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Asymmetric transfer hydrogenation of ketones with a polyethylene glycol bound Ru catalyst in water

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Abstract—A new polyethylene glycol supported Ru catalyst was synthesized and applied in the asymmetric transfer hydrogenation of various aromatic ketones in water with high chemical yields and enantioselectivities without adding any surfactants. The catalyst could be easily recycled several times without a significant loss of enantioselectivity and activity.

1. Introduction

Compound Ru-TsDPEN, developed by Noyori et al., is one of the most notable chiral catalysts for the catalytic asymmetric transfer hydrogenation of ketones.[1] A variety of aromatic ketones in an isopropanol system or HCOOH–Et_3N azeotropic system can be reduced by this catalyst with excellent chemical yields and enantioselectivities to give chiral secondary alcohols, which are valuable intermediates in organic and pharmaceutical syntheses.[2]

Water has many advantages over common organic solvents when it is used as a solvent in chemical reactions. It is economical, non-toxic, and environmentally friendly. The use of water as a solvent in catalytic asymmetric transfer hydrogenation has been investigated in recent years. Xiao et al. employed water as a solvent in the reaction of Ru-TsDPEN catalyst with HCOONa as the hydrogen donor.[3] They discovered that the reaction rates could be accelerated in water with a slight decrease in enantioselectivity. Deng et al. reported the asymmetric transfer hydrogenation of ketones with Ru-TsDPEN catalyst in water by adding surfactants to form aqueous micelles and vesicles.[4] The hydrophobic products could be separated by extraction with an organic solvent, such as hexane, and the catalyst recycled for at least six times. More recently, Fan et al. found that the asymmetric transfer hydrogenation of ketones catalyzed by Ru-TsDPEN could be successfully performed in a mixture of polyethylene glycol and water ($PEG/H_2O = 9:1$) with high enantioselectivity.[5] The catalyst could be easily recovered after extraction of the product with hexane, and was reused 14 times. Supported Ru-TsDPEN catalysts in asymmetric transfer hydrogenation have also received widespread attention. Tu et al. developed a heterogeneous catalyst through the immobilization of TsDPEN onto silica gel.[6] Xiao et al. prepared the polyethylene glycol supported ligand (PTsDPEN) and the related ruthenium catalyst.[7] Herein, we report a new supported PEG-BsDPEN catalyst (Scheme 1) for the asymmetric transfer hydrogenation of a variety of ketones in neat water with high enantioselectivity and chemical yields, without adding any surfactants.

2. Results and discussion

The poor solubility of the pre-catalyst Ru-TsDPEN and most ketones in water leads to lower reaction rates of the asymmetric transfer hydrogenation. For improving the solubility of the ligand in water, Deng et al. prepared an *ortho*-sulfonated TsDPEN ligand,[8] which achieved high reactivity and enantioselectivity in Ru-catalyzed asymmetric transfer hydrogenation for most prochiral aromatic ketones in water. On the other hand, polyethylene glycol (PEG), which is soluble in both water and organic solvents, has successfully been used as a reaction medium and additive in a variety of organic reactions. Recently, Xiao et al.

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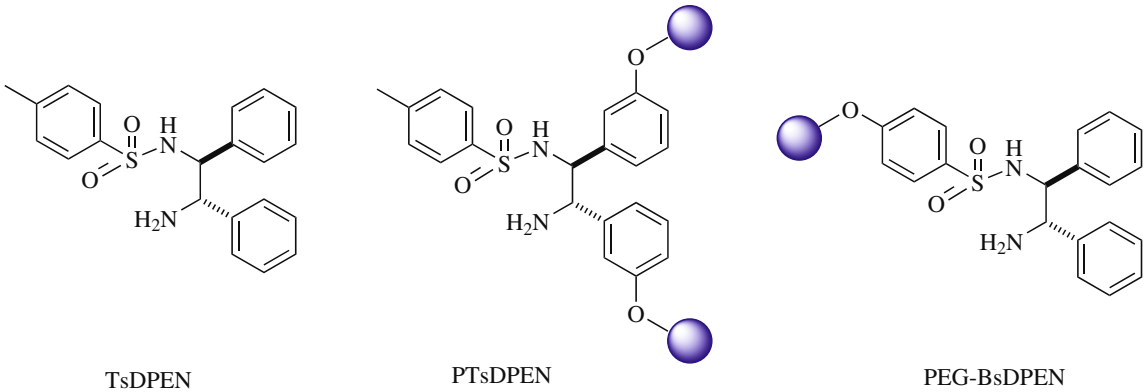
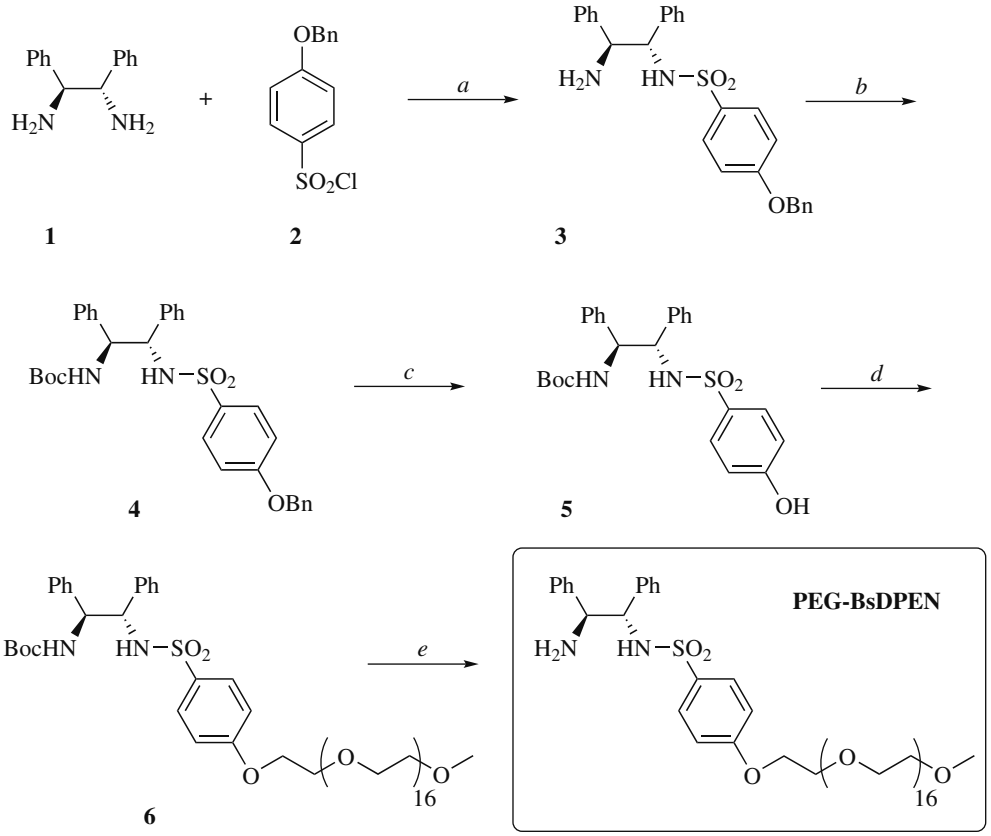


Scheme 1. TsDPEN and PEG-supported DPEN ligands.

developed a new PTsDPEN ligand which has two long polyethylene glycol chains (PEG-2000) on *meta*-position of TsDPEN's phenyl groups.[7] Comparing the results of Ru-TsDPEN catalyst in water,[3] the polyethylene glycol supported ruthenium catalyst Ru-PTsDPEN in the asymmetric transfer hydrogenation of various aromatic ketones by HCOONa in water afforded faster rates and good reusability.

As an alternative method for attaching a PEG chain onto TsDPEN-type ligands, we designed a medium-length polyethylene glycol chain (PEG-750) at the *para*-position of an aryl sulfate group, which can effectively accelerate the reaction rate of asymmetric transfer hydrogenation in water and afford good enantioselectivity and reusability.

The polyethylene glycol supported chiral ligand (PEG-BsDPEN) could be conveniently prepared from chiral 1,2-diphenylethane-1,2-diamine (Scheme 2). Chiral diamine **1** reacted with 4-(benzyloxy)-benzene-1-sulfonyl chloride **2** in the presence of triethylamine giving *N*-((1*S*,2*S*)-2-amino-1,2-diphenylethyl)-4-(benzyloxy)benzenesulfonamide **3** in 85% yield. The amino group of compound **3** was protected by reacting with DIBOC to convert into *tert*-butyl-(1*S*,2*S*)-2-(4-(benzyloxy)phenylsulfonamido)-1,2-diphenylethylcarbamate **4** with 98% yield. The deprotection of



Scheme 2. Synthetic route to the PEG-BsDPEN ligand. Reagents and conditions: (a) (*S*,*S*)-DPEDA, Et_3N, CH_2Cl_2; (b) DIBOC, Et_3N, CH_2Cl_2; (c) Pd/C, H_2, EtOH; (d) Cs_2CO_3, MeOPEGOTs, acetone; (e) CF_3COOH, CH_2Cl_2.

intermediate **4** was carried out in the presence of Pd/C under a hydrogen atmosphere to give *tert*-butyl-(1*S*,2*S*)-2-(4-hydroxyphenylsulfonamido)-1,2-diphenylethylcarbamate **5** in a quantitative yield. After reaction with polyethylene glycol monomethyl ether tosylate in the presence of Cs_2CO_3, compound **5** was converted to Boc-PEG-BsDPEN ligand **6** in good yield. Finally, the Boc deprotection by trifluoroacetic acid afforded the target chiral ligand PEG-BsDPEN **7** in 51% overall yield. The mass spectrum of PEG-BsDPEN was measured by APCI-MS, and then compared with starting material PEG-750 (Fig. 1).

PEG-BsDPEN **7** was first examined in the Ru-catalyzed asymmetric transfer hydrogenation of acetophenone in water using HCOONa as the hydrogen donor at room temperature. Common factors governing the enantioselectivity of the reaction were examined. The results shown in Table 1 indicate that the enantioselectivity was sensitive to the amounts of HCOONa used. Five equivalents were found to give the best result (entries 1–3: 1 equiv of HCOONa, 92% ee; 2.5 equiv of HCOONa, 94% ee; 5 equiv of HCOONa, 96% ee). The high ratio of substrate to catalyst (S/C) led to slower reaction rates and enantioselectivities (entry 5: S/C = 1000, 24 h was needed to complet the reaction with 90% ee).

Various aromatic ketones were used in the study of the asymmetric transfer hydrogenation of PEG-BsDPEN **7** under optimized conditions (Table 2). Ee values were found to be consistently 2–3% higher in most cases in comparison with those obtained with Ru-PTsDPEN as catalyst; this is probably attributable to the fact that the PEG chain on aryl sulfate group is far from the catalytic center and does not have negative effect on the torsional dihedral angle in PEG-BsDPEN **7**. The electronic effect of the substrates is important for the enantioselectivity of the reaction. For example, *p*-fluoroacetophenone or *p*-chloroacetophenone gave products with higher enantioselectivities (99% ee and 97% ee respectively) than those from *p*-methylacetophenone and *p*-methoxyacetophenone (92% ee and 93% ee). 2-Chloro-1-phenylethanone and 2-bromo-1-phenylethanone also afforded good to excellent enantioselectivities (entry 12: 97% ee with 95% yield and entry 13: 95% ee with 96% yield). However, the enantioselectivity decreased abruptly for heptanophenone (entries 9: 56% ee) possibly due to the larger steric bulk of the heptanyl group. The highest enantioselectivity (99%) was realized for 4′-fluoroacetophenone which contained a *p*-fluoro group on the aromatic ring (entry 4).

The recycling of catalyst Ru-PEG-BsDPEN **7** was investigated with acetophenone as the substrate and HCOONa as

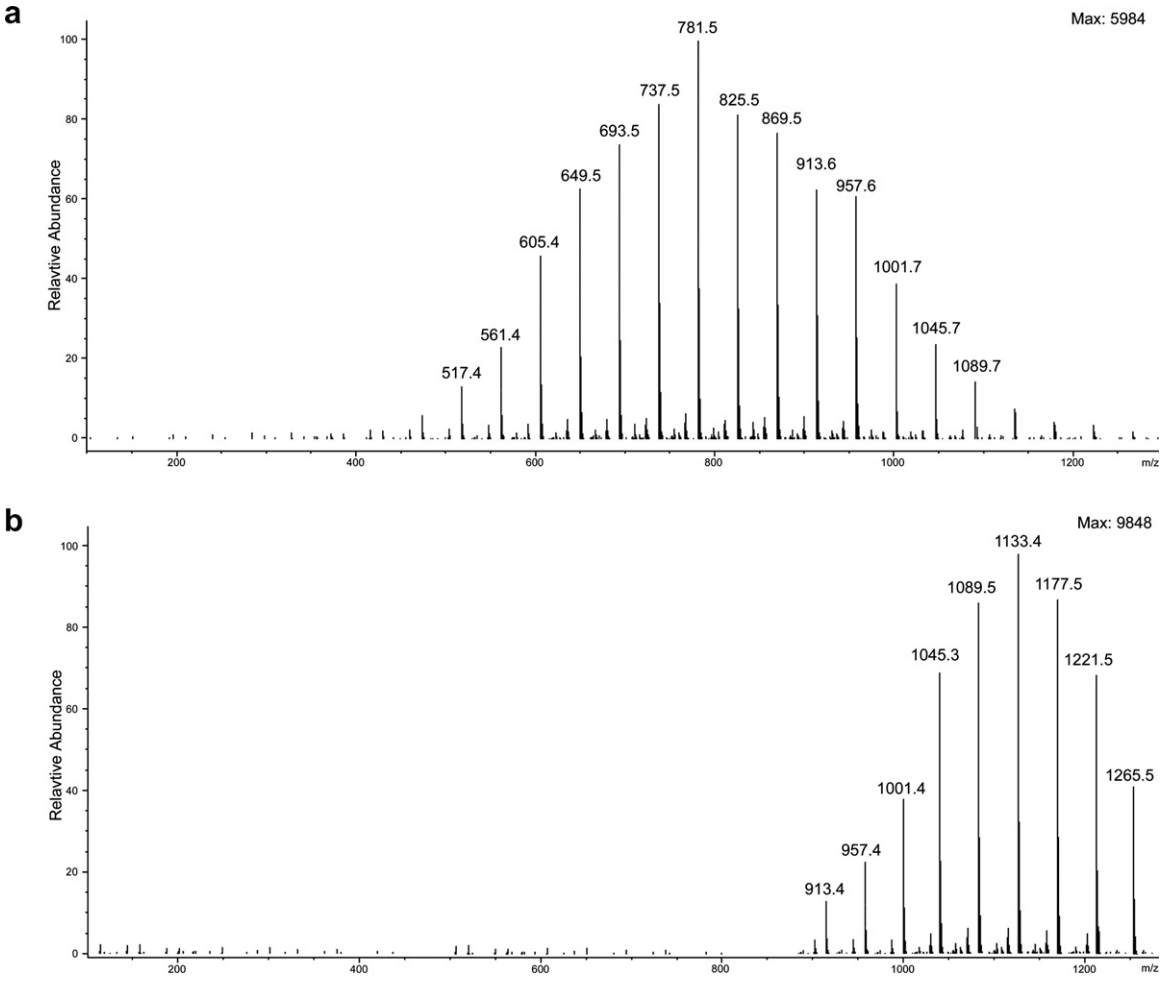
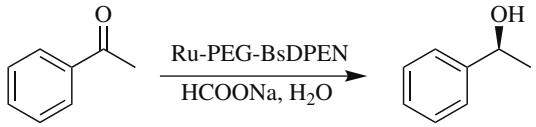


Figure 1. APCI mass spectra: (a) PEG-750; (b) PEG-BsDPEN.

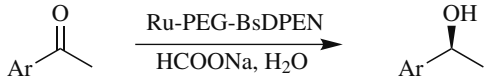
Table 1. Asymmetric transfer hydrogenation of acetophenone in water[a]



Entry	S/C Ratio	HCOONa (equiv)	Time (h)	Conversion[b] (%)	ee[c] (%)
1	100	1.0	4	99	92
2	100	2.5	2	>99	94
3	100	5.0	2	>99	96
4	500	5.0	12	>99	93
5	1000	5.0	24	>99	90

[a] Reactions were carried out with Ru-PEG-BsDPEN catalyst at room temperature in water.
[b] The conversion was determined by GC with an HP-5 capillary column.
[c] The ee value was determined by chiral HPLC with a chiralcel OD-H column.

Table 2. Asymmetric transfer hydrogenation of various ketones in water[a]



Entry	Substrates	Conversion[b] (%)	ee[c] (%)
1	Acetophenone	99	96
2	4′-Fluoroacetophenone	99	99
3	4′-Chloroacetophenone	99	97
4	4′-Bromoacetophenone	95	96
5	4′-Methoxyacetophenone	99	93
6	4′-Methylacetophenone	99	92
7	4′-Nitroacetophenone	95	89
8	Propiophenone	99	91
9	Heptanophenone	99	56
10	1-Tetralone	99	96
11	1-Indanone	99	95
12	2-Chloro-1-phenylethanone	95	97
13	2-Bromo-1-phenylethanone	96	95
14	2-Acetylnaphthalene	95	90
15	2-Acetylfuran	99	97

[a] Reactions were carried out with Ru-PEG-BsDPEN catalyst (S/C = 100/1) and 5.0 equiv HCOONa as a hydrogen donor at room temperature in water for 2 h.
[b] The conversion was determined by GC with an HP-5 capillary column.
[c] The ee value was determined by chiral HPLC with a chiralcel OD-H or OB-H column.

the hydrogen donor in water. After each catalytic cycle, hexane was added to extract the product and the residue containing the catalyst was reused by adding 1.0 equiv of formic acid to regenerate sodium formate for the next cycle. Due to a slight decrease of catalyst's reactivity, the reaction time was prolonged to 4 h in the sixth run (Table 3). However, the enantioselectivity (95% ee) was quite consistent even on the eighth run.

Table 3. Results of catalyst recycling in the asymmetric transfer hydrogenation of acetophenone in water[a]

Run	Time (h)	Conversion[b] (%)	ee[c] (%)
1	2	>99	96
2	2	>99	97
3	2	>99	96
4	2	>99	95
5	2	99	95
6	4	98	95
7	4	98	95
8	4	96	95

[a] Reactions were carried out with Ru-PEG-BsDPEN catalyst (S/C = 100/1) and 5.0 equiv of HCOONa as a hydrogen donor at room temperature in water for 2 h. After each batch, 1 equiv of HCOOH was added to regenerate HCOONa.
[b] The conversion was determined by GC with an HP-5 capillary column.
[c] The ee value was determined by chiral HPLC with a chiralcel OD-H column.

3. Conclusions

In conclusion, we have developed a new chiral ligand PEG-BsDPEN, which is practical for the Ru-catalyzed asymmetric transfer hydrogenation of aromatic ketones with HCOONa as the hydrogen donor in an environmentally friendly manner. The reactions proceeded smoothly with good yields and high enantioselectivities (up to 99% ee) in water. The unique feature was that the catalyst could be easily recovered and reused eight times without a significant loss of enantioselectivity and activity.

4. Experimental

The NMR spectra were recorded with TMS as the internal standard on a Varian 300 spectrometer. Coupling constants were given in Hertz. The enantiomeric excess was determined by HPLC on Chiralcel OB-H or OD-H columns. Optical rotations were determined on a Perkin Elmer 341 polar meter. MS spectra were recorded on an Agilent LC–MS 6120 with ESI or APCI. The reactions were monitored by thin layer chromatography coated with silica gel.

4.1. Preparation of PEG-BsDPEN ligand

4.1.1. 4-Benzyloxyphenylsulfonic acid, sodium salt. To a solution of 4-hydroxybenzenesulfonic acid (6.00 g, 26 mmol) in 150 ml of ethanol were added benzyl bromide (6.6 g, 39 mmol) and sodium hydroxide (1.0 g) in water (10 ml). The reaction mixture was stirred at reflux for 24 h. After cooling to room temperature, colorless crystals formed, which were filtrated and washed with cold CH_2Cl_2. The precipitate was dried in vacuo to afford white crystals, 4.62 g, 62% yield. ^{1}H NMR ($(CD_3)_2SO$) δ: 7.49 (d, $J = 8.8$, 2H), 7.42 (d, $J = 8.8$, 2H), 7.37–7.31 (m, 3H), 6.92 (d, 2H), 5.09 (s, 2H) ppm; ESI-MS $[M-Na]^+$ 263.2.

4.1.2. 4-(Benzyloxy)benzene-1-sulfonyl chloride. To a solution of *p*-hydroxybenzenesulfonic acid (4.62 g, 16.1 mmol) in CH_2Cl_2 (10 ml) was added PCl_5 (5 g, 24.2 mmol). The reaction mixture was stirred at 40 °C for 24 h, after which the solvent was removed using rotary evaporator. The residue was purified by chromatography (10% ethyl acetate in petroleum ether as eluents) to give a

white solid in quantitative yield, 4.5 g, 99% yield. ^{1}H NMR ($CDCl_3$) δ: 7.49 (d, $J = 9$, 2H), 7.42–7.37 (m, 5H), 6.92 (d, $J = 9$, 2H), 5.09 (s, 2H) ppm; ESI-MS $[M+H]^+$ 282.3.

4.1.3. Polyethylene glycol monomethyl ether tosylate. To polyethylene glycol monomethyl ether (MW750) (7.5 g, 10 mmol) and *p*-toluenesulfonyl chloride (7.5 g, 40 mmol) in methylene chloride (50 ml) was added 2 ml (20 mmol) of pyridine under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 5 h. The resulting solution was poured into 100 ml of 10% HCl and extracted twice with methylene chloride (50 ml). The combined organic layers were dried over anhydrous magnesium sulfate and filtered. The solvent was removed under reduced pressure to give a yellow oil. The crude product could be further purified by column chromatography (ethyl acetate/methanol = 4:1 as eluents) to yield a colorless liquid, 6.8 g, 75% yield. ^{1}H NMR ($CDCl_3$) δ: 7.79 (d, $J = 8.4$, 2H), 7.34 (d, $J = 8.4$, 2H), 4.16 (t, $J = 4.5$, 2H), 4.15 (t, $J = 4.8$, 2H), 3.68 (t, $J = 4.8$, 2H), 3.63 (m, 56H), 3.57 (s, 3H), 3.37 (s, 3H) ppm.

4.1.4. *N*-((1*S*,2*S*)-2-Amino-1,2-diphenylethyl)-4-(benzyloxy)-benzenesulfonamide. To a solution of (1*S*,2*S*)-1,2-diphenylethane-1,2-diamine (836 mg, 2 mmol) and triethylamine (0.28 ml, 2 mmol) in anhydrous dichloromethane (10 ml) was added dropwise a solution of 4-(benzyloxy)benzene-1-sulfonyl chloride (565 mg, 2 mmol) in dichloromethane (5 ml) at 0 °C. The mixture was stirred at 0 °C for 2 h and allowed to warm to room temperature. Water (5 ml) was added and the two layers were separated. The aqueous layer was extracted twice with 5 ml of dichloromethane and the combined organic layers were washed with brine and water and subsequently dried over sodium sulfate. The solvent was removed under reduced pressure. The crude *N*-((1*S*,2*S*)-2-amino-1,2-diphenylethyl)-4-(benzyloxy)benzenesulfonamide was purified by column chromatography (5% methanol in ethyl acetate as eluents) to give a white solid, 780 mg, 85% yield. ^{1}H NMR ($CDCl_3$) δ: 7.41–7.39 (m, 4H), 7.33 (d, $J = 9$, 2H), 7.14–7.10 (m, 10H), 6.71 (d, $J = 9$, 2H), 5.04 (s, 2H) 4.35 (d, $J = 5$, 1H), 4.11 (d, $J = 5$, 1H), 1.53 (br, 2H) ppm; APCI-MS $[M+H]^+$ 459.2.

4.1.5. *tert*-Butyl-(1*S*,2*S*)-2-(4-(benzyloxy)phenylsulfonamido)-1,2-diphenylethylcarbamate. A solution of *N*-((1*S*,2*S*)-2-amino-1,2-diphenylethyl)-4-(benzyloxy)benzenesulfonamide (458 mg, 1.0 mmol), DIBOC (262 mg, 1.2 mmol), and Et_3N (202 mg, 2 mmol) in 20 ml of CH_2Cl_2 was stirred at room temperature for 4 h. The solution was washed with 5% aq HCl. The organic phase was separated and dried over Na_2SO_4. The crude product was purified by chromatography (chloroform as eluents) to yield a white powder, 544 mg, 98% yield. ^{1}H NMR ($CDCl_3$) δ: 7.45 (d, $J = 8.8$ Hz, 2H), 7.38–7.40 (m, 5H), 7.34 (s, 1H), 6.78–7.16 (m, 10H), 6.76 (d, $J = 8.8$ Hz, 2H), 5.20 (s, 2H), 4.78 (m, 1H), 4.55 (m, 1H), 1.47 (s, 9H) ppm. APCI-MS $[M+H]^+$ 559.2.

4.1.6. *tert*-Butyl-(1*S*,2*S*)-2-(4-hydroxyphenylsulfonamido)-1,2-diphenylethylcarbamate. A solution of *tert*-butyl-(1*S*,2*S*)-2-(4-(benzyloxy)phenylsulfonamido)-1,2-diphenylethylcarbamate (559 mg, 1 mmol) and 10% Pd/C (11 mg, 0.1 mmol) in 20 ml of methanol was stirred at room temperature for 24 h under an atmosphere of H_2. Then the reaction mixture was filtered and washed with 5 ml of methanol. The combined organic solution was evaporated in vacuum. The residue was purified by chromatography (5% methanol in chloroform as eluents) to yield a colorless powder (465 mg, 99% yield). ^{1}H NMR ($(CD_3)_2SO$) δ: 10.07 (s, 1H), 7.95 (d, $J = 8.7$ Hz, 2H), 7.25 (s, 1H), 7.02–7.24 (m, 10H), 6.50 (d, $J = 8.7$ Hz, 2H), 4.79 (m, 1H, CH), 4.60 (m, 1H), 1.25 (s, 9 H) ppm. APCI-MS $[M+H]^+$ 469.2.

4.1.7. Boc-PEG-BsDPEN ligand. A solution of *tert*-butyl-(*1S*,2*S*)-2-(4-hydroxyphenylsulfonamido)-1,2-diphenylethylcarbamate (469 mg, 1 mmol), poly(ethylene glycol) monomethyl ether tosylate (905 mg, 1 mmol), and Cs_2CO_3 (652 mg, 2 mmol) in 10 ml of acetone was heated at reflux for 24 h. The residue was triturated with CH_2Cl_2. The extract was filtered and dried over Na_2SO_4. Evaporation of the solvent in vacuum gave the crude product, which was further purified by chromatography (5% methanol in chloroform as eluents) to yield a yellow oil, 850 mg, 65% yield. ^{1}H NMR ($CDCl_3$) δ: 8.28 (s, 1H), 7.95 (d, $J = 8.7$ Hz, 2H), 7.25 (s, 1H), 7.02–7.24 (m, 10H), 6.50 (d, $J = 8.7$ Hz, 2H), 4.79 (m, 1H, CH), 4.60 (m, 1H), 1.25 (s, 9H) ppm.

4.1.8. PEG-BsDPEN ligand. Boc-PEG-BsDPEN ligand (850 mg, 0.7 mmol) was added to a mixture of trifluoroacetic acid (10 ml) and methylene chloride (10 ml). The mixture was stirred at room temperature for 4 h and then poured into water (10 ml). Aqueous sodium hydroxide was added to adjust the pH value up to 10. The organic layer was separated and the aqueous layer was extracted twice with methylene chloride (5 ml). The combined organic layers were dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to give a yellow oil, 730 mg, 95% yield. ^{1}H NMR ($CDCl_3$) δ: 10.07 (s, 1H), 7.95 (d, $J = 8.7$ Hz, 2H), 7.25 (s, 1H), 7.02–7.24 (m, 10H), 6.50 (d, $J = 8.7$ Hz, 2H), 4.79 (m, 1H, CH), 4.60 (m, 1H), 1.25 (s, 9H) ppm. APCI-MS is shown in Figure 1.

4.2. General procedure for asymmetric transfer hydrogenation

A suspension of $[RuCl_2(p\text{-cymene})]_2$ (3 mg, 0.005 mmol) and PEG-BsDPEN [(*S*,*S*), 16 mg, 0.012 mmol] in H_2O (2 ml) was purged with argon and stirred at 40 °C for 1 h. Then, HCOONa (340 mg, 5.0 mmol) and a ketone (1.0 mmol) were introduced to the catalyst solution. The mixture was purged with argon and stirred at room temperature. After a certain period of time, the organic compounds were extracted with hexane (6 ml). The conversion was determined by GC with an HP-5 capillary column, and the enantioselectivity was determined by chiral HPLC analysis.

4.3. General procedure of catalyst recycling in asymmetric transfer hydrogenation of acetophenone in water

A suspension of $[RuCl_2(p\text{-cymene})]_2$ (3 mg, 0.005 mmol) and PEG-BsDPEN [(*S*,*S*), 16 mg, 0.012 mmol] in H_2O (2 ml) was purged with argon and stirred at 40 °C for 1 h. Then, HCOONa (340 mg, 5.0 mmol) and acetophe-

none (120 mg, 1.0 mmol) were introduced to the catalyst solution. The mixture was degassed three times, and stirred at room temperature under an argon atmosphere. After the reaction was completed, the product was extracted with *n*-hexane (1 ml) three times. The conversion was determined by GC with an HP-5 capillary column, and the enantioselectivity was determined by chiral HPLC analysis.

The aqueous solution containing the catalyst was used for the subsequent transfer hydrogenation run: HCOOH (0.039 ml, 1 equiv) was added to regenerate sodium formate and then acetophenone (120 mg, 1.0 mmol) was added into the aqueous solution for a new reaction cycle.

Acknowledgments

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