

Imidazole Functionalized Magnetic Fe₃O₄ Nanoparticles a Highly Efficient and Reusable Brønsted Acid Catalyst for the Regioselective Thiocyanation of Aromatic and Heteroaromatic Compounds at Room Temperature in Water:Ethanol

E. Rezaee Nezhad*, S. Karimian, and S. Sajjadifar

Department of Chemistry, Payame Noor University, PB BOX 19395-4697 Tehran, Islamic Republic of Iran

Received: 27 December 2014 / Revised: 30 February 2015 / Accepted: 12 July 2015

Abstract

The Magnetically recoverable Fe₃O₄ nanoparticle and the supported brønsted acidic ionic liquid 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium hydrogen sulfate (Fe₃O₄-IL-HSO₄) were synthesized and used as efficient magnetic catalysts for the regioselective thiocyanation of aromatic and heteroaromatic compounds at room temperature in Water: Ethanol. This procedure provided the target thiocyanates after short reaction times in good to excellent yields and high regioselectivity. The catalyst can be readily isolated by using an external magnet and no obvious loss of activity was observed when the catalyst was reused in seven consecutive runs. The mean size and the surface morphology of the nanoparticles were characterized by TEM, SEM, VSM, XRD and FTIR techniques.

Keywords: Magnetic nanoparticles; Ionic liquid; Thiocyanation; Regioselective; Room temperature.

Introduction

In the past decade, magnetic nanoparticles have been attracting increasing materials attention among the academic and industrial scientific, because of their high surface area, unique magnetic properties, have a broad range of potential uses in biomedical and high catalytic activity [1-3]. Moreover, they have a wide range of novel applications in various fields; such as magnetic fluids [4] catalysis [5,6] biology and medical applications [7] magnetic resonance imaging (MRI) [8, 9] data storage,[10] and environmental remediation

[11,12]. Therefore, catalytic systems developed on MNPs aids have been successfully used in catalyzing a wide range of organic reactions including knoevenagel reaction [13], nucleophilic substitution reactions of benzyl halides [14], epoxidation of alkenes [15], synthesis of α -amino nitriles [16], hydrogenation of alkynes [17], esterifications [18], CO₂ cycloaddition reactions [19], Suzuki coupling reactions [20], azidolysis of epoxides [21] and three-component condensation [22]. Organosulfur compounds are very important in organic chemistry. Among these compounds, thiocyanates play an basic role in organic

* Corresponding author: Tel: +988432228316; Fax: +988432221053; Email: e.rezaee66@yahoo.com

synthesis [23] also particularly useful for producing drugs and pharmaceuticals [24]. Thiocyanate is a versatile synthon [23], which can be readily become to other functional groups such as sulfide [25], aryl nitrile [26], thio-carbamate [27], and thionitrile [28]. Many methods have been used for thiocyanation of aromatic and heteroaromatic compounds such as bromine/potassium thiocyanate [29], N-thiocyanatosuccinimide [30], ceric ammonium nitrate (CAN) [31], acidic montmorillonite K10 clay [32], I₂/MeOH [24], Oxone [33], pentavalent iodine [34], IBX [35], potassium peroxydisulfate /copper (II) sulfate [36], H₂O₂, HCl [37], BSA/H₂O₂ [38], Mn(OAc)₃ [39], [2(Sulfooxy)ethyl] sulfamic Acid/H₂O₂ [40], BAIL, H₂O₂ [41] which have been used to the thiocyanation of aromatic and heteroaromatic compounds. However, the methods used suffer from one or more drawbacks such as difficult working conditions, low yields and long reaction time. Hence, a requirement for developing superseded synthesis routines accessible to the thiocyanation of aromatic and heteroaromatic compounds is in high demand. In this work, we describe an efficient protocol for the selective thiocyanation of aromatic and heteroaromatic using Fe₃O₄-IL-HSO₄ and thiocyanation agent. This method has some advantages including the use of an inexpensive and reusable ionic liquid, easy handling, short reaction times, high yield, and simplicity of the product isolation.

Materials and Methods

General

FeCl₂.4H₂O (99%), FeCl₃.6H₂O (98%), aromatic aldehyde and other chemical materials were purchased from Fluka and Merck and were used without further purification. Products were characterized by comparison of their physical data, IR and ¹H NMR and ¹³C NMR spectra with known samples. NMR spectra were recorded in DMSO on a Bruker Advance DPX 400 MHz instrument spectrometer using TMS as an internal standard. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates. IR spectra of the compounds were obtained on a PerkinElmer spectrometer version 10.03.06 using a KBr disk. The particle morphology was examined by SEM and TEM.

Preparation of Fe₃O₄-IL-HSO₄

The magnetite nanoparticles were prepared by the conventional co-precipitation method [42]. A schematic representation of the synthesis of magnetic nanoparticles supporting ionic liquids is shown in Scheme 1. Then, 1-methyl-3-(3-trimethoxysilylpropyl)

imidazolium chloride (IL), was prepared from the reaction of imidazole with (3-chloropropyl)trimethoxysilane was heated at 120 °C for 8 h with continuous stirring under N₂ atmosphere [43]. Then an excess amount of KHSO₄ were added into deionized water and stirred for 24 h at room temperature. KCl, which was prepared during the exchange of chloride anions with HSO₄ [44] and MNP-IL-HSO₄ was separated by magnetic decantation, washed with acetonitrile and dichloromethane, and left to dry in a desiccator.

General Procedure for Preparation of Thiocyanation Reaction

A suspension of indole (0.117 g, 1mmol), potassium thiocyanate (0.294 g, 3mmol), and catalyst (20 mg) in Water:Ethanol (1:4, 2 mL) was stirred at room temperature for 5min. Then, H₂O₂(30%) (3mmol) was added dropwise (2–5min) Scheme 2. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was extracted with CHCl₃(2 ×25mL). Anhydrous Na₂SO₄(3 g) was added to the organic layer and filtered off after 20min. CHCl₃ was removed. The yield was 0.159 g, (91%), m.p 71–73 °C. FT-IR (KBr): 2159, 3289, ¹H-NMR (FT-300MHz, CDCl₃/TMS): δppm 8.87 (br s, 1H, NH), 7.83 (1H, d, J = 8.8Hz), 7.46–7.23 (4H, m). ¹³CNMR(75MHz, CDCl₃): 136.06, 131.22, 127.66, 123.83, 121.87, 118.65, 112.24, 91.76.

Results and Discussion

Characterization of Fe₃O₄-IL-HSO₄ preparation and its structural and morphological analysis

Immobilization of Si-Im-HSO₄ functionalized MNPs combines the advantages of ionic liquids with those of heterogeneous catalysts. Fourier transform infrared (FT-IR) spectra were recorded on a FT-IR spectrometer (Perkin Elmer) with a spectral resolution of 4 cm⁻¹ in the wave number range of 450–4000 cm⁻¹. KBr pellets were used for solid samples. The magnetic properties were assessed with a vibrating sample magnetometer (VSM) (RIKEN DENSHI Co. Ltd., Japan). The magnetic properties of the particles were evaluated in terms of saturation magnetization and coactivity. Scanning electronic microscopy (SEM), the morphology of the surface of Si-Im-HSO₄ functionalized MNPs was investigated using a scanning electronic microscope of XL30 type (Netherland).

Fig. 1 presents the FTIR spectra of MNPs, IL and Fe₃O₄-IL-HSO₄. Comparing with the spectra of MNPs without modifiers (curve a), spectrum of Fe₃O₄-IL-HSO₄ (curve c) presented a new peak at 1090 cm⁻¹ and

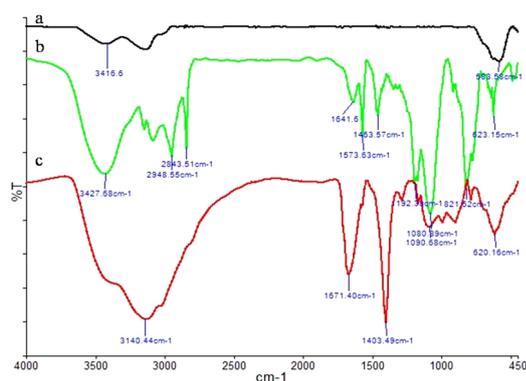


Figure 1. FT-IR spectra of (a) MNP, (b) IL, (c) Fe₃O₄-IL-HSO₄

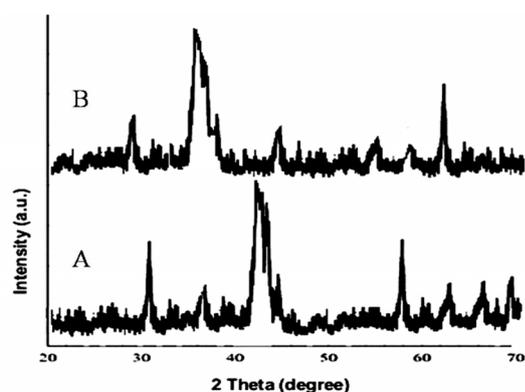


Figure 2. XRD pattern of (A) MNPs, (B) Fe₃O₄-IL-HSO₄

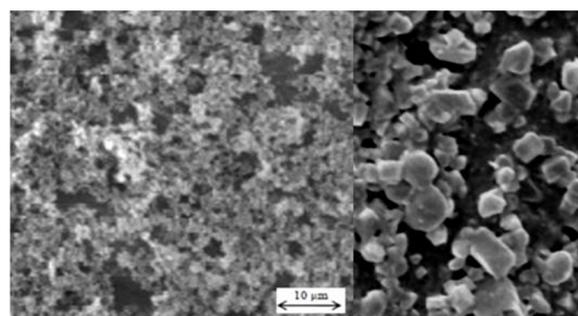
appeared to indicate the Si-O band on the Fe₃O₄. The peak wave numbers 2948 and 2843 cm⁻¹ are the stretching vibrations of CH₃ and CH₂ and the peaks at 1403 and 1287 cm⁻¹ are their bending vibrations in ionic liquid. Accordingly, one can be sure that IL has been immobilized successfully on the surface of MNPs.

The X-ray diffraction patterns of Fe₃O₄-IL-HSO₄, is shown in Fig. 2. Peaks of MNPs-IL ($2\theta = 30, 36, 37, 38, 39, 46, 55, 58$) and iron oxide phase ($2\theta = 33, 41, 63, 68$) confirms the structure of the catalyst.

The structural and morphological characterization of Fe₃O₄ and Fe₃O₄-IL-HSO₄ nanostructure were performed by measuring SEM using a Philips XL30 scanning electron microscope. The surface morphologies of the Fe₃O₄ nanoparticles without modifiers and Fe₃O₄-IL-HSO₄ were shown in Figs. 3A and 3B.

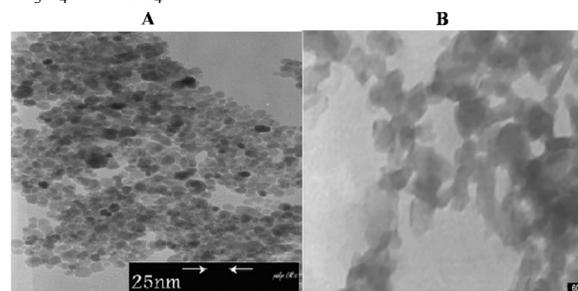
The TEM images of MNPs and Fe₃O₄-IL-HSO₄ are presented in Fig. 4, showing almost homogeneous and uniform distribution of these particles in the powder samples.

Figure 5 shows the magnetization curves of prepared



A **B**

Figure 3. SEM images of (A) Fe₃O₄ nanoparticles, (B) Fe₃O₄-IL-HSO₄



A **B**

Figure 4. TEM images of (A) MNPs, (B) Fe₃O₄-IL-HSO₄

MNPs, and Fe₃O₄-IL-HSO₄. The magnetization curve of MNPs exhibited no emanence effect (indicating the superparamagnetic property) with saturation magnetization of about 60emu/g.

Application of Fe₃O₄-IL-HSO₄ as magnetic catalyst for the regioselective thiocyanation of aromatic and heteroaromatic compounds in Water: Ethanol

To obtain suitable conditions for the reaction, we tried the thiocyanation was check at different conditions. In the absence of Fe₃O₄-IL-HSO₄, reaction

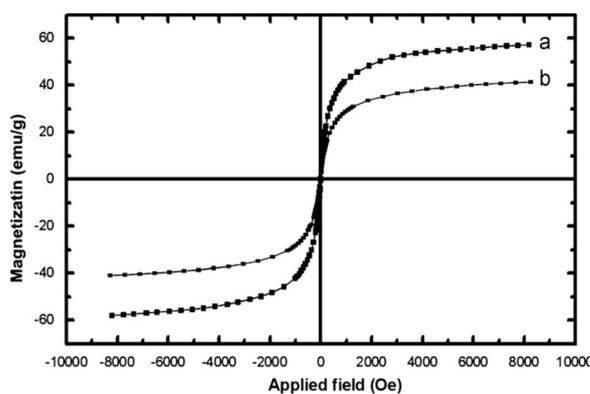
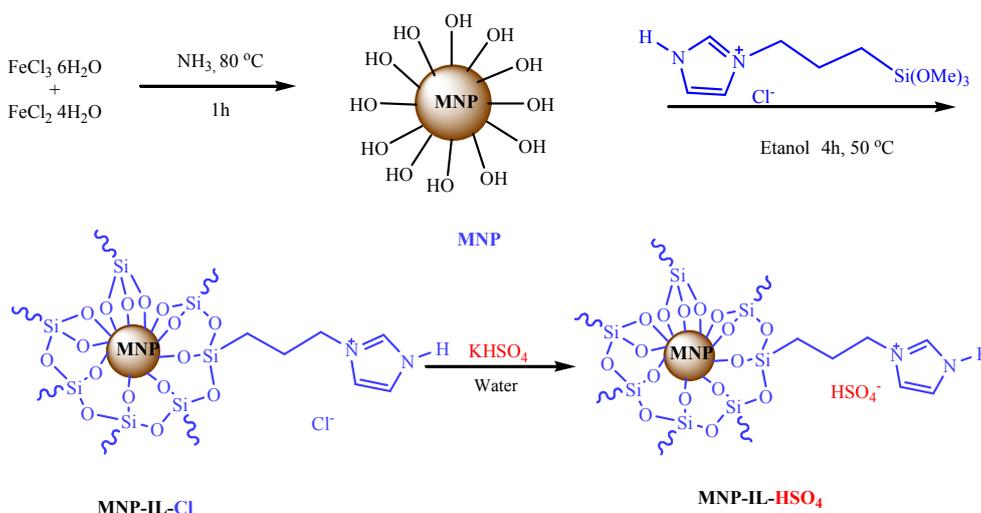


Figure 5. Magnetization curves of (a) MNPs and (b) Fe₃O₄-IL-HSO₄

Table 1. Optimization amounts of Fe₃O₄-IL-HSO₄, H₂O₂, and KSCN in Water: Ethanol (1:4, 2mL)

Entry	Fe ₃ O ₄ -IL-HSO ₄ (mg)	H ₂ O ₂ (mmol)	KSCN(mmol)	Time(min)	Yield %
1	-----	3	3	24(h)	-----
2	1	3	4	45	75
3	3	3	3	25	87
4	1	4	3	40	65
5	5	3	3	5	95
6	5	2	3	15	80
7	5	4	3	10	90
8	10	3	4	20	79
9	15	3	3	25	83
11	5	3	2	10(h)	45
12	5	-----	-----	24(h)	-----

**Scheme 1.** Synthesis of magnetic nanoparticles supported ionic liquid (MNP-IL)

was not accomplished (Table 1, Entry 1). For the synthesis of aryl thiocyanate, conversion of indole to thiocyanato indole in Water:Ethanol (1:4) and room temperature has been considered as a model reaction (Scheme 1).

In an initial experiment we examined the reaction of indole in Water:Ethanol in various values of H₂O₂ and KSCN (the results are shown in Table 1). According to the Table 1 is characterized that ratio of 1:3:3 (indole:H₂O₂:KSCN) was found to be the most suitable in presence of Fe₃O₄-IL-HSO₄ 5 mg. It should be noted that in the absence of catalyst when indole was reaction with hydrogen peroxide and KSCN, product was not observed. When the amount of catalyst was less than 5mg, the yield of product was reduced. Otherwise, increasing the catalyst loading from 5 to mg does not significantly change the yield. Also to select a suitable solvent, we tested various solvents such as H₂O, EtOH, MeOH, CH₃CN, CH₂Cl₂, THF, and AcOEt (the results are shown in Table 2). Both the yields and the reaction times were shown in Table 2. It is characterized

Table 2. Optimization of solvent in presence of Fe₃O₄-IL-HSO₄ (5 mg) for synthesis of 3-thiocyanato-1H-indole

Entry	solvent	Time (min)	Yield %
1	H ₂ O (5mL)	3(h)	57
2	Ethanol (5mL)	35	68
3	Water: Ethanol (1 : 1, 5mL)	50	59
4	Water: Ethanol (1 : 1, 10mL)	55	70
5	Water: Ethanol (1 : 2, 5mL)	45	78
6	Water: Ethanol (1 : 3, 5mL)	45	83
7	Water: Ethanol (1 : 4, 5mL)	35	85
8	Water: Ethanol (1 : 4, 2mL)	5	95
9	Water: Ethanol (1 : 5, 5mL)	45	89
10	Water: Ethanol (1 : 10, 5mL)	45	84
11	Water: Ethanol (2:1, 5mL)	40	80
12	Water: Ethanol (5:1, 5mL)	90	83
13	Water: Ethanol (2:3, 5mL)	55	68
14	MeCN	3(h)	68
15	MeOH	90	80
16	CH ₂ Cl ₂	2(h)	50
17	THF	3(h)	65
18	AcOEt	3(h)	59

that Water:Ethanol (1:4, 2mL) the best solvent for the thiocyanation in presence of Fe₃O₄-IL-HSO₄ (In this section, 5 mg Fe₃O₄-IL-HSO₄ was used). We identified that Water:Ethanol (1:4) was the best and most suitable solvent for the thiocyanation of aromatic and heteroaromatic compounds in the presence of Fe₃O₄-IL-

HSO₄.

After obtaining the optimal conditions for thiocyanation, we carried out the reaction with various aromatic and heteroaromatic compounds under the optimized conditions (the results are shown in Table 3). Most compounds used reacted under these conditions

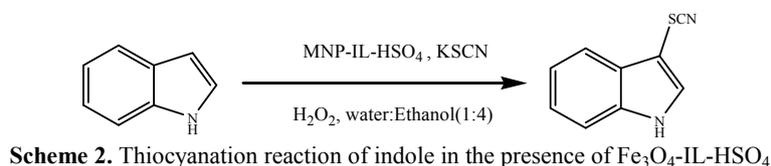


Table 3. Substrate scope in the thiocyanation reaction of arenes using KSCN/ Fe₃O₄-IL-HSO₄/H₂O₂ under room temperature

Entry	Substrate	Product	Time (min)	Yield (%)
1			5	95
2			25	97
3			10	96
4			15	88
5			20	98
6			2	98
7			8	98
8			2(h)	75
9			90	91
10			2(h)	96
11			85	92
12				
13				
14				
15				
16				
17				

Table 4. Comparison of catalytic ability of catalysts

Entry	System	Time (min)	Yield % [ref.]
1	Fe ₃ O ₄ -IL-HSO ₄ /Water: Ethanol	5	95 [This work]
2	I ₂ /MeOH	50	85[24]
3	K10clay/MeOH,80°C	2(h)	85[32]
4	Mn(OAc) ₃ /HOAc	2 (h)	83[39]
5	DDQ/MeOH	50	94[45]
6	DEAD/MeCN	45	85[46]
7	Citric acid/H ₂ O ₂ /H ₂ O	20	91[47]

Table 5. The catalytic activity of Fe₃O₄-IL-HSO₄ in 7 cycles.

Run	1	2	3	4	5	6	7
Yield (%)	95	93	93	90	91	88	86

and this reaction provided good-to-excellent yields with all the substrates tested.

The reaction was moderate and good for indoles and N,N-disubstituted anilines. According to the table 3, indole and electron-rich indoles gave the desired products in excellent yields (Table 3, Entries 1–3). Also, electron-poor indoles such as 5-bromoindole produces 5-bromo-3-thiocyanatoindoles with good yields but required longer reaction times (Table 3, Entry 5). According to Table 3 Is characterized that compounds containing electron donor groups is high speed and high yield. The thiocyanation reaction for ring indoles and N,N-disubstituted anilines, SCN group placed with highly regioselective in 3 position in indoles and para-position in N,N-disubstituted anilines.

After study thiocyanation reaction for the heteroaromatic compounds we also examined the capability of aromatic amines in the thiocyanation reaction. The samples reacted and produced corresponding arylthiocyanates in high yield (Table 3, Entries 6–11). However, compounds such as N,N,4-trimethylaniline, 1-phenylpiperazine, aniline, o-toluidine, and N,N,N-triphenylamine did not react with potassium thiocyanate and Fe₃O₄-IL-HSO₄/H₂O₂ and the product was not found (Table 3, Entries 12–16). As shown in Table 3, the substitution was highly regioselective, occurring at the para-position of the aromatics rings.

As it can be seen in Table 4, Fe₃O₄-IL-HSO₄ as a catalyst afforded good results in comparison to the other catalysts. In order to evaluate the efficiency of our introduced method, more recently developed methods were compared with our present method on the basis of the yields and reaction times parameters, the results are given in Table 4. The catalyst was consecutively reused seven times without any noticeable loss of its catalytic activity (Table 5).

Conclusion

A green methodology for the regioselective thiocyanation of aromatic and heteroaromatic compounds at room temperature in Water: Ethanol, using magnetically recoverable Fe₃O₄-IL-HSO₄. This method has advantages including the use of an inexpensive and reusable catalyst, short reaction times in comparison to the other procedures, high yield and simplicity of the product isolation. In this way, the catalyst can be easily recovered by simple magnetic decantation and reused several times with no loss of activity.

Acknowledgement

The authors gratefully acknowledge partial support of this work by Ilam Payame Noor University, I.R. of Iran.

References

- Senapati K. K., Roy S., Borgohain C., Phukan P., Palladium nanoparticle supported on cobalt ferrite: An efficient magnetically separable catalyst for ligand free Suzuki coupling. *J. Mol. Catal. A: Chem.* **352**: 128-134 (2012).
- Schladt T. D., Schneider K., Schild H., Tremel W., Synthesis and bio-functionalization of magnetic nanoparticles for medical diagnosis and treatment. *Dalton Trans.* **40**: 6315-6343 (2011).
- Sheykhan M., Ma'mani L., Ebrahimi A., Heydari A., Sulfamic acid heterogenized on hydroxyapatite-encapsulated γ -Fe₂O₃ nanoparticles as a magnetic green interphase catalyst. *J. Mol. Catal. A: Chem.* **335**: 253-261 (2011).
- Chikazumi S., Taketomi S., Ukita M., Mizukami M., Miyajima H., Setogawa M., Kurihara Y., Physics of magnetic fluids. *J. Magn. Magn. Mater.* **65**: 245-251 (1987).
- Lu A. H., Schmidt W., Matoussevitch N., Bpnnermann H., Spliethoff B., Tesche B., Bill E., Kiefer W., Schüth F., Nanoengineering of a Magnetically Separable

- Hydrogenation Catalyst. *Angew. Chem.* **116**: 4403-4406 (2004).
6. Tsang S. C., Caps V., Paraskevas I., Chadwick D., Thompsett D., Magnetically Separable, Carbon-Supported Nanocatalysts for the Manufacture of Fine Chemicals. *Angew. Chem.* **116**: 5763-5766 (2004).
 7. Gupta A. K., Gupta M., Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications. *Biomaterials* **26**: 3995-4021 (2005).
 8. Mornet S., Vasseur S., Grasset F., Verveka P., Goglio G., Demourgues A., Portier J., Pollert E., Duguet E., Magnetic nanoparticle design for medical applications. *Prog. Solid State Chem.* **34**: 237-247 (2006).
 9. Li Z., Wei L., Gao M. Y., Lei H., One-Pot Reaction to Synthesize Biocompatible Magnetite Nanoparticles. *Adv. Mater.* **17**: 1001-1005 (2005).
 10. Hyeon T., Chemical synthesis of magnetic nanoparticles. *Chem. Commun.*, 927-934 (2003).
 11. Elliott D. W., Zhang W. X., Field assessment of nanoscale bimetallic particles for groundwater treatment. *Environ. Sci. Technol.* **35**: 4922-4926 (2001).
 12. Takafuji M., Ide S., Ihara H., Xu Z., Preparation of Poly(1-vinylimidazole)-Grafted Magnetic Nanoparticles and Their Application for Removal of Metal Ions. *Chem. Mater.* **16**: 1977-1983 (2004).
 13. Karaoğlu E., Baykal A., Şenel M., Sözeri H., Toprak M. S., Synthesis and characterization of Piperidine-4-carboxylic acid functionalized Fe₃O₄ nanoparticles as a magnetic catalyst for Knoevenagel reaction. *Mater. Res. Bull.* **47**: 2480-2486 (2012).
 14. Kiasat A. R., Nazari S., Magnetic nanoparticles grafted with β-cyclodextrin-polyurethane polymer as a novel nanomagnetic polymer brush catalyst for nucleophilic substitution reactions of benzyl halides in water. *J. Mol. Catal. A: Chem.* **365**: 80-86 (2012).
 15. Kooti M., Afshari M., Phosphotungstic acid supported on magnetic nanoparticles as an efficient reusable catalyst for epoxidation of alkenes. *Mater. Res. Bull.* **47**: 3473-3478 (2012).
 16. Kassae M. Z., Masrouri H., Movahedi F., Sulfamic acid-functionalized magnetic Fe₃O₄ nanoparticles as an efficient and reusable catalyst for one-pot synthesis of α-amino nitriles in water. *Appl. Catal. A: General.* **395**: 28-33 (2011).
 17. Abu-Reziq R., Wang D., Post M., Alper H., Platinum Nanoparticles Supported on Ionic Liquid-Modified Magnetic Nanoparticles: Selective Hydrogenation Catalysts. *Adv. Synth. Catal.* **349**: 2145-2150 (2007).
 18. Jiang Y. Y., Guo C., Xia H. S., Mahmood I., Liu C. Z., Liu H. Z., Magnetic nanoparticles supported ionic liquids for lipase immobilization: Enzyme activity in catalyzing esterification. *J. Mol. Catal. B: Enzym.* **58**: 103-109 (2009).
 19. Zheng X. X., Luo S. Z., Zhang L., Cheng J. P., Magnetic nanoparticle supported ionic liquid catalysts for CO₂ cycloaddition reactions. *Green Chem.* **11**: 455-458 (2009).
 20. Taber A., Kim J. B., Jung J. Y., Ahn W. S., Jin M. J., Highly Active and Magnetically Recoverable Pd-NHC Catalyst Immobilized on Fe₃O₄ Nanoparticle-Ionic Liquid Matrix for Suzuki Reaction in Water. *Synlett.* **15**: 2477-2482 (2009).
 21. Sajjadifar S., Abbasi Z., Rezaee Nezhad E., Rahimi Moghadam M., Karimian S., Miri S., Ni²⁺ supported on hydroxyapatite-core-shell γ-Fe₂O₃ nanoparticles: a novel, highly efficient and reusable lewis acid catalyst for the regioselective azidolysis of epoxides in water. *J Iran Chem Soc.* **11**: 335-340 (2014).
 22. Rezaee Nezhad E., Abbasi Z., Rahimi Moghaddam M., Attaei M. A., Ni²⁺ supported on hydroxyapatite-core@shell γ-Fe₂O₃ nanoparticles as new and green catalyst for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones under solvent-free condition. *Iran. Chem. Commun.* **1**: 35-42 (2013).
 23. Guy R. G., Patai S., In The Chemistry of Cyanates and their Thio Derivatives, John Wiley and Sons: New York, (1977).
 24. Yadav J. S., Reddy B. V. S., Shubashree S., Sadashiv K., Iodine/MeOH: a novel and efficient reagent system for thiocyanation of aromatics and heteroaromatics. *Tetrahedron Lett.* **45**: 2951-2954 (2004).
 25. Billard T., Langlois B. R., Medebielle M., Tetrakis(dimethylamino)ethylene (TDAE) mediated addition of difluoromethyl anions to heteroaryl thiocyanates. A new simple access to heteroaryl-SCF₂R derivatives. *Tetrahedron Lett.* **42**: 3463-3465 (2001).
 26. Zhang Z. H., Liebeskind L. S., Palladium-Catalyzed, Copper(I)-Mediated Coupling of Boronic Acids and Benzylthiocyanate. A Cyanide-Free Cyanation of Boronic Acids. *Org. Lett.* **8**: 4331-4333 (2006).
 27. (a) Riemschneider R. J., Wojahn F., Orlick G., Thiocarbamates. III.1 Aryl Thiocarbamates from Aryl Thiocyanates. *J. Am. Chem. Soc.* **73**: 5905-5907 (1951). (b) J. Riemschneider R., Thiocarbamates and Related Compounds. X.1 A New Reaction of Thiocyanates. *Am. Chem. Soc.* **78**: 844-847 (1956).
 28. Lee Y. T., Choi S. Y., Chung Y. K., Microwave-assisted palladium-catalyzed regioselective cyanothiolation of alkynes with thiocyanates. *Tetrahedron Lett.* **48**: 5673-5677 (2007).
 29. Grant M. S., Snyder, Thiocyanation of Indole. Some Reactions of 3-Thiocyanoindeole. *J. Am. Chem. Soc.* **82**: 2742-2744 (1960).
 30. Toste F. D., Stefano V. D., Still I. W. J., A Versatile Procedure for the Preparation of Aryl Thiocyanates Using N-Thiocyanatosuccinimide (NTS). *Synth. Commun.* **25**: 1277-1286 (1995).
 31. Nair V., George T. G., Nair L. G., Panicker S. B., A direct synthesis of aryl thiocyanates using cerium(IV) ammonium nitrate. *Tetrahedron Lett.* **40**: 1195-1196 (1999).
 32. Chakrabarty M., Sarkar S., A clay-mediated eco-friendly thiocyanation of indoles and carbazoles. *Tetrahedron Lett.* **44**: 8131-8133 (2003).
 33. Wu G., Liu Q., Shen Y., Wu W., Wu L., Regioselective thiocyanation of aromatic and heteroaromatic compounds using ammonium thiocyanate and oxone. *Tetrahedron Lett.* **46**: 5831-5834 (2005).
 34. Chaudhari K. H., Mahajan U. S., Bhalerao D. S., Akamanchi K. G., Novel and Facile Transformation of N,N-Disubstituted Glycylamides into Corresponding Cyanamides by Using Pentavalent Iodine Reagents in Combination with Tetraethylammonium Bromide. *Synlett*

- 18: 2815-2818 (2007).
35. Yadav J. S., Reddy B. V. S. Krishna B. B. M., IBX: A Novel and Versatile Oxidant for Electrophilic Thiocyanation of Indoles, Pyrrole and Arylamines. *Synthesis* **23**: 3779-3782 (2008).
36. Kumar A., Ahmad P. Maurya R. A., Direct α -thiocyanation of carbonyl and β -dicarbonyl compounds using potassium peroxydisulfate-copper(II). *Tetrahedron Lett.* **48**: 1399-1401 (2007).
37. Khazaei A., Zolfigol M. A., Mokhlesi M., Derakhshan Panah F., Sajjadifar S., Simple and Highly Efficient Catalytic Thiocyanation of Aromatic Compounds in Aqueous Media. *Helv. Chim. Acta.* **95**: 106-114 (2012).
38. Sajjadifar S., Louie O., Regioselective Thiocyanation of Aromatic and Heteroaromatic Compounds by Using Boron Sulfonic Acid as a New, Efficient, and Cheap Catalyst in Water. *J. Chem.* (2013) 674946.
39. Wu G., Liu Q., Shen Y., Wu W., Wu L., Mn(OAc)₃-promoted regioselective free radical thiocyanation of indoles and anilines. *Tetrahedron Lett.* **50**: 347-349 (2009).
40. Sajjadifar S., Karimian S., Noorzadeh H., Veisi H., Regioselective Thiocyanation of Aromatic and Heteroaromatic Compounds Using [2-(Sulfoxy)ethyl]sulfamic Acid as an Efficient, Recyclable Organocatalyst and Novel Difunctional Brønsted Acid. *J. Catal.* 1-7 (2013).
41. Sajjadifar S., Hosseinzadeh H., Ahmadaghae S., Rezaee Nezhad E., Karimian S., 1-Methyl-3-(2-(Sulfoxy)Ethyl)-1Himidazol-3-Ium Thiocyanate as A Novel, Green, and Efficient Brønsted Acidic Ionic Liquid-Promoted Regioselective Thiocyanation of Aromatic and Heteroaromatic Compounds at Room Temperature. *Phosphorus, Sulfur Silicon Relat. Elem.* **189**: 333-342 (2014).
42. Liu X.Q., Ma Z. Y., Xing J. M., Liu H. Z., Preparation and characterization of amino-silane modified superparamagnetic silica nanospheres. *J. Magn. Magn. Mater.* **270**: 1-6 (2004).
43. Nazari S., Saadat Sh., Kazemian Fard P., Gotjizadeh M., Rezaee Nezhad E., Afshari M., Imidazole functionalized magnetic Fe₃O₄ nanoparticles as a novel heterogeneous and efficient catalyst for synthesis of dihydropyrimidinones by Biginelli reaction. *Monatsh Chem.* **144**: 1877-1882 (2013).
44. Safari J., Zarnegar Z., Brønsted acidic ionic liquid based magnetic nanoparticles: a new promoter for the Biginelli synthesis of 3,4-dihydropyrimidin-2(1H)-ones/thiones. *New J. Chem.* **38**: 358-365 (2014).
45. Zolfigol M. A., Khazaei A., Mokhlesi M., Vahedi H., Sajadifar S., Pirveysian M., Heterogeneous and Catalytic Thiocyanation of Aromatic Compounds in Aqueous Media. *Phosphorus, Sulfur Silicon Relat. Elem.* **187**: 295-306 (2012).
46. Iranpoor N., Firouzabadi H., Khalili D., Shahin R., A new application for diethyl azodicarboxylate: efficient and regioselective thiocyanation of aromatics amines. *Tetrahedron Lett.* **51**: 3508-3510 (2010).
- Khazaei A., Zolfigol M. A., Mokhlesi M., Pirveysian M., Citric acid as a trifunctional organocatalyst for thiocyanation of aromatic and heteroaromatic compounds in aqueous media. *Canad. J. Chem.* **90**: 427-432 (2012).