

**New Synthetic and Catalytic methods for the Oxidation of Benzyl
Amines, Benzyl Alcohols and Styrenes and Reduction of Levulinic Acid**

by

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Submitted

in fulfillment of the requirements of the degree of

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Dedicated

to

My Family and Teachers

CERTIFICATE

This is to certify that the thesis entitled “ *New Synthetic and Catalytic methods for the Oxidation of Benzyl Amines, Benzyl Alcohols and Styrenes and Reduction of Levulinic Acid* ” being submitted by Mr. **Pritam Dolui** to *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 him. Mr. **Pritam Dolui** 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 Ph.D. degree.

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

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ABSTRACT

The thesis entitled " *New Synthetic and Catalytic methods for the Oxidation of Benzyl Amines, Benzyl Alcohols and Styrenes and Reduction of Levulinic Acid* " presents the results obtained from the research work carried out on the development, characterization and application of organometallic, transition metal and main group based compounds as catalysts and reagents for oxidation of amines, alcohols, styrenes and reduction of levulinic acid to value-added chemicals. The accompanied research work has been divided into seven chapters.

Chapter 1 of this thesis begins with a brief discussion on the chemistry and applications of ferrocene. This is followed by a brief discussion of the literature around C-H bond functionalization of ferrocene using directing group strategy and possible methods to remove the directing groups from the functionalized ferrocene compounds. This is followed by a section on ligand promoted palladium catalyzed oxidation of alcohols and styrenes. A brief literature background on water soluble palladium complexes and six membered trimeric palladium complexes has also been provided. In the last section of this chapter, importance of levulinic acid, γ -valerolactone (GVL), pyrrolidones and why the use of biomass as a renewable energy source is significant for the development of future 'Green-Sustainable Society & Economy' has been discussed. The detailed literature background of recent developments on the synthesis of GVL and pyrrolidones has also been portrayed.

The chapter ends with the objective of the present work carried out and reported in the thesis.

Chapter 2 describes the general experimental procedures adopted in the synthesis of new compounds and details of characterization techniques utilized. Specific synthetic details of the starting materials described in the thesis are also presented.

Chapter 3 deals with picolinamide group assisted sp^3 C-H bond oxidation of methylene groups bound to the phenyl ring, or the Cp ring of metal sandwich compounds to the corresponding carbonyl compounds by using simple ferrocene as a catalyst and $Cu(OAc)_2$ or tert-butyl peroxybenzoate (TBPB) as oxidant under mild conditions. This study represents an unprecedented use of picolinamide directing group and the development of a novel methodology to remove the directing group via oxidation of a sp^3 C-H bond to the corresponding carboxylic acids starting from benzyl amines. The reaction mechanisms of these oxidative transformations both on phenyl ring as well as the Cp ring of metal sandwich compounds were proposed by taking into account the literature reports and control experiments.

Chapter 4 describes the synthesis, characterization and catalytic evaluation of new trimeric, dimeric and monomeric palladium complexes with 8-aminoquinolines. A water soluble, neutral palladium trimer complex having a $(Pd-N)_3$ core is synthesized by a single pot method using 8- aminoquinoline in reasonably good yields at room temperature. This chapter also represents the synthesis of cationic monomeric, dimeric and trimeric palladium complexes with 2-methyl 8-aminoquinoline ligands. The catalytic activity of the neutral trimeric palladium complex was explored for the oxidation of alcohols to aldehydes using water as the solvent and oxygen as the green oxidant. The cationic palladium complexes are used for the oxidation of styrenes to methyl ketones in the presence of the green oxidant hydrogen peroxide. Single crystal X- ray diffraction

studies on all the new palladium complexes synthesized in this study has also been presented.

Chapter 5 presents an efficient, metal-free, catalyst-free and solvent-free methodology for the reductive amination of levulinic acid with different anilines using HBpin as the reducing reagent. This protocol offers an excellent method to avoid solvents and added catalysts for the synthesis of different kinds of *N*-substituted pyrrolidones under metal free conditions. For the first time a hydroboration methodology is applied on biomass derived levulinic acid, which contains a keto-acid bi-functional group. In addition to substrate scope, control experiment studies and DFT studies have also been carried out to find out the possible reaction pathway.

Chapter 6 presents the synthesis of the industrially important compound γ -valerolactone (GVL) from biomass derived levulinic acid. An efficient catalytic metal-free methodology was developed for the synthesis of the green solvent γ -valerolactone directly from levulinic acid using I_2/Et_3SiH at room temperature with good yields. This methodology is also explored on different keto acids. A hydrosilylation methodology is applied in this study. The mechanism of the reaction is also proposed by taking into account the literature reports and control experiments.

Chapter 7 gives the overall conclusions of the entire work carried out in the present study.

सारांश

शोध प्रबंध जिसका शीर्षक है ' **बेंजाइल एल्कोहलो, बेंजाइलमाइन्स और स्टाइरीन का ऑक्सीकरण, लेवुलिनिक का अपचयन के लिए नए कृत्रिम तथा उत्प्रेरको का अध्ययन** ' जिसमें बेंजाइल एल्कोहलो, बेंजाइलमाइन्स और स्टाइरीन का ऑक्सीकरण, लेवुलिनिक का अपचयन मूल्य वर्धित रसायनो में करने के लिए उपयोग हुए कार्ब-धात्विक उत्प्रेरक, संक्रमण धातु और नए मुख्य समूह के विकास, लक्षण वर्णन और अनुप्रयोग पर किए गए शोध कार्यों से प्राप्त परिणामों को प्रस्तुत किया गया है। सह अनुसंधान कार्य सात अध्यायों में विभाजित है।

इस शोध प्रबंध का **अध्याय 1** फेरोसिन के रसायन और अनुप्रयोग पर एक संक्षिप्त चर्चा के साथ शुरू होता है। शोध प्रबंध का पहला अध्याय निर्देशन समूहों रणनितियों का उपयोग करके धातु सैंडविच यौगिकों में फेरोसिन के सी-एच कार्यात्मककरण तथा अन्य संभावित तरीकों से समूह निर्देशन को हटाने के साहित्य पर एक संक्षिप्त चर्चा की गयी है। इसके बाद लिगैंड सहायक पैलेडियम उत्प्रेरित एल्कोहलो और स्टाइरीन के ऑक्सीकरण पर एक खंड है। जल में घुलनशील पैलेडियम यौगिक और त्रिमेरिक पैलेडियम यौगिक पर एक संक्षिप्त चर्चा की गयी है। इस अध्याय के अंतिम भाग में, लेवुलिनिक एसिड, वेलेरोलैक्टोन, पाइरोलिडोन का महत्व और भविष्य के 'ग्रीन सस्टेनेबल सोसाइटी एंड इकोनॉमी' के विकास के लिए अक्षय उर्जा स्रोत के रूप में बायोमास का उपयोग क्यों महत्वपूर्ण है, पर चर्चा की गई है। जीवीएल और पाइरोलिड के संश्लेषण पर हात के घटनाक्रमों की विस्तृत साहित्य पृष्ठभूमि को भी चित्रित किया गया है।

अध्याय 2 नए यौगिकों के संश्लेषण में अपनाई गई सामान्य प्रायोगिक अभिक्रियाओं का वर्णन करता है और उपयोग किए गए लक्षण वर्णन तकनीकों का विवरण भी करता है। शोध प्रबंध में वर्णित शुरुआती सामग्रियों का विशिष्ट संश्लेषण विवरण भी प्रस्तुत किया गया।

अध्याय 3 पीकोलीनैमाइड सहायक फिनाइल रिंग या धातु सैंडविच यौगिकों के सीपी- रिंग से जुड़े $-CH_2$ इकाई का sp^3 सी-एच आबंध ऑक्सीकरण उनके अनुरूप कार्बोनिल उत्पाद में प्राप्त करने के लिए फेरोसिन को उत्प्रेरक तथा $Cu(OAc)_2$ या TBPB ऑक्सीडेंट का उपयोग किया गया। यह अध्ययन पीकोलीनैमाइड निर्देशन समूहों के अभूतपूर्व उपयोग और बेंजाइलमाइन्स से शुरू होने वाले संबंधित कार्बोकिजलिक एसिड के लिए एक sp^3 सी-एच आबंध के ऑक्सीकरण के माध्यम से समूह निर्देशन को हटाने के लिए प्रयोग हुए नये क्रियाविधि के विकास पर चर्चा

करता है। इन ऑक्सीडेटिव परिवर्तन की प्रतिक्रिया तंत्र दोनो फिनाइल रिंग के साथ साथ धातु सैंडविच यौगिको के सीपी- रिंग पर साहित्य रिपोर्ट और नियंत्रण प्रयोगो को ध्यान में रखते हुए प्रस्तावित किए गए है।

अध्याय 4 8-एमिनोकिनोलिन के साथ नए ट्रिमेरिक, डिमेरिक और मोनोमेरिक पैलेडियम यौगिको के संश्लेषण, लक्षण वर्णन और उत्प्रेरक मूल्यांकन का वर्णन करता है। एक जल में घुलनशील, उदासीन पैलेडियम ट्रिमेरिक यौगिको जिसमे (पीडी एन)₃ कोर होता है, को कमरे के तापमान पर अच्छी पैदावार में 8-एमिनोकिनोलिन का उपयोग करके एकल पॉट विधि द्वारा संश्लेषित किया जाता है। यह अध्याय 2- मिथाइल 8-एमिनोकिनोलिन लिगैंड के साथ धनायनी मोनोमेरिक, डिमेरिक और ट्रिमेरिक पैलेडियम यौगिको के संश्लेषण का भी प्रतिनिधित्व करता है। एल्कोहलो का ऑक्सीकरण एल्डीहाइडो में करने लिए उदासीन ट्रिमेरिक पैलेडियम यौगिको को उत्प्रेरक के रूप में, जल को विलायक के रूप तथा ऑक्सीजन को ऑक्सीडेंट की तरह उपयोग किया गया। धनायनी पैलेडियम यौगिको का उपयोग हाइड्रोजन परॉक्साइड की उपस्थिति में स्टाइरीन का किटोन में ऑक्सीकरण के लिए करते है। इस अध्याय में संश्लेषित सभी नए पैलेडियम यौगिको पर एकल क्रिस्टल XRD अध्ययन भी प्रस्तुत किया गया है।

अध्याय 5 अपचायक अभिकर्मक के रूप में एचबीपिन का उपयोग करते हुए विभिन्न एनिलिन के साथ लेवुलिनिक एसिड के रिडिक्टिव एमिनेशन के लिए एक कुशल, धातु मुक्त, उत्प्रेरक मुक्त और विलायक मुक्त कार्यप्रणाली प्रस्तुत करता है। यह प्रोटोकॉल धातु मुक्त परिस्थितियों में विभिन्न प्रकार के एन प्रतिस्थापित पाइरोलिडोन के संश्लेषण के लिए विलायक मुक्त और अतिरिक्त उत्प्रेरक से बचने के लिए एक उत्कृष्ट विधि है। पहली बार हाइड्रोबोरेशन पद्धति बायोमास व्युत्पन्न लेवुलिनिक एसिड पर लागू होती है, जिसमे कीटो एसिड द्विकार्यात्मक समूह होता है। सबस्ट्रेट स्कोप के अलावा, संभावित अभिक्रिया मार्ग का पता लगाने के लिए नियंत्रण प्रयोग का भी अध्ययन किया गया है।

अध्याय 6 बायोमास व्युत्पन्न लेवुलिनिक एसिड से औद्योगिक रूप से महत्वपूर्ण यौगिक वेलेरोलैक्टोन के संश्लेषण को प्रस्तुत करता है। यह प्रोटोकॉल धातु मुक्त परिस्थितियों में सामान्य तापमान पर I_2/Et_3SiH का उपयोग करके लेवुलिनिक एसिड से वेलेरोलैक्टोन का संश्लेषण प्रस्तुत करता है। विभिन्न कीटो एसिड पर भी इस प्रोटोकॉल का पता लगाया जाता है। इस अध्ययन में एक हाइड्रोसिलिलेशन पद्धति लागू की गई है। साहित्य रिपोर्टों तथा नियंत्रण प्रयोगो को ध्यान में रखते हुए अभिक्रिया की क्रिया-विधि भी प्रस्तावित की गई।

अध्याय 7 पूर्ण वर्तमान अध्ययन में किए गए कार्यों का संपूर्ण निष्कर्ष देता है।

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List of Abbreviations Used

Anal.	Analysis
<i>i</i> Pr	Isopropyl
Calcd.	Calculated
Cp	Cyclopentadiene
Me	Methyl
Et	Ethyl
Ph	Phenyl
Fc	Ferrocene
Mp	Melting point
RT	Room Temperature
h	Hour(s)
min	Minutes
THF	Tetrahydrofuran
UV	Ultraviolet Spectroscopy
TLC	Thin Layer Chromatography
NMR	Nuclear Magnetic Resonance Spectroscopy
HRMS	High Resolution Mass Spectroscopy
BHT	Butylated hydroxytoluene
TEMPO	(2, 2, 6, 6-tetramethylpiperidin-1-yl)oxyl
DMSO	Dimethyl sulfoxide
SCXRD	Single crystal X-ray diffraction
DCM	Dichloromethane

DMF	<i>N, N</i> -dimethyl formamide
Aq.	Aqueous
DCE	1, 2-dichloroethane
TBHP	<i>tert</i> -Butyl hydroperoxide
TBPB	<i>tert</i> -Butyl peroxybenzoate
GC-MS	Gas Chromatography Mass Spectrometry
HBpin	pinacoleborane
GVL	Gamma-valerolactone
Et ₃ SiH	Triethylsilane
PMHS	Polymethylhydrosiloxane
H ₂ O ₂	Hydrogen peroxide