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Mixture of poly(ethylene glycol) and water as environmentally friendly media for efficient enantioselective transfer hydrogenation and catalyst recycling

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Abstract

The asymmetric transfer hydrogenation of nonfunctionalized aromatic ketones catalyzed by Ru-TsDPEN was performed successfully in a mixture of poly(ethylene glycol) (PEG) and water. High activity and enantioselectivity were obtained, which were better than or comparable to those obtained in conventional organic solvents. The unmodified catalyst could be easily recovered after extraction of the reduced product with a less polar solvent such as hexane, and was reused at least 14 times without obvious loss in enantioselectivity. These results indicate that the inexpensive and non-toxic aqueous PEG can serve as a new means for the immobilization of Ru-TsDPEN catalyst and related variants without calling for catalyst modification.

Keywords: Poly(ethylene glycol); Water; Catalyst recycling; Ruthenium complex; Asymmetric transfer hydrogenation

1. Introduction

Optically active secondary alcohols are currently important intermediates for the construction of many biologically active chiral compounds. The asymmetric transfer hydrogenation of ketones provides an attractive alternative method to asymmetric hydrogenation for the preparation of chiral alcohols because of its operational simplicity and the easy availability of the hydrogen sources [1–5]. Among the various chiral catalysts reported, the most notable is Ru-TsDPEN (TsDPEN = *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylene diamine), which was developed by Noyori and co-workers in 1995 [6,7]. Since then, this catalyst and related variants have been applied successfully to a wide range of prochiral ketones and imines, leading to good to excellent enantioselectivities. However, as with other homogeneous catalysts, the expensive Ru-TsDPEN catalyst cannot be easily separated from the chiral products. To address this problem, a number of approaches for heterogenization of the catalyst have been reported [8–20]. These included immobilization either by anchoring the catalyst onto insoluble and soluble polymers [9–12], inorganic materials [13,14] and dendrimers [15,18], or by using ionic liquid biphasic systems [19,20]. All of these approaches are of interest but often require additional ligand or catalyst-modifications, which are tedious and time-consuming. In addition, the immobilized catalysts often suffered from reduced catalytic activity and/or enantioselectivity owing to the mass transfer limitation and/or degradation of the support. Most recently, Deng and co-workers reported the asymmetric hydrogenation of ketones by using an unmodified ruthenium

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catalyst in aqueous micelles and vesicles [21]. The hydrophobic catalyst could be separated by extraction with organic solvent and was recycled at least six times. This is probably the first report on the recycling of Noyori's catalyst without calling for any modification. However, in terms of catalyst activity and reusability, there is still room for improvement.

Recently, liquid polymers or low melting polymers have emerged as alternative green reaction media with unique properties such as thermal stability, commercial availability, nonvolatility, immiscibility with a number of organic solvents and recyclability. Poly(ethylene glycol)s (PEGs) are preferred over other polymers because they are inexpensive, nonhalogenated and low toxicity [22,23]. PEGs have been adopted as a new means for catalyst recycling in a broad range of catalytic reactions including polymerization and biotransformation [24–49]. However, the utilization of PEG as solvent or cosolvent for asymmetric catalytic reactions and recycling of the homogeneous chiral catalysts are rather limited [43–49]. Very recently, we reported the use of Ru, Rh and Ir complexes with chiral diphosphine ligands for the enantioselective hydrogenation of prochiral olefins, ketones and quinolines in PEG with an organic co-solvent such as methanol, isopropanol and hexane [48,49]. High enantioselectivities have been achieved, which are comparable to those obtained in conventional organic solvent systems. In continuing our efforts for developing recyclable chiral catalytic systems for asymmetric catalysis [8,48–59], we report here the highly enantioselective transfer hydrogenation in a mixture of PEG and water by using Ru catalyst with commercially available TsDPEN. The catalyst could be recycled up to 14 times without obvious decrease in enantioselectivity.

2. Experimental

2.1. General remarks

All experiments were carried out under a nitrogen atmosphere by using standard Schlenk-type techniques, or performing in a glovebox.

2.2. Materials and equipment

All solvents were dried by using standard, published methods and were distilled under nitrogen atmosphere before use. The simple ketones were distilled under reduced pressure before use. PEGs were used as received without further purification. ^{1}H NMR (300 HMz) and ^{13}C NMR (75 HMz) spectra were recorded on a Bruker-DMX 300 spectrometer. Determinations of conversions and ee values were performed on a Varian-6000 GC with an FID detector by using a Varian CP 7502 chiral column (25 m × 0.25 mm).

2.3. Preparation of (1S, 2S)-N-p-toluenesulfonyl-1,2-diphenylethylenediamine ((1S, 2S)-TsDPEN) [66]

To a solution of (*S*, *S*)-DPEN (0.5 g, 2.4 mmol) and NEt_3 (0.45 ml, 3.2 mmol) in CH_2Cl_2 (10 ml) cooled in an ice-bath was added *p*-toluenesulfonyl chloride (0.48 g, 2.5 mmol) in CH_2Cl_2 (2 ml) in a dropwise manner. The mixture was stirred for 30 min and then warmed to room temperature. The reaction progress was monitored by TLC (silica gel, EtOAc, R_f:TsDPEN = 0.7, starting material = 0 and ditosylated product = 1), and the reaction was found to complete after 16 h. The resulting mixture was washed with water (20 ml), saturated $NaHCO_3$ (20 ml), brine (20 ml) and then was dried over $MgSO_4$. Recrystallisation from ethyl acetate/pentane afforded (1*S*, 2*S*)-TsDPEN as white crystals (0.48 g, 56% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.30 (s, 3H), 2.50 (br, s, 2H), 4.12 (d, J = 5.4 Hz, 1H), 4.39 (d, J = 5.4 Hz, 1H), 6.95 (d, J = 8.2 Hz, 2H), 7.10 (m, 11H), 7.31 (d, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.4 (1C, CH_3 in *p*-Ts), 60.6 (1C, $CHNH_2$), 63.4 (1C, CHNH-*p*-Ts), 126.6, 126.9, 127.0, 127.3, 127.5, 128.2, 128.4, 129.1, 137.2, 139.3, 141.5, 142.5 (4C in Ar).

2.4. General procedure for the asymmetric transfer hydrogenation of acetophenone using 2-propanol (IPA) as the hydrogen source [6]

The catalyst was prepared *in situ* by reacting [$RuCl_2$(*p*-cymene)]$_2$ (1.3 mg, 0.002 mmol) with (1*S*, 2*S*)-TsDPEN (3.0 mg, 0.008 mmol) in degassed IPA (0.5 ml) at 80 °C for 30 min under nitrogen atmosphere. Then, acetophenone (47 μl, 0.5 mmol) and KOH (1.12 mg, 5 equiv. to Ru catalyst) were introduced. After degassed three times, the mixture was stirred at room temperature for a certain period of time. The conversion and ee values were determined by GC with a chiral column.

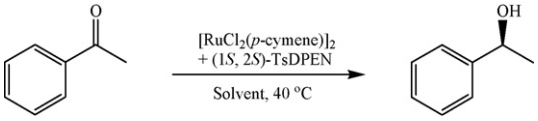
2.5. General procedure for the asymmetric transfer hydrogenation of acetophenone using HCOOH/TEA as the hydrogen source

The catalyst was prepared *in situ* by reacting [$RuCl_2$(*p*-cymene)]$_2$ (3.1 mg, 0.005 mmol) with (1*S*, 2*S*)-TsDPEN (4.4 mg, 0.012 mmol) in CH_2Cl_2 (0.5 ml) at room temperature for 30 min under nitrogen atmosphere. After removal of CH_2Cl_2 under reduced pressure, a solution of HCOOH (0.13 ml, 3.3 mmol), Et_3N (0.37 ml, 2.7 mmol) and acetophenone (118 μl, 1.0 mmol) in PEG (2 ml) was introduced. After degassed three times, the mixture was stirred at 40 °C for a certain period of time. The conversion and ee values were determined by GC with a chiral column.

2.6. General procedure for the asymmetric transfer hydrogenation of acetophenone using HCOONa as the hydrogen source

The catalyst was prepared *in situ* by reacting [$RuCl_2$(*p*-cymene)]$_2$ (3.1 mg, 0.005 mmol) with (1*S*, 2*S*)-TsDPEN (4.4 mg, 0.012 mmol) in water (0.2 ml) at 40 °C for 1 h under nitrogen atmosphere. After cooling to room temperature, a solution of ketone (118 μl, 1.0 mmol) and HCOONa (5 mmol, 340 mg) in PEG (0.6 ml) was introduced. After degassed three times, the mixture was stirred at 40 °C for a certain period of

Table 1
Asymmetric transfer hydrogenation of acetophenone in various solvent systems[a]



Entry	Solvent[b]	T (h)	Conversion (%)[c]	e.e. (%)[c]
1	PEG-400/IPA (1:1)	15	70 (88)[d]	96 (97)[d]
2	PEG-400/HCOOH–NEt_3 (4:1)	12	64 (99)[e]	96 (97)[e]
3	PEG-400/HCOOH–NEt_3 (4:1)	24	>99	96
4[f]	PEG-400/HCOOH–NEt_3/hexane (4:1:4)	16	83	96
5	PEG-400	10	50	96
6	PEG-400	24	89	96
7	PEG-400/H_2O (9:1)	8	65	96
8	PEG-400/H_2O (9:1)	15	>99	96
9	PEG-400/H_2O (6:1)	4	80	96
10	PEG-400/H_2O (3:1)	2	73	96
11	PEG-400/H_2O (3:1)	3	>99	96
12	PEG-400/H_2O (1:1)	2	>99	93
13	PEG-600/H_2O (3:1)	3	98	95
14	PEG-1000/H_2O (3:1)	3	88	94
15	PEG-2000/H_2O (3:1)	3	86	94
16[f]	PEG-400/H_2O/hexane (3:1:3)	3	64	94

[a] The reactions were performed with 0.5 mmol or 1 mmol acetophenone at S/C ratio of 100:1 (molar ratio) in 2 ml solvent at 40 °C.
[b] For entries 5–16, HCOONa (5 equiv.) was used as the hydrogen source.
[c] Determined by GC equipped with a chiral column (Chirasil-Dex CP 7502), the alcohol was in *S*-configuration.
[d] Data in brackets were obtained with pure IPA.
[e] Data in brackets were obtained with the azeotrope only.
[f] The reactions were carried out under biphasic manner.

time. The conversion and ee values were determined by GC with a chiral column.

2.7. Recycle experiment for the asymmetric transfer hydrogenation of acetophenone in PEG

Under nitrogen atmosphere, a mixture of HCOOH (0.13 ml, 3.3 mmol), Et_3N (0.37 ml, 2.7 mmol), acetophenone (118 μl, 1.0 mmol) and Ru-TsDPEN (0.01 mmol, prepared as described above) in PEG (2 ml) was stirred at 40 °C for a certain period of time. Then, the reduced product was extracted with hexane (3× 5 ml). The residual PEG phase was recharged with acetophenone (118 μl, 1.0 mmol), HCOOH (0.13 ml, 3.3 mmol) and Et_3N (0.37 ml, 2.7 mmol), and the next reaction was started under the same conditions. The conversion and ee values were determined by GC with a chiral column.

2.8. Recycle experiment for the asymmetric transfer hydrogenation of acetophenone in PEG/H_2O (9:1, v/v)

Under nitrogen atmosphere, a mixture of acetophenone (118 μl, 1.0 mmol), HCOONa (5 mmol, 340 mg) and Ru-TsDPEN (0.01 mmol, prepared as described above) in PEG/H_2O (3 ml, 9:1, v/v) was stirred at 40 °C for a certain period of time. Then, the reduced product was extracted with hexane (3× 5 ml). The residual PEG/H_2O phase was recharged with acetophenone (118 μl, 1.0 mmol) and HCOOH (45 μl, 1.1 mmol), and the next reaction was started under similar conditions. The conversion and ee values were determined by GC with a chiral column.

3. Results and discussions

The efficacy of the asymmetric transfer hydrogenation in different reaction systems was assessed using acetophenone as a model substrate (Table 1). In general, high enantioselectivities have been achieved in most cases, which are comparable to those obtained in conventional organic solvent systems. The ruthenium catalyst was prepared *in situ* by reacting $[RuCl_2(p\text{-cymene})]_2$ with TsDPEN in organic solvent or water under nitrogen atmosphere according to the published methods [6,7,64]. We initially used IPA as the hydrogen donor for testing the effect of PEG as co-solvent. When 0.5 mmol acetophenone in

Table 2
Catalyst recycling in the asymmetric transfer hydrogenation of acetophenone catalyzed by Ru-TsDPEN with HCOOH–Et_3N in PEG[a]

Run	Conversion (%)[b]	Yield (%)[c]	e.e. (%)[b]
1	99	85	96
2[d]	99	94	96
3	96	94	97
4	98	96	96
5	76	73	93

[a] The reactions were carried out with 1.0 mmol of acetophenone at S/C ratio of 100:1 (molar ratio) in 2 ml PEG and 0.5 ml HCOOH–Et_3N azeotropic mixture at 40 °C for 24–30 h.
[b] Determined by GC equipped with a chiral column (Chirasil-Dex CP 7502), the product was in the *S*-configuration.
[c] Isolated yield.
[d] Percentage of Ru leached into the product in the second run was no more than 0.068% (0.22 ppm) by ICP analysis.

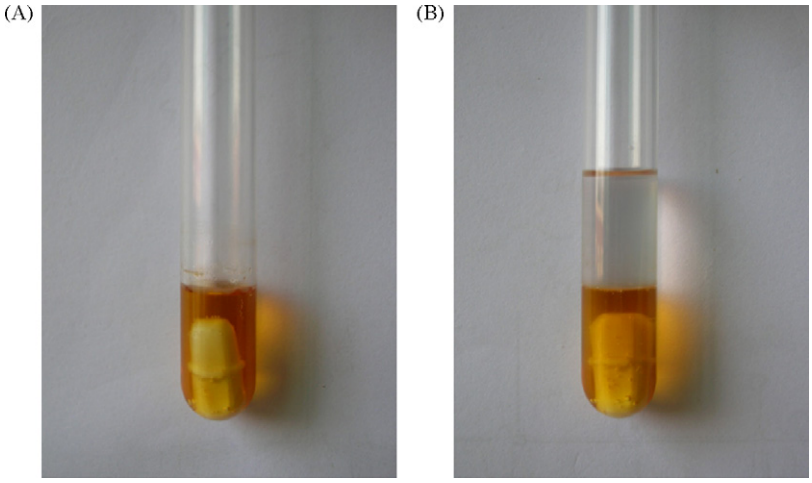


Fig. 1. Photographs of the asymmetric transfer hydrogenation catalyzed by Ru-TsDPEN in PEG/H_2O (A), and the extraction of the reduced products with hexane (B).

a mixture of IPA and PEG-400 (Mn = 400) containing the *in situ* catalyst and KOH was stirred at 40 °C for 15 h, the enantioselectivity was comparable to that obtained in pure IPA with a slight drop of conversion (entry 1). Then, we studied the reduction with the HCOOH–NEt_3 azeotropic mixtures in PEG. Similarly, high enantioselectivity was observed with low catalytic activity (entry 2). Complete conversion could be achieved at prolonged reaction time (entry 3). We also studied the biphasic catalysis by introducing hexane as the non-polar phase. As compared with the monophase reaction in PEG, similar results were obtained (entry 4 versus entry 2). When the transfer hydrogenation was performed in pure PEG with HCOONa as a hydrogen donor, the reaction was found to be sluggish, but giving comparable enantioselectivity (entries 5 and 6). This might be partially due to the high viscosity of PEG and low solubility of HCOONa in PEG, which lead to the solidification of the reaction mixture during the reaction. Most recently, Xiao's group and others reported that the Ru-TsDPEN catalyzed asymmetric transfer hydrogenation with HCOONa as a reductant could be performed in pure water and gave unexpectedly high catalytic activity [12,14,60–65]. Inspired by these results, we introduced water as a co-solvent and found that the reaction was significantly improved (entries 6–12). The reactivity increased with the increase of water. When the ratio of H_2O/PEG was increased to 1:1, the highest reaction rate was observed but at the cost of lower enantioselectivity (entry 12). When PEGs with higher molecular weight were used, slightly lower conversion and enantioselectivity were observed (entries 13–15). This was probably due to the higher viscosity of the reaction medium. Similarly, the biphasic catalyst system provided slightly lower ee value and conversion (entry 16).

To investigate the catalyst recyclability and reusability in PEG, we first chose the HCOOH–NEt_3 azeotrope as the hydrogen source and acetophenone as a standard substrate. Upon completion of the reaction, the catalyst was easily recovered

Table 3
Catalyst recycling in the asymmetric transfer hydrogenation of acetophenone catalyzed by Ru-TsDPEN with HCOONa in PEG-H_2O[a]

	Run							
	1	2[b]	3	4	5	6	7	8[b]
e.e. (%)[c]	96	96	96	95	95	95	95	94
Conversion (%)[c]	99	99	99	99	99	93	88	77
Yield (%)[d]	86	95	98	99	98	91	86	72

	Run						
	9	10	11	12	13[b]	14	15
e.e. (%)[c]	95	94	94	94	95	95	94
Conversion (%)[c]	75	99	99	99	99	97	81
Yield (%)[d]	72	98	98	96	95	96	78

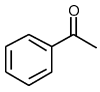
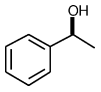
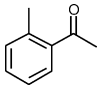
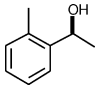
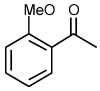
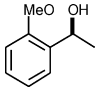
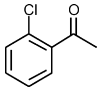
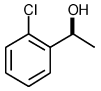
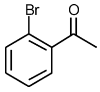
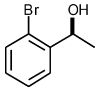
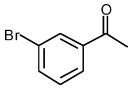
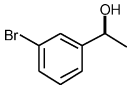
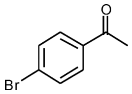
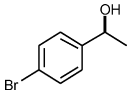
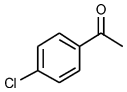
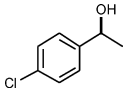
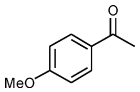
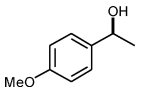
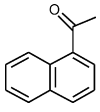
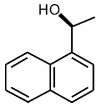
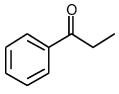
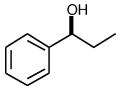
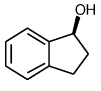
[a] The reactions were carried out with 1.0 mmol of acetophenone at S/C ratio of 100:1 (molar ratio) in 3 ml PEG/H_2O (9:1, v/v) with 5 mmol HCOONa at 40 °C in the first run. Since the second run, 1.1 mmol HCOOH was added to regenerate sodium formate in every recycling run. For reaction time: 15–20 h for run 1–9, 20–40 h for run 10–15.

[b] Percentage of Ru leached into the product in runs 2, 8 and 13 were no more than 0.064% (0.16 ppm), 0.096% (0.24 ppm) and 0.10% (0.25 ppm) respectively by ICP analysis.

[c] Determined by GC equipped with a chiral column (Chirasil-Dex CP 7502), the alcohol was in the *S*-configuration.

[d] Isolated yield.

Table 4
Asymmetric transfer hydrogenation of a variety of ketones catalyzed by Ru-TsDPEN with HCOONa in PEG-H_2O[a]

Entry	Ketone	Product	Time (h)	Conversion (%)[b]	e.e. (%)[b]
1			3	98	95
2			10	95	86
3			8	97	81
4			6	99	90
5			6	99	90
6			6	99	91
7			6	99	91
8			6	99	88
9			8	91	94
10			8	99	93
11			6	98	90
12			6	99	95

[a] The reactions were carried out with 0.5 mmol of ketone at S/C ratio of 100:1 (molar ratio) in 2 ml PEG/H_2O (3:1, v/v) with 5 equiv. HCOONa at 40 °C.
[b] Determined by GC equipped with a chiral column (Chirasil-Dex CP 7502), all products were in the *S*-configuration.

after extraction of the reduced products with a less polar solvent such as hexane (as shown in Fig. 1). The residual PEG phase containing the catalyst was recycled and reused for the next reaction by recharging substrate and azeotrope under the same conditions. In contrast to the PEG-supported Ru-TsDPEN catalyst, in which catalyst recycling led to a quick loss of catalytic activity and enantioselectivity [11], when PEG was used as solvent, the unmodified catalyst showed excellent conversion and ee up to the fourth cycle (Table 2). The mass recovery of the products (after column chromatography) was found to be low (85%) in the first cycle, but high isolated yields have been achieved from the second catalytic run. The low conversion (76%) for the fifth run was probably due to the dilution effect, resulting from the gradually increasing reaction volume. In addition, when hexane was used for extraction, a very low degree of PEG leaching (<0.5 wt%) was observed. Furthermore, inductively coupled plasma (ICP) spectroscopy analysis showed that less than 0.068% (0.22 ppm) catalyst was extracted into the product.

Considering the higher stability of the Ru-TsDPEN catalyst in the aqueous-phase than in the HCOOH–NEt_3 azeotrope [12], we further explored the recyclability of the catalyst by using HCOONa as the hydrogen source. Although the unmodified Ru-TsDPEN catalyst was highly effective for ketone reduction by HCOONa in water, the recycle of the catalyst has proven to be rather difficult due to the high solubility of the catalyst in common solvents [12,61]. In our study, we used a mixture of PEG/H_2O (9:1, v/v) as the reaction solvent and found that this catalytic system showed excellent recyclability (Table 3). The

unmodified catalyst was reused at least 14 times without obvious loss in enantioselectivity. Although the reactivity decreased after the eighth run, complete conversion could be achieved at prolonged reaction time. Notably, the recovery and reuse of the catalyst were very simple and reliable. After extraction of the reduced product with hexane, only formic acid was added into the residual PEG/H_2O phase to regenerate sodium formate. Acetophenone was then recharged and the next catalytic reaction was started. In addition, based on the ICP analysis, more than 99.9% catalyst was retained in the PEG phase. To the best of our knowledge, this represents the most efficient recyclable catalyst system in asymmetric transfer hydrogenation in terms of catalyst recyclability, activity and enantioselectivity.

Having established the superior recyclability and reusability of the unmodified Ru-TsDPEN catalyst, we then extended the reaction to a variety of simple aromatic ketones. Table 4 summarized the results obtained. Various ketones including 2-substituted, electron-rich and electron-deficient substrates were reduced with good to excellent enantioselectivities and reactivities by using HCOONa as the reductant and a mixture of PEG and H_2O (3:1, v/v) as the solvent. It was found that the substituted groups on the ortho position in the acetophenones influenced the enantioselectivity greatly. The electron-donating substrates gave low enantioselectivities. For example, the reduction of *o*-methylacetophenone and *o*-methoxylacetophenone afforded the corresponding alcohols with 81% ee and 86% ee, respectively (entries 2 and 3). In contrast, *p*-methoxylacetophenone was reduced to (*S*)-1-*p*-methoxylphenylethanol in 91% conversion and 94% ee (entry 9). For other ketones, the reductions also proceeded smoothly with almost complete conversions and high enantioselectivities (entries 10–12). On the other hand, the reaction rates for all ketones were much faster than those obtained with a similar catalyst in the HCOOH–NEt_3 azeotrope [7,11]. Particularly noteworthy is the reduction of 1-acetonaphthone, achieving 99% conversion and 93% ee in 8 h (entry 10). In contrast, about 60 h were required to complete the reduction (83% ee) at S/C = 200 and 28 °C with the azeotrope under Noyori's conditions. Furthermore, for most ketones investigated, especially for the *ortho*-substituted ketones, enantioselectivities were found to be higher than those obtained in water, albeit at the cost of low catalytic activity. For example, reduction of *o*-methoxylacetophenone by HCOONa for 8 h in PEG/H_2O furnished (*S*)-1-*o*-methoxylphenylethanol with 81% ee and 97% conversion (entry 3). In contrast, 72% ee and 96% conversion were observed in water under similar conditions [61].

4. Conclusions

We have developed a practical and green protocol for the asymmetric transfer hydrogenation of nonfunctionalized aromatic ketones catalyzed by Ru-TsDPEN in a mixture of PEG/water and for the catalyst recycle. High catalytic activity and enantioselectivity were achieved with HCOONa as a reductant, which were better than or comparable to those obtained in conventional solvent systems. The unique feature of this protocol was that the catalyst could be easily recovered and reused (up to 14 times) without calling for any catalyst modification. These results indicate that the inexpensive and non-toxic aqueous PEG can serve as an environmentally friendly alternative to water and room temperature ionic liquids, and as a novel means for the immobilization of homogeneous catalysts.

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