

Osmium-catalyzed dihydroxylation of alkenes by H₂O₂ in room temperature ionic liquid co-catalyzed by VO(acac)₂ or MeReO₃

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Abstract

Room temperature ionic liquid [bmim]PF₆ was used to immobilize a bimetallic catalytic system for H₂O₂-based dihydroxylation of alkenes. Osmium tetroxide was used as the substrate-selective catalyst with either VO(acac)₂ or MeReO₃ as co-catalyst. The latter serve as an electron transfer mediator (ETM) and activates H₂O₂. For an increased efficiency *N*-methylmorpholine is required as an additional ETM in most cases. A range of alkenes were dihydroxylated using this robust bimetallic system and it was demonstrated that for some of the alkenes the catalytic system can be recycled and used up to five times.

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1. Introduction

Osmium-catalyzed dihydroxylation of alkenes is a synthetically important reaction and many oxidation systems have been developed for this transformation [1,2]. From an environmental point of view it is of interest to use oxidants such as hydrogen peroxide or molecular oxygen, which give no waste products [2–5].

We have recently developed several methods for the osmium-catalyzed dihydroxylation of alkenes by hydrogen peroxide [5–8]. The principle of these oxidation systems is that the hydrogen peroxide reacts with a co-catalyst (electron transfer mediator) to give a reactive peroxy or hydroperoxide intermediate, which efficiently can reoxidize Os(VI) to Os(VIII), often with the aid of an additional electron transfer mediator (ETM). The latter ETM, if required, is a redox catalyst that lowers the barrier for electron transfer and *N*-methylmorpho-

line/*N*-methylmorpholine-*N*-oxide (NMM/NMO) has been used for this purpose.

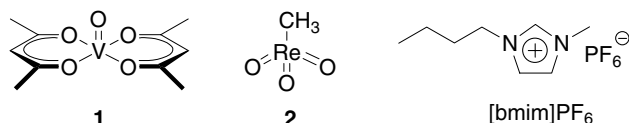
In the original version of the hydrogen peroxide-based dihydroxylation [5] an organocatalyst, a flavin, was used as the H₂O₂-activating catalyst. The flavin generates a flavin hydroperoxide, which rapidly oxidizes NMM to NMO in situ. The latter (NMO), in turn, rapidly oxidizes Os(VI) back to Os(VIII).

In a modified version of the H₂O₂-based dihydroxylation, VO(acac)₂ or MeReO₃ (MTO) was employed in place of the flavin for the activation of H₂O₂ [6]. One problem encountered with MTO was that it underwent slow decomposition [9] under the reaction conditions employed. VO(acac)₂ worked better but also this co-catalyst was less efficient than the flavin employed in the original version.

Ionic liquids are attracting a growing interest as solvents for organometallic reactions [10,11]. The use of ionic liquids in osmium-catalyzed dihydroxylation was reported by four different groups in 2002 [12], and recently we [8] developed a H₂O₂-based version of the dihydroxylation in an ionic liquid. The latter procedure

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employed a flavin as the H_2O_2 -activating catalyst. In the present paper, we report on a robust bimetallic catalytic system, employing co-catalysts $\text{VO}(\text{acac})_2$ (**1**) and MTO (**2**) in an ionic liquid for the efficient dihydroxylation of alkenes by hydrogen peroxide.



2. Results and discussion

Dihydroxylation of alkenes by H_2O_2 was carried out in the ionic liquid $[\text{bmim}]\text{PF}_6$ with acetone as co-solvent employing K_2OsO_4 as catalyst and either MTO or $\text{VO}(\text{acac})_2$ as co-catalysts for H_2O_2 -activation.

2.1. $\text{VO}(\text{acac})_2$ as co-catalyst

All reactions were carried out at room temperature with slow addition of hydrogen peroxide (8 h). Reaction of styrene with 30% aqueous hydrogen peroxide in $[\text{bmim}]\text{PF}_6$ /acetone employing 2 mol% of K_2OsO_4 and 2 mol% of $\text{VO}(\text{acac})_2$ together with 23 mol% of *N*-methylmorpholine (NMM) afforded 81% diol after workup (Table 1, entry 1). Also, β - and α -methylstyrene worked well and gave the corresponding diol in 82% and 91% yield, respectively (Table 1, entries 2 and 3). Several different alkenes were oxidized using these reaction conditions and the results are given in Table 1. Cyclohexene and acyclic aliphatic olefins gave good to high yields of the corresponding diols (Table 1, entries 6–10).

2.2. MTO as co-catalyst

The use of MTO as the H_2O_2 -activating catalyst in osmium-catalyzed dihydroxylations is associated with the problem that MTO decomposes at alkaline pH by aq. H_2O_2 . A solution to this problem was recently provided by allowing the reaction to occur under slightly acidic conditions [13]. We have now immobilized this system in ionic liquid $[\text{bmim}]\text{PF}_6$ at room temperature. Reaction of styrene with hydrogen peroxide in $[\text{bmim}]\text{PF}_6$ /acetone catalyzed by $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$ (2 mol%) and MTO (2 mol%) in the presence of citric acid afforded the corresponding diol in excellent yield (Table 2, Method A, entry 1). Although the less basic protocol utilizing citric acid worked well for some of the olefins we encountered problems with cleavage of the double bond in the case of aliphatic olefins as well

as with some of the aromatic ones (Table 2, Method A). In particular, the more substituted aliphatic olefins were problematic. Thus, 1-octene was the only aliphatic olefin that gave a clean reaction and a high yield using only 5 mol% of citric acid (Table 2, entry 8).

Since the method based on citric acid gave considerable amounts of double bond cleavage for the aliphatic olefins, and it is well known that this cleavage is faster at lower pH, we replaced citric acid with tetraethyl ammonium acetate (TEAA) as in the $\text{VO}(\text{acac})_2$ -co-catalyzed protocol. This proved to be successful and we obtained high yields for all the aliphatic olefins (Table 2, Method B, entries 7–10). Also the aromatic olefins worked quite well with this method to give satisfactory to good yields,



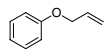
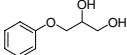
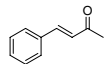
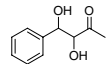
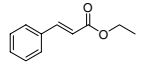
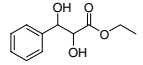



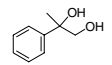
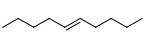
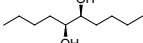
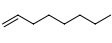
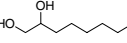
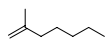
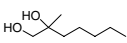


Table 1
Osmium-catalyzed dihydroxylation of alkenes in ionic liquid using $\text{VO}(\text{acac})_2$ as co-catalyst^a

Entry	Olefin	Product	Yield ^b
1			81%
2			82%
3			91%
4			81%
5			73%
6			91%
7			80%
8			81%
9			86%
10			87%

^a Experimental conditions: 7.2 mg of $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$ (2 mol%), 5.3 mg of $\text{VO}(\text{acac})_2$ (2 mol%), 25 μL of *N*-methylmorpholine (NMM) (23 mol%), and $\text{Et}_4\text{N}^+\text{OAc}^-$ (TEAA) (2 equiv.) were stirred in 0.5 mL of $[\text{bmim}]\text{PF}_6$, 3.8 mL of acetone and 1.2 mL of H_2O were added as co-solvents together with the olefin (1 mmol). 30% H_2O_2 (1.5 mmol) was added over 8 h followed by 8 h of reaction.

^b Isolated yields.

Table 2
Osmium-catalyzed dihydroxylation of alkenes in ionic liquid using MTO as co-catalyst

Entry	Substrate	Product	Method A ^a Yield ^c %	Method B ^b Yield ^c (%)
1			95	74 ^d
2			86	68
3			51	48
4			77	56
5			51	73
6			99	86
7			18	85
8			78	90
9			n.d. ^e	85
10			41	72

^a Method A: $K_2OsO_4 \cdot 2H_2O$ (7.2 mg, 2 mol%), MTO (5.5 mg, 2 mol%), *N*-methylmorpholine (NMM) (22 μ L, 20 mol%) and Citric acid (9.6 mg, 5 mol%) were stirred in 0.5 mL of [bmim]PF₆. Acetone (1 mL) and H₂O (0.2 mL) were added as co-solvents together with the olefin (1 mmol). H₂O₂ (30% aq., 1.5 mmol) was added over 4 h followed by 4–16 h of reaction.

^b Method B: $K_2OsO_4 \cdot 2H_2O$, (7.2 mg, 2 mol%), MTO (5.5 mg, 2 mol%), *N*-methylmorpholine (NMM) (22 μ L, 20 mol%) and TEAA (2 equiv.) were stirred in 0.5 mL of [bmim]PF₆. Acetone (3 mL) and H₂O (0.2 mL) were added as co-solvents together with the olefin (1 mmol). H₂O₂ (30% aq., 1.5 mmol) was added over 8 h followed by 8 h of reaction.

^c Isolated yields.

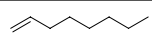
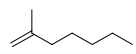

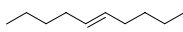

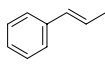
^d H₂O₂ was added over 4 h followed by an additional 16 h of stirring.

^e Not determined due to poor conversion.

but some of these olefins worked better with the citric acid-assisted method (Method A).

In order to investigate the significance of the direct oxidation of OsO₃ to OsO₄ by MTO we run the TEAA based method with six different olefins without any NMM present (Table 3). According to the results, 95% yield of diol from 1-octene (Table 3, entry 1) and 2-methyl-1-heptene (Table 3, entry 2) was obtained. Also, cyclohexene gave a good yield (88%) of diol (Table 3, entry 3). However, *E*-5-decene, styrene and β -methylstyrene gave lower yields (Table 3, entries 4–6) compared with the methods utilizing NMM as electron transfer mediator (cf. Tables 1 and 2). The re-

Table 3
Osmium-catalyzed dihydroxylation of alkenes in ionic liquid using MTO as co-catalyst without NMM^a

Entry	Olefin	Yield of diol (%)
1		95
2		95
3		88
4		75
5		74
6		67

^a $K_2OsO_4 \cdot 2H_2O$ (7.2 mg, 2 mol%), MTO (5.5 mg, 2 mol%), and TEAA (2 equiv.) were stirred in 0.5 mL of [bmim]PF₆. Acetone (3 mL) and H₂O (0.2 mL) were added as co-solvents together with the olefin (1 mmol). H₂O₂ (30% aq., 1.5 mmol) was added over 8 h followed by 8 h of reaction.

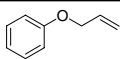

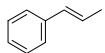
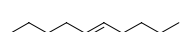
sults show that direct oxidation of OsO₃ to OsO₄ by MTO works well with some substrates but for others the presence of NMM improves the outcome of the dihydroxylation.

2.3. Recycling experiments

The catalytic system used here is immobilized in the ionic liquid. To find out if there is some loss of the catalysts during the extraction the recycling of the catalytic system (catalytic soup) [8] was studied. For our initial experiments we chose to study the dihydroxylation of allyl phenyl ether, styrene, and β -methylstyrene as model olefins. The results from five cycles using the OsO₄/NMM/VO(acac)₂/H₂O₂ triple catalytic system show that it is possible to recycle the catalytic system (Table 4, entries 1–3). Allyl phenyl ether, styrene and β -methylstyrene gave good yield for all five recycling experiments. However, the aliphatic olefins (*E*)-5-decene gave moderate yields in our initial second recycling experiment.

Whereas the recycling of the coupled catalytic system was successful using VO(acac)₂ as co-catalyst the MTO supported system unfortunately turned out to be less productive. The citric acid-based method showed severe contamination of cleaved product already in the third run (Table 5, entry 1). Since the method utilizing TEAA together with MTO (method B) gave high yields with the aliphatic olefins we chose this method for the recycling experiments for the aliphatic olefins. The yields of the diols resulting from the linear aliphatic olefins, 1-octene and 2-methyl-1-heptene, dropped steadily for each recycling of the ionic liquid-catalyst system (Table 5, entries

Table 4
Recycling of the bimetallic OsO₄-VO(acac)₂ catalytic system^a

Entry	Olefin	Yield (%) ^b				
		Run 1	Run 2	Run 3	Run 4	Run 5
1		81	88	74	80	82
2		81	83	84	78	83
3		82	79	81	74	63
4		87	43	n.d. ^c	n.d. ^c	n.d. ^c

^a K₂OsO₄ · 2H₂O (7.2 mg, 2 mol%), VO(acac)₂ (5.1 mg, 2 mol%), *N*-methylmorpholine (NMM) (22 μL, 20 mol%) and TEAA (2 equiv.) were stirred in 0.5 mL of [bmim]PF₆. Acetone (3.8 mL) and H₂O (1.2 mL) were added as co-solvents together with the olefin (1 mmol). H₂O₂ (30% aq., 1.5 mmol) was added over 8 h followed by 8 h of reaction.

^b Isolated yields.


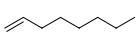
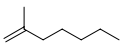

^c Not determined.

1–2). However, for the cyclohexane-1,2-diol the yields remained good through 4 runs.

2.4. Mechanism of the H₂O₂-based dihydroxylation

The mechanism of the coupled bimetallic catalytic system can be described as shown in Scheme 1. In this coupled catalytic system OsO₄ is the substrate-selective catalyst that dihydroxylates the alkene to give diol and

Table 5
Recycling of the OsO₄-MTO catalytic system^a

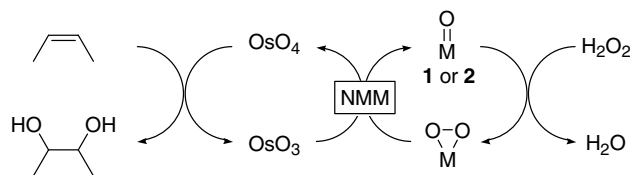
Entry	Olefin	Yield (%)			
		Run 1	Run 2	Run 3	Run 4
1 ^b		81	38 ^c	n.d. ^d	
2		98	76	59	n.d. ^d
3		98	61	47	n.d. ^d
4		72	70	84	46

^a Method B: K₂OsO₄ · 2H₂O (7.2 mg, 2 mol%), MTO (5.5 mg, 2 mol%), *N*-methylmorpholine (NMM) (22 μL, 20 mol%) and TEAA (2 equiv.) were stirred in 0.5 mL of [bmim]PF₆. Acetone (3 mL) and H₂O (0.2 mL) were added as co-solvents together with the olefin (1 mmol). H₂O₂ (30% aq., 1.5 mmol) was added over 8 h followed by 8 h of reaction.

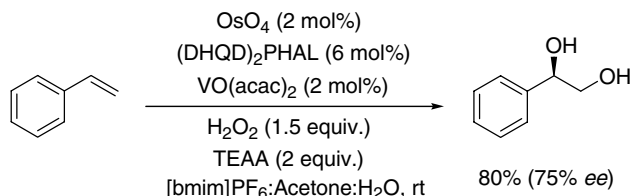
^b K₂OsO₄ · 2H₂O (1.8 mg, 0.5 mol%), MTO (2.5 mg, 1 mol%), of *N*-methylmorpholine (NMM) (22 μL, 20 mol%) and Citric acid (0.144 g, 75 mol%) were stirred in 0.5 mL of [bmim]PF₆. Acetone (3 mL) and H₂O (0.2 mL) were added as co-solvents together with the olefin (1 mmol). H₂O₂ (30% aq., 1.5 mmol) was added over 4 h followed by 8 h of reaction.

^c H₂O₂ was added over 8 h and the reaction stirred for additional 8 h.

^d Not determined due to poor conversion.



Scheme 1. Coupled bimetallic catalytic system for dihydroxylation of olefins immobilized in ionic liquid.



Scheme 2. Asymmetric dihydroxylation using (DHQD)₂PHAL in the osmium-VO(acac)₂ catalytic system.

reduced osmium. Hydrogen peroxide reacts with the metal oxo complex to give a reactive peroxy complex. This peroxy complex can react directly with the reduced form of the osmium catalyst, OsO₃, to regenerate OsO₄. The selectivity of this reoxidation is increased by the use of catalytic amounts of *N*-methylmorpholine (NMM). In the latter case the amine is oxidized to the corresponding *N*-oxide (NMO), which efficiently transfers an oxygen atom to osmium.

An interesting question is if the hydrogen peroxide-based dihydroxylation in ionic liquid is compatible with chiral ligands. In a preliminary experiment we found that chiral ligand (DHQD)₂PHAL gave an *ee* of 75% in the dihydroxylation of styrene utilizing the osmium-VO(acac)₂ catalytic system (Scheme 2). In this reaction the chiral ligand is also working as an electron transfer mediator. Further studies are required to improve the enantioselectivity of the H₂O₂-based reaction in ionic liquid.

3. Conclusions

Hydrogen peroxide-based osmium-catalyzed dihydroxylation using two different metal complexes, VO(acac)₂ and MTO, as co-catalysts (electron transfer mediators) in room temperature ionic liquid [bmim]PF₆ has been investigated. The two protocols of the bimetallic catalytic system were tested with a variety of aromatic and aliphatic olefins and were found to yield the corresponding 1,2-diols in good to excellent yields. Electron transfer from the co-catalyst to osmium is facilitated by the presence of catalytic amounts of NMM as an additional electron transfer mediator. It was demonstrated that in some cases direct electron transfer from MTO to osmium is efficient without added NMM.

Immobilization and recycling of the catalytic system (catalytic soup) has been demonstrated by extraction

of the product and reuse of the catalytic system with no or moderate loss of activity. The bimetallic catalytic system in room temperature ionic liquid gives a simple and reusable “catalytic soup” with hydrogen peroxide as the terminal oxidant, which is environmentally friendly since the only by-product is water.

4. Experimental

4.1. General methods

^1H and ^{13}C NMR spectra were recorded on a Varian Unity 400 (400 MHz ^1H , 100 MHz ^{13}C) or a Varian Unity 300 (300 MHz ^1H , 75 MHz ^{13}C) spectrometer. Chemical shifts (δ) are reported in ppm, using residual solvent as internal standard. Millipore Matrex silica gel (60 Å pore size, 35–70 μm) was used for flash chromatography. Potassium osmate and tetraethylammonium acetate (TEAA) were purchased from Aldrich. 1-Butyl-3-methyl imidazolium hexafluorophosphate ([bmim]PF₆) was purchased from Acros. All olefins, VO(acac)₂ (**1**) and MeReO₃ (**2**) were obtained from commercial suppliers and used without further purification.

4.2. Procedure for osmium-catalyzed dihydroxylation of olefins by H₂O₂ with VO(acac)₂ as co-catalyst (Table 1, all entries)

Ionic liquid [bmim]PF₆ (0.5 mL) was placed in a 20 mL vial with a small stir bar. K₂OsO₄·2H₂O (7.2 mg, 0.02 mmol, 2 mol%), VO(acac)₂ (5.1 mg, 0.02 mmol, 2 mol%), and TEAA·4H₂O (523 mg, 2 mmol) were added and mixed by gentle stirring. Acetone (3.8 mL) and water (1.2 mL) were introduced, followed by *N*-methylmorpholine (NMM) (28 μL , 0.23 mmol, 23 mol%) and olefin (1 mmol). Aqueous hydrogen peroxide (170 μL , 30% solution, 1.5 equivalents) was added over 8 h via syringe pump. The reaction mixture was allowed to stir for another 8 h, and the volatile solvents were removed under reduced pressure. The residue of [bmim]PF₆ was extracted three times with 10 mL portions of diethyl ether. The ether layers were combined, and reduced in volume to yield the crude diol. The crude diol was chromatographed on silica gel with 1:1 EtOAc/pentane to yield the purified product.

4.3. Procedure for osmium-catalyzed dihydroxylation of olefins by H₂O₂ with MeReO₃ (MTO) as co-catalyst using method A (Table 2, all entries)

Ionic liquid [bmim]PF₆ (0.5 mL) was placed in a 20 mL vial with a small stir bar. K₂OsO₄·2H₂O (7.2 mg, 0.02 mmol, 2 mol%), MeReO₃ (5.5 mg,

0.02 mmol, 2 mol%), and citric acid (9.6 mg, 0.05 mmol) were added and mixed by gentle stirring. Acetone (1 mL) and water (0.2 mL) were introduced, followed by *N*-methylmorpholine (NMM) (22 μL , 0.2 mmol, 20 mol%) and olefin (1 mmol). Aqueous hydrogen peroxide (170 μL , 30% solution, 1.5 equivalents) was added over 4 h via syringe pump followed by additional 8 h stirring after which the volatile solvents were removed under reduced pressure. The resulting residue of [bmim]PF₆ was then extracted three times with 10 mL portions of diethyl ether. The ether layers were combined, and reduced in volume to yield the crude diol. The crude diol was chromatographed on silica gel with 1:1 or 1:2 EtOAc/pentane to yield the purified product.

4.4. Procedure for osmium-catalyzed dihydroxylation of olefins by H₂O₂ with MeReO₃ (MTO) as co-catalyst using method B (Table 2, all entries)

Ionic liquid [bmim]PF₆ (0.5 mL) was placed in a 20 mL vial with a small stir bar. K₂OsO₄·2H₂O (7.2 mg, 0.02 mmol, 2 mol%), MeReO₃ (5.5 mg, 0.02 mmol, 2 mol%), and TEAA·4H₂O (523 mg, 2 mmol) were added and mixed by gentle stirring. Acetone (3 mL) and water (0.2 mL) were introduced, followed by *N*-methylmorpholine (NMM) (28 μL , 0.23 mmol, 23 mol%) and olefin (1 mmol). Aqueous hydrogen peroxide (170 μL , 30% solution, 1.5 equivalents) was added over 8 h via syringe pump followed by additional 8 h stirring after which the volatile solvents were removed under reduced pressure. The resulting residue of [bmim]PF₆ was then extracted three times with 10 mL portions of diethyl ether. The ether layers were combined, and reduced in volume to yield the crude diol. The crude diol was chromatographed on silica gel with 1:1 or 1:2 EtOAc/pentane to yield the purified product.

4.5. Procedure for osmium-catalyzed dihydroxylation of olefins by H₂O₂ with MeReO₃ (MTO) as co-catalyst without *N*-methylmorpholine (NNM) (Table 3, all entries)

Same as method B but without NMM.

4.6. Recycling and reuse of ionic liquid-immobilized catalytic system using VO(acac)₂ as co-catalyst (Table 4, runs 2–5)

Acetone (3.8 mL) and water (1.2 mL) were added to the ionic liquid layer from the first reaction, followed by 1 mmol of olefin. Aqueous hydrogen peroxide (170 μL , 30% solution, 1.5 equivalents) was added over 8 h. After stirring for another 8 h, the volatile solvents were removed, and the remaining ionic liquid was extracted three times with 10 mL portions of diethyl ether.

The ether layers were combined and reduced in volume, and the resulting crude product was chromatographed on silica gel with 1:1 EtOAc/pentane to yield purified diol. The subsequent reaction runs 3–5 were carried out in exactly the same manner as described here.

4.7. Recycling and reuse of ionic liquid-immobilized catalytic system using MeReO_3 (MTO) as co-catalyst (Table 5, runs 2–5)

Acetone (3 mL) and water (0.2 mL) were added to the ionic liquid layer from the first reaction, followed by 1 mmol of olefin. Aqueous hydrogen peroxide (170 μL , 30% solution, 1.5 equivalents) was added over 8 h. After stirring for another 8 h, the volatile solvents were removed, and the remaining ionic liquid was extracted three times with 10 mL portions of diethyl ether. The ether layers were combined and reduced in volume, and the resulting crude product was chromatographed on silica gel with 1:1 or 1:2 EtOAc/pentane to yield purified diol. The subsequent reaction runs 3–4 were carried out in exactly the same manner as described herein.

4.8. Procedure for asymmetric dihydroxylation of styrene by OsO_4 -(DHQD)₂PHAL-VO(acac)₂ catalytic system (Scheme 2)

$\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$ (7.2 mg, 0.02 mmol, 2 mol%), VO(acac)₂ (5.1 mg, 0.02 mmol, 2 mol%), and TEAA \cdot 4H₂O (523 mg, 2 mmol) were placed in a 20 mL vial with a small stir bar. Ionic liquid [bmim]PF₆ (0.5 mL), acetone (3.8 mL) and water (1.2 mL) were introduced and mixed by gentle stirring, followed by (DHQD)₂PHAL (46 mg, 0.06 mmol, 6 mol%) and styrene (1 mmol). Aqueous hydrogen peroxide (170 μL , 30% solution, 1.5 equivalents) was added over 8 h via syringe pump. The reaction mixture was allowed to stir for another 8 h, and the volatile solvents were removed under reduced pressure. The resulting residue of [bmim]PF₆ was then extracted three times with 10 mL portions of diethyl ether. The ether layers were combined, and reduced in volume to yield the crude diol. The crude diol was chromatographed on silica gel with 1:1 EtOAc/pentane to yield the purified product in 80% isolated yield. Analysis by HPLC [5b] showed that the product was of 75% *ee*. (1*R*)-1-phenyl-1,2-ethanediol (HPLC (Daicel Chiralcel OD-H column, 95:5 *iso*-hexane/2-propanol, flow rate 0.5 mL/min): t_{R} (major) = 29.9 min, t_{R} (minor) = 31.6 min).

4.9. The NMR data of the diols were in accordance with those previously reported

1-Phenyl-1,2-ethanediol [3b], 2-phenyl-1,2-propanediol [3b], 5,6-decenediol [3b], *cis*-1,2-cyclohexanediol [14], 2,3-octanediol [15], 1-phenyl-1,2-propanediol [16],

3-phenoxy-1,2-propanediol [17], 1-phenyl-1,2-cyclohexane-diol [18], 2-methyl-1,2-heptanediol [19], 1,2-octanediol [20], 3,4-dihydroxy-4-phenyl-2-butanone [21], 2,3-dihydroxy-3-phenyl ethyl propionate [22].

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