

## **$\beta$ -Cyclodextrin conjugated imidazolium cation: A neutral, eco-friendly and water-miscible dicationic ionic liquid in the regioselective ring opening of epoxides**

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### ABSTRACT

The present study, for the first time, presents a feasible protocol for the preparation of  $\beta$ -cyclodextrin/ imidazolium based dicationic ionic liquid,  $[\beta\text{CD}/\text{Im}](\text{OTs})_2$ , and its application as an efficient and eco-friendly microvessel and host ionic liquid system for the regioselective ring opening of the epoxides in water. No evidence for the formation of diol by-products or side reactions, such as isomerization, epimerization and rearrangements was observed and 1,2-disubstituted products,  $\beta$ -azidoalcohols,  $\beta$ -cyanohydrins, and  $\beta$ -thiocyanohydrins, obtained in pure form. Short reaction time, easy reaction conditions, simple work-up procedure, high yield, reusability, and use of an eco-friendly catalyst are some of the striking features of the present protocol.

**Keywords:** Dicationic ionic liquid,  $\beta$ -Cyclodextrin conjugated imidazolium cation, Regioselective ring opening of the epoxides,  $\beta$ -azidoalcohols,  $\beta$ -cyanohydrins,  $\beta$ -thiocyanohydrins.

### 1. Introduction

Due to their versatility and reactivity with a range of nucleophiles, epoxides are often used as starting materials and intermediates in organic synthesis [1]. The products of the nucleophilic addition, 1,2-disubstituted products, are important classes of organic compounds which applied as precursors in the syntheses of many biologically active compounds. Although some reagents and catalysts have been recently reported for the conversion of epoxides to 1,2-disubstituted vicinal compounds,  $\beta$ -azido alcohols,  $\beta$ -cyanohydrins and  $\beta$ -thiocyanohydrins [2-6], disadvantages such as long reaction times, low yields, difficulty in the preparation and/ or the storage of reagents or catalysts, tedious workup, and, in most cases, low regioselectivity, clearly identify a need for introducing new methods for such functional group transformations [7-8]. Therefore it is not surprising the extent of literature covering the chemistry of this class of compounds.

Green chemistry is a multi-faceted discipline that has been created as a contribution of chemistry to sustainable development, avoiding damage to the environment [9]. The green chemistry revolution is providing an enormous number of challenges to those who practice chemistry in industry, education and research. Another aspect which is receiving increasing attention is the use of alternative reaction media that circumvent the problems associated with many of the traditional volatile organic solvents. Consequently, it is highly desirable to develop environmentally benign processes that can be conducted in aqueous media. In several cases, by exploiting the unique properties of water it has been possible to realize more selective and efficient processes than those performed in organic media [10]. Again, organic synthesis in aqueous media is limited by the low solubility of organic compounds in water. One of the most important strategies to overcome this limitation is the utilization of phase transfer catalyst such as ionic liquids [11].

Ionic liquids (ILs) have aroused increasing interest for their promising role in the field of organic synthesis, catalysis, material science, chemical engineering,

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electrochemistry as a result of their unique chemical and physical properties [12-14]. ILs can dissolve a wide spectrum of organic, organometallic, and inorganic compounds [14]. Also, they have no detectable vapor pressure and are relatively thermal stable [15]. Therefore, ILs are a new generation of chemicals that have a great potential for contributing to the greenness of chemical processes and developing new applications.

On the other hand, nowadays molecular host-guest systems have been attracted enormous interest. By careful selection of host and guest molecules, specific properties of the resulting inclusion compounds can be targeted [16-17]. The ability of cyclodextrins to sequester hydrophobic moieties makes them interesting and valuable in many areas of research such as enantiomeric separation [18], targeted drug delivery [19], and removal of contaminants from wastewater [20]. In this field, cyclodextrins (CDs) play major roles in many disciplines such as supramolecular chemistry, analytical chemistry, catalysis and biomedicine are widely used as hosts to form noncovalent inclusion complexes with a wide variety of organic molecules by taking up a whole molecule, or some part of it into their lipophilic cavity [21].

By considering all the above-mentioned points and in continuation of our research [7-8] to develop green chemistry by using water as reaction medium, application of molecular host-guest systems and dicationic room temperature ionic liquid in organic transformation, herein,  $\beta$ -cyclodextrin/imidazolium based dicationic ionic liquid,  $[\beta\text{CD}/\text{Im}](\text{OTs})_2$ , was successfully prepared and its performance as eco-friendly microvessel and host ionic liquid system for the regioselective ring opening of the epoxides with azide, cyanate and thiocyanate anions in water was investigated.

## 2. Experimental

### 2.1. General

Chemical materials were purchased from Fluka and Merck and used without further purification.  $\beta$ -Cyclodextrin was heated at 80°C under vacuum for 30 min before use to remove traces of moisture. Products were characterized by comparison of their physical and spectroscopic data with known samples. The purity determination of the products and reactions monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates. The infrared spectroscopy (FT-IR) spectra of  $[\beta\text{CD}/\text{Im}](\text{OTs})_2$  was measured as potassium bromide discs on a BOMEM MB-Series 1998 FT-IR Spectrophotometer.

### 2.2. Preparation of pure 6-O-Monosyl- $\beta$ -cyclodextrin, mono-Ts- $\beta$ CD

The 6-O-Monosyl-  $\beta$ -cyclodextrin, mono-Ts- $\beta$ CD, was synthesized by reacting  $\beta$ -CD with tosyl chloride, TsCl, according to improved Tripodo's procedure [22]. Briefly NaOH (2 mmol) and  $\beta$ -CD (1 mmol) was dissolved in 10 mL of distilled water in a 100 mL round bottom flask at room temperature. 10 mL THF was injected into the mixture and stirred for 15 min at 0-5 °C. To the suspension, 1 mmol of TsCl in 10 mL of THF was added dropwise. Then the mixture was stirred at 0-5 °C for 20 min. After neutralization by HCl (2 N), the mixture was stirred at 0-5 °C for 1 h. The reaction mixture was poured in ice and white precipitate filtered off and washed with acetone several times. Yield: 90% (based on starting  $\beta$ -cyclodextrin), Melting point: 160–162 °C.

### 2.3. Preparation of 1,4-bis(imidazol-1-yl)-butane

A mixture of imidazole (3.4 g, 50 mmol) and NaOH (2.0 g, 50 mmol) in DMSO (10 mL) was stirred at 60°C for 1 h. 1,4- Dibromobutane (5.4 g, 25 mmol) was added to the mixture and stirred at 60°C for 2 h. The mixture poured into 100 mL of water and a white solid formed immediately, which weighed 4.1 g after drying in air [23].

### 2.4. Preparation of $\beta$ -Cyclodextrin/ imidazolium based dicationic ionic liquid, $[\beta\text{CD}/\text{Im}](\text{OTs})_2$

To a solution of 1,4-bis(imidazol-1-yl)-butane (0.5 mmol) in DMF (2.5 mL), solution of 1 mmol of mono-Ts- $\beta$ CD in 2.5 mL DMF was added dropwise. After 2 h stirring of the reaction mixture at 40°C, the temperature increased to 65°C and suspension was stirred for 6 h. The white precipitate filtered off and washed with  $\text{CCl}_4$  several times.

### 2.5. General procedure for the regioselective ring opening of the epoxides, preparation of $\beta$ -azidoalcohols, $\beta$ -cyanohydrins, and $\beta$ -thiocyanohydrins in water

A suspension of epoxide (1 mmol), nucleophile (3 mmol),  $[\beta\text{CD}/\text{Im}](\text{OTs})_2$  (0.005 g), and water (5 mL) were heated at 90 °C and stirred for appropriate time (Table 2). The progress of the reaction was monitored by TLC (eluent: n-hexane-EtOAc 80:20). After completion of the reaction, the catalyst was separated by simple filtration and mixture extracted with ether (2  $\times$  10 mL). The combined organic extracts (dried over  $\text{CaCl}_2$ ) were evaporated under reduced pressure. The desired product was obtained in high isolated yields. The separated catalyst after washing with water and methanol, was dried at 70 °C and then reused.

Selected spectral data

3-Phenoxy-2-hydroxypropyl thiocyanate [26]:

IR (neat):  $\bar{\nu} = 2156$  (SCN)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.27$  (2H, m, Ar-H), 7.01 (1H, m, Ar-H), 6.9 (2H, m, Ar-H), 4.29 (1H, m, CHOH), 4.04 (2H, d,  $\text{OCH}_2$ ), 3.78 (1H, s, OH), 3.30 (2H, d,  $\text{CH}_2\text{SCN}$ ) ppm.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 158.5$  (C), 129.9 (m-CH), 121.3 (p-CH), 114.6 (o-CH), 113.0 (SCN), 69.5 ( $\text{OCH}_2$ ), 68.0 (CHOH), 37.4 ( $\text{CH}_2\text{SCN}$ ) ppm.

2-Hydroxycyclohexyl thiocyanate [26]:

IR (neat):  $\bar{\nu} = 2151$  (SCN)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 3.34$  (1H, m, CHOH), 3.14 (1H, m, CHSCN), 2.35 (1H, s, OH), 1.98 (2H, m,  $\text{CH}_2\text{CHOH}$ ), 1.69 (2H, m,  $\text{CH}_2\text{CH}_2\text{CHOH}$ ), 1.21–1.29 (4H, m,  $\text{CH}_2\text{CH}_2\text{CHSCN}$ ) ppm.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 110.5$  (SCN), 76.4 (CHOH), 52.6 (CHSCN), 31.5 ( $\text{CH}_2\text{CHOH}$ ), 30.5 ( $\text{CH}_2\text{CHSCN}$ ), 25.1 ( $\text{CH}_2\text{CH}_2$ ), 22.2 ( $\text{CH}_2\text{CH}_2$ ) ppm.

2-Hydroxycyclohexyl azide [7d]:

IR (neat):  $\bar{\nu} = 2097$  ( $\text{N}_3$ )  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 3.28$ – $3.42$  (1H, m, CHOH), 3.10– $3.22$  (1H, m,  $\text{CHN}_3$ ), 2.52 (1H, s, OH), 2.00– $2.07$  (2H, m,  $\text{CH}_2\text{CHOH}$ ), 1.72– $1.78$  (2H, m,  $\text{CH}_2\text{CH}_2\text{CHOH}$ ), 1.20– $1.36$  (4H, m,  $\text{CH}_2\text{CH}_2\text{CHN}_3$ ) ppm.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 73.79$  (CHOH), 62.14 ( $\text{CHN}_3$ ), 33.14

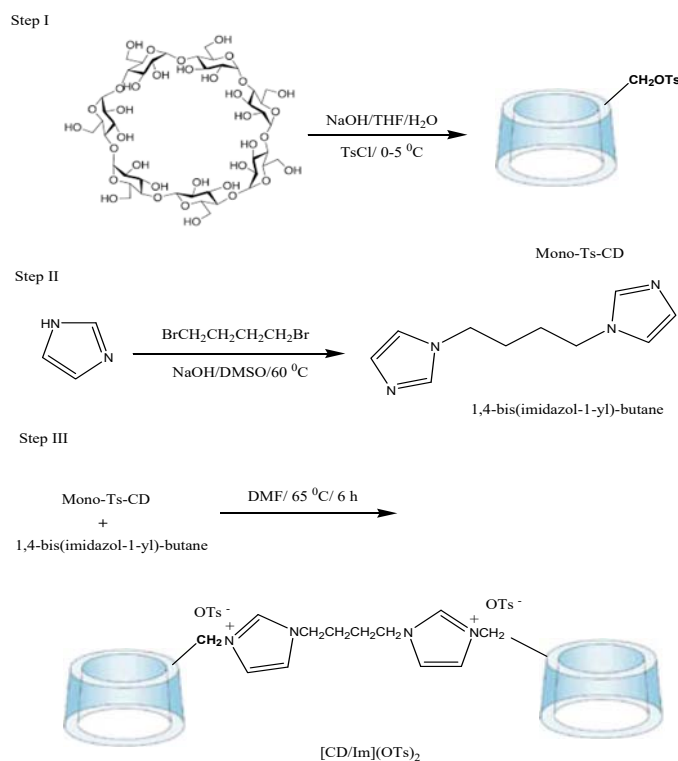
( $\text{CH}_2\text{CHOH}$ ), 24.51 ( $\text{CH}_2\text{CHN}_3$ ), 24.48 ( $\text{CH}_2\text{CH}_2$ ), 24.38 ( $\text{CH}_2\text{CH}_2$ ) ppm.

2-Azido-2-phenyl-1-ethanol [7a, 7d]:

IR (neat):  $\bar{\nu} = \text{N}_3$  (2102  $\text{cm}^{-1}$ ).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 7.34$ – $7.44$  (5H, m, Ar-H), 4.67 (1H, m,  $\text{CHN}_3$ ), 3.74 (2H, m,  $\text{CH}_2\text{OH}$ ), 3.37 (1H, s, OH) ppm.  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 136.47.0$  (C), 128.61.0 (m-CH), 128.49 (o-CH), 127.49 (p-CH), 68.03 ( $\text{CH}_2\text{OH}$ ), 66.37( $\text{CH}_2 \text{N}_3$ ) ppm.

3. Results and Discussion

A general synthetic route for the preparation of the  $\beta$ -Cyclodextrin/ imidazolium based dicationic ionic liquid,  $[\beta\text{CD}/\text{Im}](\text{OTs})_2$  is presented in Scheme 1. First, 6-O-Monotosyl-  $\beta$ -cyclodextrin, mono-Ts- $\beta\text{CD}$ , was synthesized by nucleophilic substitution of *p*-toluene sulfonyl chloride with  $\beta$ -CD, with molar ratio 1:1, under controlled conditions and verified by FT-IR spectra. The new peak at 1579  $\text{cm}^{-1}$  correspond to stretch vibrating of aromatic ring and the presence of peaks at 1364 and 1170  $\text{cm}^{-1}$  due to the asymmetric and symmetric stretching vibrations of sulfonyl groups shows that OH group are converted to the tosylate. This modified procedure had a good yield (90%) as compared to Tripodo's procedure (35%) [22] and other procedure (38%) [24-25].



Scheme 1. General synthetic route for the preparation of the  $[\beta\text{CD}/\text{Im}](\text{OTs})_2$ .

In the next step, 1,4-dibromo butane in DMSO reacted with two equivalents of Imidazole in basic conditions to afford 1,4-bis(imidazol-1-yl)-butane. In the last step,  $[\beta\text{CD}/\text{Im}](\text{OTs})_2$  was prepared by the nucleophilic substitution of mono-Ts- $\beta\text{CD}$  with 1,4-bis(imidazol-1-yl)-butane under controlled conditions and verified by FT-IR spectra.

The FT-IR spectrum of this host ionic liquid system (Fig 1) show characteristic adsorption bands at 1650 and 1515  $\text{cm}^{-1}$  correspond to stretch vibrating of C=N and C=C of aromatic ring. The asymmetric and symmetric stretching vibrations of sulfonate anion ( $\text{SO}_2$ ) were also observed at 1297 and 1230  $\text{cm}^{-1}$ . In addition, all the significant peaks of  $\beta\text{-CD}$  in the range of 900–1200  $\text{cm}^{-1}$  are present in the spectrum of  $[\beta\text{CD}/\text{Im}](\text{OTs})_2$  with a small shift.

After successful verification of the  $[\beta\text{CD}/\text{Im}](\text{OTs})_2$  by recording the FT-IR spectrum, it was decided to evaluate its catalytic activity in the ring opening of epoxides with different nucleophiles in water. In the beginning, ring opening of phenyl glycidyl ether was investigated with  $\text{NaN}_3$  in the presence of  $[\beta\text{CD}/\text{Im}](\text{OTs})_2$ . TLC analysis of the reaction mixture interestingly showed that this catalyst acted very efficiently in  $\text{H}_2\text{O}$ , and that 0.005 g of the catalyst was enough to convert 1 mmol of different epoxides,

carrying electron-donating or withdrawing groups, to their corresponding  $\beta$ -azidoalcohols in high yields (Scheme 2, Table 1).

As shown in Table 1, the desired  $\beta$ -azidoalcohols were obtained with a reversal of regioselectivity indicating attack at the less substituted carbon of the aliphatic epoxides, while styrene oxide as an aryl epoxide formed the product by attack at the benzylic position. In all cases, a very clean reaction was observed and careful examination of the  $^1\text{H}$ NMR spectra of the crude products clearly indicated the formation of only one regioisomer in each case. The probable reason may be that, in styrene oxide, the positive charge on the oxygen appears to be localized on the more highly substituted benzylic carbon leading to the major product [7a] whereas in the case of aliphatic epoxides, steric factors predominate over electronic factors, thereby facilitating attack at the less hindered carbon atom of the epoxide ring. Also, in the case of cyclohexene oxide, the reaction was completely antistereoselective, and the trans product was obtained. The structures of all of the products were determined from their analytical and spectral (IR,  $^1\text{H}$  NMR) data and by direct comparison with authentic samples.

It is noteworthy that no evidence for diols formation as reaction by-product was observed.

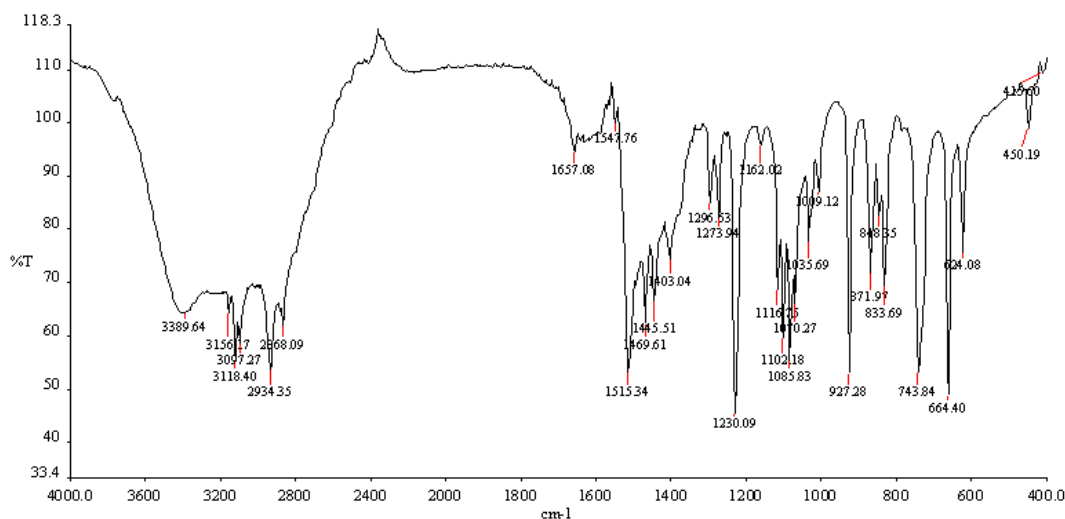
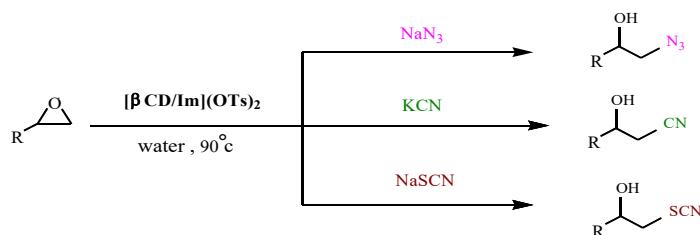


Fig. 1. FT-IR spectrum of  $[\beta\text{CD}/\text{Im}](\text{OTs})_2$ .



Scheme 2. Preparation of  $\beta$ -azido alcohols,  $\beta$ -cyanohydrins, and  $\beta$ -thiocyanohydrins catalyzed by  $[\beta\text{CD}/\text{Im}](\text{OTs})_2$ .

**Table 1.** Optimization of reaction conditions for the preparation of  $\beta$ -azido alcohol from phenyl glycidyl ether, in the presence of  $[\beta\text{CD}/\text{Im}](\text{OTs})_2$  in aqueous medium.

Entry	$\text{NaN}_3$ (mmol)	Nanocomposite (g)	Temp. ( $^\circ\text{C}$ )	Time (min)
1	2	0.03	90	30
2	3	0.03	90	30
3	3	0.02	90	15
4	3	0.01	90	10
5	3	None	90	360
6	3	0.005	90	10
7	3	0.02	60	50

This reaction was also performed in similar manner with weaker nucleophiles,  $\text{CN}^-$  and  $\text{SCN}^-$ , to obtain  $\beta$ -cyanohydrins and  $\beta$ -thiocyanohydrins, respectively. The collection of results was shown in Table 2. The structure of all the products were settled from their analytical and spectral (IR, NMR) data and by direct comparison with authentic sample.

This dicationic ionic liquid contains two different units linked together and we believed each unit has especial role in the ring opening of epoxides.

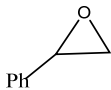
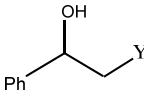
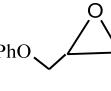
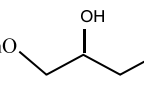
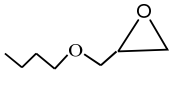
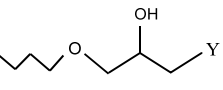
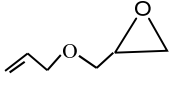
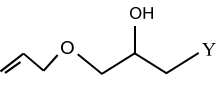
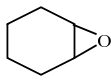
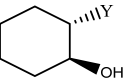
Cyclodextrins (CDs) are trous-shaped cyclic oligosaccharides with the hydrophilic outer surfaces and an interior hydrophobic cavity. Thus in water, central cavities of  $\beta$ -CD units in  $[\beta\text{CD}/\text{Im}](\text{OTs})_2$  can be act as microvessel and accommodate nonpolar parts of epoxides. In addition the hydrophilic exterior due to the outer OH of the  $\beta$ -CD cavity formed complexes with cation and these complexes cause the anion to be

activated. In addition, the imidazolium units introduced ionic liquid property to the catalyst.

The reusability of the catalyst is important for the large scale operation and industrial point of view. For this purpose, the catalyst was quantitatively separated and reused after washing with water and methanol and drying at  $70^\circ\text{C}$ . The reusability of the catalyst was investigated in the ring opening reaction of phenyl glycidyl ether with azide anion. The results showed that the catalyst can be used five times with consistent yield. The yields were 95, 93, 89, 85 and 85%, respectively.

In order to show the merit of our procedure in the ring opening reaction, we have shown the advantages of present procedure by comparing our results with those previously reported in the literature. As shown in Table 3,  $[\beta\text{CD}/\text{Im}](\text{OTs})_2$  has greater efficiency and shorter reaction time than other catalysts.

**Table 2.** Ring opening reaction of epoxides with different nucleophiles,  $\text{NaN}_3$ /  $\text{KCN}$ /  $\text{NaSCN}$ , catalysed by  $[\beta\text{CD}/\text{Im}](\text{OTs})_2$  in water.

Entry	Substrate	Product	Nucleophile(Y)	Time(min)	Yield(%)
1			$\text{N}_3$ (CN)(SCN)	7(10)(7)	95(90)(91)
2			$\text{N}_3$ (CN)(SCN)	10(10)(7)	93(91)(92)
3			$\text{N}_3$ (CN)(SCN)	20(25)(20)	87(80)(85)
4			$\text{N}_3$ (CN)(SCN)	20(20)(20)	90(89)(88)
5			$\text{N}_3$ (CN)(SCN)	10(20)(20)	(85)(80)(82)

**Table 3.** Comparison of azidolysis of styrene oxide with reported methods in the literature.

Entry	Catalyst	Solvent	Temp. (°C)	Time (h)	Yield (%)	Ref
1	LiClO <sub>4</sub>	CH <sub>3</sub> CN	80	5	92	[8a]
2	(TBA) <sub>4</sub> PF <sub>6</sub> MO <sub>3</sub> .3H <sub>2</sub> O	CH <sub>3</sub> CN-H <sub>2</sub> O	80	4.5	85	[8b]
3	Dowex-PEG	H <sub>2</sub> O	100	0.5	85	[7a]
4	PEG300	PEG300	60	1.5	85	[7b]
5	SiO <sub>2</sub> -PEG	H <sub>2</sub> O	100	1	80	[7c]
6	MPTC <sup>a</sup>	H <sub>2</sub> O	90	0.5	85	[7d]
7	Network polymer	H <sub>2</sub> O	80	1.5	85	[7e]
8	Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> /BNC	H <sub>2</sub> O	90	0.25	95	[7f]
9	MCM-crown	H <sub>2</sub> O	90	0.33	89	[7g]
10	[βCD/Im](OTs) <sub>2</sub>	H <sub>2</sub> O	90	0.16	91	This work

<sup>a</sup>Multi-site phase-transfer catalyst.

#### 4. Conclusion

Regarding the green chemistry's goals, heterogeneous dicationic ionic liquid open up new avenue to introduce an amazing and efficient system for facilitating catalyst recovery in different organic reactions. In this paper, in summary, we describe a novel, eco-friendly, and efficient protocol for the regioselective ring opening of epoxides with different anions using [βCD/Im](OTs)<sub>2</sub> as an inexpensive and green heterogeneous dicationic ionic liquid. This method offers several advantages including mild reaction conditions, high conversions, greater regioselectivity, short reaction times, clean reaction profiles, and high isolated yields which make it a useful and attractive process for the synthesis of 1,2-disubstituted products.

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