the C-3 thioalkylation of quinoxalin-2(1*H*)-one with an extended alkyl chain without utilizing any photocatalyst. This thesis features a remarkable strategy for inserting an amino group on quinolin-2(1*H*)-one using photo-driven skeletal rearrangement. Furthermore, a series of regioselective aryl sulfone systems is prepared using an inexpensive photocatalyst.

Chapter 1 enumerates the progress made since the field of C-H functionalization began in terms of synthetic techniques for activating ubiquitous, non-reactive C-H bonds to facilitate efficient organic transformations. With regard to the access of complex organic scaffolds, in particular, the functionalization of C-H bonds has made it possible to create C-C, C-N, C-S, and C-X bonds immediately and with the least amount of pre-activation. Photocatalytic methods have gained considerable attention due to their sustainability, milder reaction conditions, and the facilitation of inaccessible reactions without adding any hazardous waste to the environment. Further, we have briefly remarked on the different radical-mediated photoredox techniques and how they overcome the challenges in functionalizing C-H bonds to architect organic frameworks. Using similar cases from our work, this chapter also illustrated ongoing scientific developments and the potential significance of our findings in mitigating existing challenges.

Chapter 2: Activation of C(sp^3)-H bonds directly utilizing easily accessible feedstock chemicals to functionalize diverse heterocycles has grown tremendously in synthetic chemistry. Still, ubiquitous properties of C(sp^3)-H bonds render them impractical for various applications. Here, an intriguing and efficient method is discussed for the selective alkylation of quinoxalin-2(1*H*)-one with a broad class of hydrocarbons having different C(sp^3)–H bonds with varying bond strengths using di-*tert*-butyl peroxide (DTBP) as an alkoxyl radical mediator for hydrogen atom

transfer (HAT). This protocol exhibits good functional group compatibility and selectivity regarding heterocycles and unactivated alkanes. We also illustrate the applicability of this C(sp^2)–H/C(sp^3)–H cross-coupling for practical access to bioactive pharmaceuticals and gram-scale synthesis.

Chapter 3 describes a decarboxylative alkylation approach of quinoxalin-2(1*H*)-one, which is mediated by a light-driven ligand to metal charge transfer utilizing the cerium catalyst. This inexpensive catalytic approach provides a viable solution regarding a precious photocatalyst system to generate alkyl radicals from various unactivated carboxylic acids, such as primary, secondary, tertiary, biologically active amino acids, and pharmaceutically active acids. This protocol also displays compatibility with quinolone, providing the regioselective alkylated product. Detailed mechanistic experiments are conducted using several spectroscopic studies to corroborate the hypothesis of photoinduced LMCT and decarboxylation events.

Chapter 4 describes a light-driven cascade reaction strategy for thioalkylation of quinoxalin-2(1*H*)-one with alkene and aryl disulfide. This greener approach eliminates the requirement of any external photocatalyst to generate the key radical synthons from various aryl disulfides. This protocol also manifests compatibility with alkyne, providing the regioselective vinylated quinoxalin-2(1*H*)-one. The practical applicability of this methodology is illustrated by scale-up experiments and late-stage modification of pharmaceutically active compounds. Detailed mechanistic experiments are performed using several spectroscopic studies to prove the hypothesis of quinoxalin-2(1*H*)-one as a photosensitizer.

Chapter 5 deals with the selective introduction of an amino group on heterocyclic moiety, which is crucial for manufacturing various bioactive compounds. It became essential to move beyond the limitations of conventional approaches that utilize elevated temperatures or extreme acidic conditions, ensuring site selectivity. We have developed a skeletal editing approach for regioselective denitrogenative amination to access C-3 aminoquinolin-2(1*H*)-ones. We have explored various 3-ylideneoxindoles substituted with sensitive functional groups as synthetic precursors for quinolin-2(1*H*)-one backbone. Several spectroscopic studies are carried out to understand the photocatalytic involvement in the skeletal editing of the triazoline intermediate. The practical utility of this approach is depicted by scale-up experiments and efficient synthesis of pharmaceutically active compounds.

Chapter 6 discusses the organophotocatalytic approach for the site-selective sulfonylation of

C(sp^2)−H bonds of anilide and quinoline amide derivatives. We have explored various anilides and sulfonyl chlorides substituted with sensitive functional groups as synthetic precursors for aryl sulfone moieties. This protocol also manifests compatibility with quinoline amides for regioselective sulfonylated products. Detailed mechanistic experiments are conducted using several spectroscopic studies, cyclic voltammetry, and DFT calculations to corroborate the photocatalytic involvement in the regioselective sulfonylation in both the proximal and distal positions.

Chapter 7 gives the overall conclusions of all the research carried out in the current studies and provides an outline for future scope in this area of research.

सारांश

थीसिस जिसका शीर्षक है "**सी(एसपी2)-एच बॉन्ड फंक्शनलाइजेशन ऑफ (हेटेरो)एरोमैटिक्स के लिए कैटेलिटिक सिस्टम का विकास**" सी-सी, सी-एन और सीएस बॉन्ड उत्पन्न करने के लिए हेटरोसायकल और एरोमैटिक सिस्टम के सी-एच बॉन्ड सक्रियण के लिए पर्यावरण के अनुकूल और टिकाऊ सिंथेटिक मार्गों को विकसित करने से संबंधित है। इस थीसिस में, हमने फीडस्टॉक अग्रदूतों से सी(एसपी2)-एच बांड कार्यात्मकता को प्रदर्शित करने के लिए एक सस्ती और हल्की उत्प्रेरक प्रणाली विकसित की है। हम निष्क्रिय अल्केन्स और कार्बोक्जिलिक एसिड जैसे फीडस्टॉक्स का उपयोग करके अल्काइलेटेड हेटेरोएरोमैटिक्स को संश्लेषित करने के लिए क्रॉस-डीहाइड्रोजनिंग और डीकार्बोक्सिलेटिव युग्मन दृष्टिकोण का वर्णन करते हैं। हमने किसी फोटोकैटलिस्ट का उपयोग किए बिना एक विस्तारित एल्काइल श्रृंखला के साथ क्विनॉक्सालिन -2 (1 एच)-वन के सी-3 थायोअल्काइलेशन के लिए एक फोटोप्रेरित रेडिकल-कैस्केड प्रोटोकॉल भी तैयार किया है। यह थीसिस फोटो-संचालित कंकाल पुनर्व्यवस्था का उपयोग करके क्विनोलिन-2(1*H*)- वन पर एक अमीनो समूह सम्मिलित करने के लिए एक उल्लेखनीय रणनीति पेश करती है। इसके अलावा, एक सस्ते फोटोकैटलिस्ट का उपयोग करके रीजियोसेलेक्टिव एरिल सल्फोन सिस्टम की एक श्रृंखला तैयार की जाती है।

अध्याय 1 कुशल जैविक परिवर्तनों को सुविधाजनक बनाने के लिए सर्वव्यापी, गैर-प्रतिक्रियाशील सी-एच बांड को सक्रिय करने के लिए सिंथेटिक तकनीकों के संदर्भ में सी-एच कार्यात्मकता के क्षेत्र की शुरुआत के बाद से हुई प्रगति की गणना करता है। जटिल कार्बनिक मचानों की पहुंच के संबंध में, विशेष रूप से, सी-एच बांड के कार्यात्मककरण ने सी-सी, सी-एन, सीएस और सी-एक्स बांड तुरंत और कम से कम पूर्व-सक्रियण के साथ बनाना संभव बना दिया है। फोटोकैटलिटिक विधियों ने अपनी स्थिरता, हल्की प्रतिक्रिया स्थितियों और पर्यावरण में किसी भी खतरनाक अपशिष्ट को शामिल किए बिना दुर्गम प्रतिक्रियाओं की सुविधा के कारण काफी ध्यान आकर्षित किया है। इसके अलावा, हमने अलग-अलग रेडिकल-मध्यस्थता वाले फोटोरेडॉक्स तकनीकों पर संक्षेप में टिप्पणी की है और कैसे वे आर्किटेक्ट ऑर्गेनिक फ्रेमवर्क के लिए सी-एच बांड को क्रियाशील करने में आने वाली चुनौतियों से निपटते हैं। हमारे काम से मिलते-जुलते मामलों का उपयोग करते हुए, इस अध्याय में चल रहे वैज्ञानिक विकास और मौजूदा चुनौतियों को कम करने में हमारे निष्कर्षों के संभावित महत्व को भी दर्शाया गया है।

अध्याय 2: विविध हेटरोसायकल को कार्यान्वित करने के लिए आसानी से सुलभ फीडस्टॉक रसायनों का सीधे उपयोग करते हुए $C(sp^3)$-H बांड का सक्रियण सिंथेटिक रसायन विज्ञान में काफी बढ़ गया है। फिर भी,

$C(sp^3)$-H बांड के सर्वव्यापी गुण उन्हें विभिन्न अनुप्रयोगों के लिए अव्यावहारिक बनाते हैं। यहां, डि-टर्ट-ब्यूटाइल पेरोक्साइड (डीटीबीपी) का उपयोग करके अलग-अलग बॉन्ड ताकत वाले विभिन्न $C(sp^3)$-H बॉन्ड वाले हाइड्रोकार्बन के एक व्यापक वर्ग के साथ क्विनॉक्सालिन -2 (1 एच) -वन के चयनात्मक क्षारीकरण के लिए एक दिलचस्प और कुशल विधि पर चर्चा की गई है। हाइड्रोजन परमाणु स्थानांतरण (एचएटी) के लिए एक एल्कोक्सिल रेडिकल मध्यस्थ के रूप में। यह प्रोटोकॉल हेटरोसायकल और निष्क्रिय अल्केन्स के संबंध में अच्छी कार्यात्मक समूह अनुकूलता और चयनात्मकता प्रदर्शित करता है। हम बायोएक्टिव फार्मास्यूटिकल्स और ग्राम-स्केल संश्लेषण तक व्यावहारिक पहुंच के लिए इस $C(sp^2)$-H/$C(sp^3)$-H क्रॉस-कपलिंग की प्रयोज्यता का भी वर्णन करते हैं।

अध्याय 3 में क्विनॉक्सालिन-2(1*H*)-वन के डीकार्बोक्सिलेटिव एल्किलेशन दृष्टिकोण का वर्णन किया गया है, जो कि सेरियम उत्प्रेरक का उपयोग करके धातु चार्ज स्थानांतरण के लिए प्रकाश-संचालित लिगैंड द्वारा मध्यस्थ होता है। यह सस्ता उत्प्रेरक दृष्टिकोण प्राथमिक, माध्यमिक, तृतीयक, जैविक रूप से सक्रिय अमीनो एसिड और फार्मास्युटिकल रूप से सक्रिय एसिड जैसे विभिन्न निष्क्रिय कार्बोक्जिलिक एसिड से एल्काइल रेडिकल उत्पन्न करने के लिए एक कीमती फोटोकैटलिस्ट प्रणाली के संबंध में एक व्यवहार्य समाधान प्रदान करता है। यह प्रोटोकॉल क्विनोलोन के साथ अनुकूलता भी प्रदर्शित करता है, जो रीजियोसेलेक्टिव एल्काइलेटेड उत्पाद प्रदान करता है। फोटोप्रेरित एलएमसीटी और डीकार्बाक्सिलेशन घटनाओं की परिकल्पना को पुष्ट करने के लिए कई स्पेक्ट्रोस्कोपिक अध्ययनों का उपयोग करके विस्तृत यंत्रवत प्रयोग किए जाते हैं।

अध्याय 4 में एल्कीन और एरिल डाइसल्फ़ाइड के साथ क्विनॉक्सालिन-2(1*H*)-वन के थायोअल्काइलेशन के लिए प्रकाश-चालित कैस्केड प्रतिक्रिया रणनीति का वर्णन किया गया है। यह हरित दृष्टिकोण विभिन्न एरिल डाइसल्फ़ाइड्स से प्रमुख रेडिकल सिंथॉन उत्पन्न करने के लिए किसी भी बाहरी फोटोकैटलिस्ट की आवश्यकता को समाप्त कर देता है। यह प्रोटोकॉल एल्काइन के साथ अनुकूलता भी प्रदर्शित करता है, जो रीजियोसेलेक्टिव विनाइलेटेड क्विनॉक्सालिन-2(1*H*)-वन प्रदान करता है। इस पद्धति की व्यावहारिक प्रयोज्यता को बड़े पैमाने पर प्रयोगों और फार्मास्युटिकल रूप से सक्रिय यौगिकों के अंतिम चरण के संशोधन द्वारा चित्रित किया गया है। फोटोसेंसिटाइज़र के रूप में क्विनॉक्सालिन-2(1*H*)-वन की परिकल्पना को साबित करने के लिए कई स्पेक्ट्रोस्कोपिक अध्ययनों का उपयोग करके विस्तृत यंत्रवत प्रयोग किए जाते हैं।

अध्याय 5 विषमचक्रीय भाग पर एक अमीनो समूह के चयनात्मक परिचय से संबंधित है, जो विभिन्न जैव सक्रिय यौगिकों के निर्माण के लिए महत्वपूर्ण है। पारंपरिक दृष्टिकोणों की सीमाओं से आगे बढ़ना आवश्यक हो गया है जो ऊंचे तापमान या अत्यधिक अम्लीय स्थितियों का उपयोग करते हैं, जिससे साइट की चयनात्मकता सुनिश्चित होती है। हमने C-3 अमीनोक्विनोलिन-2(1H)-ऑन तक पहुंचने के लिए रीजियोसेलेक्टिव डेनाइट्रोजनेटिव एमिनेशन के लिए एक कंकाल संपादन दृष्टिकोण विकसित किया है। हमने क्विनोलिन-2(1H)-वन बैकबोन के लिए सिंथेटिक अग्रदूतों के रूप में संवेदनशील कार्यात्मक समूहों के साथ प्रतिस्थापित विभिन्न 3-यलिडीनॉक्सिंडोल्स की खोज की है। ट्रायज़ोलिन इंटरमीडिएट के कंकाल संपादन में फोटोकैटलिटिक भागीदारी को समझने के लिए कई स्पेक्ट्रोस्कोपिक अध्ययन किए गए हैं। इस दृष्टिकोण की व्यावहारिक उपयोगिता को बड़े पैमाने पर प्रयोगों और औषधीय रूप से सक्रिय यौगिकों के कुशल संश्लेषण द्वारा दर्शाया गया है।

अध्याय 6 एनिलाइड और क्विनोलिन एमाइड डेरिवेटिव के सी(एसपी2)-एच बांड के साइट-चयनात्मक सल्फोनाइलेशन के लिए ऑर्गेनोफोटोकैटलिटिक दृष्टिकोण पर चर्चा करता है। हमने एरिल सल्फोन मौएटीज़ के लिए सिंथेटिक अग्रदूतों के रूप में संवेदनशील कार्यात्मक समूहों के साथ प्रतिस्थापित विभिन्न एनिलाइड्स और सल्फोनील क्लोराइड्स की खोज की है। यह प्रोटोकॉल रीजियोसेलेक्टिव सल्फोनिलेटेड उत्पादों के लिए क्विनोलिन एमाइड्स के साथ संगतता भी प्रकट करता है। समीपस्थ और दूरस्थ दोनों स्थितियों में रीजियोसेलेक्टिव सल्फोनाइलेशन में फोटोकैटलिटिक भागीदारी को पुष्ट करने के लिए कई स्पेक्ट्रोस्कोपिक अध्ययन, चक्रीय वोल्टामेट्री और डीएफटी गणना का उपयोग करके विस्तृत यंत्रवत प्रयोग किए जाते हैं।

अध्याय 7 वर्तमान अध्ययनों में किए गए सभी शोधों के समग्र निष्कर्ष देता है और अनुसंधान के इस क्षेत्र में भविष्य के दायरे की रूपरेखा प्रदान करता है ।

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LIST OF ABBREVIATIONS

CDC	cross-dehydrogenative coupling
TM	transition metal
PC	photoredox catalyst
EnT	energy transfer
ET	electron transfer
PCET	proton-coupled electron transfer
ISC	intersystem crossing
SOMO	singly occupied molecular orbital
GC	gas chromatography
TLC	thin layer chromatography
$KMnO_4$	potassium permanganate
δ	chemical shift
^{1}H NMR	proton nuclear magnetic resonance
^{13}C NMR	carbon nuclear magnetic resonance
$CDCl_3$	deuterated chloroform
DMSO-d6	deuterated dimethyl sulfoxide
Hz	Hertz
ppm	parts per million
HRMS	high-resolution mass spectra
ESI-TOF	electrospray ionization time-of-flight
HAT	hydrogen-atom transfer
NHC	*N*-heterocyclic carbene
TBAI	tetrabutylammonium iodide
DCE	dichloroethane
^{t}BuOH	tertiary butanol
EtOAc	ethyl acetate
DMSO	dimethyl sulfoxide
TBHP	*tert*-butyl hydroperoxide
TBPB	*tert*-butyl peroxybenzoate
DTBP	di-*tert*-butyl peroxide
DCP	dicumyl peroxide
TEMPO	2,2,6,6-tetramethylpiperidin-1-yl-oxidanyl

BHT	2,6-di-*tert*-butyl-4-methylphenol
DIPEA	*N*,*N*-Diisopropylethylamine
DMAP	4-(dimethylamino)pyridine
DCC	dicyclohexyl carbodiimide
EY	Eosin Y
RB	Rose Bengal
OH^-	hydroxide anion
$^tBuO^\bullet$	*tert*-butoxyl radical
$^tBuOO^\bullet$	*tert*-butyl peroxy radical
SET	single-electron transfer
BDE	bond-dissociation energy
ΔH_{HA}	hydrogen atom affinities
LMCT	ligand-to-metal charge transfer
LSF	late-stage functionalization
GC–MS	gas chromatography–mass spectrometry
HPLC	high-performance liquid chromatography
FTIR	Fourier transform infrared
DFT	density functional theory
CV	cyclic voltammetry
SCE	saturated calomel electrode
PET	photoinduced electron transfer
RCRs	radical cascade reactions