

Imidazol-1-yl-acetic Acid as a Green Simple Bifunctional Organocatalyst for the Regioselective Conversion of Epoxides to 1,2-azido Alcohols and β -hydroxythiocyanates

Simin Nazari^{a*}, Nasir Iravani^b, Amanollah Zarei Ahmady^c, Masoumeh Vafae-nezhad^b and Mosadegh Keshavarz^{d*}

^aDepartment of Chemistry, Sousangerd Branch, Islamic Azad University, Sousangerd 44181-6189, Iran; ^bDepartment of Chemistry, Gachsaran Branch, Islamic Azad University, Gachsaran, Iran; ^cNanotechnology Research Center, Faculty of Pharmacy, Jundishapur University of Medical Sciences, Ahvaz, Iran; ^dDepartment of Gas and Petroleum, Yasouj University, P.O. Box 353, Yasouj, 75918-74831 Iran

Abstract: Imidazol-1-yl-acetic acid is introduced as a new, efficient and recyclable green bifunctional organocatalyst for the synthesis of β -hydroxythiocyanate and 1,2-azido alcohols under mild conditions. This catalyst can be recovered by simple filtration and recycled up to 8 consecutive runs without losing any of its efficiency. Various advantages associated with this protocol include simple workup procedure, short reaction times, high product yields, greater regioselectivity.

Keyword: Imidazol-1-yl-acetic acid, epoxide, ring opening, bifunctional organocatalyst, sodium azide, sodium thiocyanate, green chemistry, nucleophile, electrophile, regioselective.

1. INTRODUCTION

The future challenges in resources, environmental and economical sustainability need the development of more efficient and atom economic technologies in chemical reactions. Green chemistry principles focus on minimizing the hazards and maximizing the efficiency of any chemical choice [1]. They have attracted an enormous interest over the past decade. One of the most promising approach uses water as a reaction medium. Water is an abundant, cheap and non-toxic solvent [2]. In addition, Organocatalysis, which involves the use of small organic molecules to catalyze organic reactions, is another step forward towards developing the green chemical synthesis. Organocatalytic reactions are becoming dominant tools for the production of complex molecular skeletons [3]. In contrast to the conventional catalysts, these organic catalysts are easily available, more stable to air and water, easy to handle, less toxic, and can promote an organic reaction by several activation modes. Epoxides are among the most valuable synthetic intermediates on the way to the synthesis of many biologically active compounds. Their electrophilic reactions with different nucleophiles have been an interesting subject in organic synthesis [4, 5]. Literature review shows that NH_4SCN /Zeolite Molecular Sieve 4 Å [6], $\text{Al}(\text{HSO}_4)_3$ /silica gel [7], PEG- SO_3H [8], Dowex-50X8 [9], $\text{B}(\text{HSO}_4)_3$ [10], silica sulfuric acid [11], GaCl_3 [12], thioxanthenone-fusedazacrown ethers [13], $\text{HN}_3/\text{Co}(\text{salen})$ [14], 2,6-bis[2-(*o*-aminophenoxy)methyl]-4-bromo-1-methoxybenzene (BABMB) [15], selectfluor [16], metallopor-

phyrins [17], dichloro(5,10,15,20-tetraphenylporphyrin) phosphorus (V) chloride [$\text{P}(\text{TPP})\text{Cl}_2$] Cl [18], tetraarylporphyrins [19], 2-phenyl-2-(2-pyridyl)imidazolidine (PPI) [20], HSCN [21], DDQ [22], $\text{Ti}(\text{O}-i\text{Pr})_4$ [23], are the reagents which efficiently produce β -hydroxythiocyanate.

1,2-Azido alcohols are essential intermediates in the synthesis of amino sugar [24], carboxylic nucleosides [25], lactams [26], oxazolines [27], and aminoalcohols [28]. These compounds are prepared through the ring opening of epoxides by using different azides in suitable solvents. The reagents for azidohydrin synthesis are the combined use of NaN_3 or TMSN_3 and a Lewis acid or a chiral catalyst zirconium alkoxides linked with chiral trialkanolamines [29]. Application of polymer-supported azide anion [30], NaN_3 supported on porous solid supports (zeolite, alumina, and silica gel) has also been reported for this purpose [31]. Moreover azidolysis of epoxides was also studied in water by Polyethylene glycol immobilized on silica gel [32] and B-Podands [33]. Unfortunately, some of these methods are not always fully satisfactory and suffer from disadvantages such as these methods require hazardous or toxic reagents high reaction temperature or relative long reaction times, difficulty in preparation and/or storage of reagents or catalysts, difficulty in work-up and isolation of products or low regioselectivity. Consequently, it seems that there is still a need for development of newer methods that proceed under mild and economically appropriate conditions. This paper aims to introduce imidazol-1-yl-acetic acid as an efficient, green, water-soluble and simply recoverable bifunctional organocatalyst for the preparation of 1,2-azido alcohols and β -hydroxythiocyanate by regioselective ring opening of epoxides with sodium azide and ammonium thiocyanate under mild conditions.

*Address correspondence to these authors at the Department of Chemistry, Sousangerd Branch, Islamic Azad University, Sousangerd 44181-6189, Iran and Department of Gas and Petroleum, Yasouj University, P.O. Box 353, Yasouj, 75918-74831 Iran; Tel: 986113361969; Fax: 986113738382; E-mails: Siminnazari@yahoo.com; chem.mosadegh@gmail.com

2. MATERIALS AND METHODS

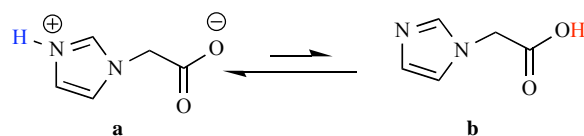
All of the products were prepared by our procedure; their spectroscopic and physical data were compared with those of authentic samples. NMR spectra were recorded in CDCl₃ on Bruker-AC 400 MHz instrument spectrometers using TMS as internal standard. IR spectra were recorded on a BOMEMMB-Series 1998 FT-IR spectrometer. Chemicals were purchased from Fluka, Merck and Aldrich Chemical companies. Yields refer to isolated pure products.

2.1. General Procedure

Imidazol-1-yl-acetic acid (0.037 g, 30mol%) was added to a mixture of epoxide (1 mmol) and NH₄SCN or NaN₃ (2 mmol) in water (10 mL). The mixture was heated under reflux condition. Progress of the reaction was monitored by TLC using CCl₄-ether (5:1). After completion of reaction, the mixture was cooled to room temperature and the product was extracted with ether (3 × 10 mL). The solvent was dried with MgCl₂ and evaporated under reduced pressure. The desired thiocyanohydrins or 1,2-azido alcohols were obtained in good to excellent isolated yields (82-88%). Evaporation of the aqueous phase gave the recovered catalyst which purified by recrystallization in cool methanol (30 mL), dried at 50 °C and reused in the next consecutive runs.

3. RESULT AND DISCUSSION

Organocatalysts are small organic molecules and their success in the reaction catalysis could most possibly be attributed to their bifunctionality, bearing a Lewis/Bronsted acidic moiety for the activation of electrophiles, and a Lewis/Bronsted basic moiety for the activation of nucleophiles. Imidazol-1-yl-acetic acid is an example of bifunctional organocatalysts. This amino acid has two forms: neutral and ionized form. It is almost always in ionized form (Scheme 1a), unless in the gaseous state or in an aprotic solvent (Scheme 1b).



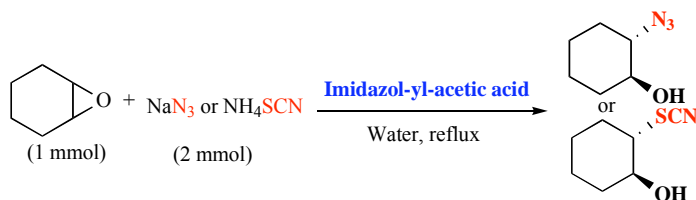
Scheme 1. The two forms of imidazol-1-yl-acetic acid.

This molecule contains both acidic and basic functionalities. Such functionalities make this molecule to be an ideal bifunctional organocatalyst for condensation reactions and nucleophile-electrophile interactions. In fact the bifunctional catalytic activities of imidazol-1-yl-acetic acid arise from its ionized form (Scheme 1a). Recently we have investigated the catalytic activity of this simple and interesting bifunctional organocatalyst for the preparation of 1,8-dioxooctahydroxanthenes [34]. Herein, we wish to report the catalytic activity of the title catalyst in the ring opening of the epoxides by using ammonium thiocyanate and sodium azide as nucleophiles.

To evaluate the catalytic activity, various amounts of imidazol-1-yl-acetic acid were examined for the nucleophilic ring opening of cyclohexene oxide by NaN₃ and NH₄SCN in water as model reactions. The reactions were performed under reflux condition with 2/1 molar ratios of NaN₃ or NH₄SCN and cyclohexene oxide. The results are summarized in (Table 1).

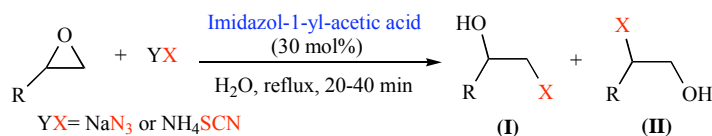
As shown in (Table 1), in the absence of the catalyst, trace amounts of the desired products were obtained after 4 h (Table 1, entry 1). However, in the presence of imidazol-1-yl-acetic acid (0.1 mmol per 1 mmol of cyclohexene oxide), the desired products were afforded at tolerable times in moderate yields (Table 1, entry 2). By increasing the molar ratio of the catalyst and cyclohexene oxide to 0.3:1, a significant improvement in the yield of the products was observed and the reaction times were considerably decreased (Table 1, entry 4). An increase in the catalyst loading had no distinguished effect on the reaction rates as well as the yields (Table 1, entry 5). According to the obtained results, the opti-

Table 1. Influence of the amount of imidazol-1-yl-acetic acid catalyst on the rate and yield of the ring opening of cyclohexene oxide by azide and thiocyanate.



Entry	Catalyst (mol%)	NaN ₃		NH ₄ SCN	
		Time (min)	Yield (%) ^a	Time (min)	Yield (%) ^a
1	0	240	Trace	240	Trace
2	10	40 (did not complete)	70	60 (did not complete)	75
3	20	40 (completed)	85	60 (completed)	83
4	30	20 (completed)	87	20 (completed)	85
5	40	20 (completed)	89	20 (completed)	83

^aIsolated yield

Table 2. Ring opening of various epoxides with NaN_3 and NH_4SCN in the presence of imidazol-1-yl-acetic acid in water.

Entry	Substrate	NaN_3		NH_4SCN	
		Time (min)	Yield (%) ^a	Time (min)	Yield (%) ^a
1		20	87(I, II)	20	85 (I, II)
2		20	85 (I, II) ^b 96:4	20	88 (I, II) ^b 95:5
3		30	83 (I)	40	84 (I)
4		30	85 (I)	35	87 (I)
5		25	87 (I)	30	85 (I)
6		25	82 (I)	30	88 (I)

^aIsolated yield^bGC yield

mized molar ratio of the catalyst:epoxide was chosen to be 3:1.

To extend the scope of the reactions and to generalize the procedure, various epoxides were subjected to ring opening reaction in water catalyzed by imidazol-1-yl-acetic acid using NaN_3 and NH_4SCN as nucleophilic reagents under optimized reaction conditions. (Table 2) represents the ring opening of epoxides using NaN_3 and NH_4SCN as nucleophiles.

Epoxides bearing activated and deactivated groups were quickly and efficiently converted to the virtually pure azido-hydrin and β -hydroxythiocyanate products in high isolated yields. No evidence for the formation of diols or thiiranes as byproducts of the reactions was observed and the products were obtained in pure form without further purification. All the products were characterized and identified by comparison of their spectral data (IR, ^1H NMR and ^{13}C NMR) with those of authentic samples. After completion of the reaction (Table 2), the mixture was cooled and organic phase was extracted with diethyl ether. Evaporation of organic solvent gave the desired products. In order to recover the catalyst, the aqueous phase was evaporated to dryness and recrystallized from cool methanol. The obtained precipitate was filtered and dried at 50°C . The recovered catalyst was reused in the next consecutive similar runs (7 runs). No appreciable yield decrease was observed during reusing processes. Typically, the yield difference between the first and 8th runs of the ring opening of cyclohexene oxide with NaN_3 and

NH_4SCN are outlined in (Fig. 1). These observations indicate that the efficiency and catalytic activity of the introduced bifunctional organocatalyst is almost completely maintained over 8 runs.

Most probably, the catalytic activity of imidazol-1-yl-acetic acid in the ring opening of epoxides arises from its dual role. Since water has been used as green solvent, this simple bifunctional organocatalyst exists completely in its ionic form (Scheme 1a). During the reaction, the formation of hydrogen bonding between two acidic hydrogens of imidazolium part of the catalyst and oxygen from epoxide activates the substrate for the nucleophilic ring opening reaction. Moreover, and more importantly, the acetate anion part of imidazole-1-yl-acetic acid strongly attracts the counterions (Na^+ and NH_4^+) of nucleophiles (N_3^- and SCN^-) which makes these nucleophiles to be free and activated for the nucleophilic attack on the activated epoxides. The proposed mechanism for the ring opening of epoxides by NaN_3 catalyzed by using imidazole-1-yl-acetic acid is outlined in (Scheme 2).

(Table 3) represents the efficiency of the introduced method in comparison with some of the reported methodologies. The reaction times for the preparation of 1,2-azido alcohols by our procedure are shorter than reported methods. Although in some previous reports the rate of the reaction for the preparation of thiocyanohydrins is faster than the present method, the superiorities of this work are: the introduced catalyst is completely green, cheap, easy to handle and does

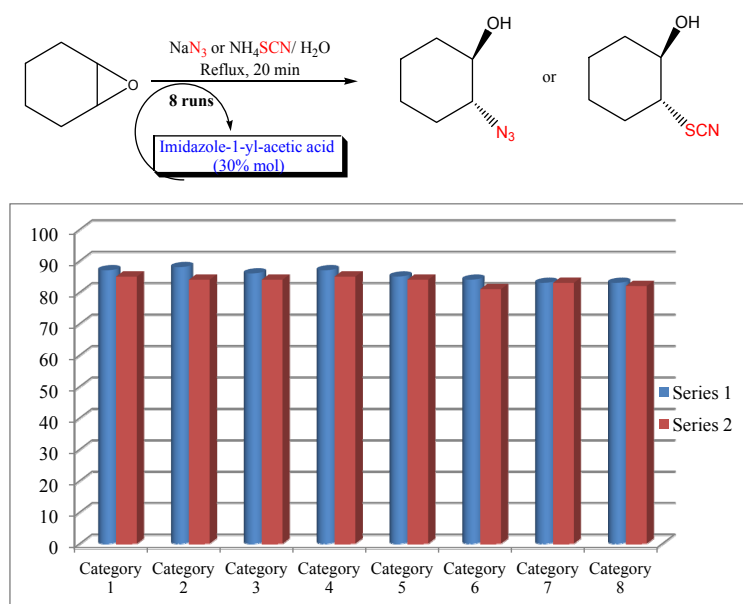
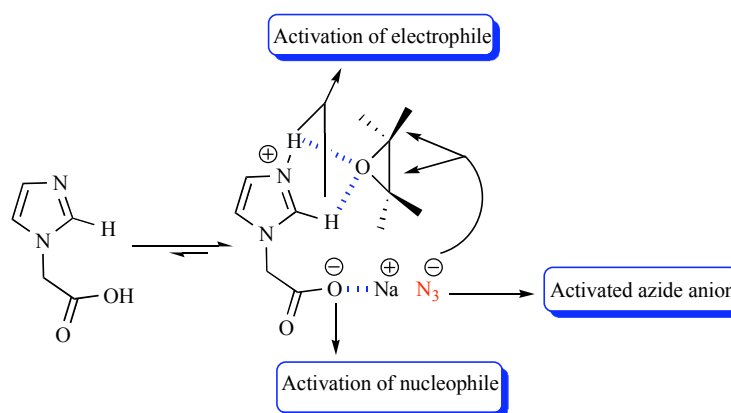


Fig. (1). Recyclability and reusability study of imidazol-1-yl-acetic acid as bifunctional organocatalyst for the ring opening of epoxides by NaN_3 (Series 1; cylindrical columns) and NH_4SCN (Series 2; cubic columns).



Scheme 2. Proposed mechanism for the ring opening of epoxides with NaN_3 catalyzed by imidazol-1-yl-acetic acid.

Table 3. Evaluation of the introduced methodology in comparison with some of the previously reported methods for the reaction of styrene oxide with thiocyanate and azideanions.

Entry	NaN_3				NH_4SCN			
	Reagent and Reaction Conditions	Time (min)	Yield (%)	[Ref.]	Reagent and Reaction Conditions	Time (min)	Yield (%)	[Ref.]
1	NaN_3 / Imidazol-1-yl-acetic/ H_2O /reflux	20	85 (96:4)	[a]	NH_4SCN /Imidazol-1-yl-acetic/ H_2O /reflux	20	88 (90:10)	[a]
2	NaN_3 /MPTC/ H_2O /90 °C	30	85	[35]	NH_4SCN /ZMS-4 solvent-free/rt	5	98	[6]
3	NaN_3 /PEG/60°C	90	85 (90:10)	[36]	NH_4SCN / $\text{Al}(\text{HSO}_4)_3$ /SiO ₂ / solvent-free/rt	5	96	[7]
4	NaN_3 /SiO ₂ -OPEG(300)/ H_2O / reflux	60	80 (95:5)	[32]	NH_4SCN /SiO ₂ /Silica sulfuric acid/ solvent-free/rt	5	70 (96:4)	[11]
5	Azide exchange resin/EtOH/50 °C	60	30	[37]	NH_4SCN /PEG-SO ₃ H/ H_2O /rt	60	84	[8b]

Table 3. Contd.....

Entry	NaN ₃				NH ₄ SCN			
	Reagent and Reaction Conditions	Time (min)	Yield (%)	[Ref.]	Reagent and Reaction Conditions	Time (min)	Yield (%)	[Ref.]
6	TMSN ₃ /β-CD/H ₂ O/60 °C	300	45	[38]	NH ₄ SCN /PEG-SO ₃ H/CH ₂ Cl ₂ /rt	60	83 (96:4)	[8a]
7	NaN ₃ /(TBA) ₄ PfEW11039.3H ₂ O/ CH ₃ CN-H ₂ O	270	85	[39]	NH ₄ SCN/SiO ₂ /Dowex-50WX8/ solvent-free/rt	6	89 (90:10)	[9]
8	HN ₃ /Co(salen)/TBME/0 °C	480	49.6	[14]	NH ₄ SCN/SiO ₂ /B(HSO ₄)/solvent-free/rt	4	91 (92:8)	[10]
9	NaN ₃ /CeCl ₃ / CH ₃ CN-H ₂ O/reflux	180	96	[40]	NH ₄ SCN/GaCl ₃ / H ₂ O/rt	18	92	[12]
10	NaN ₃ / DMSO/80 °C	180	99	[28]	NH ₄ SCN/[P(TPP)Cl ₂]Cl/CH ₃ CN/reflux/N ₂	22	96 (20:80)	[18]
11	NaN ₃ /PTC/ H ₂ O/rt	360	95	[41]	NH ₄ SCN /PPI/CH ₃ CN/reflux	45	95 (17:83)	[20]

[a] The present method.

not have any corrosion property. More importantly, its bifunctional activity can efficiently catalyze this ring opening reaction by simultaneous activation of both electrophilic and nucleophilic sites during the reaction progress.

4. CONCLUSION

In conclusion, imidazol-1-yl-acetic acid is introduced as a novel green bifunctional organocatalyst for the preparation of 1,2-azido alcohols and thiocyanohydrins from epoxides.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

We are thankful to the Research Council of Islamic Azad University, Sousangerd branch for financial support.

SUPPLEMENTARY MATERIAL

Supplementary material is available on the publishers Web site along with the published article.

REFERENCES

- Tu, N.P.; Hochlowski, J.E.; Djuric, S.W. Ultrasound-assisted click chemistry in continuous flow. *Mol. Divers.*, **2012**, *16*, 53-58.
- Hailes, H.C. The potential of water as a solvent for organic transformations. *Org. Process Res. Dev.*, **2007**, *11*, 114-120.
- Kirschning, A.; Monenschein, H.; Wittenberg, R. Functionalized polymers—emerging versatile tools for solution-phase chemistry and automated parallel synthesis. *Angew. Chem. Int. Ed.*, **2001**, *40*, 650-671.
- Iranpoor, N.; Kazemi, F.; Salehi, P. Highly region- and stereoselective synthesis of beta-halohydrins from epoxides catalyzed with ceric ammonium nitrate. *Synth. Commun.*, **1997**, *27*, 1247-1258.
- Salehi, P.; Khodaei, M.M.; Zolfigol, M.A.; Keyvan, A. Magnesium hydrogensulfate: A cheap and efficient catalyst for the conversion of epoxides into β-alkoxyalcohols, vicinal-diols, and thiranes. *Synth. Commun.*, **2003**, *33*, 3041-3048.
- Eisavi, R.; Zeynizadeh, B.; Baradarani, M.M. Fast, efficient and regioselective conversion of epoxides to β-hydroxythiocyanates with NH₄SCN/Zeolite molecular sieve 4 Å under solvent-free conditions. *Bull. Korean Chem. Soc.*, **2011**, *32*, 630-634.
- Kiasat, A.R.; Mouradzadegan, A.; Elahi, S.; Fallah, M.M. Al(HSO₄)₃/silica gel as a novel catalytic system for the ring opening of epoxides with thiocyanate anion under solvent-free conditions. *Chin. Chem. Lett.*, **2010**, *21*, 146-150.
- (a) Kiasat, A.R.; Fallah, M.M. PEG-SO₃H as soluble acidic polymeric catalyst for regioselective opening of epoxides: a high-efficient synthetic approach to β-hydroxythiocyanates. *Synth. Commun.*, **2008**, *38*, 2995-3002. (b) Kiasat, A.R.; Fallah, M.M. PEG-SO₃H as eco-friendly polymeric catalyst for regioselective ring opening of epoxides using thiocyanate anion in water: an efficient route to synthesis of β-hydroxythiocyanate. *Catal. Commun.*, **2008**, *9*, 1497-1500.
- Kiasat, A.R.; Fallah, M.M. Dowex as reusable acidic polymeric catalyst in the efficient and regioselective conversion of epoxides into β-hydroxythiocyanates under solvent free conditions. *J. Chin. Chem. Soc.*, **2008**, *55*, 1119-1124.
- Kiasat, A.R.; Fallah, M.M. B(HSO₄)₃: a novel and efficient solid acid catalyst for the regioselective conversion of epoxides to thiocyanohydrins under solvent-free conditions. *J. Braz. Chem. Soc.*, **2008**, *19*, 1595-1599.
- Kiasat, A.R.; Zayadi, M.; Fallah, M.M. Regioselective ring opening of epoxides using NH₄SCN/silica sulfuric acid: an efficient approach for the synthesis of β-hydroxythiocyanate under solvent-free conditions. *Chin. Chem. Lett.*, **2008**, *19*, 665-668.
- Chen, X.; Wu, H.; Xu, R.; Liu, M.; Ding, J.; Su, W. Gallium trichloride-promoted highly regioselective opening of epoxides with NH₄SCN and NaN₃ in water. *Synth. Commun.*, **2008**, *38*, 1855-1865.
- Sharghi, H.; Salimi, B.A.; Khalifeh, R. Synthesis of some novel thioxanthone-fused azacrownethers, and their use as new catalysts in the efficient, mild, and regioselective conversion of epoxides to β-hydroxythiocyanates with ammonium thiocyanate. *Helv. Chim. Acta.*, **2007**, *90*, 1373-1385.
- Chen, S.W.; Thakur, S.S.; Li, W.; Shin, C.K.; Kawthekar, R.B.; Kim, G.J. Efficient catalytic synthesis of optically pure 1,2-azido alcohols through enantioselective epoxide ring opening with HN₃. *J. Mol. Catal. A-Chem.*, **2006**, *259*, 116-120.
- Niknam, K. Conversion of epoxides into 2-hydroxyethyl thiocyanates with NH₄SCN in the presence of 2,6-bis[2-(O-amino phenoxy)methyl] -4-bromo-1-methoxybenzene (BABMB) as catalyst. *Phosphorus Sulfur Silicon Relat. Elem.*, **2004**, *179*, 499-506.
- Yadav, J.S.; Reddy, B.V.S.; Srinivas R.C. Selectfluor™: a novel and efficient reagent for the synthesis of β-hydroxythiocyanates. *Tetrahedron Lett.*, **2004**, *45*, 1291-1293.

- [17] Sharghi, H.; Hasani, N.A.; Nasser, M.A. Metalloporphyrins as new catalysts in the mild, efficient and regioselective conversion of epoxides to β -hydroxythiocyanates with NH_4SCN . *N. J. Chem.*, **2004**, *28*, 946-951.
- [18] Sharghi, H.; Hasani, N.A. Dichloro(5,10,15,20-tetraphenylporphyrin)phosphorus(V) chloride as a new catalyst for conversion of 1,2-epoxyethanes to 2-hydroxyethyl thiocyanates with ammonium thiocyanate. *Phosphorus Sulfur Silicon Relat. Elem.*, **2004**, *179*, 2297-2305.
- [19] Sharghi, H.; Nasser, M.A.; Hasani, N.A. Efficient synthesis of β -hydroxythiocyanates from epoxides and ammonium thiocyanates using tetraarylporphyrins as new catalysts. *J. Mol. Catal. A: Chem.*, **2003**, *206*, 53-57.
- [20] Sharghi, H.; Nasser, M.A. 2-Phenyl-2-(2-pyridyl)imidazolidine (PPI) as new catalyst in the efficient, mild, and regioselective conversion of epoxides to thiocyanohydrins with ammonium thiocyanate. *Phosphorus Sulfur Silicon Relat. Elem.*, **2003**, *178*, 1353-1359.
- [21] Gao, Y.; Sharpless, K.B. Vicinal diol cyclic sulfates. Like epoxides only more reactive. *J. Am. Chem. Soc.*, **1988**, *110*, 7538-7539.
- [22] Iranpoor, N.; Kohmareh, G.A. DDQ catalyzes the conversion of epoxides to β -hydroxythiocyanates with NH_4SCN . *Phosphorus Sulfur Silicon Relat. Elem.*, **1999**, *152*, 135-139.
- [23] Najera, C.; Sansano, J.M. β,γ -efoxysulfones in organic synthesis. Part 2: preparation of β,γ -bifunctionalized sulfones. *Tetrahedron*, **1991**, *47*, 5193-5202.
- [24] Balakrishnan, T.; Murugan, E.; Siva, A. Synthesis and characterization of novel soluble multi-site phase transfer catalyst; its efficiency compared with single-site phase transfer catalyst in the alkylation of phenylacetonitrile as a model reaction. *Appl. Catal. A: Gen.*, **2004**, *273*, 89-97.
- [25] Coe, D.M.; Myers, P.L.; Parry, D.M.; Roberts, S.M.; Storer, R. Synthesis of compounds active against HIV. Part 2. Preparation of some 2',3'-dideoxy-6'-fluorocarbo-cyclic nucleosides. *J. Chem. Soc. Chem. Commun.*, **1990**, *2*, 151-153.
- [26] Smith, B.T.; Gracias, V.; Aube, J. Regiochemical studies of the ring expansion reactions of hydroxyazides with cyclic ketones. *J. Org. Chem.*, **2000**, *65*, 3771-3774.
- [27] Badiang, J.G.; Aube, J. One-step conversion of aldehydes to oxazolines and 5,6-dihydro-4H-1,3-oxazines using 1,2- and 1,3-azido alcohols. *J. Org. Chem.*, **1996**, *61*, 2484-2487.
- [28] Cho, B.T.; Kang, S.K.; Shin, S.H. Application of optically active 1,2-diol monosylates for synthesis of β -azido and β -amino alcohols with very high enantiomeric purity. Synthesis of enantiopure (R)-octopamine, (R)-tembamide and (R)-aegeline. *Tetrahedron Asymmetry*, **2002**, *13*, 1209-1217.
- [29] Kazemi, F.; Kiasat, A.R.; Ebrahimi, S. Regioselective azidolysis of epoxides catalyzed with LiBF_4 . *Synth. Commun.*, **2003**, *33*, 999-1004.
- [30] Lakshman, M.; Nadkarni, D.V.; Lehr, R.E. Regioselective ring opening of polycyclic aromatic hydrocarbon epoxides by polymer-supported azide anion. *J. Org. Chem.*, **1990**, *55*, 4892-4897.
- [31] Onaka, M.; Sugita, K.; Izumi, Y. Solid-supported sodium azide reagents: their preparation and reactions with epoxides. *J. Org. Chem.*, **1989**, *54*, 1116-1123.
- [32] Kiasat, A.R.; Zayadi, M. Polyethylene glycol immobilized on silica gel as a new solid-liquid phase-transfer catalyst for regioselective azidolysis of epoxides in water: an efficient route to 1,2-azido alcohols. *Catal. Commun.*, **2008**, *9*, 2063-2067.
- [33] Kiasat, A.R.; Ataiean, F.; Fallah, M.M. B-pond as efficient catalysts for the ring opening of epoxides in water: a versatile and atom economical method for the synthesis of vicinal azidoalcohols. *Iran. J. Catal.*, **2012**, *2*, 1-5.
- [34] Nazari, S.; Keshavarz, M.; Karami, B.; Irvani, N.; Vafae-nezhad, M. Imidazol-1-yl-acetic acid as a novel green bifunctional organocatalyst for the synthesis of 1,8-dioxooctahydroxanthenes under solvent-free conditions. *Chin. Chem. Lett.*, **2014**, *25*, 317-320.
- [35] Kiasat, A.R.; Mirzajani, R.; Shalhaf, H.; Tabatabaei, T.; Fallah, M. M. Green regioselective azidolysis of epoxides catalyzed by multi-site phase-transfer catalyst. *J. Chin. Chem. Soc.*, **2009**, *56*, 594-599.
- [36] Kiasat, A.R.; Fallah, M.M. An efficient catalyst-free ring opening of epoxides in peg-300: a versatile method for the synthesis of vicinal azidoalcohols. *J. Iran. Chem. Soc.*, **2009**, *6*, 542-546.
- [37] Tamami, B.; Iranpoor, N.; Rezaie, R. Synthesis of azidoalcohols, nitroalcohols and nitratealcohols from epoxides using azide, nitrite and nitrate exchange resins. *Iran. Polym. J.*, **2004**, *13*, 495-501.
- [38] Kamel, A.; Arifuddin, M.; Maddamsetty, V. Rao. Enantioselective ring opening of epoxides with trimethylsilylazide (TMSN_3) in the presence of β -cyclodextrin: an efficient route to 1,2-azido alcohols. *Tetrahedron Asymmetry*, **1999**, *10*, 4261-4264.
- [39] Yadollahi, B.; Danafar, H. A facile synthesis of 1,2-azidoalcohols by $(\text{TBA})_4\text{PFeW}_{11}\text{O}_{39}\cdot 3\text{H}_2\text{O}$ -catalyzed azidolysis of epoxides with NaN_3 . *Catal. Lett.*, **2007**, *113*, 120-123.
- [40] Sabitha, G.; Babu, R.S.; Rajkumar, M.; Yadav, J.S. Cerium(III) chloride promoted highly regioselective ring opening of epoxides and aziridines using NaN_3 in acetonitrile: a facile synthesis of 1,2-azidoalcohols and 1,2-azidoamines. *Org. Lett.*, **2002**, *4*, 343-345.
- [41] Tamami, B.; Mahdavi, H. Synthesis of azidoalcohols from epoxides using quaternized amino functionalized cross-linked polyacrylamide as a new polymeric phase-transfer catalyst. *Tetrahedron Lett.*, **2001**, *42*, 8721-8724.