

**METAL-ORGANIC FRAMEWORKS SUPPORTED
EARTH-ABUNDANT METAL CATALYSTS FOR
SUSTAINABLE CHEMICAL SYNTHESIS**

NAVED AKHTAR



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
APRIL 2024**

© Indian Institute of Technology Delhi (IITD), New Delhi, 2024

**METAL-ORGANIC FRAMEWORKS SUPPORTED
EARTH-ABUNDANT METAL CATALYSTS FOR
SUSTAINABLE CHEMICAL SYNTHESIS**

by

NAVED AKHTAR

Department of chemistry

Submitted

In fulfillment of the requirements of the degree of

Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY, DELHI

APRIL 2024

Dedicated to my Family

CERTIFICATE

This is to certify that the thesis entitled, “**Metal-Organic Frameworks Supported Earth-Abundant Metal Catalysts for Sustainable Chemical Synthesis**”, being submitted by **Mr. Naved Akhtar** 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 him. Mr. Naved Akhtar worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained 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.

(Dr. Kuntal Manna)

Associate Professor

Department of Chemistry

Indian Institute of Technology Delhi

New Delhi-110016

Acknowledgments

Despite contemplating quitting almost every other day, I find myself on the brink of completing a significant milestone – my Ph.D. degree. This journey has been a challenging endeavor spanning nearly five years. The end of this journey wouldn't have been possible without the support of numerous individuals who have been associated with me in various capacities throughout these five years. While words may fall short of fully expressing the significant contributions of each person, it is the least I can do to acknowledge and appreciate their invaluable support.

*The first and foremost person is my Ph.D. advisor, **Prof. Kuntal Manna**. He is the individual under whose guidance I commenced my research career from scratch. His extensive knowledge in the field of catalysis, particularly heterogeneous catalysts, played a crucial role in addressing various research problems that emerged during my research journey. Thanks to his invaluable suggestions and timely input, I have completed my Ph.D. work. Beyond our professional relationship, he has been very supportive on a personal level, consistently motivating me when I fall behind or lose focus. I am immensely grateful to my Ph.D. advisor for all the research-oriented and scientific knowledge I gained from him. He is the one who successfully instilled a scientific temperament in me, and more specifically, the person I have become in the field of research is majorly owed to my advisor.*

I extend my sincere gratitude to my SRC members, Prof. Ravi Shankar, Prof. Sayantan Paria, and Prof. Josemon Jacob, for their consistent suggestions and valuable inputs that I received periodically. I am thankful to my committee members for their continuous availability, offering their valuable time, and guiding me during every SRC meeting over the course of 5 years.

I express my gratitude to Prof. S. Pandey, the current head of the department, as well as the previous departmental heads Prof. A. K. Ganguly, Prof. A. J. Elias, and Prof. N. D. Kurur, for their consistent support and guidance through the official channels of the department.

Analytical instruments and instrument labs constitute a crucial aspect of the Ph.D. journey for scientific researchers, without which no researcher could have progressed to this extent. Therefore, it would be inadequate not to acknowledge the individuals responsible for ensuring the efficient operation of the instrumental lab in the chemistry department. I extend my heartfelt thanks to the incharge of the instrument lab, N. Kuily, as well as S. Gupta, B. Kar, and Sandeep for their continuous efforts in facilitating the seamless functioning of the instrument lab.

I would also like to thank the office bearers of the chemistry department, Mrs. Dimple Hindwani, Mr. Vinod Kumar, Mr. Shiv, and Mr. Ashish who are always there to help me regarding official work. I would also like to thank Mr. Manoj and Mrs. Poornima for their help in operating NMR.

The prevailing belief is that the workplace and the individuals you work with play a pivotal role in shaping your professional journey. It is worth noting the names of every past and current lab member, Sakshi Shukla, Neha Antil, Wahida Begum, Manav Chauhan, Rahul Kalita, Poorvi Gupta, Chhaya Thadhani, Bharti Rana, Akanksha Choudhary, Manhar Singh Rawat, Ajay Kumar with whom I have shared the highs and lows of my Ph.D. journey in past years. These individuals are not just colleagues but also significant sources of support for me, both professionally and personally.

Furthermore, it is well said that fortunate are those who manage to find good friends and co-workers in the same individual. In this list first and foremost, I want to give special acknowledgment to Neha Antil, who has been a constant source of inspiration and support throughout my Ph.D. journey. She is among the few individuals who played a crucial role in helping me overcome the challenges of the initial years of my degree. Wahida Begum is another individual who has been with me from commencement to the completion of my degree. She is one of the liveliest individuals who significantly contributed to making the past few years truly memorable. Next, I'd like to acknowledge my younger brothers cum junior lab mates, Manav Chauhan and Rahul Kalita. The second half of my degree would have been unimaginable without them; they are the ones with whom I can freely share any thoughts of mine. Additionally, I would like to extend special recognition to Dr. Ajay Kumar, my senior in the lab, with whom I successfully acquired knowledge of the theoretical aspects of chemical reactions.

I want to extend a heartfelt mention to Namra Siddiqui for being a driving force and a continual source of encouragement, urging me to accomplish tasks and ensuring that I reach this point as early as possible.

Outside the laboratory, life carries its importance, and to infuse it with genuine memories and vibrancy, I want to convey my appreciation to my friends Sanjay, Prakash, Abu, Shashank, Vikas, Rahul, Bhuvanesh, Ravi, Ifkhar, Abu Taha, Nauman, Farman, Maroof and many other. They have been there in the past and I hope will continue to be there with me in the years ahead.

I express my gratitude to my family for their unwavering belief in me and their immense love throughout my Ph.D. journey. This appreciation extends to my parents, Mrs. Shabnam Akhtar,

and Mr. Parvez Akhtar, as well as prayers of my grandparents, Mrs. Mehar Bano and the Late Mr. Akhtar Hussain. Furthermore, I want to give special recognition to my chacha, Mr. Jamshed Akhtar; who has been more than a father figure to me, consistently being there for me since my childhood. In addition, I am deeply grateful to both of my aunts, as well as my friends from birth, Mrs. Nazma Akhtar and Mrs. Shadma Akhtar, for their unconditional love and unwavering support for me. I would also like to acknowledge the sincere love and affection given to me by my paternal uncles, Mr. Javed Akhtar (tauji) and Mr. Naseem Akhtar (chachaji), as well as my uncles Parvez Alam and Shah Alam. Finally, it is worth mentioning my brothers and sisters, namely Naurish, Gungun, Suburi, Nouman, Uzair, Obaid, Maheeb, and the youngest one, Omera. They consistently create a joyous atmosphere in the family and are among the main reasons for my happiness throughout my Ph.D. journey.

I would like to acknowledge the Present and Previous Director of IIT Delhi, Prof. Ram Gopal Rao and Prof. Rangan Banerjee.

Naved Akhtar

Abstract

The work in the thesis titled “Metal-Organic Frameworks Supported Earth-Abundant Metal Catalysts for Sustainable Chemical Synthesis” includes the fabricating of MOF materials as catalytic systems to carry out different types of organic transformations using earth-abundant base metals as active catalytic sites. The different sorts of chemical transformations involved in this work are asymmetric reductions, amine formylation using CO₂, nitro reductions with hydrosilanes, etc. This thesis is comprised of six chapters.

Chapter 1: This chapter commences with an introductory overview of heterogeneous catalysts, emphasizing the fundamental distinctions between single-site and multi-site solid supports. Following a concise definition of single-site solid supports, the narrative delves into a comprehensive examination of metal-organic frameworks (MOFs), tracing their historical evolution. The discussion extends to various modification methods and the tailored structuring of frameworks to achieve specific properties in MOFs-based materials. Additionally, the chapter provides an elaborate exploration of diverse synthetic approaches for MOF synthesis, elucidating their applications in processes such as drug delivery, chemical sensing, gas storage, and heterogeneous catalysis. The latter part of the chapter intricately examines UiO-type MOFs, offering insights into their isoreticular nature and core characteristics.

Chapter 2: This chapter provides a comprehensive account of the general experimental techniques utilized in conducting research projects. It offers detailed descriptions of the chemicals employed, including various solvents and reagents. Additionally, the chapter covers the handling of air and moisture-sensitive reactions, cleaning and drying of glassware, the purification of reagents and products, and the method for drying solvents, all discussed in thorough detail. Furthermore, the chapter delves into an in-depth exploration of various instrumentation techniques used for characterizing catalysts and studying reaction pathways. It also includes a brief discussion of the software employed for in-depth theoretical studies and a detailed examination of reaction mechanisms.

Chapter 3: This work presents a novel approach to advancing environmentally benign asymmetric catalysis, with a specific focus on developing heterogeneous single-site enantioselective catalysts derived from naturally occurring amino acids and abundant metals. The methodology encompasses the deliberate grafting of amino acids into the pores of a MOF, followed by subsequent post-synthetic metalation using an iron precursor. The resulting MOF-based catalyst, designated as L-valim-UiO-Fe, demonstrates outstanding efficacy in catalysing

hydrosilylation of carbonyl compounds, achieving enantiomeric excesses surpassing 99 % in large number of examples. Remarkably, L-valim-UiO-Fe exhibits exceptional catalytic activity, boasting high turnover numbers reaching up to 10,000. Furthermore, the catalyst showcases remarkable recyclability, enduring over 15 cycles without noticeable diminishing of activity and enantioselectivity. L-valim-UiO-Fe outperforms its homogeneous counterpart by establishing a robust single-site catalytic environment within the MOF through effective site isolation. Hence the work included in this chapter contributes to a significant advancement of asymmetric catalysis, offering an efficient, recyclable, and highly selective catalyst system in line with green and sustainable chemistry principles.

Chapter 4: The development of heterogeneous chiral catalysts for enantioselective synthesis of optically active compounds, utilizing cost-effective earth-abundant base metals, is of paramount importance. This study focuses on the development of a MOF catalyst functionalized with amino alcohol for the enantioselective reduction of unsymmetrical carbonyl groups into enantiopure alcohols, employing earth-abundant iron as the active base-metal. The chiral vol-UiO-68-FeCl catalyst was synthesized by grafting enantiopure amino alcohol into the porous framework via imine formation. Metalation of the resulting MOF with FeCl₂ in THF yielded the desired vol-UiO-68-FeCl(THF)₃ MOF catalyst, vol-UiO-68-FeCl(THF)₃, exhibiting octahedral coordination around the Fe²⁺ active sites, as confirmed by X-ray absorption spectroscopy (XAS) analysis. Treatment of vol-UiO-68-FeCl with LiCH₂SiMe₃ generated vol-UiO-68-Fe, an active catalyst for the asymmetric hydrosilylation and hydroboration of unsymmetrical ketones. The vol-UiO-68-Fe displayed high activity and enantioselectivity, achieving up to 99 % enantiomeric excess (ee) and an impressive turnover number of 15,000. Furthermore, the catalyst demonstrated robust reusability without a significant loss in its activity. In-depth mechanistic characterizations of the synthesized catalyst were conducted through spectroscopic, computational, and kinetic studies. The mechanistic insights suggest that Fe-H serves as an active catalytic precursor, undergoing hydride insertion followed by sigma-bond metathesis, resulting in optically pure silyl ether. This work underscores the significance of MOFs as chiral heterogeneous catalysts, derived from naturally occurring feedstocks such as base metals and chiral amino acids, for carrying out asymmetric conversions.

Chapter 5: N-Formylation of amines with CO₂ as a cheap and non-toxic C1-feedstock and hydrosilane reducing agent is a practical and environment-friendly method to synthesize formamides. This study describes an efficient and chemoselective mono-N-formylation of

amines using CO₂ and phenylsilane under mild conditions using a porous MOF-supported single-site cobalt catalyst (pyrim-UiO-Co). The pyrim-UiO-Co MOF has a UiO-topology, and its organic linkers bear a pyridylimine ligated Co catalytic moiety. A wide range of aliphatic and aromatic amines are transformed into desired *N*-formamides in moderate to excellent yields under 1–5 bar CO₂. Pyrim-UiO-Co is tolerant to various functional groups and could be recycled and reused at least 10 times. Mechanistic investigation using kinetic, spectroscopic, and density functional theory studies suggests that the formylation of benzylamine proceeds sequentially *via* oxidative addition of PhSiH₃ and CO₂ insertion, followed by a turn-over limiting reaction with an amine. Our work highlights the importance of MOF-based Earth-abundant metal catalysts for the practical and eco-friendly synthesis of fine chemicals using cheap feedstocks.

Chapter 6: Reducing nitro compounds to amines is a fundamental reaction in producing valuable chemicals in industry. In this work we report the synthesis and characterization of a zirconium MOF-supported salicylaldimine-cobalt(II) chloride (salim-UiO-CoCl), and its application in the catalytic reduction of nitro compounds. Salim-UiO-Co displayed excellent catalytic activity in chemoselective reduction of aromatic and aliphatic nitro compounds to the corresponding amines in the presence of phenylsilane as a reducing agent under mild reaction conditions. Salim-UiO-Co catalyzed nitro reduction had a broad substrate scope with excellent tolerance to diverse functional groups, including easily reducible ones such as aldehyde, keto, nitrile, and alkene. Salim-UiO-Co MOF catalyst could be recycled and reused at least 14 times without noticeable losing activity and selectivity. Density functional theory (DFT) studies along with spectroscopic analysis were employed to get into a comprehensive investigation of the reaction mechanism. This work underscores the significance of MOF-supported single-site base-metal catalysts for the sustainable and cost-effective synthesis of chemical feedstocks and fine chemicals.

सारांश

"सस्टेनेबल केमिकल सिंथेसिस के लिए मेटल-ऑर्गेनिक फ्रेमवर्क समर्थित पृथ्वी-प्रचुर मात्रा में धातु उत्प्रेरक" शीर्षक वाली थीसिस में सक्रिय उत्प्रेरक साइटों के रूप में पृथ्वी-प्रचुर आधार धातुओं का उपयोग करके विभिन्न प्रकार के कार्बनिक परिवर्तनों को पूरा करने के लिए उत्प्रेरक प्रणालियों के रूप में एमओएफ सामग्रियों का निर्माण शामिल है। इस कार्य में शामिल विभिन्न प्रकार के रासायनिक परिवर्तन हैं असममित कटौती, CO₂ का उपयोग करके सूत्रीकरण, हाइड्रोसिलेन के साथ कटौती, आदि। इस थीसिस में छह अध्याय शामिल हैं।

अध्याय 1: यह अध्याय विषम उत्प्रेरकों के परिचयात्मक अवलोकन के साथ शुरू होता है, जिसमें एकल-साइट और बहु-साइट ठोस समर्थन के बीच मूलभूत अंतर पर जोर दिया गया है। एकल-साइट ठोस समर्थन की एक संक्षिप्त परिभाषा के बाद, कथा धातु-कार्बनिक ढांचे (एमओएफ) की व्यापक जांच में उनके ऐतिहासिक विकास का पता लगाती है। चर्चा एमओएफ-आधारित सामग्रियों में विशिष्ट गुणों को प्राप्त करने के लिए विभिन्न संशोधन विधियों और रूपरेखाओं की अनुरूप संरचना तक फैली हुई है। इसके अतिरिक्त, अध्याय एमओएफ संश्लेषण के लिए विविध सिंथेटिक दृष्टिकोणों की विस्तृत खोज प्रदान करता है, जो दवा वितरण, रासायनिक संवेदन, गैस भंडारण और विषम उत्प्रेरण जैसी प्रक्रियाओं में उनके अनुप्रयोगों को स्पष्ट करता है। अध्याय का उत्तरार्द्ध भाग यूआईओ-प्रकार के धातु-कार्बनिक ढांचे की गहनता से जांच करता है, जो उनके आइसोरेटिकुलर प्रकृति और मुख्य विशेषताओं में अंतर्दृष्टि प्रदान करता है।

अध्याय 2: यह अध्याय अनुसंधान परियोजनाओं के संचालन में उपयोग की जाने वाली सामान्य प्रयोगात्मक तकनीकों का एक व्यापक विवरण प्रदान करता है। यह विभिन्न सॉल्वैंट्स और अभिकर्मकों सहित प्रयुक्त रसायनों का विस्तृत विवरण प्रदान करता है। इसके अतिरिक्त, अध्याय में हवा और नमी-संवेदनशील प्रतिक्रियाओं से निपटने, कांच के बर्तनों की सफाई और सुखाने, अभिकर्मकों और उत्पादों की शुद्धि, और सॉल्वैंट्स को सुखाने की विधि, सभी पर विस्तार से चर्चा की गई है। इसके अलावा, अध्याय उत्प्रेरकों को चिह्नित करने और प्रतिक्रिया मार्गों का अध्ययन करने के लिए उपयोग की जाने वाली विभिन्न उपकरण तकनीकों की गहन खोज पर प्रकाश डालता है। इसमें गहन सैद्धांतिक अध्ययन के लिए नियोजित सॉफ्टवेयर की संक्षिप्त चर्चा और प्रतिक्रिया तंत्र की विस्तृत जांच भी शामिल है।

अध्याय 3: यह कार्य पर्यावरणीय रूप से सौम्य असममित कटौतिसीस को आगे बढ़ाने के लिए एक नया दृष्टिकोण प्रस्तुत करता है, जिसमें प्राकृतिक रूप से पाए जाने वाले अमीनो एसिड और प्रचुर धातुओं से प्राप्त विषम एकल-साइट एनेटियोसेलेक्टिव उत्प्रेरक विकसित करने पर विशेष ध्यान दिया गया है। इस

पद्धति में धातु-कार्बनिक ढांचे (एमओएफ) के छिद्रों में अमीनो एसिड की जानबूझकर ग्राफ्टिंग शामिल है, इसके बाद लोहे के अग्रदूत का उपयोग करके पोस्ट-सिंथेटिक धातुकरण किया जाता है। परिणामी MOF-आधारित उत्प्रेरक, जिसे L-valim-UiO-Fe के रूप में नामित किया गया है, कार्बोनिल यौगिकों के हाइड्रोसिलिलेशन को उत्प्रेरित करने में उत्कृष्ट प्रभावकारिता प्रदर्शित करता है, बड़ी संख्या में उदाहरणों में 99% से अधिक एनैन्टीओमेरिक आधिक्य प्राप्त करता है। उल्लेखनीय रूप से, L-valim-UiO-Fe असाधारण उत्प्रेरक गतिविधि प्रदर्शित करता है, जो 10,000 तक पहुंचने वाली उच्च टर्नओवर संख्या का दावा करता है। इसके अलावा, उत्प्रेरक उल्लेखनीय पुनर्चक्रण क्षमता प्रदर्शित करता है, जो गतिविधि और ऊर्जा चयनात्मकता में उल्लेखनीय कमी के बिना 15 से अधिक चक्रों तक कायम रहता है। L-valim-UiO-Fe प्रभावी साइट अलगाव के माध्यम से MOF के भीतर एक मजबूत एकल-साइट उत्प्रेरक वातावरण स्थापित करके अपने सजातीय समकक्ष से बेहतर प्रदर्शन करता है। इसलिए इस अध्याय में शामिल कार्य असममित उत्प्रेरण की महत्वपूर्ण प्रगति में योगदान देता है, जो हरित और टिकाऊ रसायन विज्ञान सिद्धांतों के अनुरूप एक कुशल, पुनः प्रयोज्य और उच्च चयनात्मक उत्प्रेरक प्रणाली की पेशकश करता है।

अध्याय 4: लागत प्रभावी पृथ्वी-प्रचुर आधार धातुओं का उपयोग करते हुए, ऑप्टिकली सक्रिय यौगिकों के एनेंटियोसेलेक्टिव संश्लेषण के लिए विषम चिरल उत्प्रेरक का विकास अत्यंत महत्वपूर्ण है। यह अध्ययन अमीनो अल्कोहल के साथ कार्यात्मक धातु-कार्बनिक ढांचे (एमओएफ) उत्प्रेरक के विकास पर केंद्रित है, जो कि असममित कार्बोनिल समूहों को एनैन्टीओप्योर अल्कोहल में कम करने के लिए सक्रिय आधार-धातु के रूप में पृथ्वी-प्रचुर मात्रा में लोहे को नियोजित करता है। चिरल वॉल्यूम-UiO-68-FeCl उत्प्रेरक को इमाइन गठन के माध्यम से छिद्रपूर्ण ढांचे में एनेंटिओप्योर अमीनो अल्कोहल को ग्राफ्ट करके संश्लेषित किया गया था। THF में FeCl₂ के साथ परिणामी MOF के धातुकरण से वांछित vol-UiO-68-FeCl(THF)₃ MOF उत्प्रेरक, vol-UiO-68-FeCl(THF)₃ प्राप्त हुआ, जो Fe²⁺ सक्रिय साइटों के चारों ओर अष्टफलकीय समन्वय प्रदर्शित करता है, जैसा कि पुष्टि की गई है एक्स-रे अवशोषण स्पेक्ट्रोस्कोपी (एक्सएस) विश्लेषण। LiCH₂SiMe₃ के साथ वॉल्यूम-UiO-68-FeCl का उपचार, उत्पन्न वॉल्यूम-UiO-68-Fe, असममित हाइड्रोसिलिलेशन और असममित कीटोन्स के हाइड्रोबोरेशन के लिए एक सक्रिय उत्प्रेरक। Vol-UiO-68-Fe ने उच्च गतिविधि और एनैन्टीओसेलेक्टिविटी प्रदर्शित की, जिससे 99% एनैन्टीओमेरिक अतिरिक्त (ईई) और 15,000 की प्रभावशाली टर्नओवर संख्या प्राप्त हुई। इसके अलावा, उत्प्रेरक ने अपनी गतिविधि में किसी महत्वपूर्ण नुकसान के बिना मजबूत पुनः प्रयोज्यता का प्रदर्शन किया। संश्लेषित उत्प्रेरक के गहन यंत्रवत लक्षण वर्णन स्पेक्ट्रोस्कोपिक, कम्प्यूटेशनल और गतिज अध्ययनों के माध्यम से किए गए थे। यंत्रवत अंतर्दृष्टि से पता चलता है कि Fe-H एक सक्रिय

उत्प्रेरक अग्रदूत के रूप में कार्य करता है, जो सिग्मा-बॉन्ड मेटाथिसिस के बाद हाइड्राइड सम्मिलन से गुजरता है, जिसके परिणामस्वरूप ऑप्टिकली शुद्ध सिलिल ईथर होता है। यह कार्य असममित रूपांतरणों को पूरा करने के लिए बेस मेटल्स और चिरल अमीनो एसिड जैसे प्राकृतिक रूप से पाए जाने वाले फीडस्टॉक्स से प्राप्त चिरल विषम उत्प्रेरक के रूप में एमओएफ के महत्व को रेखांकित करता है।

अध्याय 5: एक सस्ते और गैर विषैले सी¹-फीडस्टॉक और हाइड्रोसिलेन कम करने वाले एजेंट के रूप में सीओ₂ के साथ एमाइन का एन-फॉर्माइलेशन फॉर्मामाइड को संश्लेषित करने का एक व्यावहारिक और पर्यावरण-अनुकूल तरीका है। यह अध्ययन एक झरझरा धातु-कार्बनिक ढांचे (एमओएफ)-समर्थित एकल-साइट कोबाल्ट उत्प्रेरक (पाइरिम-यूआईओ-सीओ) का उपयोग करके हल्के परिस्थितियों में सीओ₂ और फेनिलसिलेन का उपयोग करके एमाइन के एक कुशल और कीमोसेलेक्टिव मोनो-एन-फॉर्माइलेशन का वर्णन करता है। पाइरिम-यूआईओ-सीओ एमओएफ में यूआईओ-टोपोलॉजी है, और इसके कार्बनिक लिंकर्स में पाइरिडाइलिमाइन लिगेटेड सह उत्प्रेरक अंश होता है। एलिफैटिक और एरोमैटिक एमाइन की एक विस्तृत श्रृंखला 1-5 बार सीओ₂ के तहत मध्यम से उत्कृष्ट पैदावार में वांछित एन-फॉर्माइड में बदल जाती है। पिरिम-यूआईओ-सीओ विभिन्न कार्यात्मक समूहों के प्रति सहिष्णु है और इसे कम से कम 10 बार पुनर्नवीनीकरण और पुनः उपयोग किया जा सकता है। काइनेटिक, स्पेक्ट्रोस्कोपिक और घनत्व कार्यात्मक सिद्धांत अध्ययनों का उपयोग करते हुए यंत्रवत जांच से पता चलता है कि बेज़िलमाइन का फॉर्मूलेशन PhSiH₃ और CO₂ सम्मिलन के ऑक्सीडेटिव जोड़ के माध्यम से क्रमिक रूप से आगे बढ़ता है, इसके बाद एक एमाइन के साथ टर्न-ओवर सीमित प्रतिक्रिया होती है। हमारा काम सस्ते फीडस्टॉक का उपयोग करके बढ़िया रसायनों के व्यावहारिक और पर्यावरण-अनुकूल संश्लेषण के लिए एमओएफ-आधारित पृथ्वी-प्रचुर धातु उत्प्रेरक के महत्व पर प्रकाश डालता है।

अध्याय 6: नाइट्रो यौगिकों को एमाइन में कम करना उद्योग में मूल्यवान रसायनों के उत्पादन में एक मौलिक प्रतिक्रिया है। इस कार्य में हम जिंकोनियम धातु-कार्बनिक ढांचे-समर्थित सैलिसिलिडिमाइन-कोबाल्ट (II) क्लोराइड (सैलिम-यूआईओ-सीओसीएल) के संश्लेषण और लक्षण वर्णन और नाइट्रो यौगिकों की उत्प्रेरक कमी में इसके अनुप्रयोग की रिपोर्ट करते हैं। सलीम-यूआईओ-सीओ ने हल्के प्रतिक्रिया स्थितियों के तहत एक कम करने वाले एजेंट के रूप में फेनिलसिलेन की उपस्थिति में सुगंधित और स्निग्ध नाइट्रो यौगिकों की कीमोसेलेक्टिव कमी में उत्कृष्ट उत्प्रेरक गतिविधि प्रदर्शित की। सलीम-यूआईओ-सीओ उत्प्रेरित नाइट्रो कटौती में विविध कार्यात्मक समूहों के लिए उत्कृष्ट सहनशीलता के साथ एक व्यापक सबस्ट्रेट दायरा था, जिसमें एल्लिहाइड, कीटो, नाइट्राइल और एल्केन जैसे आसानी से कम करने योग्य समूह शामिल थे। सलीम-यूआईओ-सीओ एमओएफ उत्प्रेरक को गतिविधि और

चयनात्मकता में उल्लेखनीय कमी के बिना कम से कम 14 बार पुनर्नवीनीकरण और पुनः उपयोग किया जा सकता है। प्रतिक्रिया तंत्र की व्यापक जांच के लिए स्पेक्ट्रोस्कोपिक विश्लेषण के साथ घनत्व कार्यात्मक सिद्धांत (डीएफटी) अध्ययन को नियोजित किया गया था। यह कार्य रासायनिक फीडस्टॉक्स और बढ़िया रसायनों के टिकाऊ और लागत प्रभावी संश्लेषण के लिए एमओएफ-समर्थित एकल-साइट बेस-मेटल उत्प्रेरक के महत्व को रेखांकित करता है।

Table of contents

| | |
|---|---------------|
| Certificate..... | i |
| Acknowledgements..... | ii |
| Abstract..... | v |
| List of Figures..... | xx |
| List of Tables..... | xxviii |
| List of Schemes..... | xxx |
| Chapter 1: Introduction..... | 1 |
| 1.1. Heterogeneous catalysts..... | 2 |
| 1.2. Metal-organic framework..... | 3 |
| 1.3. Initial advancements in MOF..... | 5 |
| 1.3.1. Historical background..... | 5 |
| 1.3.2. Nomenclature of MOF..... | 6 |
| 1.4. Diverse methods for synthesis of MOF..... | 7 |
| 1.4.1. Solvothermal method..... | 10 |
| 1.4.2. Mechanochemical method..... | 10 |
| 1.4.3. Electrochemical method..... | 11 |
| 1.4.4. Microwave-assisted method..... | 11 |
| 1.5. Strategies employed for activation of MOF..... | 12 |
| 1.5.1. Solvent exchange..... | 13 |
| 1.5.2. Guest removal..... | 13 |
| 1.6. Tailoring of MOF for catalysis..... | 14 |
| 1.6.1. MOF functionalization via unsaturation over metal clusters..... | 14 |
| 1.6.2. Functionalization of MOF by utilizing Metal complexes in organic linkers..... | 15 |
| 1.6.3. MOF functionalization via post-synthetic route..... | 16 |
| 1.6.3.1. PSMs over organic linkers..... | 17 |
| 1.6.3.2. PSMs over metal nodes (SBUs)..... | 18 |
| 1.6.3.3. PSMs via metal ion exchange..... | 19 |
| 1.7. Applications of MOF..... | 19 |

| | |
|--|-----------|
| 1.7.1. MOF as gas storage and separation materials..... | 21 |
| 1.7.2. MOF as drug delivery agents..... | 22 |
| 1.7.3. MOF as chemical sensors..... | 22 |
| 1.7.4. MOF as in crystalline sponge method..... | 23 |
| 1.7.5. MOF as heterogeneous catalysts..... | 26 |
| 1.7.5.1. Catalysis reactions at metal nodes..... | 27 |
| 1.7.5.2. Catalysis reactions at organic linkers..... | 32 |
| 1.7.5.3. MOF-based biomimetic catalysis..... | 37 |
| 1.8. UiO MOF..... | 39 |
| 1.8.1. Isoreticular nature of UiO MOF..... | 40 |
| 1.9. Outline of thesis..... | 41 |
| 1.10. References..... | 42 |
| | |
| Chapter 2: General experimental procedure and techniques..... | 50 |
| 2.1. Starting materials, solvents, and reagents..... | 50 |
| 2.2. Glassware cleaning and drying procedure..... | 50 |
| 2.3. Procedure of solvents and reagent drying..... | 51 |
| 2.4. Instrumental methods..... | 51 |
| 2.5. Handling and sampling of air-sensitive reactions and compounds..... | 51 |
| 2.6. Analytical or instrumental techniques..... | 52 |
| 2.6.1. GC-MS/GC-FID..... | 52 |
| 2.6.2. HPLC..... | 52 |
| 2.6.3. BET..... | 52 |
| 2.6.4. FT-IR..... | 53 |
| 2.6.5. PXRD..... | 53 |
| 2.6.6. TGA..... | 53 |
| 2.6.7. NMR..... | 53 |
| 2.6.8. ICP-OES..... | 53 |
| 2.6.9. SEM-EDS..... | 54 |
| 2.6.10. TEM..... | 54 |
| 2.6.11. XPS..... | 54 |

| | |
|--|----|
| 2.6.12. HRMS..... | 54 |
| 2.6.13. XAS..... | 54 |
| 2.7. Theoretical studies and details of software employed..... | 55 |

Chapter 3: Utilizing amino acid-functionalized metal-organic frameworks for

| | |
|---|-----------|
| asymmetric base-metal catalysis..... | 58 |
| 3.1. Introduction..... | 58 |
| 3.2. Results and discussions..... | 62 |
| 3.2.1. Synthesis and characterization of the L-valim-UiO-Fe MOF..... | 62 |
| 3.2.2. L-valim-UiO-Fe catalyzed asymmetric hydrosilylation of ketones..... | 64 |
| 3.2.3. Mechanistic investigation for L-valim-UiO-Fe catalyzed asymmetric hydrosilylation of ketones..... | 68 |
| 3.3. Experimental section..... | 70 |
| 3.3.1. General experiment..... | 70 |
| 3.3.2. Synthesis and characterization of chiral L-valim-UiO MOF..... | 70 |
| 3.3.2.1. Synthesis of dimethyl-2'-amino-[1,1':4',1''-terphenyl]-4,4''- dicarboxylate..... | 70 |
| 3.3.2.2. Synthesis of 2'-amino-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid..... | 71 |
| 3.3.2.3. Synthesis of L-val-UiO-MOF via PSM of UiO-68-NH ₂ | 72 |
| 3.3.2.4. PSM of L-val-UiO MOF to L-valim-UiO MOF..... | 73 |
| 3.3.3. Synthesis of L-valim-UiO-FeCl MOF..... | 76 |
| 3.3.4. Synthesis of chiral L-valim-UiO-Fe MOF..... | 79 |
| 3.3.5. Catalytic reactions with L-valim-UiO-Fe MOF..... | 79 |
| 3.3.5.1. General procedure for L-valim-UiO-Fe MOF catalysed hydrosilylation of ketones..... | 79 |
| 3.3.5.2. Heterogeneity test of L-valim-UiO-Fe MOF..... | 80 |
| 3.3.5.3. Recyclability test for hydrosilylation of ketones..... | 81 |
| 3.3.6. Synthesis and catalysis with homogeneous control (L-valim-FeCl)..... | 83 |
| 3.3.6.1. Synthesis of (<i>S,E</i>)-3-methyl-N-phenyl-2-((pyridin-2- ylmethylene)amino)butanamide..... | 83 |

| | |
|--|-----|
| 3.3.6.2. Metalation of (<i>S,E</i>)-3-methyl- <i>N</i> -phenyl-2-((pyridin-2-ylmethylene)amino)butanamide with FeCl ₂ | 84 |
| 3.3.6.3. Homogeneous control L-valim-Fe catalyzed hydrosilylation of acetophenone..... | 85 |
| 3.3.7. Investigation of the role of chiral amino acid moiety in catalytic activity and enantioselectivity of chiral MOF-catalysts..... | 85 |
| 3.3.7.1. Synthesis of pyrim-UiO-FeCl ₂ | 85 |
| 3.3.7.2. Pyrim-UiO-Fe catalyzed hydrosilylation of acetophenone..... | 86 |
| 3.3.8. Determination of the rate law for L-valim-UiO-Fe MOF catalyzed hydrosilylation of acetophenone..... | 86 |
| 3.3.9. Characterization and analysis of % ee of products by NMR, GC and HPLC analysis..... | 88 |
| 3.3.9.1. NMR analysis..... | 88 |
| 3.3.9.2. Analysis of products by GC-MS and GC-FID..... | 95 |
| 3.3.10. DFT calculations..... | 97 |
| 3.3.10.1. Cartesian coordinates of optimized structures..... | 100 |
| 3.3.11. X-ray absorption spectroscopic analysis..... | 104 |
| 3.3.11.1. XANES analysis..... | 104 |
| 3.3.11.2. EXAFS fitting..... | 104 |
| 3.3.12. GC-FID spectra..... | 108 |
| 3.3.13. NMR spectra..... | 123 |
| 3.3.14. Mass spectra..... | 126 |
| 3.4. Conclusion..... | 127 |
| 3.5. References..... | 128 |

Chapter 4: Chiral Iron(II)-Catalyst within Valinol-Grafted Metal-Organic

| | |
|---|------------|
| Frameworks for Enantioselective Reduction of Ketones..... | 135 |
| 4.1. Introduction..... | 136 |
| 4.2. Results and discussions..... | 138 |
| 4.2.1. Synthesis and characterization of the vol-UiO-68-Fe MOF..... | 138 |
| 4.2.2. Vol-UiO-68-Fe catalyzed asymmetric hydrosilylation of ketones..... | 140 |

| | |
|---|-----|
| 4.2.3. Investigating the Mechanism of asymmetric hydrosilylation of ketones catalyzed by vol-UiO-68-Fe..... | 144 |
| 4.2.4. Vol-UiO-68-Fe catalyzed asymmetric hydroboration of ketones..... | 148 |
| 4.3. Experimental Section..... | 149 |
| 4.3.1. General Experiment..... | 149 |
| 4.3.2. Synthesis and characterization of L-valinol-functionalized UiO-68 MOF (vol-UiO-68 MOF)..... | 150 |
| 4.3.2.1. Synthesis of 2'-formyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid..... | 150 |
| 4.3.2.2. Synthesis of vol-UiO-68 MOF via PSM of UiO-68-CHO MOF..... | 152 |
| 4.3.3. Synthesis and characterization of vol-UiO-68-FeH..... | 153 |
| 4.3.3.1. Synthesis of vol-UiO-68-FeH..... | 153 |
| 4.3.3.2. Characterization of vol-UiO-68-FeH by quantification of H ₂ after reaction with water..... | 153 |
| 4.3.4. Catalytic reactions with vol-UiO-68-Fe MOF..... | 156 |
| 4.3.4.1. General procedure for vol-UiO-68-Fe MOF catalyzed hydrosilylation of ketones..... | 156 |
| 4.3.4.2. General procedure for vol-UiO-68-Fe MOF catalyzed hydrosilylation of ketones using phenylsilane..... | 157 |
| 4.3.4.3. General procedure for vol-UiO-68-Fe MOF catalyzed hydroboration of ketones..... | 157 |
| 4.3.4.4. Heterogeneity test of vol-UiO-68-Fe MOF..... | 158 |
| 4.3.4.5. Recyclability test..... | 158 |
| 4.3.4.6. Comparative study between vol-UiO-68 and its homogenous control for hydrosilylation of ketone..... | 161 |
| 4.3.5. Determination of the rate law for vol-UiO-68-Fe MOF catalyzed hydrosilylation of 4-methoxyacetophenone..... | 162 |
| 4.3.6. Characterization and analysis of % ee of products by NMR, GC and HPLC..... | 164 |
| 4.3.6.1. NMR analysis..... | 164 |
| 4.3.6.2. Analysis of products by GC-MS and GC-FID..... | 167 |
| 4.3.7. DFT calculations..... | 169 |
| 4.3.7.1. Cartesian coordinates of optimized structures..... | 172 |

| | |
|--|-----|
| 4.3.8. X-ray absorption spectroscopic analysis..... | 175 |
| 4.3.8.1. XANES analysis..... | 175 |
| 4.3.8.2. EXAFS fitting..... | 176 |
| 4.3.9. XPS analysis of vol-UiO-68-FeCl MOF and vol-UiO-68-FeH..... | 180 |
| 4.3.10. GC-FID and HPLC spectra..... | 182 |
| 4.3.11. NMR analysis..... | 191 |
| 4.4. Conclusion..... | 195 |
| 4.5. References..... | 196 |

Chapter 5: A supported pyridylimine–cobalt catalyst for *N*-formylation of

| | |
|---|------------|
| amines using CO₂..... | 202 |
| 5.1. Introduction..... | 203 |
| 5.2. Results and discussions..... | 205 |
| 5.2.1. Synthesis and characterization of the pyrim-UiO-Co(THF) MOF..... | 205 |
| 5.2.2. Pyrim-UiO-Co(THF) catalyzed <i>N</i> -formylation of primary amines and anilines using CO ₂ and PhSiH ₃ | 209 |
| 5.2.3. Pyrim-UiO-Co(THF) catalyzed <i>N</i> -formylation of secondary amines..... | 214 |
| 5.2.4. Identification of the active sites and catalyst resting state..... | 216 |
| 5.2.5. Mechanistic investigation of Pyrim-UiO-Co(THF) catalyzed <i>N</i> -formylation of amines using CO ₂ and PhSiH ₃ | 217 |
| 5.3. Experimental section..... | 221 |
| 5.3.1. General experiment..... | 221 |
| 5.3.2. Synthesis and characterization of pyridylimine-functionalized UiO-68 MOF..... | 221 |
| 5.3.2.1. Synthesis of UiO-68-NH ₂ MOF..... | 221 |
| 5.3.2.2. Post synthetic modification of synthesized UiO-68-NH ₂ MOF..... | 221 |
| 5.3.2.3 Analysis of digested pyrim-UiO MOF by ¹ H NMR..... | 222 |
| 5.3.3. Post synthetic metalation of pyrim-UiO-MOF..... | 223 |
| 5.3.3.1. Synthesis of pryim-UiO-CoCl ₂ | 223 |
| 5.3.4. Synthesis of pyrim-UiO-Co(THF)..... | 224 |
| 5.3.5. Catalytic reactions with pyrim-UiO-Co(THF)..... | 225 |

| | |
|---|-----|
| 5.3.5.1. General procedure for pyrim-UiO-Co(THF) catalyzed <i>N</i> -formylation of amines using phenylsilane..... | 225 |
| 5.3.5.2. A Typical procedure for pyrim-UiO-Co(THF) catalyzed <i>N</i> -formylation of benzylamine..... | 225 |
| 5.3.5.3. Test for “heterogeneity” of pyrim-UiO-Co(THF) in <i>N</i> -formylation of amines..... | 226 |
| 5.3.5.4. Hg test..... | 227 |
| 5.3.5.5. Recycling of pyrim-UiO-Co(THF) for the <i>N</i> -formylation of benzylamines..... | 228 |
| 5.3.5.6. Investigation of the effect of pore sizes on the rate of catalysis. | 229 |
| 5.3.6. Determination of the rate law for pyrim-UiO-Co(THF) catalyzed <i>N</i> -formylation of benzylamine..... | 231 |
| 5.3.7. Analysis of products by GC-MS..... | 231 |
| 5.3.8. X-ray absorption spectroscopic analysis..... | 234 |
| 5.3.8.1. XANES analysis..... | 234 |
| 5.3.8.2. EXAFS fitting using DFT optimized structures..... | 234 |
| 5.3.9. DFT calculations..... | 241 |
| 5.3.9.1. Cartesian coordinates of optimized structures..... | 244 |
| 5.3.10. XPS analysis..... | 248 |
| 5.4. Conclusion..... | 250 |
| 5.5. References..... | 251 |

**Chapter 6: Selective Reduction of Nitro Compounds by Organosilanes Catalyzed
by a Zirconium Metal–Organic Framework Supported**

| | |
|---|------------|
| Salicylaldimine-Cobalt(II) Complex..... | 258 |
| 6.1. Introduction..... | 259 |
| 6.2. Results and discussions..... | 260 |
| 6.2.1. Synthesis and characterization of the salim-UiO-CoCl MOF..... | 260 |
| 6.2.2. Salim-UiO-CoCl catalyzed reduction of nitroarenes and its derivatives..... | 263 |
| 6.2.3. Mechanistic investigation of the catalytic reduction..... | 268 |
| 6.3. Experimental section..... | 272 |
| 6.3.1. General experiment..... | 272 |
| 6.3.2. Synthesis and characterization of salicylaldehyde-functionalized | |

| | |
|--|------------|
| UiO-68 MOFs..... | 272 |
| 6.3.2.1.Synthesis of UiO-68-NH ₂ MOF..... | 272 |
| 6.3.2.2. Post synthetic modification of as-synthesized UiO-68-NH ₂ MOF..... | 273 |
| 6.3.2.3. Analysis of digested salim-UiO MOF by ¹ H NMR..... | 273 |
| 6.3.3. Post synthetic metalation of salim-UiO-MOF..... | 274 |
| 6.3.3.1. Synthesis of salim-UiO-CoCl..... | 274 |
| 6.3.4. Catalytic reactions with salim-UiO-CoCl..... | 275 |
| 6.3.4.1. General procedure for salim-UiO-CoCl catalyzed reduction of nitro functional group compounds using phenylsilane..... | 275 |
| 6.3.4.2. A typical procedure for salim-UiO-CoCl catalyzed reduction of nitrobenzne..... | 275 |
| 6.3.4.3. Test for “heterogeneity” of salim-UiO-CoCl in reduction of 1-nitronaphthalene..... | 277 |
| 6.3.4.4. Hg test..... | 278 |
| 6.3.4.5. Recycling of salim-UiO-CoCl for the reduction of nitrobenzene to aniline..... | 278 |
| 6.3.5. Characterization of products..... | 281 |
| 6.3.5.1. GC-MS analysis..... | 281 |
| 6.3.5.2. NMR analysis..... | 282 |
| 6.3.6. X-ray absorption spectroscopy..... | 288 |
| 6.3.6.1. XANES analysis..... | 288 |
| 6.3.6.2. EXAFS fitting using DFT optimized structures..... | 288 |
| 6.3.7. DFT calculations..... | 290 |
| 6.3.7.1. Cartesian coordinates of optimized structures..... | 293 |
| 6.3.8. XPS analysis..... | 297 |
| 6.4. Conclusion..... | 300 |
| 6.5. References..... | 301 |
| Reflecting on overall PhD work: Insights, Lessons Learned, and Future Impact..... | 306 |
| List of Publications..... | 309 |
| Authors profile..... | 311 |

List of Figures

| Figure captions..... | Page no. |
|---|-----------------|
| 1.1. Schematic representation of Single-site heterogeneous catalyst..... | 3 |
| 1.2. Schematic representation of MOF and its constituents..... | 4 |
| 1.3. Examples of various types of SBUs involve in synthesis of MOF..... | 8 |
| 1.4. Examples of various types of organic linkers involve in synthesis of MOF..... | 9 |
| 1.5. Schematic representation of the methods used for activation of MOF..... | 13 |
| 1.6. Metal-functionalized 2-pymo and bzim based organic linkers..... | 16 |
| 1.7. Different methods for post-synthetic functionalization of MOF..... | 17 |
| 1.8. Proline functionality over Cr SBUs of MIL-101 via PSM..... | 18 |
| 1.9. Distinct applications associated with MOFs..... | 21 |
| 1.10. Various sites of catalysis functionalities within the MOF..... | 26 |
| 1.11. Facile coordination of substrate via expansion of co-ordination sites or by displacement of ligand on metal center..... | 27 |
| 1.12. Removal of co-ordinating solvent to create vacant site therefore a substrate can bind or interact with the metal center..... | 28 |
| 1.13. Methods for introducing active catalytic sites on MOF linkers..... | 33 |
| 1.14. Structures of various ligands discussed in section 1.7.4.2..... | 34 |
| 1.15. Isorecticular MOFs based on the size of organic linkers..... | 40 |
| 1.16. Isorecticular MOFs based on the difference in functionalities over organic linkers..... | 40 |
| 1.17. Different ligands employed in isorecticular Zr-based MOFs..... | 41 |
| 3.1. Synthesis of chiral D-POST-1..... | 60 |
| 3.2. Post-synthetic grafting of oligopeptides within the pores of MOF..... | 61 |
| 3.3. Synthesis of L-valine functionalized chiral MOF and its metalation with FeCl ₂ | 62 |
| 3.4. Plots showing the correlation of % conversion of 1a and the corresponding % ee of product 2a with time (min) using L-valim-UiO-68-Fe (0.5 mol% Fe)..... | 67 |
| 3.5. a) Proposed catalytic cycle and the stereochemical models of hydrosilylation at 298 K..... | 69 |
| b) DFT-calculated reaction energy profile diagram of L-valim-UiO-Fe catalyzed asymmetric hydrosilylation of acetophenone at 298 K..... | 69 |

| | |
|--|----|
| 3.6. ¹ H NMR spectrum (400 MHz, DMSO- <i>d</i> ₆) of L-val-UiO MOF digested in K ₃ PO ₄ /D ₂ O followed by neutralization..... | 73 |
| 3.7. ¹ H NMR spectrum (400 MHz, DMSO- <i>d</i> ₆) of L-valim-UiO-MOF digested in K ₃ PO ₄ /D ₂ O/DMSO- <i>d</i> ₆ | 74 |
| 3.8. IR spectra of L-val-UiO-MOF (black) and L-valim-UiO-MOF (red)..... | 75 |
| 3.9. TGA curve of freshly prepared L-valim-UiO MOF..... | 75 |
| 3.10. Images of L-valim-UiO MOF (left) and L-valim-UiO-FeCl MOF (right)..... | 76 |
| 3.11. (a) TGA curve of freshly prepared L-valim-UiO-FeCl MOF..... | 77 |
| (b) TGA curve of freshly prepared L-valim-UiO-FeCl MOF (black) and L-valim-UiO MOF (red) from 200-800 °C..... | 77 |
| 3.12. PXRD patterns of UiO-68-MOFs..... | 77 |
| 3.13. Nitrogen sorption isotherms (77 K) of L-valim-UiO, L-valim-UiO-FeCl, and L-valim-UiO-Fe after run 16 of hydrosilylation of acetophenone..... | 78 |
| 3.14. HK pore size distribution of L-valim-UiO and L-valim-UiO-FeCl..... | 78 |
| 3.15. TEM image of L-valim-UiO-FeCl..... | 78 |
| 3.16. Heterogeneity test of L-valim-UiO-Fe catalysed asymmetric reduction of Cyclopropylphenylketone..... | 80 |
| 3.17. Plot for % GC-yield and the corresponding % ee of silyl ether (2a) at various runs in the recycle of L-valim-UiO-Fe for hydrosilylation of acetophenone..... | 82 |
| 3.18. PXRD patterns of L-valim-UiO-Fe MOF after catalysis..... | 82 |
| 3.19. Synthesis of L-valim-FeCl..... | 83 |
| 3.20. Synthesis of pyrim-UiO-FeCl ₂ MOF..... | 85 |
| 3.21. Kinetic plots of initial rates (d[<i>product</i>]/dt) for hydrosilation of 1a versus initial concentrations of iron and 1a for the first 30 min..... | 87 |
| 3.22. Plot of initial rate (d[<i>product</i>]/dt) versus [(EtO) ₂ MeSiH] _{initial} for first 30 min (10 % conversion) in THF..... | 87 |
| 3.23. Optimized structure of L-valim-FeCl(THF)..... | 97 |
| 3.24. Atomic charge distribution of L-valim-FeCl(THF)..... | 98 |
| 3.25. Optimized structure of L-valim-Fe[Si(OEt) ₂ Me] (INT-1) and atomic charge distribution of L-valim-Fe[Si(OEt) ₂ Me] (INT-1) as calculated by NBO population analysis..... | 98 |
| 3.26. Optimized structure of INT-2(<i>S</i>) (L-valim-Fe[<i>S</i>]-C(Ph){OSi(OEt) ₂ Me}(Me))..... | 99 |

| | |
|--|-----|
| 3.27. Optimized structure of the TS-1(<i>S</i>) of <i>S</i> -pathway at room temperature..... | 100 |
| 3.28. Fe <i>K</i> -edge XANES spectra of FeCl ₂ , L-valim-UiO-FeCl, and (L-valim)Fe-[(<i>S</i>)C(Ph)(Me){OSiMe(OEt) ₂ }] after hydrosilylation of 1a..... | 104 |
| 3.29. EXAFS spectra and fits in R-space at the Fe <i>K</i> -edge of L-valim-UiO-FeCl(THF)... | 105 |
| 3.30. EXAFS fitting of L-valim-UiO-Fe recovered after hydrosilylation of 1a..... | 105 |
| 3.31. GC trace and integration data of racemic 1-phenylethanol..... | 108 |
| 3.32. GC trace and integration data of (<i>S</i>)-1-phenylethanol..... | 108 |
| 3.33. GC trace and integration data of racemic 4-(1-hydroxyethyl)phenol..... | 109 |
| 3.34. GC trace and integration data of (<i>S</i>)-4-(1-hydroxyethyl)phenol..... | 109 |
| 3.35. GC trace and integration data of racemic 4-(1-hydroxy-2-methylpropyl)phenol | 110 |
| 3.36. GC trace and integration data of (<i>S</i>)-4-(1-hydroxy-2-methylpropyl)phenol..... | 110 |
| 3.37. GC trace and integration data of racemic 1-(4-bromophenyl)ethanol..... | 111 |
| 3.38. GC trace and integration data of (<i>S</i>)-1-(4-bromophenyl)ethanol..... | 111 |
| 3.39. GC trace and integration data of racemic of cyclopropyl(phenyl)methanol..... | 112 |
| 3.40. GC trace and integration data of (<i>R</i>)-cyclopropyl(phenyl)methanol..... | 112 |
| 3.41. GC trace and integration data of racemic phenyl(<i>o</i> -tolyl)methanol..... | 113 |
| 3.42. GC trace and integration data of (<i>S</i>)-phenyl(<i>o</i> -tolyl)methanol..... | 113 |
| 3.43. GC trace and integration data of racemic 1-(pyridine-2-yl)ethanol..... | 114 |
| 3.44. GC trace and integration data of (<i>S</i>)-1-(pyridin-2-yl)ethanol..... | 114 |
| 3.45. GC trace and integration data of racemic (2-aminophenyl)(phenyl)methanol..... | 115 |
| 3.46. GC trace and integration data of (<i>R</i>)-(2-aminophenyl)(phenyl)methanol..... | 115 |
| 3.47. GC trace and integration data of racemic 1-(pyridin-4-yl)ethanol..... | 116 |
| 3.48. GC trace and integration data of (<i>R</i>)-1-(pyridin-4-yl)ethanol..... | 116 |
| 3.49. GC trace and integration data of racemic 1-(naphthalen-2-yl)ethanol..... | 117 |
| 3.50. GC trace and integration data of (<i>S</i>)-1-(naphthalen-2-yl)ethanol..... | 117 |
| 3.51. GC trace and integration data of racemic 1-(4-methoxyphenyl)ethanol..... | 118 |
| 3.52. GC trace and integration data of (<i>S</i>)-1-(4-methoxyphenyl)ethanol..... | 118 |
| 3.53. GC trace and integration data of racemic 1-(4-nitrophenyl)ethanol..... | 119 |
| 3.54. GC trace and integration data of (<i>S</i>)-1-(4-nitrophenyl)ethanol..... | 119 |
| 3.55. HPLC trace and integration data of racemic 3-(1-hydroxyethyl)phenol..... | 120 |
| 3.56. HPLC trace and integration data of (<i>S</i>)-3-(1-hydroxyethyl)phenol..... | 120 |
| 3.57. GC trace and integration data of racemic 1-(thiophen-2-yl)ethanol..... | 121 |
| 3.58. GC trace and integration data of (<i>S</i>)-1-(thiophen-2-yl)ethanol..... | 121 |

| | |
|--|-----|
| 3.59. GC trace and integration data of racemic 6-methylhept-5-en-2-ol prepared..... | 122 |
| 3.60. GC trace and integration data of (<i>R</i>)-6-methylhept-5-en-2-ol..... | 122 |
| 3.61. ¹ H NMR (400 MHz, DMSO- <i>d</i> ₆) spectra of 2'-amino-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid..... | 123 |
| 3.62. ¹³ C NMR (100 MHz, DMSO- <i>d</i> ₆) spectra of 2'-amino-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid..... | 123 |
| 3.63. ¹ H NMR spectrum (400 MHz, DMSO- <i>d</i> ₆) of digested L-valim-UiO-MOF after hydrosilylation of acetophenone..... | 124 |
| 3.64. ¹ H NMR (400 MHz, DMSO- <i>d</i> ₆) spectrum of (<i>S</i>)-tert-butyl (3-methyl-1-oxo-1-(phenylamino)butan-2-yl)carbamate (boc-protected L-val)..... | 124 |
| 3.65. ¹ H NMR (400 MHz, DMSO- <i>d</i> ₆) spectra of (<i>S</i>)-2-amino-3-methyl-N-phenylbutanamide (L-val)..... | 125 |
| 3.66. ¹ H NMR (400 MHz, DMSO- <i>d</i> ₆) spectra of (<i>S,E</i>)-3-methyl-N-phenyl-2-((pyridin-2-ylmethylene)amino)butanamide (L-valim)..... | 125 |
| 3.67. m/z of (<i>S,E</i>)-3-methyl-N-phenyl-2-((pyridin-2-ylmethylene)amino)butanamide..... | 126 |
| 3.68. GC-MS spectra of (<i>S,E</i>)-3-methyl-N-phenyl-2-((pyridin-2-ylmethylene)amino)butanamide (L-valim)..... | 126 |
| 3.69. L-valim-UiO-Fe MOF carrying out asymmetric reductions with excellent ee of up to 99 %..... | 127 |
| 4.1. Immobilization of chiral auxiliaries into the heterogeneous supports..... | 137 |
| 4.2. Solid supported chiral [Co(Salen)] complex..... | 137 |
| 4.3. Synthesis of aldehyde-functionalized UiO-68-MOF, its postsynthetic functionalization with L-valinol and, the metalation of chiral valinol-functionalized UiO-68 MOF (vol-UiO-68) with iron..... | 139 |
| 4.4. PXRD patterns of simulated UiO-68 MOF, freshly prepared pristine UiO-68-CHO, vol-UiO-68, and vol-UiO-68-FeCl..... | 140 |
| 4.5. BET nitrogen sorption isotherms (77 K) of vol-UiO-68, and vol-UiO-68-FeCl..... | 140 |
| 4.6. PXRD patterns of vol-UiO-68-Fe after hydrosilylation & hydroboration of 4-methoxyacetophenone..... | 144 |
| 4.7. Mechanistic proposal for vol-UiO-68-Fe catalyzed asymmetric hydrosilylation of ketones..... | 146 |
| 4.8. DFT-calculated Gibbs free enthalpy reaction profile diagram of vol-UiO-Fe catalyzed hydrosilylation of 4-methoxyacetophenone..... | 147 |
| 4.9. IR spectra UiO-68-CHO, vol-UiO-68, vol-UiO-68-FeCl, and vol-UiO-68-FeH..... | 154 |

| | |
|---|-----|
| 4.10. TGA curve of freshly prepared vol-UiO-68 and vol-UiO-68-FeCl..... | 155 |
| 4.11. a) TEM image of vol-UiO-68-FeCl, b) TEM-EDX analysis of vol-UiO-68-FeCl..... | 156 |
| 4.12. Heterogeneity test of vol-UiO-68-Fe for the hydrosilylation of isobutyrophenone... | 158 |
| 4.13. % GC-yield and the corresponding % ee of silyl ether (2a) at several runs in the recycle of vol-UiO-68-Fe for hydrosilylation of 4-methoxyacetophenone..... | 160 |
| 4.14. % GC-yield and the corresponding % ee of borate ester (4a) at several runs in the recycle of vol-UiO-68-Fe for hydroboration of 4-methoxyacetophenone..... | 161 |
| 4.15. Plots of initial rates $-(d[\textit{substrate}]/dt)$ for hydrosilylation of 4-methoxyacetophenone vs iron and substrate concentration..... | 163 |
| 4.16. Plot for initial rate $(d[\textit{product}]/dt)$ versus $[(\text{EtO})_2\text{MeSiH}]$ | 164 |
| 4.17. (a) DFT-optimized structure of vol-UiO-68-FeCl(THF) ₃ , and (b) Atomic charge distribution of vol-UiO-68-FeCl(THF) ₃ | 169 |
| 4.18. DFT-optimized structures of intermediates and transition states of the proposed catalytic cycle..... | 171 |
| 4.19. $\mu(\text{E})$ XAS spectra of metallic Fe(0), vol-UiO-68-FeCl, vol-UiO-68-FeH, vol-UiO-68-Fe after hydrosilylation of 4-methoxyacetophenone and FeCl ₂ | 176 |
| 4.20. DFT optimized model and Fe <i>K</i> -edge EXAFS spectra of vol-UiO-68-FeCl and its fits in R-space..... | 177 |
| 4.21. DFT optimized model and EXAFS spectra and fits in R-space at the Fe <i>K</i> -edge of vol-UiO-68-Fe after hydrosilylation of 4-methoxyacetophenone..... | 179 |
| 4.22. XPS data of vol-UiO-68-FeCl..... | 180 |
| 4.23. Fe 2p XPS spectrum of vol-UiO-68-FeCl..... | 180 |
| 4.24. Zr 3d XPS spectrum of vol-UiO-68-FeCl..... | 181 |
| 4.25. XPS data of vol-UiO-68-FeH..... | 181 |
| 4.26. Fe 2p XPS spectrum of vol-UiO-68-FeH..... | 182 |
| 4.27. Zr 3d XPS spectrum of vol-UiO-68-FeH..... | 182 |
| 4.28. GC trace and integration data of racemic 4-(1-hydroxyethyl)phenol..... | 183 |
| 4.29. GC trace and integration data (<i>S</i>)-4-(1-hydroxyethyl)phenol..... | 183 |
| 4.30. GC trace and integration data of racemic 4-(1-hydroxy-2-methylpropyl)phenol..... | 184 |
| 4.31. GC trace and integration data of (<i>S</i>)-4-(1-hydroxy-2-methylpropyl)phenol..... | 184 |
| 4.32. GC trace and integration data of racemic 1-(4-nitrophenyl)ethanol..... | 185 |
| 4.33. GC trace and integration data of (<i>S</i>)-1-(4-nitrophenyl)ethanol..... | 185 |
| 4.34. GC trace and integration data of racemic 1-(thiophen-2-yl)ethanol..... | 186 |

| | |
|---|-----|
| 4.35. GC trace and integration data of (<i>S</i>)-1-(thiophen-2-yl)ethanol..... | 186 |
| 4.36. GC trace and integration data of racemic 1-(naphthalen-2-yl)ethanol..... | 187 |
| 4.37. GC trace and integration data of (<i>S</i>)-1-(naphthalen-2-yl)ethanol..... | 187 |
| 4.38. GC trace and integration data of racemic 6-methylhept-5-en-2-ol..... | 188 |
| 4.39. GC trace and integration data of (<i>R</i>)-6-methylhept-5-en-2-ol..... | 188 |
| 4.40. HPLC trace and integration data of racemic 3-(1-hydroxyethyl)phenol..... | 189 |
| 4.41. HPLC trace and integration data of (<i>S</i>)-3-(1-hydroxyethyl)phenol..... | 189 |
| 4.42. HPLC trace and integration data of racemic 3-(1-hydroxyethyl)phenol..... | 190 |
| 4.43. HPLC trace and integration data of (<i>S</i>)-3-(1-hydroxyethyl)phenol..... | 190 |
| 4.44. ¹ H NMR of (2,5-dibromophenyl)methylene diacetate..... | 191 |
| 4.45. ¹³ C NMR of (2,5-dibromophenyl)methylene diacetate..... | 191 |
| 4.46. ¹ H NMR of dimethyl 2'-formyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate..... | 192 |
| 4.47. ¹³ C NMR of dimethyl 2'-formyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylate..... | 192 |
| 4.48. ¹ H NMR of 2'-formyl-[1,1':4',1''-terphenyl]-4,4''-dicarboxylic acid..... | 193 |
| 4.49. ¹ H NMR spectrum of UiO-68-CHO MOF digested in K ₃ PO ₄ /D ₂ O/DMSO- <i>d</i> ₆ | 193 |
| 4.50. ¹ H NMR spectrum of vol-UiO-68 MOF digested in K ₃ PO ₄ /D ₂ O/DMSO- <i>d</i> ₆ | 194 |
| 4.51. ¹ H NMR of synthesized (<i>S,E</i>)-2-(benzylideneamino)-3-methylbutan-1-ol..... | 194 |
| 4.52. Vol-UiO-68-Fe catalyzed asymmetric reduction reactions..... | 195 |
| 5.1. Synthesis of UiO-MOF supported single-site pyridylimine-cobalt catalyst for <i>N</i> -formylation of amines using CO ₂ | 206 |
| 5.2. PXRD patterns of the simulated UiO-68 MOF, pristine UiO-68-NH ₂ , pyrim-UiO-MOF, and pyrim-MOF-CoCl ₂ | 206 |
| 5.3. SEM image of a pyrim-MOF-Co particle..... | 208 |
| 5.4. SEM-EDX mapping of Co and Zr in the respective pyrim-MOF-Co particle..... | 208 |
| 5.5. Co <i>K</i> -edge XANES spectra of Co-foil, CoCl ₂ , pyrim-UiO-CoCl ₂ , pyrim-UiO-Co(THF) and pyrim-UiO-Co after catalysis..... | 209 |
| 5.6. PXRD patterns of simulated UiO-68 MOF and as-synthesized UiO-68-NH ₂ MOF, pyrim-UiO-68 MOF, pyrim-UiO-CoCl ₂ , pyrim-MOF-Co(THF), and pyrim-MOF-Co after hydroformylation of benzyl amine using PhSiH ₃ | 217 |
| 5.7. Proposed catalytic cycle of pyrim-UiO-Co(THF) catalyzed <i>N</i> -formylation of amines using CO ₂ and phenylsilane..... | 218 |
| 5.8. Kinetic plots of initial rates (d[benzyl amine]/dt) for <i>N</i> -formylation of | |

| | |
|---|-----|
| benzylamine versus initial concentrations of cobalt and benzylamine..... | 219 |
| 5.9. Kinetic plots of initial rates ($d[\textit{benzyl amine}]/dt$) for <i>N</i> -formylation of benzylamine versus initial concentrations of PhSiH ₃ and initial P _{CO₂} | 219 |
| 5.10. The DFT calculated free energy diagram at 353 K for pyrim-UiO-Co(THF) catalyzed <i>N</i> -formylation of benzyl amines using CO ₂ and silane..... | 220 |
| 5.11. ¹ H NMR spectrum (500 MHz, DMSO-d ₆) of pyrim-UiO MOF digested in K ₃ PO ₄ /D ₂ O/DMSO-d ₆ | 222 |
| 5.12. TGA curve of freshly prepared (a) UiO-68-NH ₂ , and (b) pyrim-UiO-CoCl ₂ . (c) TGA curve from 200-650 °C..... | 224 |
| 5.13. Heterogeneity test of pyrim-UiO-Co(THF) for the <i>N</i> -formylation of amines..... | 226 |
| 5.14. Hg test in the <i>N</i> -formylation with pyrim-UiO-Co(THF)..... | 227 |
| 5.15. Recycle and reuse of pyrim-UiO-Co(THF) in <i>N</i> -formylation of benzylamine..... | 228 |
| 5.16. Plot for % GC-yield of <i>N</i> -benzylformamide at various runs in the recycle experiments of pyrim-MOF-Co catalyst in formylation of benzyl amine..... | 229 |
| 5.17. <i>N</i> -formylation of 4-methoxybenzylamine catalyzed by pyrim-UiO-Co(THF) with that of pyrim-UiO-66-Co under identical reaction conditions..... | 230 |
| 5.18. EXAFS spectrum and fits of pyrim-MOF-CoCl ₂ in R-space at the Co <i>K</i> -edge..... | 234 |
| 5.19. DFT-optimized structure of (pyrim)CoCl ₂ (THF) ₂ | 235 |
| 5.20. EXAFS spectrum and fits of pyrim-MOF-Co(THF) in R-space at the Co <i>K</i> -edge..... | 237 |
| 5.21. DFT-optimized structure of pyrim-UiO-Co(THF)..... | 237 |
| 5.22. EXAFS spectrum and fits of pyrim-MOF-Co after <i>N</i> -formylation of benzylamine in R-space at the Co <i>K</i> -edge..... | 239 |
| 5.23. DFT-optimized structure of pyrim-UiO-Co(THF)..... | 239 |
| 5.24. EXAFS spectra in R space are 0-6 Å of pyrim-UiO-Co(THF), pyrim-UiO-Co after catalysis and Co foil..... | 241 |
| 5.25. DFT-optimized structure of (pyrim)CoCl ₂ (THF) ₂ | 242 |
| 5.26. DFT-optimized structure of pyrim-UiO-Co(THF) (INT-1)..... | 242 |
| 5.27. DFT-optimized structures of intermediates and transition states of the catalytic cycle in pyrim-UiO-Co catalyzed <i>N</i> -formylation reaction..... | 243 |
| 5.28. XPS data of pyrim-UiO-CoCl ₂ | 248 |
| 5.29. Co 2p XPS spectrum of pyrim-UiO-CoCl ₂ | 248 |
| 5.30. Zr 3d XPS spectrum of pyrim-UiO-CoCl ₂ after catalysis..... | 249 |
| 5.31. Co 2p XPS spectrum of pyrim-UiO-Co(THF)..... | 249 |

| | |
|--|-----|
| 5.32. Pyrim-UiO-Co(THF) MOF for <i>N</i> -formylation of amines..... | 250 |
| 6.1. Pyrim-UiO-Co(THF) MOF for <i>N</i> -formylation of amines..... | 260 |
| 6.2. PXRD patterns of the simulated UiO-68 MOF, pristine UiO-68-NH ₂ , salim-UiO-MOF, and salim-UiO-CoCl..... | 261 |
| 6.3. TGA curve of freshly prepared (a) UiO-68-NH ₂ and (b) salim-UiO-CoCl (c) TGA curve of freshly prepared UiO-68-NH ₂ and salim-UiO-CoCl from 200-700 °C..... | 262 |
| 6.4. Co <i>K</i> -edge XANES spectra of Co-foil, CoCl ₂ , and salim-UiO-CoCl..... | 263 |
| 6.5. PXRD patterns of the simulated UiO-68 MOF, pristine UiO-68-NH ₂ , and salim-UiO-Co recovered after catalysis..... | 269 |
| 6.6. SEM image of salim-UiO-Co particles recovered after catalysis and the SEM-EDX mapping of Co and Zr of the respective particles..... | 269 |
| 6.7. Co <i>K</i> -edge XANES spectra of Co-foil, CoCl ₂ , salim-UiO-CoCl, and salim-UiO-Co after catalysis..... | 270 |
| 6.8. Proposed catalytic cycle of salim-UiO-Co catalyzed reduction of nitroarenes..... | 270 |
| 6.9. DFT-calculated Gibbs free enthalpy reaction profile diagram..... | 271 |
| 6.10. ¹ H NMR spectrum of salim-UiO MOF digested in K ₃ PO ₄ /D ₂ O/DMSO- <i>d</i> ₆ | 274 |
| 6.11. Heterogeneity test of salim-UiO-CoCl for the reduction of 1-nitronaphthalene..... | 277 |
| 6.12. Hg test in the reduction of 1-fluoro-4-nitrobenzene with salim-UiO-CoCl..... | 278 |
| 6.13. Recycle and reuse of salim-UiO-CoCl in reduction of nitrobenzene..... | 279 |
| 6.14. Recycle plot of salim-UiO-CoCl in reduction of nitrobenzene..... | 279 |
| 6.15. (a) EXAFS spectra and fits of salim-UiO-CoCl in the R space at the Co <i>K</i> -edge (b) DFT optimized structure of salim-CoCl moiety in salim-UiO-CoCl..... | 289 |
| 6.16. EXAFS spectrum of salim-UiO-Co fitted with different % metallic Co..... | 289 |
| 6.17. DFT optimized structure of salim-UiO-CoCl(THF)..... | 291 |
| 6.18. DFT-optimized structures of intermediates and transition states..... | 293 |
| 6.19. XPS data of salim-UiO-CoCl before catalysis..... | 297 |
| 6.20. Co 2p XPS spectra of salim-UiO-CoCl MOF before catalysis..... | 297 |
| 6.21. Zr 3d XPS spectra of salim-UiO-CoCl MOF before catalysis..... | 298 |
| 6.22. XPS data of salim-UiO-Co after catalysis..... | 298 |
| 6.23. Co 2p XPS spectrum of salim-UiO-Co after catalysis..... | 299 |
| 6.24. Zr 3d XPS spectrum of salim-UiO-Co after catalysis..... | 299 |
| 6.25. Salim-UiO-Co catalyst for chemoselective reduction of nitro compounds..... | 300 |

List of Tables

| Table no. | Title of the table | Page no. |
|------------------|--|-----------------|
| Table 3.1. | L-valim-UiO-Fe-catalyzed asymmetric hydrosilylation of ketones..... | 65 |
| Table 3.2. | Optimization of L-valim-UiO-Fe MOF catalyzed hydrosilylation of ketones..... | 80 |
| Table 3.3. | % Yield, % ee, and % leaching of metals during the recycling..... | 81 |
| Table 3.4. | The GC retention time of products..... | 95 |
| Table 3.5. | NBO charge population analysis of L-valim-FeCl(THF)..... | 99 |
| Table 3.6. | NBO charge population analysis of L-valim-Fe[Si(OEt) ₂ Me]..... | 99 |
| Table 3.7. | Summary of EXAFS fitting parameters L-valim-UiO-FeCl(THF)..... | 106 |
| Table 3.8. | Summary of EXAFS fitting parameters INT-2(S)..... | 107 |
| Table 4.1. | Asymmetric hydrosilylation of ketones catalyzed by Vol-UiO-68-Fe MOFs..... | 142 |
| Table 4.2. | Asymmetric hydroboration of ketones catalyzed by vol-UiO-68-Fe MOFs..... | 148 |
| Table 4.3. | % Yield, % ee, and leaching of metals during the recycling..... | 159 |
| Table 4.4. | GC-MS and GC-FID analysis of products..... | 168 |
| Table 4.5. | NBO charge population analysis of vol-UiO-68-FeCl(THF) ₃ | 170 |
| Table 4.6. | Summary of EXAFS fitting parameters vol-UiO-68-FeCl(THF) ₃ | 178 |
| Table 4.7. | Summary of EXAFS fitting parameters vol-UiO-68- -Fe(S-OCH(Me)(Ar ^{OMe})) after hydrosilylation..... | 179 |
| Table 5.1. | Formylating agents commonly used in <i>N</i> -formylation of amines..... | 203 |
| Table 5.2. | Optimization reaction conditions for the <i>N</i> -formylation of benzylamine..... | 210 |
| Table 5.3. | Pyrim-UiO-Co(THF)-catalyzed <i>N</i> -formylation of primary benzylamines and anilines using CO ₂ and PhSiH ₃ | 212 |
| Table 5.4. | % GC-Yield of <i>N</i> -benzylformamide, the leaching of Co at various runs of the recycling of pyrim-UiO-Co(THF)..... | 229 |
| Table 5.5. | The GC-MS retention times of the arene substrates and the products..... | 232 |
| Table 5.6. | Atoms coordinates used for EXAFS fitting of pyrim-UiO-CoCl ₂ (THF) ₂ | 235 |
| Table 5.7. | Summary of EXAFS fitting parameters of pyrim-UiO-CoCl ₂ (THF) ₂ | 236 |
| Table 5.8. | Atoms coordinates used for EXAFS fitting of pyrim-UiO-Co(THF)..... | 237 |
| Table 5.9. | Summary of EXAFS fitting parameters of pyrim-UiO-Co(THF)..... | 238 |
| Table 5.10. | Summary of EXAFS fitting of pyrim-UiO-Co recovered after hydroformylation of benzyl amine with PhSiH ₃ | 240 |
| Table 6.1. | Optimization for salim-UiO-Co catalyzed reduction of nitrobenzene..... | 264 |
| Table 6.2. | Salim-UiO catalyzed reduction of nitroarenes derivatives..... | 266 |

| | |
|--|-----|
| Table 6.3. Optimization reaction conditions for the reduction of nitrobenzene..... | 276 |
| Table 6.4. % GC-Yield of aniline, the leaching of Co at various runs..... | 280 |
| Table 6.5. The GC-MS retention times of the arene substrates and the products..... | 281 |
| Table 6.6. Summary of EXAFS fitting parameters of salim-UiO-CoCl(THF)..... | 290 |

List of schemes

| Scheme no. | Scheme caption | Page no. |
|------------|--|----------|
| 1.1. | MOF-5 catalyzed <i>p</i> -alkylation of aromatic compounds..... | 6 |
| 1.2. | Thermal activation of Cu metal sites in HKUST-1 MOF..... | 15 |
| 1.3. | Synthesis of gold (Au) functionalized IRMOF-3 via PSM on organic linkers..... | 18 |
| 1.4. | Metal-ion exchange in MOF SBUs via post-synthetic ion exchange..... | 19 |
| 1.5. | MIL-101-SO ₃ H catalysed Nozaki-Hiyama allenylation reaction..... | 28 |
| 1.6. | UiO-66-(COOH) ₂ catalysed Levulinic acid esterification in presence of ethanol..... | 29 |
| 1.7. | Conversion of Glucose to HMF by phosphorylated NU-1000 MOF..... | 29 |
| 1.8. | In-MOF catalysed reduction of nitro groups present in organic compounds..... | 31 |
| 1.9. | Al ₂ (BDC) ₃ MOF catalysed hydrogenation of olefins..... | 31 |
| 1.10. | Pd-MOF catalysed Suzuki-coupling reaction..... | 31 |
| 1.11. | Asymmetric esterification reaction catalysed by chiral MOF (POST-1)..... | 35 |
| 1.12. | Synthesis of gold (Au) functionalized IRMOF-3 via PSM on organic linkers..... | 36 |
| 5.1. | Pyrim-UiO-Co(THF) catalyzed <i>N</i> -formylation of secondary amines..... | 215 |