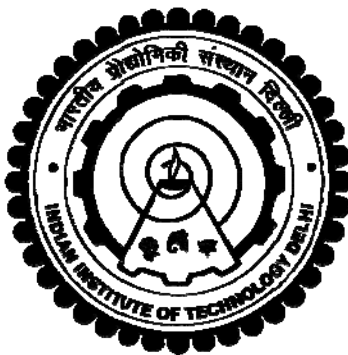


**STEREOSELECTIVE CASCADE APPROACHES INVOLVING
1,2-PHOSPHA BROOK REARRANGEMENT/CONJUGATE
ADDITION AND CYCLOADDITION REACTIONS**

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INDIAN INSTITUTE OF TECHNOLOGY DELHI
JUNE 2025**

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Stereoselective Cascade Approaches involving 1,2-Phospha Brook Rearrangement/Conjugate Addition and Cycloaddition Reactions

by

RAVNEET KAUR

DEPARTMENT OF CHEMISTRY

Submitted

**In fulfillment of the requirements of the degree of Doctor of Philosophy
to the**



INDIAN INSTITUTE OF TECHNOLOGY, DELHI

JUNE 2025

This Ph.D. thesis is dedicated to my Family.

*Special gratitude to my parents and my
brother for their blessings, unconditional
love, friendship and support.*

CERTIFICATE

This is to certify that the thesis entitled, “**Stereoselective Cascade Approaches involving 1,2-Phospha Brook Rearrangement/Conjugate Addition and Cycloaddition Reactions**”, being submitted by **Ms. Ravneet Kaur** to the *Indian Institute of Technology Delhi* for the award of the degree of **Doctor of Philosophy** in Chemistry is a record of bonafide research work carried out by her. **Ms. Ravneet Kaur** worked under my guidance and supervision and has fulfilled the requirements for the submission of a Ph.D. thesis, which to my knowledge has reached the requisite standard.

The results illustrated and incorporated in this dissertation have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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Ravneet Kaur

ABSTRACT

The thesis titled “*Stereoselective Cascade Approaches Involving [1,2]-Phospha Brook Rearrangement/Conjugate Addition and Cycloaddition Reactions*” is structured into four chapters that primarily focus on the development of stereoselective C-C and C-X bond-forming methodologies involving [1,2]-phospha Brook rearrangement, conjugate addition, and cycloaddition reactions. Chapters 2 and 3 detail the role of the [1,2]-phospha Brook rearrangement in stereoselective addition reactions, while Chapter 4 focuses on (5+2) cycloaddition reactions for constructing complex cyclic molecules.

Chapter 1: This chapter provides a concise overview of general organic chemistry, chirality, and its significance in everyday life, along with a discussion on asymmetric catalysis, with a particular focus on organocatalysis and its various activation modes. The chapter further elaborates on the concepts of aminocatalysis, the [1,2]-Phospha Brook Rearrangement, and cycloaddition reactions.

Chapter 2: This chapter introduces an aminocatalytic enantioselective conjugate addition reaction involving [1,2]-phospha-Brook rearrangement. Here, a simple aminocatalyst featuring both primary/secondary amine and tertiary amine functionalities, enabling the simultaneous activation of α,β -unsaturated enones and the generation of anionic nucleophiles *via* the Pudovik addition/[1,2]-phospha-Brook rearrangement. The approach provides a simple one-pot process employing a stable, additive-free catalytic system, yielding a variety of oxindole derivatives with two adjacent stereocenters, achieved in high yields and exceptional stereoselectivities.

Chapter 3: This work describes a highly regio- and diastereoselective approach for synthesizing phosphate-substituted dihydrocoumarins through the [1,2]-phospha-Brook rearrangement catalysed by a Brønsted base. The method employs a two-step, one-pot process involving the Michael addition of α -phosphonyloxy enolates formed through the coupling of dialkyl phosphite with α -ketoesters to *o*-quinone methides, followed by intramolecular cyclization. This strategy efficiently produces 3,4-dihydrocoumarin frameworks in high yields with excellent diastereoselectivity.

Chapter 4: This section presents a base-catalysed intermolecular (5+2) cycloaddition/oxa-Michael addition between α -arylidene pyrazolones and acylated pyranone acetals. The reaction proceeds through a sequential vinylogous aldol-Michael addition of alkyldiene pyrazolones to

oxidopyrylium ylides, generated in situ from the acylated pyranone acetals. This process yields bridged cycloaddition products, which subsequently undergo oxa-Michael addition. The method offers a highly regioselective and stereoselective route to synthesize 8-oxobicyclo[3.2.1]octane cores, achieving moderate to good yields with excellent diastereoselectivity.

सार

इस शोधप्रबंध का शीर्षक “स्टीरियोसिलेक्टिव कैस्केड दृष्टिकोण जिनमें [1,2]-फॉस्फा ब्रूक पुनर्व्यवस्था/संयुग्मित अभिक्रिया और साइक्लोएडिशन अभिक्रियाएं शामिल हैं” है। यह चार अध्यायों में विभाजित है, जो मुख्य रूप से [1,2]-फॉस्फा ब्रूक पुनर्व्यवस्था, संयुग्मित अभिक्रिया, और साइक्लोएडिशन अभिक्रियाओं के माध्यम से स्टीरियोसिलेक्टिव C-C और C-X बंध निर्माण पद्धतियों के विकास पर केंद्रित हैं। अध्याय 2 और 3 में स्टीरियोसिलेक्टिव संयोजन अभिक्रियाओं में [1,2]-फॉस्फा ब्रूक पुनर्व्यवस्था की भूमिका का विवरण दिया गया है, जबकि अध्याय 4 जटिल चक्रीय अणुओं के निर्माण के लिए (5+2) साइक्लोएडिशन अभिक्रियाओं पर केंद्रित है।

अध्याय 1: यह अध्याय सामान्य कार्बनिक रसायन विज्ञान, चिरलिटी और इसके दैनिक जीवन में महत्व का संक्षिप्त अवलोकन प्रस्तुत करता है। इसमें विषम उत्प्रेरण पर चर्चा की गई है, जिसमें विशेष रूप से ऑर्गेनोकैटालिसिस और इसके विभिन्न सक्रियण विधियों पर ध्यान केंद्रित किया गया है। अध्याय में आगे अमीनोकैटालिसिस, [1,2]-फॉस्फा ब्रूक पुनर्व्यवस्था, और साइक्लोएडिशन अभिक्रियाओं की अवधारणाओं को विस्तार से समझाया गया है।

अध्याय 2: यह अध्याय [1,2]-फॉस्फा ब्रूक पुनर्व्यवस्था से संबंधित अमीनोकैटालिटिक एंटियोसिलेक्टिव संयुग्मित अभिक्रिया का परिचय देता है। इसमें एक साधारण अमीनोकैटालिस्ट का उपयोग किया गया है, जिसमें प्राथमिक/माध्यमिक अमीन और तृतीयक अमीन कार्यात्मकताएं शामिल हैं, जो α,β -असंतृप्त इनोन्स को सक्रिय करने और पुदोविक अभिक्रिया/[1,2]-फॉस्फा ब्रूक पुनर्व्यवस्था के माध्यम से एनीऑनिक न्यूक्लियोफाइल उत्पन्न करने में सक्षम हैं। यह प्रक्रिया एक सरल वन-पॉट विधि प्रदान करती है, जिसमें स्थिर और एडिटिव-मुक्त उत्प्रेरक प्रणाली का उपयोग किया गया है, जिससे दो निकटवर्ती स्टीरियोसेंटर्स के साथ ऑक्सिडोल व्युत्पन्न उच्च उपज और उत्कृष्ट स्टीरियोसेलेक्टिविटी के साथ प्राप्त होते हैं।

अध्याय 3: यह कार्य [1,2]-फॉस्फा ब्रूक पुनर्व्यवस्था द्वारा ब्रॉस्टेड बेस उत्प्रेरण के तहत फॉस्फेट-प्रतिस्थापित डाइहाइड्रोकोमरिन्स के संश्लेषण के लिए एक अत्यधिक क्षेत्र- और डायस्टेरियोसेलेक्टिव दृष्टिकोण का वर्णन करता है। यह विधि एक दो-चरणीय, वन-पॉट प्रक्रिया का उपयोग करती है, जिसमें डायल्काइल फॉस्फाइट और α -किटोएस्टर्स के संयोजन से बने α -फॉस्फोनिओक्सी एनोलाट्स का माइकल अभिक्रिया α -क्विनोन मिथाइड्स के साथ किया जाता है, जिसके बाद अंतःआणविक चक्रीयकरण

होता है। यह रणनीति उच्च उपज और उत्कृष्ट डायस्टेरियोसेलेक्टिविटी के साथ 3,4-डाइहाइड्रोकोमरिन ढांचे का कुशलतापूर्वक निर्माण करती है।

अध्याय 4: यह खंड α -एरिलिडीन पायराज़ोलॉस और एसीलेटेड पायरोनोन एसीटल्स के बीच एक बेस-कैटालाइज्ड इंटरमॉलिक्यूलर (5+2) साइक्लोएडिशन/ऑक्सा-माइकल अभिक्रिया प्रस्तुत करता है। यह अभिक्रिया एसीलेटेड पायरोनोन एसीटल्स से इन-सीटू उत्पन्न ऑक्सीडोपायरीलियम यलाइड्स के साथ अल्काइलिडीन पायराज़ोलॉस के क्रमिक विनाइलोगस एल्डोल-माइकल अभिक्रिया के माध्यम से होती है। इस प्रक्रिया से बने ब्रिज्ड साइक्लोएडिशन उत्पादों में आगे ऑक्सा-माइकल अभिक्रिया होती है। यह विधि 8-ऑक्सोबाइसाइक्लो[3.2.1]ऑक्टेन कोर के संश्लेषण के लिए एक अत्यधिक क्षेत्र- और स्टीरियोसेलेक्टिव मार्ग प्रदान करती है, जो मध्यम से अच्छी उपज और उत्कृष्ट डायस्टेरियोसेलेक्टिविटी के साथ प्राप्त होती है।

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List of Abbreviations

Abbreviation	Full form
Ac	Acetate
MeCN/CH ₃ CN/ACN	Acetonitrile
Ar	Aryl
AI	Artificial Intelligence
^t Bu	<i>tert</i> -Butyl
CDCl ₃	Deuterated chloroform
CH ₂ Cl ₂ /DCM	Dichloromethane
CPA	Chiral Phosphoric Acid
cm ⁻¹	Wavenumbers
°C	Degrees Celsius
<i>dr</i>	Diastereomeric ratio
d	Doublet
dd	Doublet of doublets
DMSO- <i>d</i> ₆	Deuterated dimethyl sulfoxide
δ	Chemical shift
<i>er</i>	Enantiomeric ratio
<i>ee</i>	Enantiomeric excess
ESI-TOF	Electrospray ionization - Time-of-flight
EtOAc	Ethyl acetate
Et ₂ O	Diethyl ether
H ₂ O	Water
hr	Hour
HOMO	Highest occupied molecular orbital
HPLC	High-performance liquid chromatography
HRMS	High resolution mass spectroscopy
<i>J</i>	Coupling constant
λ	Wavelength
LUMO	Lowest unoccupied molecular orbital
min	Minute
MTBE	Methyl <i>tert</i> -butyl ether

m	Multiplet
MHz	Megahertz
mL	Millilitre
μL	Microlitre
NHC	N-Heterocyclic carbenes
Na_2SO_4	Sodium Sulphate
NBS	N-Bromosuccinimide
NaHCO_3	Sodium bicarbonate
NaCl	Sodium chloride
NMR	Nuclear Magnetic Resonance
N_2	Nitrogen gas
<i>o</i>	Ortho
<i>p</i> -TsOH	<i>para</i> -Toluenesulfonic acid
PTC	Phase Transfer Catalyst
PhCl	Chlorobenzene
<i>i</i> Pr	Isopropyl
<i>p</i>	para
rt	room temperature
s	Singlet
SOMO	Singly unoccupied molecular orbital
TLC	Thin Layer Chromatography
TfOH	Triflic acid
THF	Tetrahydrofuran
TMS	Tetramethylsilane
UV	Ultraviolet