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Metal Complexes Immobilized on Magnetic Nanoparticles

Seyed Mohsen Sadeghzadeh and Mehdi Mogharabi

Additional information is available at the end of the chapter

Abstract

The reusability of valuable catalysts in organic reaction without change in properties is known as an important feature in the evolution of green processes. The imobilization of metal catalysts on magnetic nanoparticles makes them recoverable and can be used as building blocks for the fabrication of various functional systems, which are applied in several fields such as catalysis, environmental remediation magnetic resonance imaging, data storage, and biotechnology. Applying magnetic nanoparticles in organic reaction as a scaffold for the immobilization of metal complexes is reviewed as well as the improvement of the methods of production and applying catalysts with magnetic properties in organic reaction.

Keywords: Recyclable catalyst, superparamagnetic nanoparticle, nanocatalyst, recyclable support matrix, magnetic separation

1. Introduction

The concept of "green chemistry" has emerged as one of the main principles of environmentally benign organic synthesis approaches. Using nanoparticles (NPs) in organic synthesis has become a subject of intense investigation. In particular, magnetic nanoparticles (MNPs) offer several advantages in clean and sustainable chemistry such as nontoxic effects, readily accessible, and retrievable. In addition, the activity and selectivity of magnetic nanocatalysts can be manipulated surface modification.

2. Green and sustainable catalysis

Green and sustainable chemistry is a philosophy of chemical research and engineering that encourages the design of products and processes, minimizing the use and generation of hazardous materials. Green catalysis as a subchapter of green chemistry but probably the most important one is associated with the synthetic protocols and reaction conditions, which plays a pivotal role in recent years toward the goal of switching to increasingly efficient and benign processes avoiding the use of volatile organic solvents, toxic reagents, hazardous and/or harsh reaction conditions, as well as challenging and time-consuming wasteful separations. Among the various principles of green chemistry, the use of alternative energy sources, benign solvents, and efficient reusable catalytic materials are contributed to the development of greener synthetic methods for a wide range of applications related to medicine, the environment, and nanoscience. In this sense, the search for environmentally benign, sustainable, and efficiently reusable alternative catalytic systems has become critical [1].

3. Homogeneous and heterogeneous catalysis

Catalysts are broadly divided into two types: homogeneous and heterogeneous. In a homogeneous catalysis, the active sites and the reactants are in the same phase, which allows for easier interaction between the components leading to better action. Homogeneous ones have other advantages such as high selectivities, high turnover numbers, and effortless optimization of activity. It is also possible to control the chemo-, regio-, and enantioselectivity of product by adapting the active molecules.

These catalysts are widely used in industrial processes, but the separation of the final product is one of the most important drawbacks of homogeneous types. After separation the homogeneous catalyst from the reaction mixture, trace amounts of are likely remains in the final product. It is essential to remove the catalyst completely and avoiding metal contamination in final products especially in the food and pharmaceutical industry. One efficient way to overcome this is the immobilization on the heterogeneous supports. Heterogenization is commonly achieved by entrapment or grafting of the active molecules on surfaces or inside the pores of a solid support such as silica, alumina, or ceria. Grafting can be achieved by covalent binding or by simple adsorption of the active catalytic molecules, but covalent binding is preferred because of it is sufficiently robust to survive the harsh reaction conditions; this binding and adsorption process not only minimizes catalyst leaching but also allows the reusability of catalyst. However, the active sites in heterogeneous catalysts are not as accessible as in a homogeneous system, and thus the activity of the catalyst may be reduced. There are many attempts to make all active sites on solid supports available for reactions, but only sites on the external surface of a porous solid support are available for reaction, and thus the overall reactivity of the catalyst system decreases. Consequently, we need a system that not only shows high activity and selectivity but also possesses the ease of separation and recovery. These goals can be achieved by nanocatalysis. Nanocatalysts bridge the gap between homogeneous and heterogeneous catalysts, preserving the desirable attributes of both systems [2].

4. Nanocatalysis

Nanoparticles have emerged as sustainable alternatives to conventional materials. The nanosized particles increase the exposed surface area of the component of the catalyst and enhance the contact between reactants and catalyst dramatically and mimic the homogeneous catalysts. However, their insolubility in reaction solvents makes them easily separable from the reaction mixture, which in turn makes the product isolation stage effortless. In addition, the selectivity of nanocatalyst can be manipulated by tailoring chemical and physical properties such as size, shape, composition, and morphology. One challenge is the synthesis of specific size and shape of nanocatalysts to allow the easy movement of materials in the reacting phase and control over the morphology of nanostructures to tailor their physical and chemical properties. However, the rapid advancement of nanotechnology made possible the preparation of a variety of nanoparticles with controlled size, shape, morphology, and composition [3].

5. Magnetic nanocatalysts

Nanocatalysts possess some advantages over conventional systems; however, the isolation and recovery of these nanocatalysts from the reaction mixture is not so easy, and conventional filtration methods are not efficient because of the nanosize of the catalyst. To overcome such limitations, the use of magnetic nanosupport has emerged as one of the best alternatives; their insoluble and paramagnetic nature enables easy and efficient separation of the catalysts from the reaction mixture with an external magnet. In addition, the design of the materials that are specifically needed for a particular application is possible by the control of properties, including size, shape, morphology, and dispersity. The isolation and separation of magnetic nanoparticle-supported catalysts can be achieved using an external magnet, thus offering a promising option that can meet the requirements of high accessibility with improved reusability [4]. Catalyst recovery and reusability are the two most important features for many catalytic processes; most heterogeneous systems require a filtration or centrifugation step or a time-consuming workup of the final reaction mixture to recover them, while magnetically supported nanocatalysts can be recovered with an external magnet.

5.1. Synthesis of magnetic catalysts

There are several protocols reported in the literature for preparing a wide variety of catalytic magnetic materials, some of them are discussed in the following sections. It is important to note that the practicality and cost-effectiveness of these processes have a direct effect on the sustainability of the catalytic protocols based on these materials.

5.2. Carbonaceous magnetic materials

Magnetic carbon nanoparticles were obtained from the carbonization of iron-doped polypyrrole nanoparticles [5, 6]. Carbonization was performed at 800°C and yielded microporous carbonaceous nanomaterials with approximately 4–5 wt% nitrogen. Palladium nanoparticles were subsequently deposited onto the surface of the microporous carbon using a conventional

impregnation/deposition methodology and using Pd(NO$_3$)$_2$ as a metal precursor in aqueous media. The synthesized material possesses a remarkably high palladium content that is comprised of homogeneously and well-dispersed PdNP on the porous surface, with a reasonably narrow particle size distribution. Carbonaceous materials and a carbon black are prepared by thermal decomposition of methane using dc thermal plasma processing, provided poorly dispersed Pd NP on the material surface [6]. Zhu et al. [7] prepared magnetic porous carbon microspheres via carbonization of chitosan microspheres containing iron precursors (a negatively charged iron oxalate) that were absorbed due to the cationic and swelling properties of chitosan. In general, this biomass-derived material possessed large surface areas and good magnetic separation properties. Interestingly, Fe Mossbauer spectroscopic experiments indicated that the temperature of carbonization affected the type of Fe species observed in the sample [8]. Thus, samples calcinated at 700°C contained γ-Fe$_2$O$_3$, Fe$_3$C, and α-Fe, whereas samples carbonized at 900°C and 1000°C exhibited peaks that indicated Fe$_3$C and α-Fe. It was claimed to result from the reaction of maghemite with carbon and subsequent decomposition into metallic Fe. Because of these promising features and the potential adsorption properties of carbon, high temperature calcinated materials were tested for the adsorption of potential pollutants in aqueous solutions. A relatively similar magnetically ordered mesoporous carbon containing super paramagnetic FePt NP [7] was prepared via a simple nanocasting route, with polyfurfuryl alcohol formed after polymerization of furfural in the channels of a mesoporous silica employed as a hard template [8] and FePt sources introduced in the framework of PFA through incipient wetness impregnation. Subsequent thermal treatment of the material in argon at 700°C and extraction of the silica rendered template-free mesoporous FePt/C materials with large surface areas and important adsorption properties.

5.3. Metal oxide-derived magnetic materials

A range of novel materials based on titanium silicate mesoporous solids have been recently reported by Barmatova et al. [9, 10]. These materials were prepared following the so-called solid core-mesoporous shell morphology synthetic approach, originally developed by Yoon et al. [11]. The novel materials composed of quasi-spherical particles covered by a titanium silicate mesoporous shell containing isolated Ti atoms were modified by previously synthe-sized magnetic nanoparticles. According to physicochemical studies, these iron oxide NPs were stabilized within the particle core, and thus they did not interfere with the catalytic application such as selective oxidation processes. Wang et al. [12] recently reported a facile chemical route to these interesting materials, which have photocatalytic applications. These hybrid nanoparticles have been reported to be spherical, 100 nm in diameter, and decorated with several Fe$_2$O$_3$ particles as cores distributed within the titania matrix. The silica layers intercalated between magnetic cores and titania shells. Similarly, Xu et al. [13] recently reported the preparation of a visible-light active TiO$_2$/ZnFe$_2$O$_4$ photocatalyst via conventional liquid-phase transformation using the sol-gel method. The formation of highly dispersed zinc ferrite nanoparticles (less than 5 nm in size, with imperfect crystallization) on the TiO$_2$ material prevented the formation of the rutile phase to some extent. The advantage of this material was the coupling of the relatively narrow band gap for ZnFe$_2$O$_4$ (light absorbing semiconductor) and the wide band gap of titania resulting in a semiconductor system with an enhanced

primary charge separation and photocatalytic activity under visible light irradiation. A magnetically recoverable material composed of palladium nanoparticles supported on hydroxyapatite-encapsulated maghemite nanocrystallites (Pd-HAP-γ-Fe$_2$O$_3$) was also reported in the dehalogenation of organic compounds with molecular hydrogen [14]. Pd deposition on the magnetic support was achieved via simple impregnation with a solution of PdCl$_2$(PhCN)$_2$ in acetone. Monomeric PdCl$_2$ species were grafted by chemisorption onto the PdO groups of the support, which were subsequently reduced under H$_2$ atmosphere to give Pd metallic MNP [15, 16]. The synthesized catalyst were used in the dechlorination of 4-chlorophenol as a model compound, with quantitative yields to products obtained in 40 min [17].

5.4. Polymer-derived magnetic materials

Polymer-derived Fe$_3$O$_4$-polyaniline-Au magnetic nanocomposites have been prepared via a two-step process [18]. In the first step, a super paramagnetic Fe$_3$O$_4$-polyaniline (PANI) with a well-defined core-shell nanostructure was synthesized using an ultrasound-assisted in situ surface polymerization method. Aniline monomers were added to an aqueous solution of carboxylic acid-functionalized Fe$_3$O$_4$ microspheres and partially reacted with the surface carboxylic groups to generate COO$^-$H$_3$N$^+$, followed by aniline polymerization [19] on the surface of particle to form the mono-dispersed Fe$_3$O$_4$-PANI core/shell structure [20]. Negatively charged discrete Au nanoparticles with particle sizes of approximately 4 nm were effectively loaded onto the positively charged magnetic support surface by electrostatic attraction. These materials were found to be catalytically active in the reduction of rhodamine B using NaBH$_4$ as a reducing agent.

6. Catalyst and application

Catalysts can be loaded onto MNP either by modification of MNP shells or by coprecipitation during the MNP synthesis, in which the functional ligands also act as stabilizers [21]. Zhu and coworkers [22] successfully immobilized the second-generation Hoveyda–Grubbs catalyst over MNPs (Scheme 1) by using the surface-modification strategy. In this procedure, commercially available MNPs were coated with orthoisopropoxystyrene ligands by covalent bonds. The reaction of the supported ligands with the second-generation Grubbs catalyst formed the supported Hoveyda–Grubbs catalyst, which displayed high activity for both self- and cross-metathesis of methyl oleate (MO).

Polshettiwar et al. [23] used silica coated nanoferrite for the synthesis of magnetically retrievable ruthenium–arene–PTA complexes (Scheme 2) and developed a simple strategy to modify a catalyst that worked efficiently for the hydration of nitriles and various isomerization reactions in aqueous media.
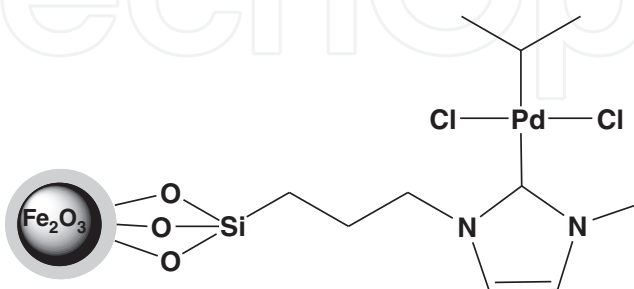
Philip D. Stevens and coworkers reported the use of superparamagnetic nanoparticles (Scheme 3) as a new type of matrices for supporting catalytic homogeneous Suzuki, Heck, and Sonogashira cross-coupling reactions (Scheme 4).
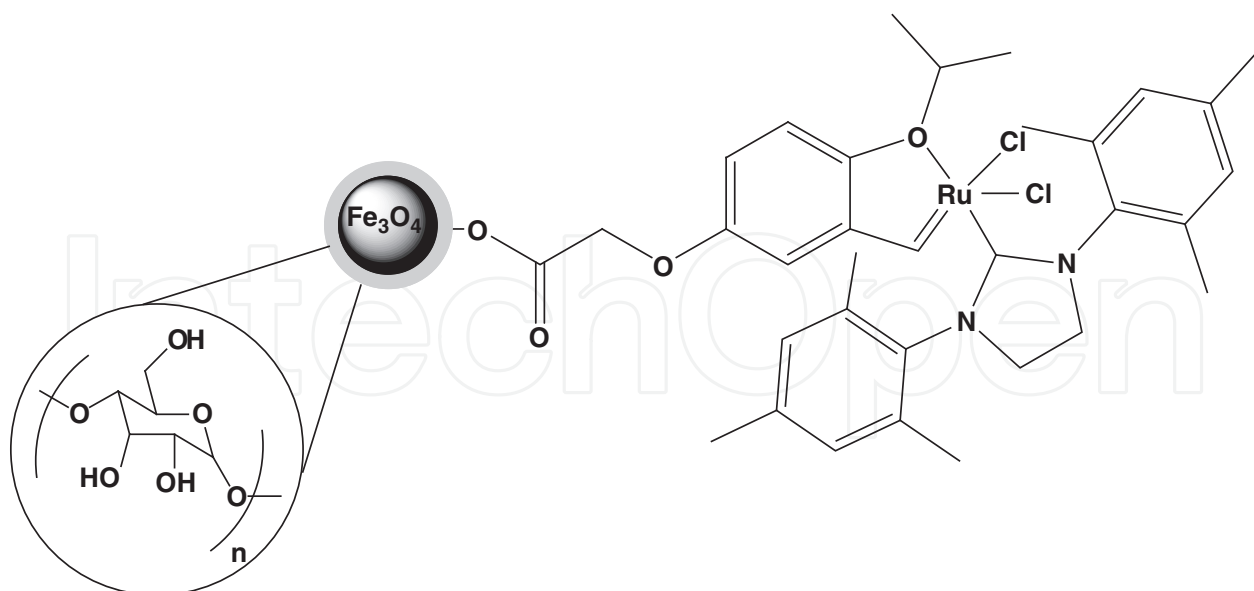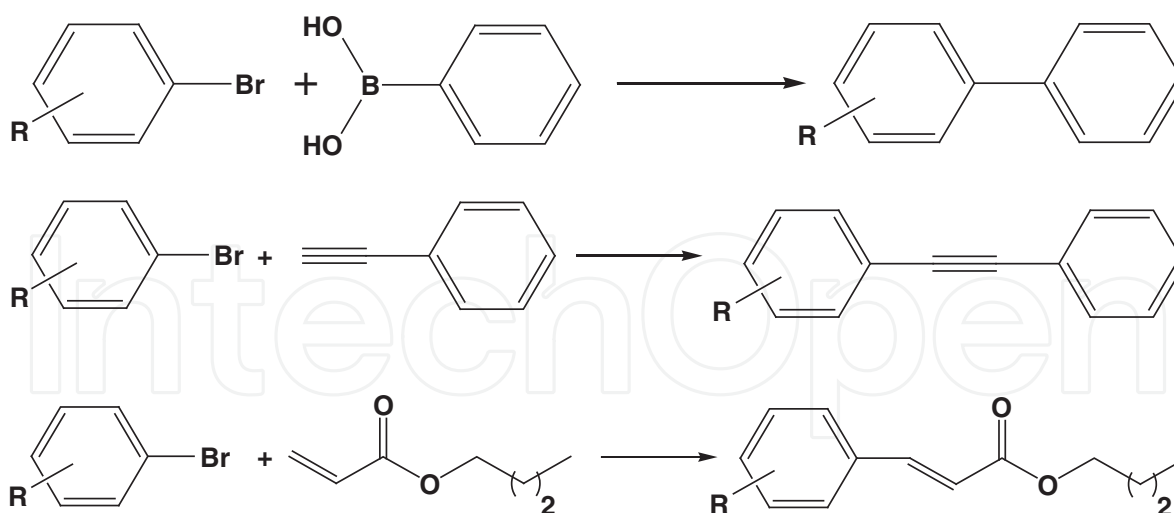
Scheme 1. Synthesis of magnetic Hoveyda–Grubbs catalyst.
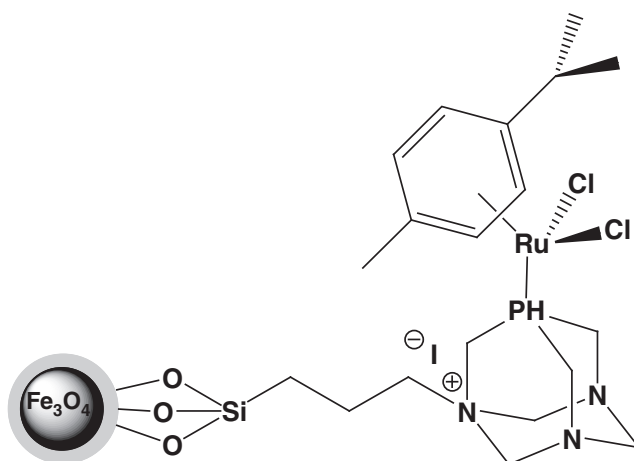
Scheme 2. Magnetically retrievable ruthenium–arene–PTA (RAPTA) complex.


Scheme 3. Structures of maghemite nanoparticle-supported polystyrene (PS) resin-supported NHC–Pd catalyst (solid phase–Pd).

Scheme 4. Supporting catalytic homogeneous Suzuki, Heck, and Sonogashira cross-coupling reactions.

Gao et al. [24] also developed an emulsion polymerization methodology as a novel route for the immobilization of a Pd-NHC catalyst on core/shell super paramagnetic nanoparticles that consisted of a highly crystalline γ-Fe$_2$O$_3$ core and a very thin polymeric shell wall (Scheme 5).
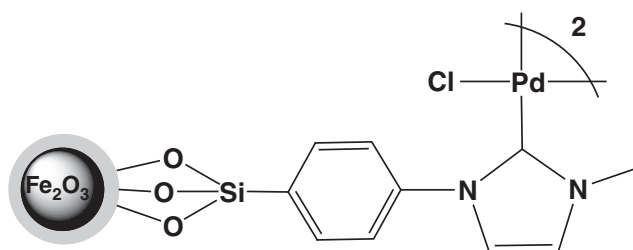
Scheme 5. Emulsion polymerization synthesis of core/shell iron oxide/polymer nanocrystals.

As-synthesized catalyst showed excellent activities in the Suzuki coupling of various aryl iodides and bromides with phenyl boronic acid, using DMF as a solvent (Scheme 6). However, the coupling of aryl chlorides was not reported for this system. The recovery of the catalysts was easily achieved by applying an external permanent magnet, and recycling of the catalytic system was examined for five consecutive rounds in the synthesis of 4-phenyltoluene from 4-iodotoluene and phenylboronic acid. No significant loss of catalytic activity consequently observed during the five consecutive reactions.
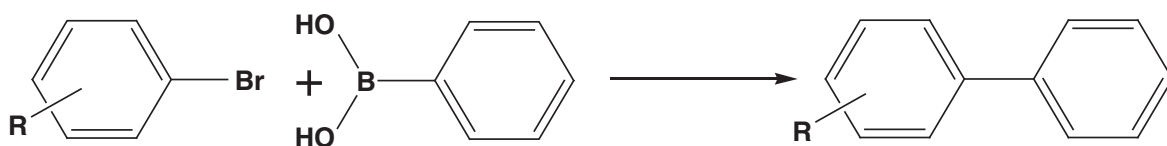
Scheme 6. Maghemite nanoparticle-supported Suzuki cross-coupling reactions.

Jin et al. [25] designed a remarkably active magnetic nanoparticle-supported (β-oxoiminato) (phosphanyl) palladium catalyst via the immobilization of a triethoxysilyl-functionalized palladium complex on the surface of robust SiO_2/Fe_3O_4 in refluxing toluene (Scheme 7).
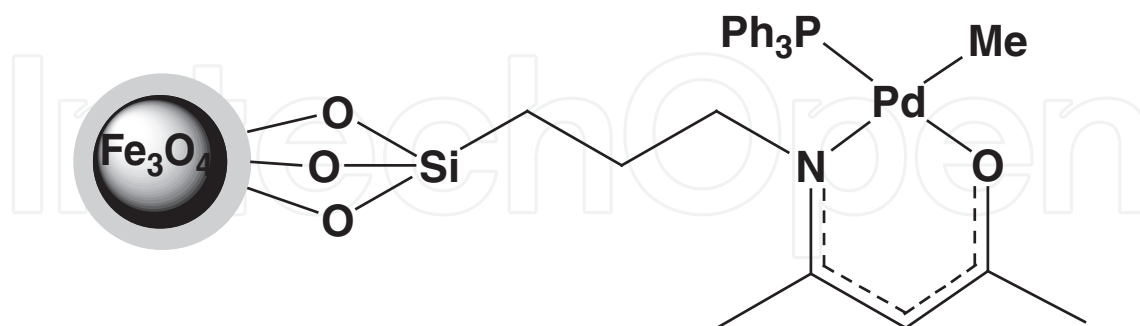
Scheme 7. Synthesis of the MNP-supported (β-oxoiminato) (phosphanyl) palladium complex.

The activity of this catalyst was evaluated in the Suzuki coupling of a series of aryl chlorides with arylboronic acid in aqueous solution and in the presence of K_2CO_3 as a base and tetra-butylammonium bromide as a phase-transfer agent. Reactions of phenylboronic acid with activated aryl chlorides led to the desired products with excellent yields after 3 h at 60°C. The system was particularly efficient for the coupling of phenylboronic acid with deactivated aryl chlorides, including 4-chloroanisole, 4-chlorotoluene, 4-chlorophenol, 2-chloroanisole, and 2-chlorotoluene (Scheme 8).
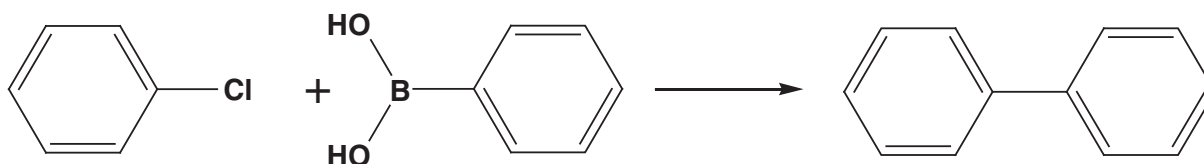
Scheme 8. Suzuki cross-coupling of deactivated aryl chlorides and phenylboronic acid.

Thiel and coworkers [26] reported trimethoxysilyl-functionalized palladium (II)-phosphine complexes on magnetic nanoparticles, which were successfully used as heterogeneous catalysts in the Suzuki reaction of aryl bromides and iodides (Scheme 9). In the presence of 1 mol% of this catalyst, the best results were obtained with Cs_2CO_3 as the base in dioxane at 80°C for 15 h (Scheme 10).

Heuze et al. [27] have synthesized a metallodendron functionalized with a dicyclohexyl-diphosphino palladium complex (Scheme 11). The grafting of this dendron onto core-shell γ-Fe_2O_3/polymer 300 nm MNPs was studied on the basis of the peptide reaction via covalent bond formation between the terminal primary amino group and the carboxyl group of the MNP polymer shell.
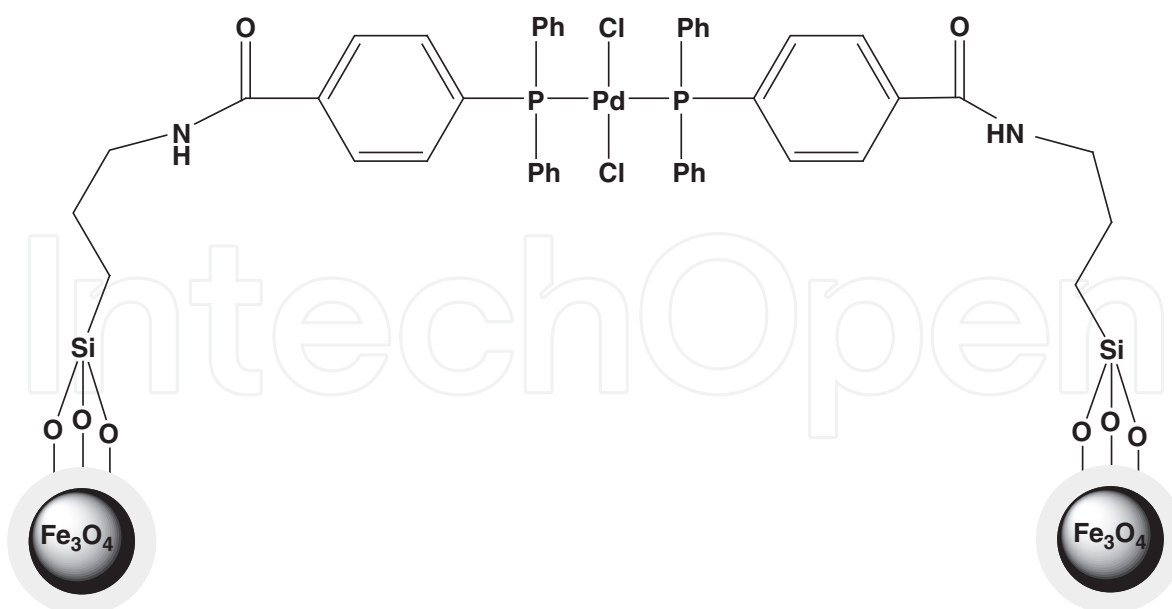
Scheme 9. Pd(II)–phosphine complexes supported on magnetic nanoparticles.
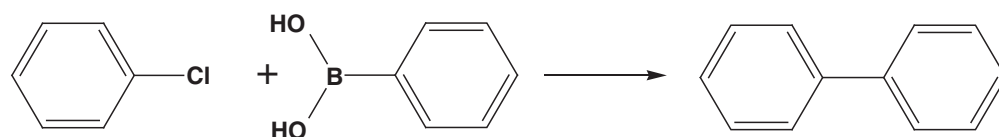
**Scheme 10.** Scheme 8 Suzuki coupling of bromobenzene and phenylboronic acid.
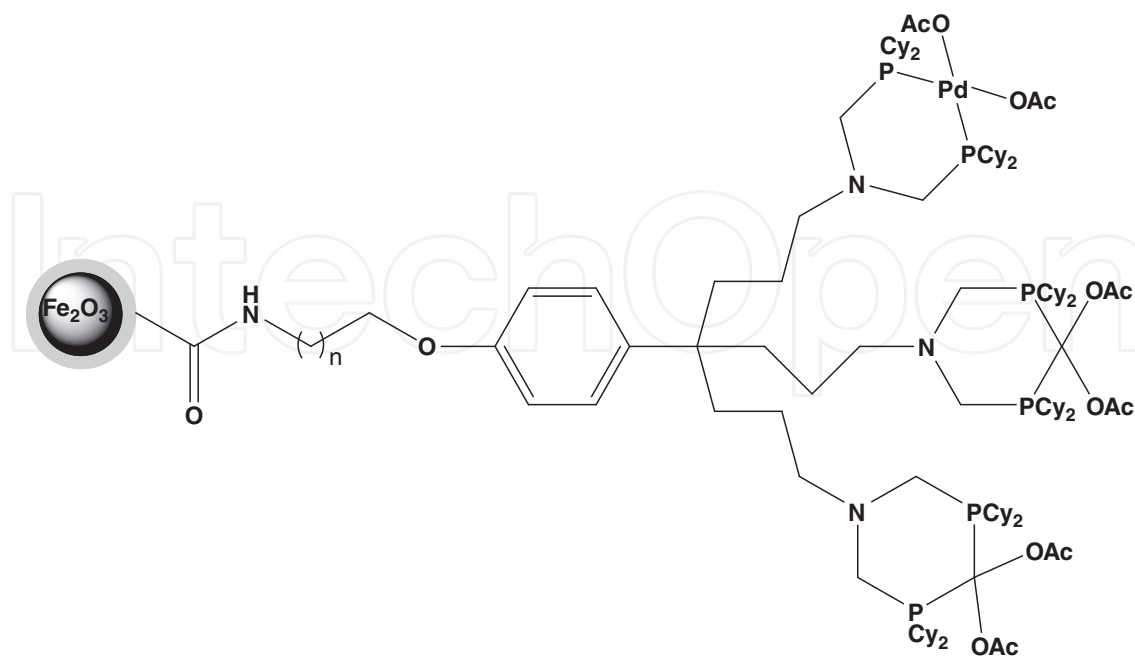
Scheme 11. Dendron-functionalized core-shell super paramagnetic nanoparticles.

This catalyst showed excellent catalytic activities for the coupling of a range of iodo and aryl bromides, which were obtained in good to excellent yields. However, the coupling of aryl chlorides with phenylboronic acid required higher catalyst loading, longer reaction times, and higher temperatures (Scheme 12).
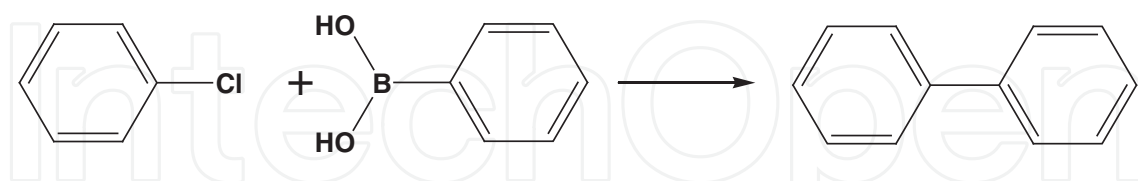
Scheme 12. Suzuki cross-couplings of aryl chlorides with phenylboronic acid using grafted MNPs.

Baig and Varma [28] synthesized a nano-FeDOPACu bimetallic catalyst (Scheme 13) and demonstrated its application for C-S coupling of aryl halides and thiophenols under micro-wave conditions.
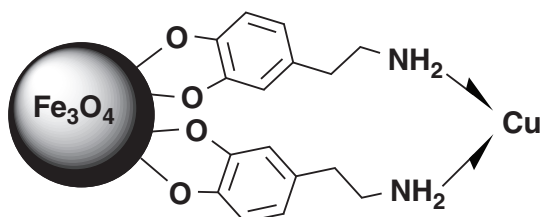
Scheme 13. Nano-Fe$_3$O$_4$-DOPA-Cu catalyst (nano-FeDOPACu).

Thiel and coworkers [29] reported an organic–inorganic hybrid catalyst, obtained by cova-lently anchoring [(L-L)MoO(O$_2$)$_2$] (LL=(3-triethoxysilylpropyl)[3-(2-pyridyl)-1-pyrazolyl]acet-amide) on silica MNPs as a robust magnetically separable epoxidation catalyst (Scheme 14).
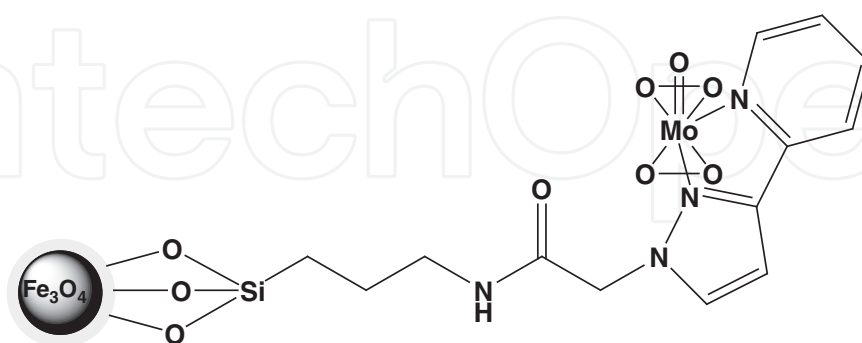
Scheme 14. Magnetic molybdenumperoxo catalyst for olefin epoxidation.

Reiser and co-workers [30] synthesized azabis(oxazoline)copper(II) complexes immobilized on magnetic silica nanoparticles, which displayed selectivities in the asymmetric benzoylation of 1,2-diols in high yields (Scheme 15).
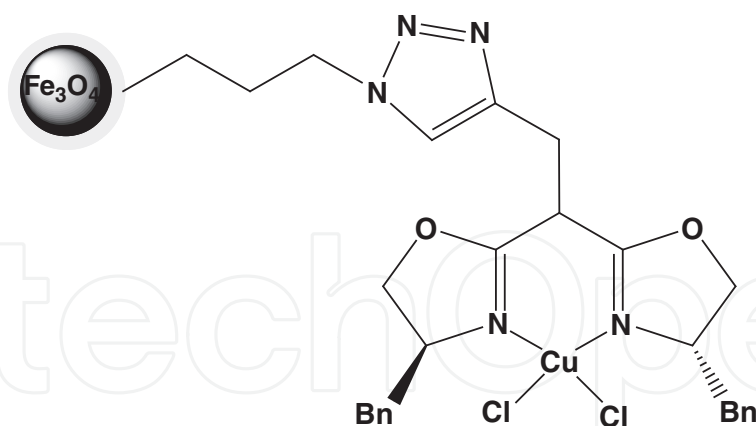
Scheme 15. Asymmetric benzoylation using magnetically separable azabis(oxazoline)copper(II) nanocatalysts.

Claesson et al. [31] employed a stable dispersion to synthesize monodisperse magnetizable colloidal silica particles functionalized with a homogeneous catalyst, i.e., PCP–pincer Pd complex (Scheme 16). This complex is known to catalyze the aldol condensation reaction between benzaldehyde and methyl isocyanoacetate to produce oxazolines (Scheme 17).
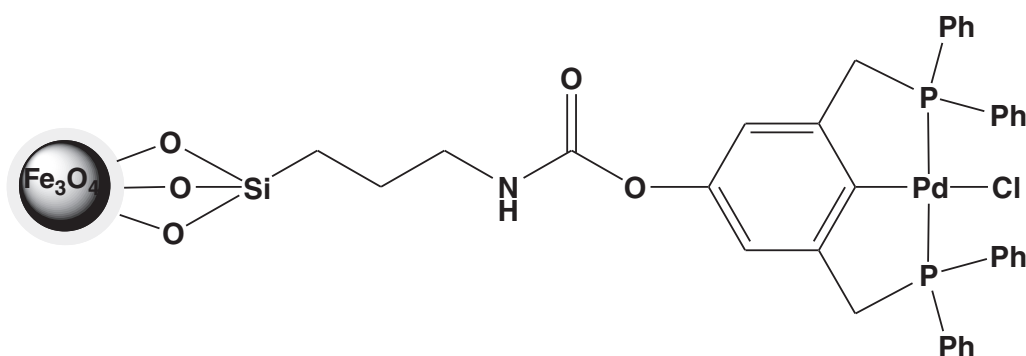

Scheme 16. PCP–pincer Pd complex-immobilized silica-coated nanocatalyst.
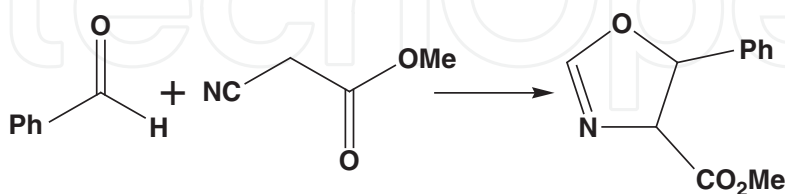
Scheme 17. Catalytic activity for cross-aldol condensation reactions.

Masteri-Farahani and Tayyebi [32] synthesized a highly efficient catalyst by covalent binding of a Schiff base ligand (*N,N′*-bis(3-salicylidenaminopropyl)amine) (salpr) onto the surface of silica-encapsulated magnetite nanoparticles (Si-MNPs) followed by complexation with $MoO_2(acac)_2$ (Scheme 18).
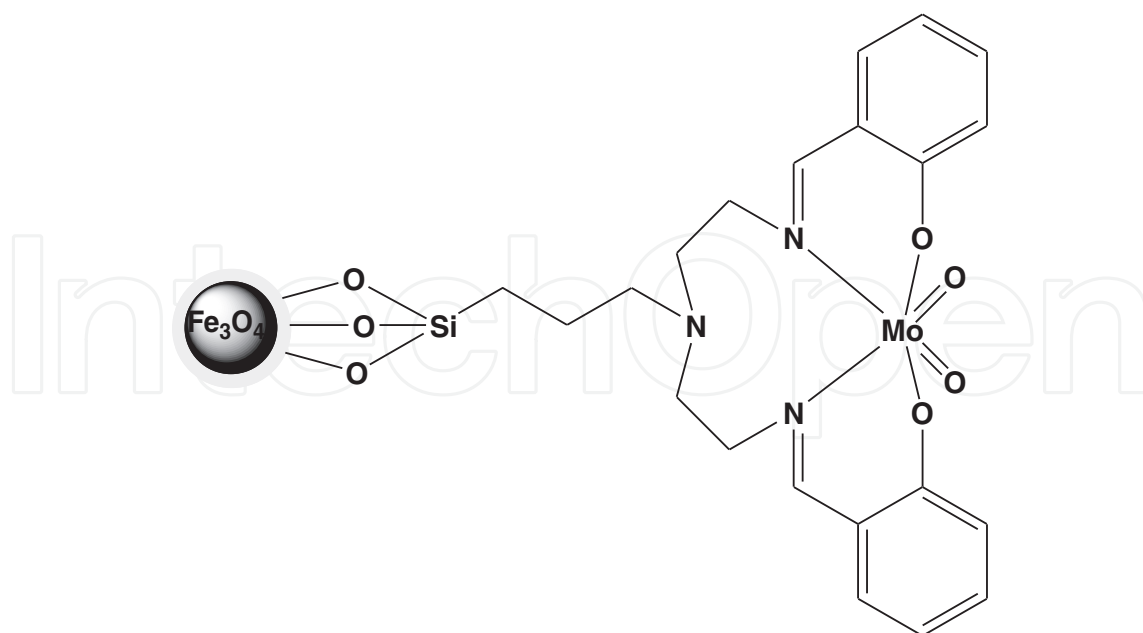
Scheme 18. MoO$_2$ salpr-immobilized silica-coated nanocatalyst.

The catalytic activity of the prepared MoO2salpr/SI-MNPs nanocatalyst was examined in the epoxidation of olefins with tert-butyl hydroperoxide (TBHP) and cumene hydroperoxide (CHP) (Scheme 19).
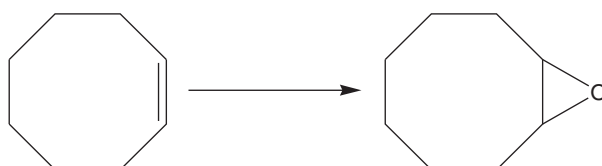
Scheme 19. Epoxidation of olefins.

Benign and economic [33] reported silica-coated magnetically recoverable Mn-porphyrin catalytic system (Scheme 20).

This catalyst is used for oxidation of industrially and biologically important substrates including olefins, saturated hydrocarbons, alcohols, and organosulfur compounds in water applying tert-butyl hydroperoxide (Scheme 21).

Sun and coworkers [34] reported organic–inorganic hybrid heterogeneous nanocatalysts via covalent anchoring of cobalt(II) or copper(II) acetylacetonate complexes ([Co(acac)$_2$] or [Cu(acac)$_2$]) onto core–shell structured Fe$_3$O$_4$/SiO$_2$ previously functionalized with 3-amino-propyltriethoxysilane (APTES) (Scheme 22).

Sharma et al. [35] reported the fabrication of a highly efficient magnetically separable nano-catalyst by the covalent immobilization of a copper (II) acetylacetonate complex onto amine-functionalized silica magnetite NPs (Cu(acac)$_2$@Si-MNP) (Scheme 22).
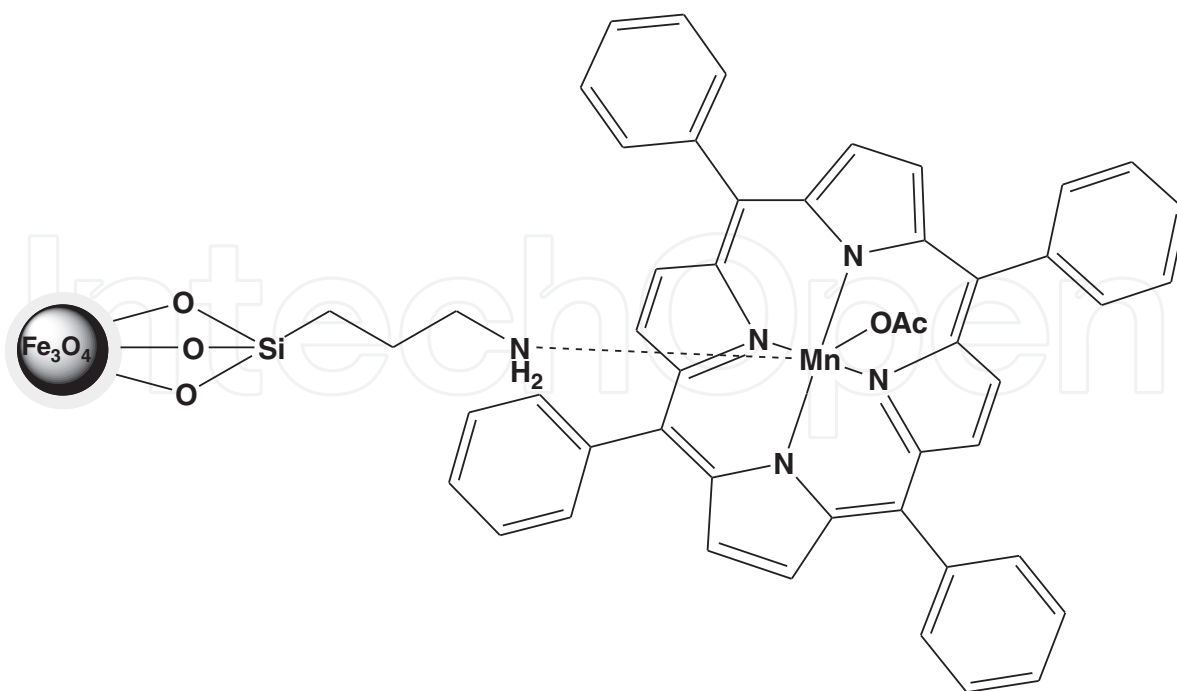
Scheme 20. Silica-coated magnetically recoverable Mn-porphyrin catalytic system.
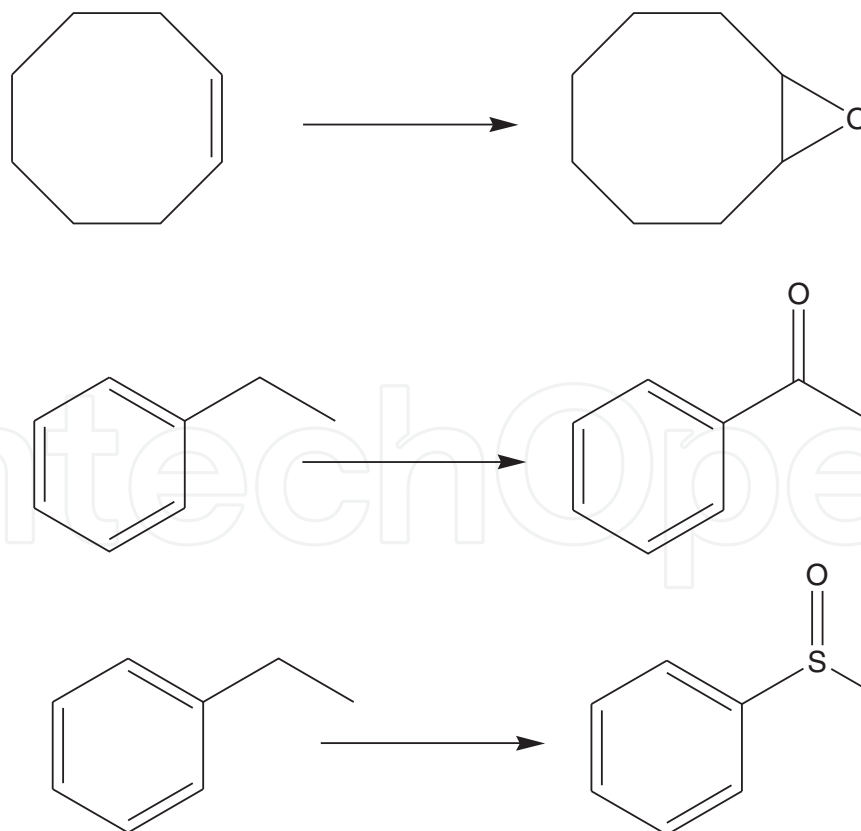

Scheme 21. Oxidation of different arenes.
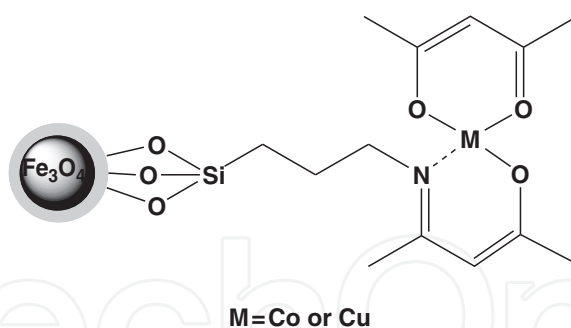
Scheme 22. Magnetically recoverable heterogeneous nanocatalysts $Fe_3O_4/SiO_2–NH_2–M$ (M=Cu or Co).

The application of the synthesized nanocomposites was examined for the degradation of various organic nitro-analogues in aqueous medium at room temperature using sodium borohydride as a source of hydrogen (Scheme 23). The reported nanocatalytic system was able to selectively reduce the nitro group even in presence of other sensitive functional groups.
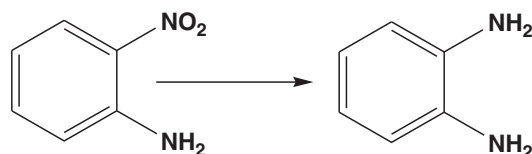
Scheme 23. $Cu(acac)_2$@Am-Si-MNPs catalyzed reduction of nitro compounds.

Byrenes et al. [36] synthesized a nanocatalyst in one step from a commercially available second-generation Grubbs catalyst by the immobilization of the homogeneous catalyst onto magnetically separable silica coated nanosized iron oxide particles (Scheme 24).
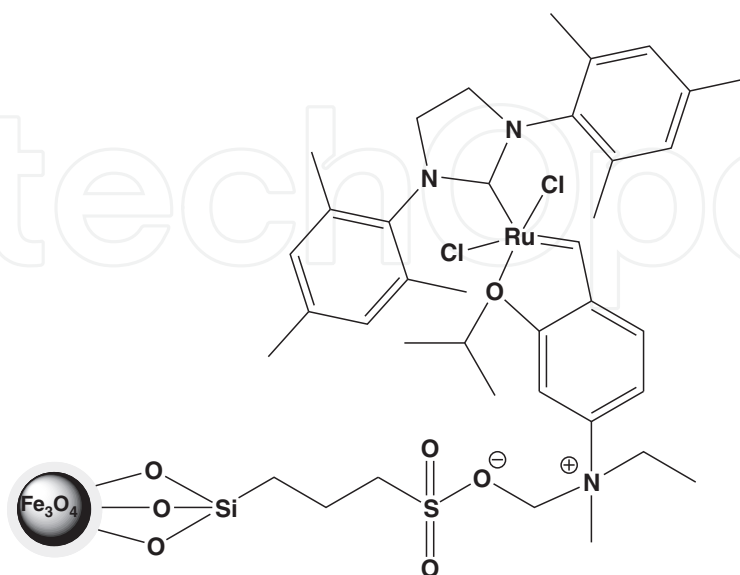
Scheme 24. Ruthenium alkylidene-immobilized silica-coated nanocatalyst.
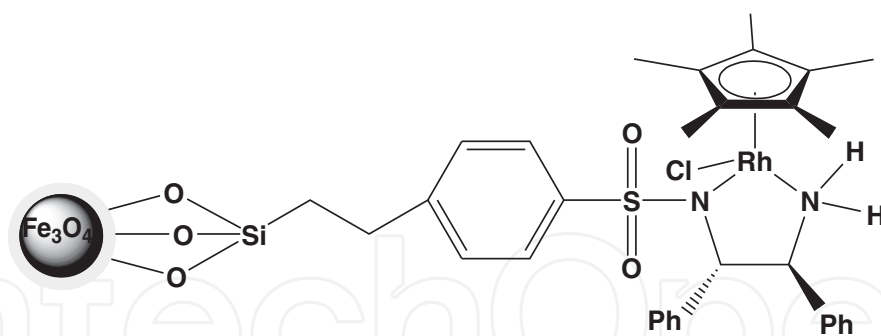
Scheme 25. Preparing magnetic catalysts through direct complexation of [Cp*RhCl$_2$]$_2$ with (S,S)-TsDPEN and [Cp*RhCl$_2$]$_2$ with (R,R)-TsDACH modified SiO$_2$-coated Fe$_3$O$_4$ nanoparticles.

Liu and coworkers [37, 38] reported a convenient method for preparing three magnetic catalysts (Scheme 25) through direct complexation of [Cp*IrCl$_2$]$_2$ or [Cp*RhCl$_2$]$_2$ with (S,S)-TsDPEN and [Cp*RhCl$_2$]$_2$ with (R,R)-TsDACH modified SiO$_2$-coated Fe$_3$O$_4$ nanoparticles.

In 2004, Xu and coworkers [39] developed a simple and efficient functionalization protocol for ferrites using dopamine as an anchor. These functionalized materials with Ni-complex (Scheme 26) displayed high specificity for protein separation and excellent stability to heating and high salt concentrations.
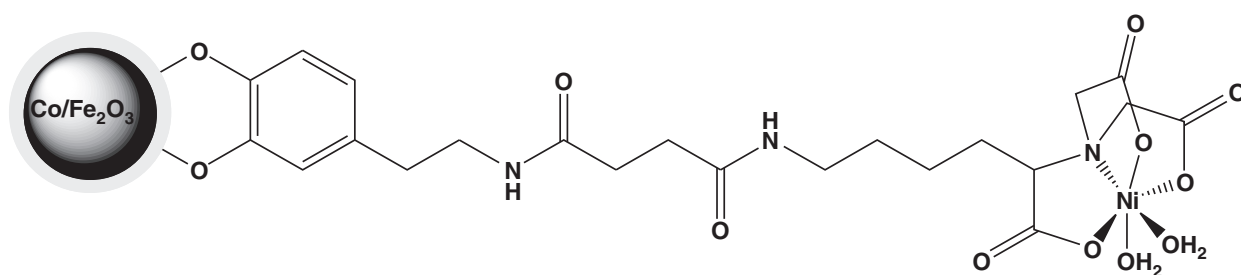
**Scheme 26.** Dopamine functionalization of ferrites.

Lin et al. [40] designed a magnetite nanoparticle-supported chiral catalyst by Ru-complex formation with BINAP followed by functionalization on the ferrite surfaces (Scheme 27). The catalyst could be recovered by using an external magnet and was used up to 14 times without any change in activity.

This catalyst was then used for the hydrogenation of a wide range of aromatic ketones to their corresponding secondary alcohols and exhibited high reactivity and enantioselectivity. The enantiomeric excess (ee) values were significantly higher than those of the parent homogeneous catalyst [Ru(BINAP)(DPEN)-Cl$_2$] and were comparable to the values of its homogeneous counterpart. The stability of the recovered catalyst was investigated in the asymmetric hydrogenation of 1-acetonaphthone. In this reaction, the catalyst could be recycled 14 times with no decrease in conversion and/or enantiomeric excess. However, the MSCs tend to aggregate slightly, presumably because the [Ru(BINAPPO3)(DPEN)Cl$_2$] moieties on the MNP
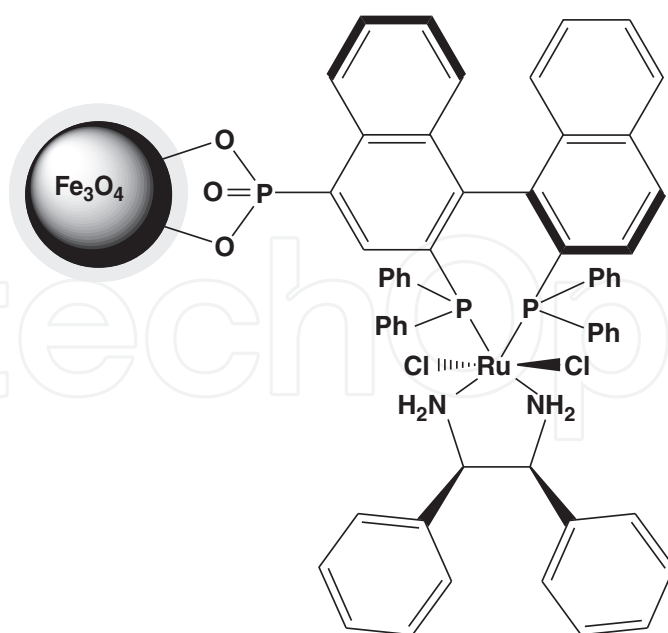
Scheme 27. Nanoparticle-supported chiral Ru-catalyst.

surfaces are less effective in preventing the aggregation of the MNPs than that of widespread coating agents such as oleic acid (Scheme 28).
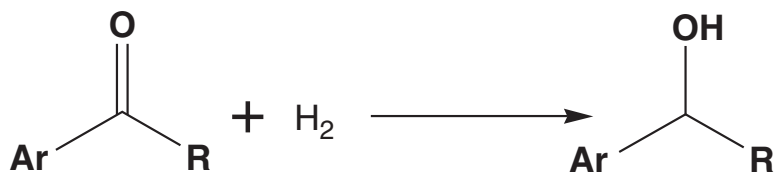

Scheme 28. Magnetite chiral Ru catalyst for asymmetric hydrogenation of aromatic ketones.

Kitamura and colleagues [41] prepared a heterogeneous deallylation catalyst by immobilizing $[CpRu(\eta^3\text{-}C_3H_5)(2\text{-pyridinecarboxylato}]PF_6$ onto silica-coated nanoferrite particles. The obtained materials showed high saturation magnetization and high levels of dispersibility with weak coercive forces. It was highly active for deallylation reactions and could operate in alcoholic solvents in the absence of any extra additives to complete the reaction (Scheme 29).
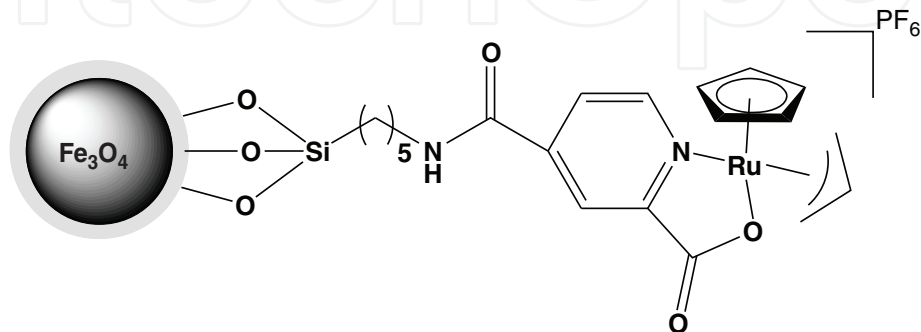

Scheme 29. Heterogeneous deallylation catalyst.

The catalyst was highly active for deallylation reactions (Scheme 30), and no extra additives were needed to complete the reaction. Only volatile allyl ethers were the coproducts of the reaction. The catalyst was removed using an external magnet and reused, making the protocol economical.
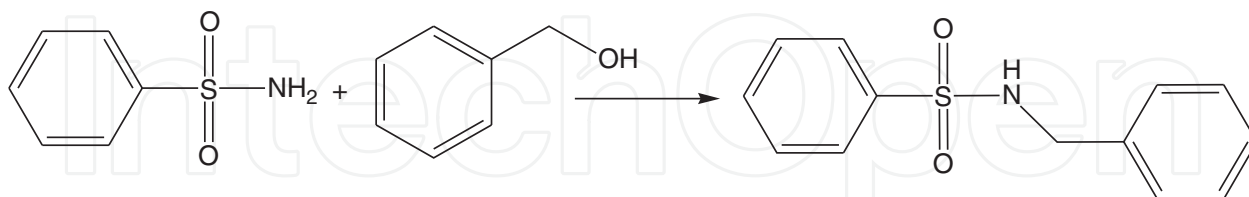

Scheme 30. Magnetically separable Ru catalyst for synthesis of sulfonamides.

Gao and colleagues [42] reported the synthesis of a novel magnetic nanoparticle-supported di(2-pyridyl)methanol palladium dichloride complex via click chemistry (Scheme 31).
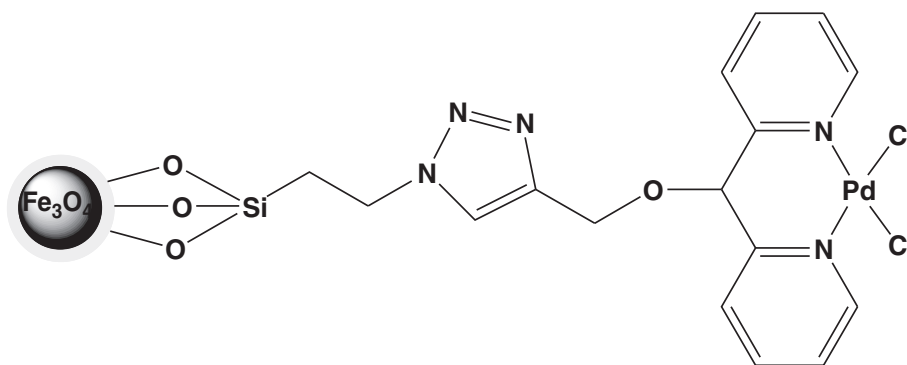
Scheme 31. Preparation of an MNP-supported Di(2-pyridyl)-methanol-Pd complex via click chemistry.

The catalyst was then initially used in the Suzuki coupling of phenylboronic acid with bromobenzene. Optimized results were achieved with a 0.2 mol% catalyst and the use of K_2CO_3 as base in DMF at 100°C. Under these conditions, fairly good to excellent yields were obtained in the coupling of aryl bromides containing electron-donating and electron-with-drawing substituents (Scheme 32).
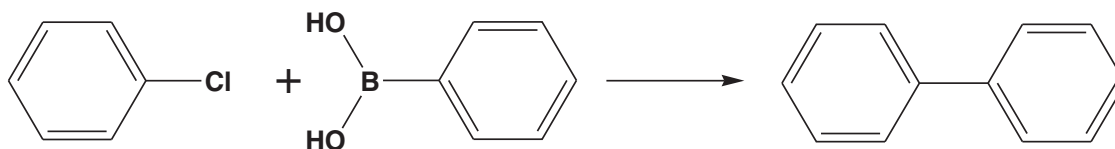
**Scheme 32.** Coupling reactions using MSC-supported complexes.

Interestingly, Che et al. [43] developed a novel type of Hoveyda–Grubbs catalyst by assembling magnetic nanoparticles with a Grubbs I catalyst. Scheme 33 describes the synthesis of the

magnetic nanoparticle-supported Hoveyda–Grubbs catalyst. The isopropoxystyrene deriva-
tive was first treated with glutaric anhydride in the presence of Et3N and DMAP to create
5-(4-isopropoxy-3-vinylbenzyloxy)-5-oxopentanoic acid, which was further reacted with
amino-functionalized ferrite. The as-synthesized material was then coupled with a first-
generation Grubbs catalyst in the presence of CuCl to produce the desired magnetic Hoveyda–
Grubbs catalyst.
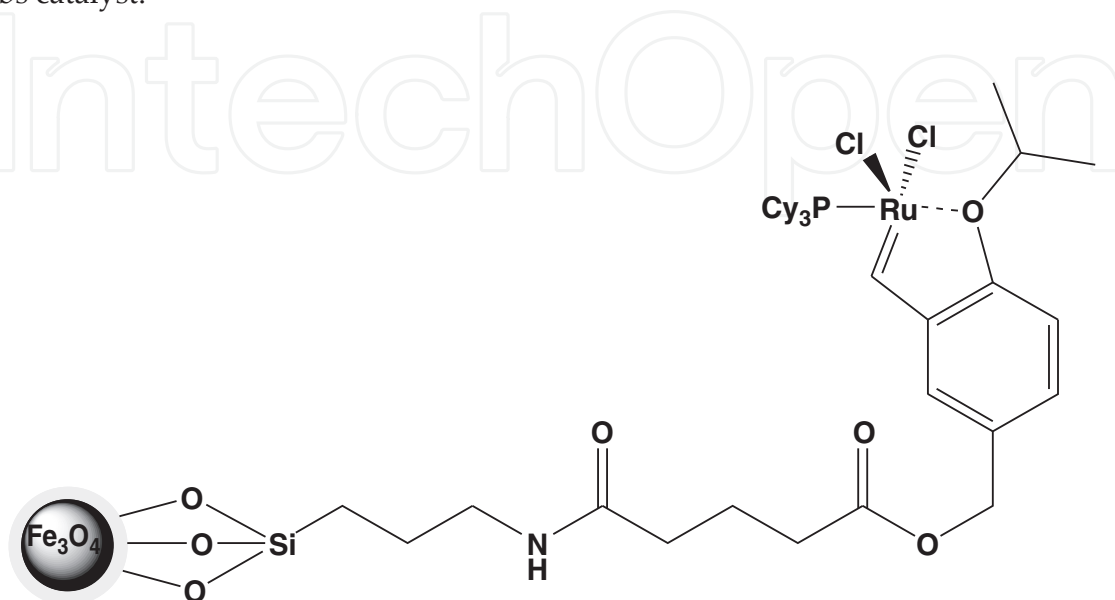
Scheme 33. Preparation of the magnetic Hoveyda–Grubbs catalyst.

Recently, Li et al. [44] synthesized a magnetite-supported copper(I)pybox magnetically
retrievable catalyst (Scheme 34).
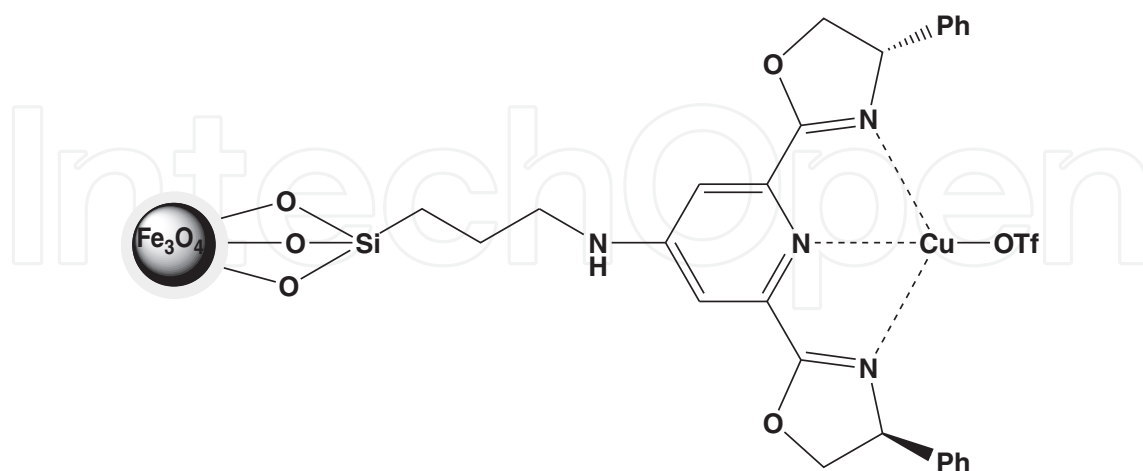
**Scheme 34.** Magnetite-supported copper (I) pybox.

More recently, Glorious et al. [45] reported an enantioselective allylation reaction on a
magnetite-supported NHC catalyst. The immobilization of an enantiomerically pure imida-

zolium salt on the surface of magnetite leading to the formation of a molecular Pd complex is presented in Scheme 35.
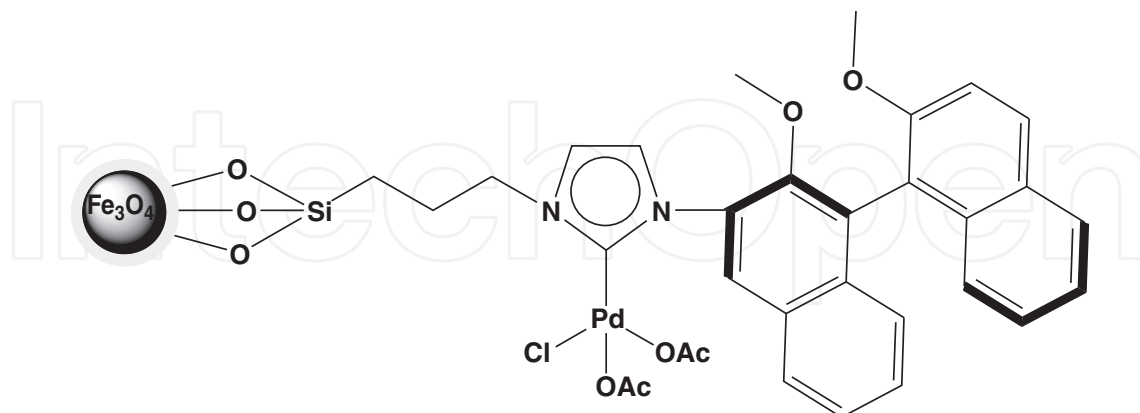
**Scheme 35.** Synthesis of magnetite-supported chiral NHC.

Shijie Ding et al. [46] used regular shaped Fe3O4 magnetic nanoparticles (20–30 nm) to support the catalyst for atom transfer radical polymerization (ATRP). It was tethered onto the magnetic nanoparticles (Scheme 1). The supported catalyst could mediate ATRP with a control over polymerization unattainable by heterogeneous catalysts. The separation of nanosized magnetic supports could be easily achieved by applying a magnetic field (Scheme 36).
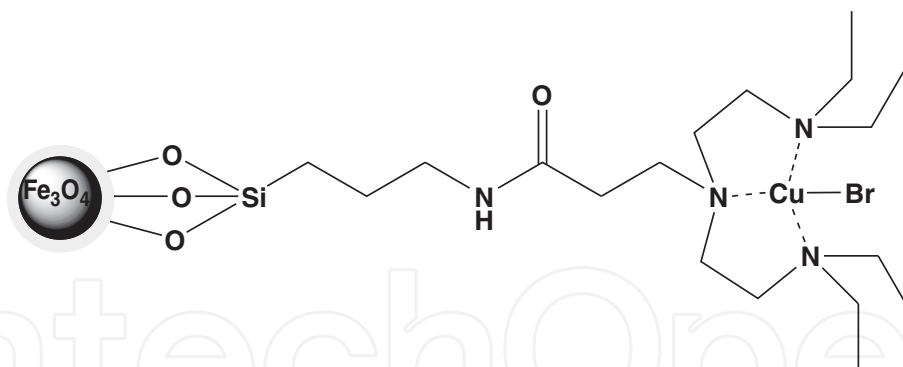

Scheme 36. Immobilization of the ligand tetraethyldiethylenetriamine (TEDETA) and the catalyst onto Fe_3O_4 magnetic nanoparticles.

The Fe_3O_4 magnetic nanoparticle-supported porphyrinato cobalt III (MNP-P) has been designed, synthesized (Scheme 37), and evaluated as a recoverable catalyst for coupling reaction of epoxide and CO_2 (Scheme 38) [47].

Barahman Movassagh et al. [48] introduced a new heterogeneous, recyclable, heat- and air-stable silica-coated magnetic nanoparticle (MNP)-supported palladium(II)-crypt and complex [$Fe_3O_4/SiO_2/C22$–Pd(II)] catalyst (Scheme 39) as a highly efficient catalytic system for performing the Suzuki–Miyaura reaction and S-arylation of thiols (Scheme 40).
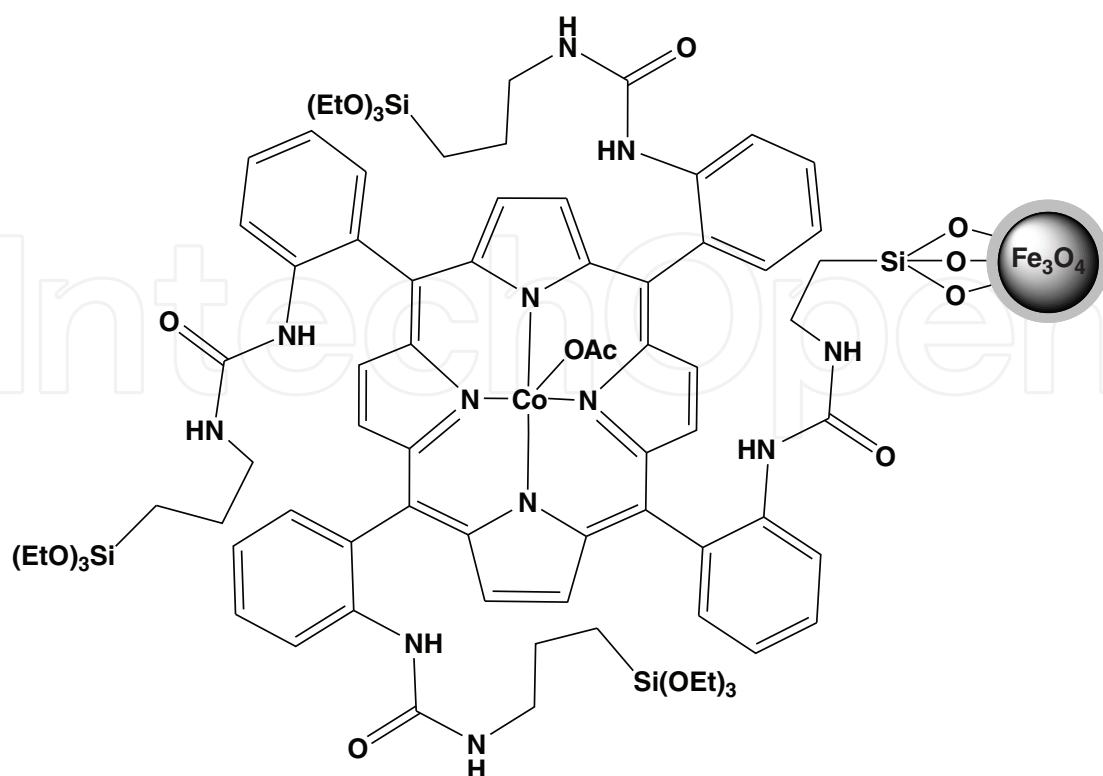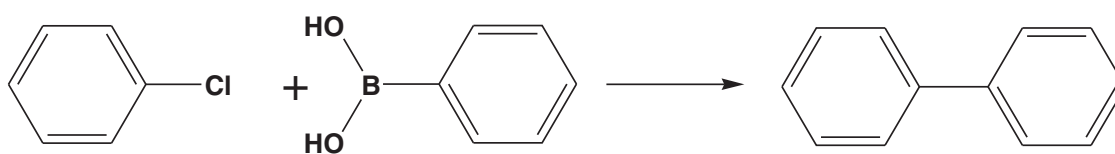
Scheme 37. The Fe_3O_4 magnetic nanoparticle-supported porphyrinato cobalt III.
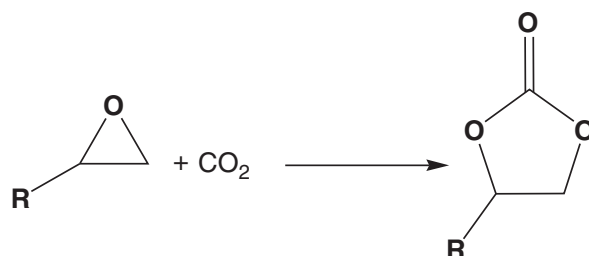
**Scheme 38.** Coupling reaction catalyzed by MNP-P/PTAT.
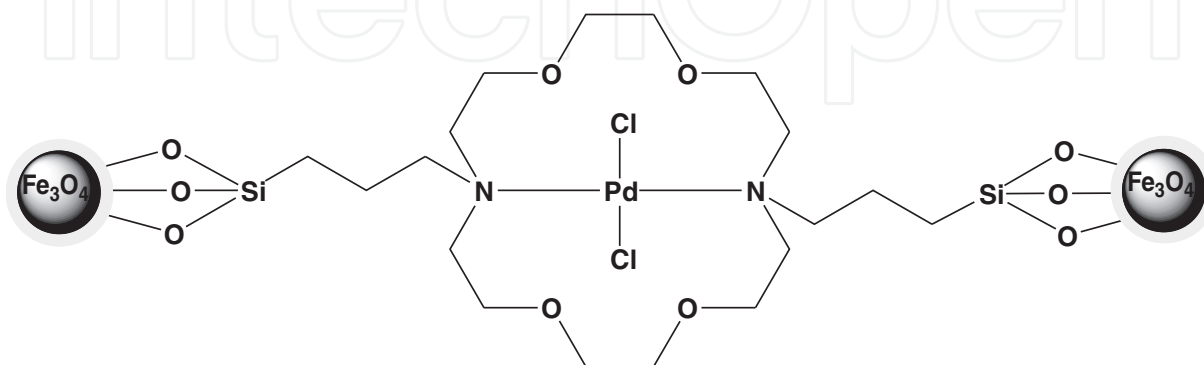
**Scheme 39.** Synthetic schemes of $Fe_3O_4/SiO_2/C22$–Pd(II) catalyst.

Scheme 40. Suzuki cross-couplings of aryl chlorides with phenylboronic acid using grafted MNPs.

Pinhua Li et al. [49] developed a highly active air- and moisture-stable and easily recoverable magnetic nanoparticle-supported palladium catalyst (Scheme 41) for the Suzuki, Sonogashira, and Heck reactions. A wide range of substrates was coupled successfully under aerobic conditions (Scheme 42).
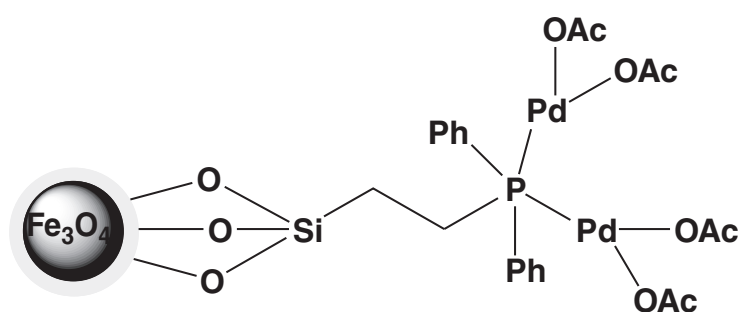

**Scheme 41.** Preparation of the magnetic nanoparticle-supported palladium catalyst.
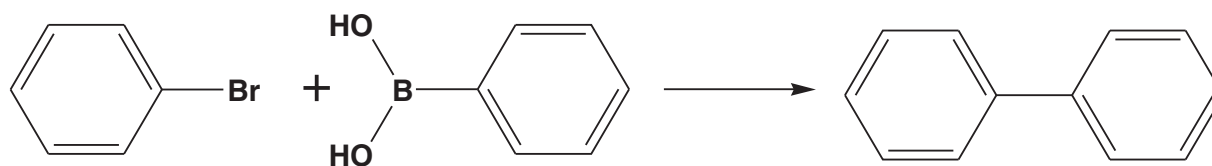
Scheme 42. Applications in Suzuki, Sonogashira, and Heck reactions.

Xingquan Xiong et al. [50] reported a green, inexpensive and scale-up synthesis of 1,4-disubstituted 1,2,3-triazoles from benzyl/alkyl halides, functional alkynes and sodiumazides in water, which were catalyzed by heterogeneous, recyclable, and commercially available Fe_3O_4-supported Cu(I) catalysts (MNPs–CuBr) via a combination of one-pot multi-component CuAAC reaction and microwave irradiation (Scheme 43).

Fe_3O_4 was successfully prepared by coprecipitation with $FeCl_2$ and $FeCl_3$ as reaction substrate, polystyrene (PS) as surfactant and aqueous NH_3 as precipitant And then the core-shell Fe_3O_4/SiO_2 nanospheres were prepared by a modified Stober method. A mild, convenient, and efficient protocol developed for the synthesis of 1- and 5-substituted 1H-tetrazoles from nitriles and amines using magnetically separable Fe_3O_4/SiO_2/ligand/Cu(II) nanoparticles as an efficient and recyclable catalyst (Scheme 44) [51].
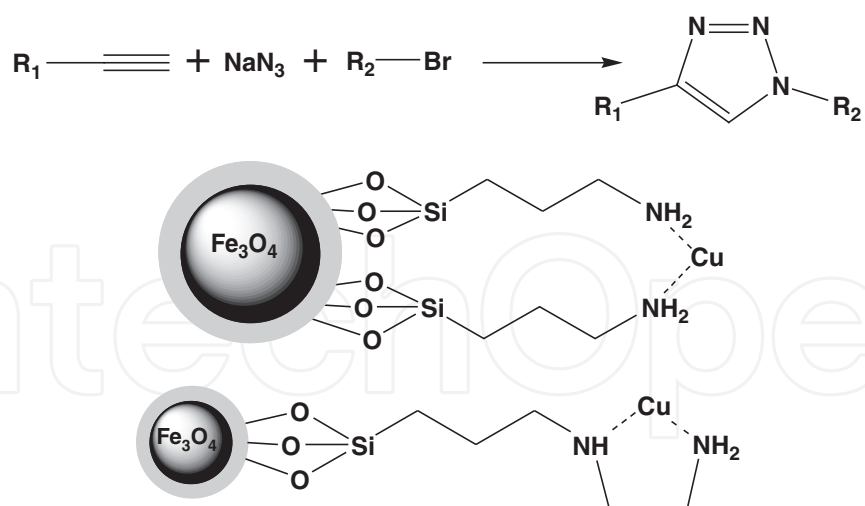
Scheme 43. MNPs–CuBr catalyzed one-pot synthesis of 1,4-disubstituted 1,2,3-triazoles in water under microwave irradiation conditions.
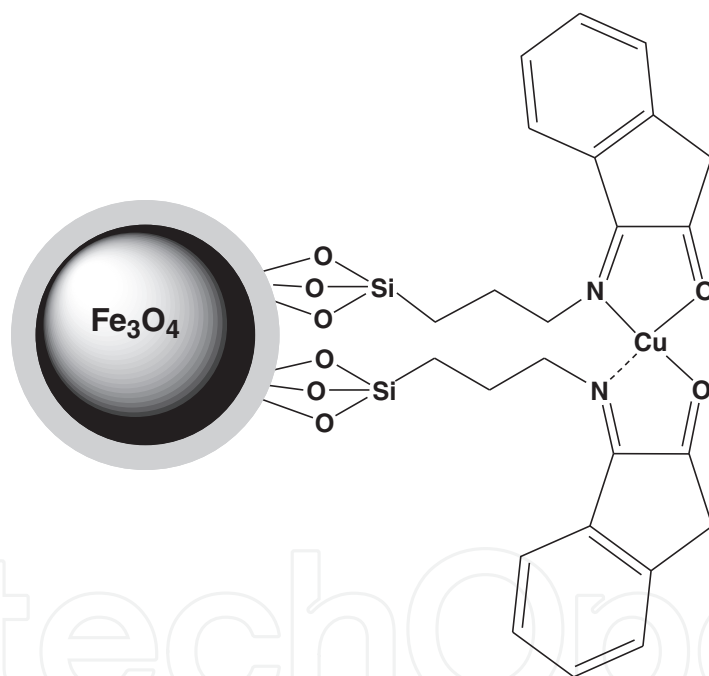
Scheme 44. Cu(II) complex functionalized Fe$_3$O$_4$/SiO$_2$ nanoparticle.

The immobilized copper complex was used as an efficient catalyst for synthesis of 1- and 5-substituted 1H-tetrazoles from nitriles and amines in good to excellent yields (Scheme 45).
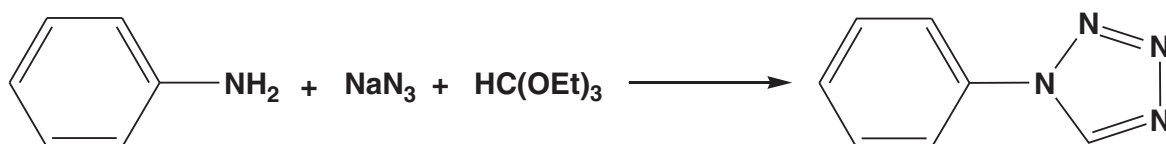
Scheme 45. Synthesis of 1- and 5-substituted 1H-tetrazoles from nitriles and amines.

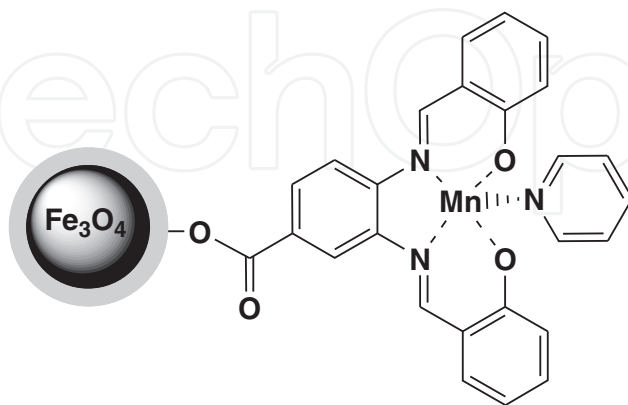Functionalized magnetic iron ferrite (Fe_3O_4) synthesized by complexation with various metals and applied in organic synthesis. A new Fe_3O_4 magnetic nanoparticle-supported manganese–salen complex was successfully prepared by attaching manganese acetates to a novel *N,N′*-bis(salicylidine)ethylenediamine ligand functionalized Fe_3O_4 (Scheme 46) [52].

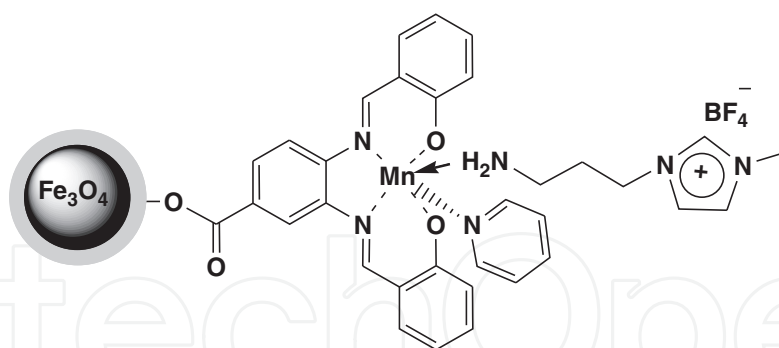**Scheme 46.** Schematic illustration of the synthesis for Fe_3O_4\SiO_2\Salen\Mn nanoparticles.

This catalyst was used as a magnetically recyclable heterogeneous catalyst for the efficient one-pot synthesis of benzopyranopyrimidines from the reaction of 2-hydroxybenzaldehyde, malononitrile, and amine with high product yields (Scheme 47).
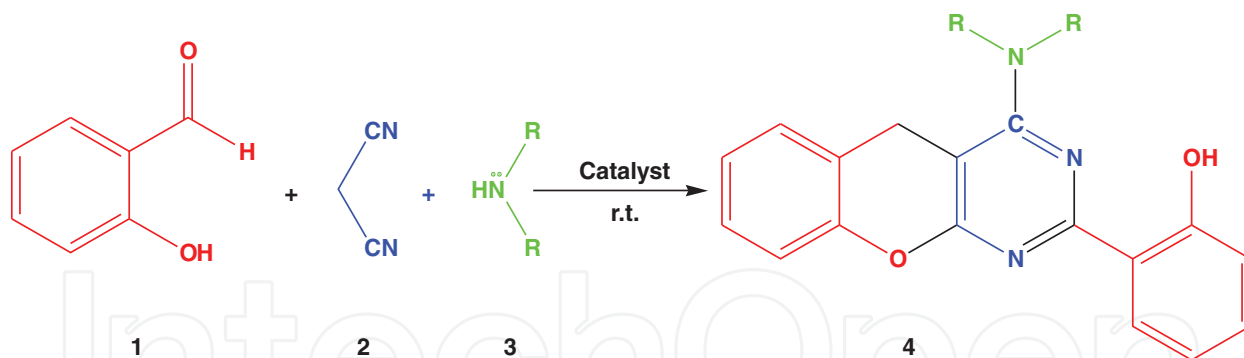
Scheme 47. Synthesis of benzopyranopyrimidines from salicylic aldehydes, malononitrile, and amine in the presence of Fe_3O_4\SiO_2\Salen\Mn MNPs.

The Fe_3O_4/SiO_2 core shell was synthesized by a simple method and then functionalized by the Schiff base complex of Mn (III), which had been obtained by the reaction between Mn (III) acetate and the Schiff base prepared from 1,2-benzenediamine and salicylaldehyde, according to Scheme 48 and its catalytic activity in the multicomponent reaction (Scheme **49**) [53].

Magnetite–polyoxometalate hybrid nanomaterials, Fe_3O_4/SiO_2/salen/Mn/IL/HPW, were prepared by grafting $H_3PW_{12}O_{40}$ on ionic liquid-functionalized Fe3O4 magnetite nanoparticles (Scheme 50) [54].

Scheme 48. Schematic illustration of the synthesis for Fe$_3$O$_4$/SiO$_2$/Salen/Mn/IL nanoparticles.
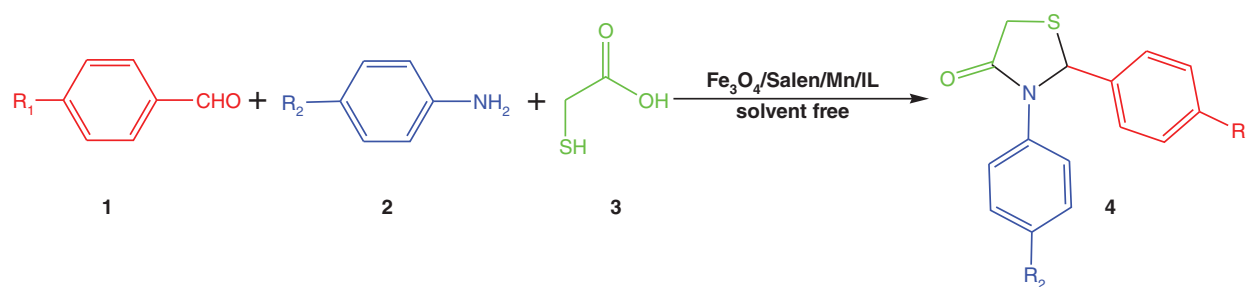
Scheme 49. Synthesis of 1,3-thiazolidin-4-one in the presence of Fe$_3$O$_4$/SiO$_2$/Salen/Mn/IL MNPs.
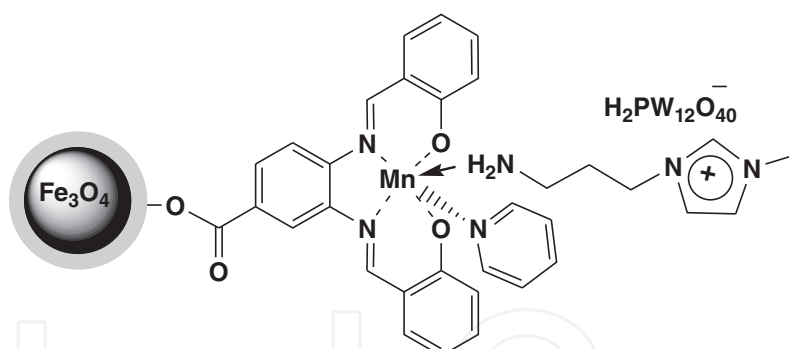

Scheme 50. Schematic illustration of the synthesis of MNPs-HPW.

This catalyst is a recoverable catalyst for the one-pot synthesis of thiazoloquinolines in high to excellent yield under solvent-free conditions (Scheme 51).

A new Fe$_3$O$_4$ magnetic nanoparticle-supported gold dipyridine complex was successfully prepared by attaching sodium tetrachloroaurate(III) hydrate to a novel dipyridine ligand functionalized Fe$_3$O$_4$. The catalyst was prepared by sonicating nanoferrites with dipyridine (which acts as a robust anchor and avoids Au(III)) in absolute MeOH, followed by addition of sodium tetrachloroaurate(III) hydrate. Material with Au(III) on the functionalized nanoferrites was obtained in excellent yield (Scheme 52), which catalyzed the 2,6-dihydropyrimido[2,1-a]isoindole derivatives (4) in aqueous media (Scheme 53) [55].
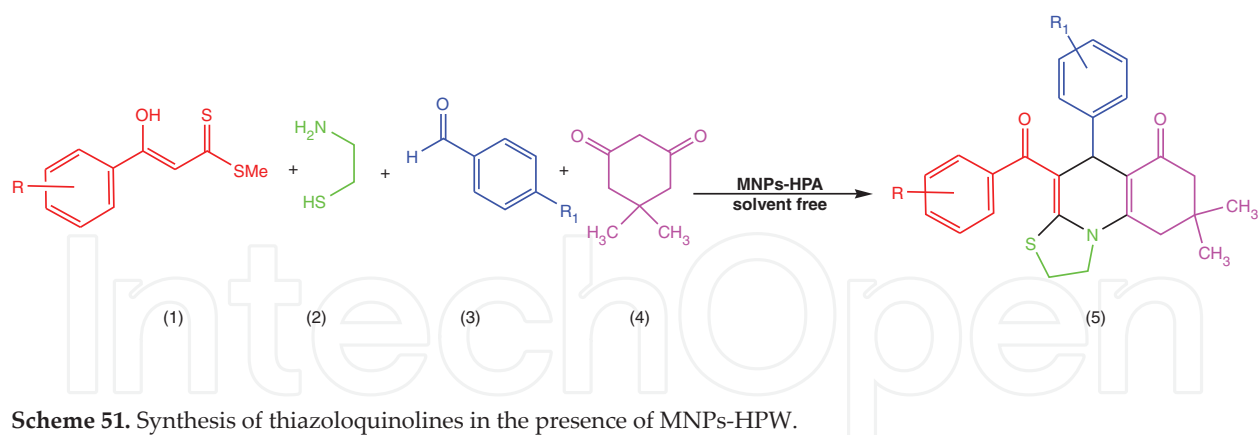
Scheme 51. Synthesis of thiazoloquinolines in the presence of MNPs-HPW.
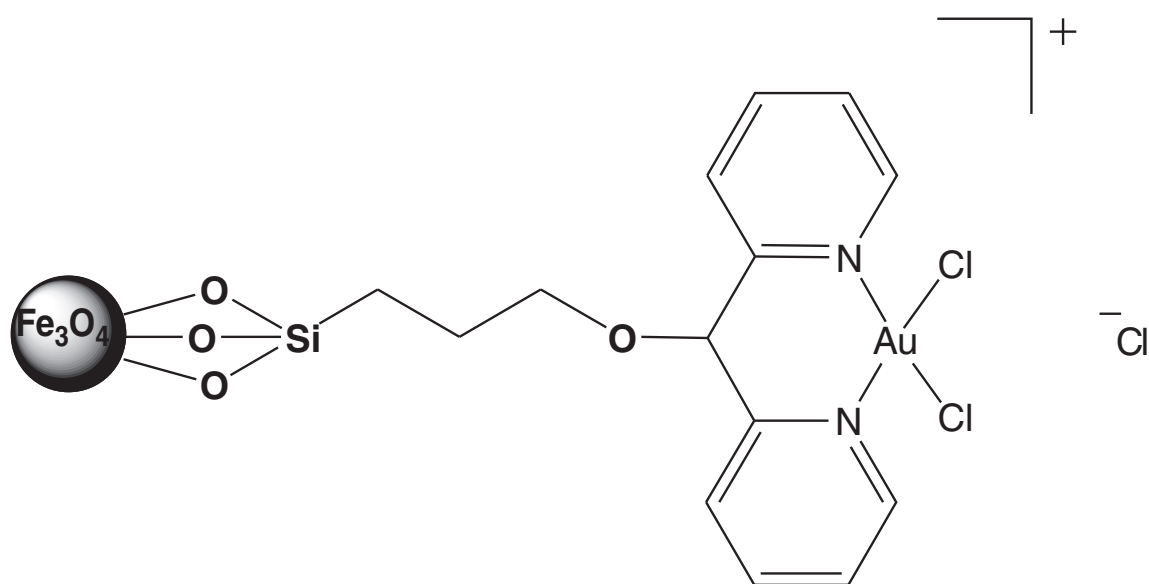
Scheme 52. It was found to be an efficient catalyst for the synthesis 2,6-dihydro[2,1-a]isoindole in aqueous medium.
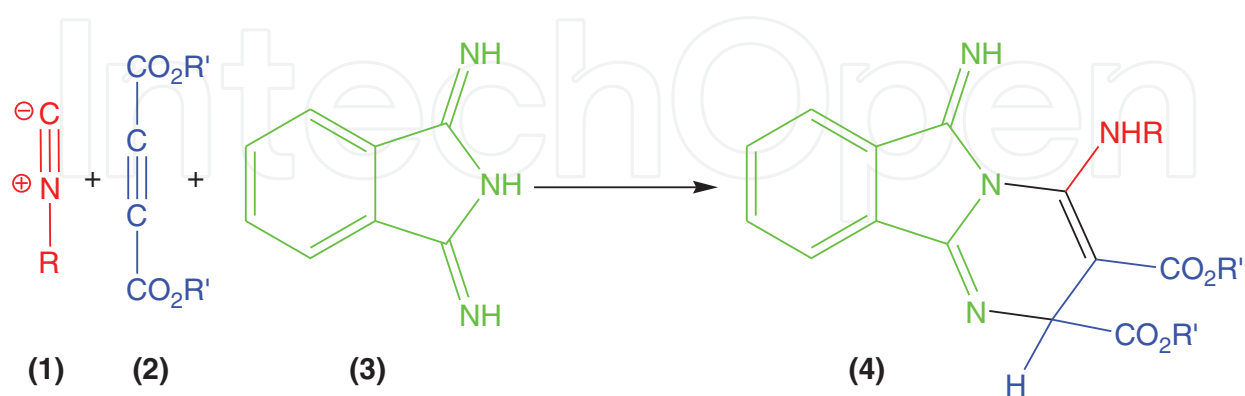
Scheme 53. Reaction pathways for the condensation of alkyl isocyanides (1) and dialkyl acetylenedicarboxylates (2) with 1,3-diimino isoindoline (3).

7. Conclusion

The heterogenization of catalysts using magnetic supports is a new direction for modern organic chemistry, which is associated with the efficient isolation, reusability, and recyling of precious catalysts or reagents. Magnetic separation not only reduces the costs of production but also prevents the production and accumulation of toxic waste. These reasons explain why the development of magnetically separable nanocatalysts is growing exponentially, with uses in sustainable and benign chemical transformations. The high-surface area and cost-effective solid supports are important features, but the main problem when using MNPs is the unwanted aggregation of tiny magnetic particles. This problem has been mitigated by grafting catalyst species onto presynthesized MNPs, as well as by the functionalization and modification of MNPs with suitable ligands, and coating or encapsulating with stabilizing materials such as silica, polymers, ionic liquids, and carbon. The application of magnetically supported catalysts may affect most types of organic reactions such as cyclo-addition, oxidation, reduction, and coupling, including their asymmetric equivalents. Major progress has been made in the synthesis and application of magnetically recoverable chiral catalysts, as well as their applications in asymmetric organic synthesis, but maintaining their persistent activity, selectivity, and asymmetric induction over a period of time is challenging due to the leaching or poisoning of the catalysts in the reaction conditions. Thus, the development of new magnetic materials, their functionalization, and the immobilization of asymmetric catalysts demand further research to overcome these problems. The particle size, size distributions, and coherent functionalization are the most important features because of their important roles in the activity and strength of catalysts. In addition, there should be an emphasis on bringing these magnetic materials closer to industrial applications by employing them in multikilogram-scale processes in a cost-effective manner. Finally, the use of magnetic nanocatalysts in continuous flow synthesis needs to be exploited. The automated recycling of magnetic nanocatalysts needs to be studied to demonstrate their usefulness as supports for use in parallel and high-throughput synthesis.

Author details

Seyed Mohsen Sadeghzadeh[1*] and Mehdi Mogharabi[2,3]

*Address all correspondence to: sadeghzadeh_sm@yahoo.com

1 Department of Chemistry, College of Sciences, Sina Masihabadi Student Research, Neishabour, Iran

2 Department of Pharmaceutical Biotechnology, Faculty of Pharmacy and Biotechnology Research Center, Tehran University of Medical Sciences, Tehran, Iran

3 Pharmaceutical Sciences Research Center, Tehran University of Medical Sciences, Tehran, Iran

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