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Faculty of Sciences

M.Sc. Thesis in Organic Chemistry

**SYNTHESIS OF METALLOSALENS AND THEIR
IMMOBILIZATIONS ONTO ACTIVATED CARBON
AS NEW NANOPARTICLE HETEROGENEOUS
CATALYSTS IN ORGANIC REACTIONS**

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IN THE NAME OF GOD

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IMMOBILIZATIONS ONTO ACTIVATED CARBON AS NEW
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ORGANIC REACTIONS**

BY:

Mahdi Aberi

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Dedicated to:

My Mother and My Father

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ABSTRACT

SYNTHESIS OF METALLOSALENS AND THEIR IMMOBILIZATIONS ONTO ACTIVATED CARBON AS NEW NANOPARTICLE HETEROGENEOUS CATALYSTS IN ORGANIC REACTIONS

By:

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In this thesis, some Schiff base compounds and new bifunctional salen and metallosalen complexes have been synthesized. Among them cobalt salen complex **31** was utilized in a convenient and efficient procedure for the synthesis of 2-arylbenzimidazole derivatives at room temperature as catalyst.

Then, in continuation of study, we developed the immobilization of the metallosalen onto activated carbon to afford nanoparticle metallosalen as a new and reusable heterogeneous catalyst in organic reactions. Various 2-arylbenzimidazoles were synthesized from phenylenediamines and aromatic aldehydes via a one-step process in the presence of a catalytic amount of cobalt salen complex supported on activated carbon (CoxO-Co(salen) **35**) at room temperature. The reactions were performed in ethanol and the catalyst could be reused for several cycles without a decrease in activity. The heterogeneous catalyst was characterized by powdered X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), inductively coupled plasma (ICP) and thermogravimetric (TG) method for analysis of nitrogen adsorption and FT-IR spectroscopy. Leaching experiments showed that the catalyst is most strongly anchored to the activated support after 10 times of reuse.

Another objective of this study is preparation of cobalt-on-carbon as a reusable heterogeneous catalyst for a convenient one-pot synthesis of 2-arylbenzimidazole derivatives. This catalyst exhibit a higher catalytic activity than Co(OAc)₂ for the synthesis of 2-arylbenzimidazole derivatives. The catalyst was easily recovered by a simple extraction and could be reused for several cycles without a decrease in the activity. The heterogeneous catalyst was characterized by XRD, SEM, AFM, ICP, TG for analysis the nitrogen adsorption and FT-IR spectroscopy.

We have also reported a regioselective aminomethylation of 2,4-dihydroxybenzoyl compounds at the C(3) positions on the silica gel in the absence of solvents. Treatment of paraformaldehyde and secondary amines with 2,4-dihydroxybenzoyl compounds under solvent free conditions gave the corresponding products in good to excellent yields in a short reaction time.

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ABBREVIATION

The following abbreviations are used in this thesis:

AFM	Atomic force microscopy
ICP	Inductively coupled plasma
SEM	Scanning electron microscopy
TGA	Thermo gravimetric analysis
XRD	X-ray diffraction
ee	enantiomeric excess

CHAPTER ONE

INTRODUCTION AND LITERATURE
REVIEW

CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEW

1.1. Introduction

The word “salen” is an acronym widely used to denote a family of bisimine compounds having a structure derived from the *N,N'*-bis(salicylidine) ethylenediamine.

The condensation of an amine with an aldehyde, forming what is called a Schiff base, is one of the oldest reactions in chemistry.¹ Schiff bases are among the most general N ligands, because the basicity of the sp^2 -hybridized N lone pair, although lower than that of amines (sp^3 hybridization), is well suited to form complexes with metal ions.² The salicylidene imine group is prone to undergo an acid-catalyzed hydrolysis, reverting to the corresponding salicylaldehyde and diamine in the presence of water. However, the stability of the Schiff base group increases considerably upon coordination with a metal ion and formation of the salen-metal complex. For this reason, in contrast to the salen ligand, the salen-metal complex can be used in wet solvents or even in aqueous media without undergoing hydrolysis. When a diamine was first combined with 2 equiv of salicylaldehyde, the salen ligands came into being (Scheme 1).³

The first salen-metal complex was probably reported by Pfeiffer et al. in 1933.⁴ The ligands feature two covalent and two coordinate covalent sites situated in a planar array. This makes the ligands ideal for the equatorial coordination of transition metals, leaving the two axial sites open for