Magnetically Recoverable Nanoparticles: Highly Efficient Catalysts for Asymmetric Transfer Hydrogenation of Aromatic Ketones in Aqueous Medium

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Abstract: Two magnetic chiral iridium and rhodium catalysts were prepared *via* directly postgrafting 1,2-diphenylethylenediamine-derived organic silica or 1,2-cyclohexanediamine-derived organic silica onto the silica-coated iron oxide nanoparticles followed by complexation with iridium(III) or rhodium(III) complexes. During the asymmetric transfer hydrogenation of aromatic ketones in aqueous medium, the magnetic chiral catalysts exhibited high catalytic ac-

Introduction

Heterogeneous catalysts for asymmetric catalysis have attracted a great deal of interest due to their general advantages of easy separation and efficient recycling.^[1] Among these heterogeneous catalysts explored so far, magnetic catalysts show some salient features.^[2] Their intrinsically superparamagnetic properties provide a more convenient strategy to remove the magnetic catalyst by an appropriate external magnetic field, which make recovery and recycling of catalyst much easily. Furthermore, magnetic nanoparticles can be functionalized easily through appropriate surface coatings/modification, which are able to load various functionalities. In particular, magnetic catalysts show remarkable chemical and mechanical stability, which can enhance the durability of recycling catalysts. Due to these advantages, exploitation of the functionality of homogeneous catalysts on magnetic nanoparticles represents a rapidly growing field that is on the verge of being applied in industry.

Recently, some magnetic nanoparticles have been used successfully in asymmetric catalysis.^[3-7] The pioneering work reported by Lin's group^[4a] utilized bare tivities (up to 99% conversion) and enantioselectivities (up to 92% *ee*). Both catalysts could be recovered easily by magnetic separation and be reused ten times without significantly affecting their catalytic activities and enantioselectivities.

Keywords: asymmetric transfer hydrogenation; catalyst recycling; enantioselectivity; magnetic nanoparticles; magnetic separation

Fe₃O₄ nanoparticles as a support and directly postmodified chiral ruthenium complexes onto magnetic nanoparticles, which exhibited excellent enantioselectivity and remarkable reusability in the asymmetric hydrogenation of aromatic ketones. Recently, a similar strategy for enantioselective acylation has also appeared in the literature.^[4b] Additionally, a practical strategy employing magnetic mesocellular materials as magnetic supports for asymmetric catalysis also revealed high catalytic efficiency and reusability. The group of Hyeon and Kim reported that a chiral Cinchona alkaloid ligand trapped in magnetic mesocellular materials exhibited a high enantioselectivity in Oscatalyzed asymmetric dihydroxylation,^[5a] Similarly, the magnetic mesocellular foam materials developed by the groups of Li and Yang^[5b] has been applied in the Ru-catalyzed asymmetric transfer hydrogenation of imines and aromatic ketones. Although these successful samples employing magnetic materials as supports have been explored, however, these researches mainly focused on bare magnetic nanoparticles^[4] and magnetic mesocellular materials.^[5] Their intrinsic disadvantages, such as magnetic aggregation of bare magnetic nanoparticles and magnetic loss of magnetic

mesocellular materials, do still hinder their application in industry. Thus, searching for more suitable magnetic materials to overcome these restrictions is still a challenge for realizing practical applications. Recently, the development of other magnetic materials has obtained great achievements.^[6] In particular, the use of SiO₂-coated Fe₃O₄ as a support shows an obvious superiority in catalysis fields.^[7] This strategy of outside surface coatings does not only reduce greatly magnetic aggregation of bare magnetic nanoparticles, but also does avoid the magnetic losses of magnetic mesocellular materials. More importantly, the functionality of chiral catalysts on the outside surface of magnetic nanoparticles can remain in the same chiral microenvironment as the homogeneous catalyst, showing highly catalytic efficiency in stereocontrol performance.

Chiral η^5 -Cp*-M (M=Ru, Rh and Ir) complexes bearing *N*-sulfonylated 1,2-diamines are a type of highly effective catalyst for the asymmetric hydrogenation of ketones as well as cyclic imines.^[8] In particular, some of catalysts can accelerate significantly the asymmetric transfer hydrogenation of ketones in aqueous medium,^[9–11] which is economic and environmentally friendly. Thus, the immobilization of chiral η^5 -Cp*-Rh-TsDACH^[10] [DACH=1,2-cyclohexanediamine] or η^5 -Cp*-Ir-TsDEPN catalysts^[11] [DPEN= 1,2-diphenylethylenediamine] onto magnetic nanoparticle materials for asymmetric transfer hydrogenation of ketones in water-medium does not only solve the problem of expensive transition metal catalyst recycling but also does match the needs of green chemistry.

Recently, we report a series of heterogeneous catalysts for green catalysis,^[12] some of them have exhibited excellent catalytic activity and enantioselectivity in asymmetric hydrogenation reactions.^[12a-c] As part of our ongoing research aimed at the development of reusable catalysts for asymmetric hydrogenation, we herein report the development of a convenient method for the preparation of two magnetic, *N*-sulfonylated diamine-based chiral iridium and rhodium catalysts **5** and **6** through direct complexation of $[Cp*IrCl_2]_2$ with (*S*,*S*)-TsDPEN modified SiO₂-coated Fe₃O₄ nanoparticles or of $[Cp*RhCl_2]_2$ with (*R*,*R*)-TsDACH modified SiO₂-coated Fe₃O₄ nanoparticles, and apply them to the asymmetric transfer hydrogenation of aromatic ketones in aqueous medium. Our attentions focus on construction of a uniform shape of the magnetic catalysts, investigation of the tailored structure and surface chemistry of SiO₂-coated magnetic catalysts, and exploration of catalyst's reusability.

Results and Discussion

Syntheses and Characterization of the Catalysts

The magnetic chiral iridium and rhodium catalysts, abbreviated as Cp*IrTsDPEN-MNPs (5) and Cp*RhTsDACH-MNPs (6), were prepared by a postgrafting method. As shown in Scheme 1, the SiO₂coated Fe₃O₄ magnetic nanoparticles denoted as $SiO_2@Fe_3O_4$ (4) were synthesized readily via a similar solvothermal method to that reported,^[13] followed by an SiO₂-coated procedure.^[14] The silica source, (S,S)-TsDPEN-derived chiral ligand 2 or (R,R)-TsDACHderived chiral ligand $3_{\bullet}^{[15]}$ was then grafted onto the magnetic nanoparticles through refluxing in toluene for 24 h. Finally, the crude products 5 and 6 were successfully obtained via direct complexation of (S,S)-TsDPEN-modified magnetic nanoparticles [(denoted as (S,S)-TsDPEN-MNPs)] with $[Cp*IrCl_2]_2$ or (R,R)-TsDACH-modified magnetic nanoparticles [(denoted as (R,R)-TsDACH-MNPs)] with $[Cp*RhCl_2]_2$ using NEt₃ as a basic reagent. In order to remove unreacted starting materials, the crude products were Soxlet extracted thoroughly in toluene to afford the pure catalysts 5 and 6 as red powders. Elemental analyses of 5 and 6 calculated from the mass % of N (0.40 and 0.34%) showed that the loading amounts of nitrogen atoms were 0.286 and 0.243 mmol per gram catalyst. As compared with the data [27.6 mg (0.144 mmol) of Ir and 12.5 mg (0.121 mmol) of Rh per gram catalyst] of the inductively coupled plasma (ICP) optical emis-



Scheme 1. Preparation of the magnetic catalysts 5 and 6.

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sion spectrometer analyses, a 1:2 mole ratio of M(Ir or Rh)/nitrogen indicated that one equivalent of *N*-sulfonylated 1,2-diamine moieties coordinated with one metal atom. Such a structural arrangement was consistent with the structure reported in the literature.^[8] In addition, as compared with the metal loading amounts of **5** and **6** with the theoretically initial values in synthetic experiments, it was found that about 10% of the organometallic complexes could be incorporated onto the magnetic nanoparticles, which was further confirmed by the data of the thermogravimetric analyses (TGA) that 11.11% of the mass loss in **5** and 9.48% of the mass loss in **6** were obtained (see Figure S2 in Supporting Information).

FT-IR spectra of **4–6** (Figure 1) displayed strong bands around 3400, 1096 and 464 cm⁻¹, which are ascribed to the characteristic bands of v(O-H), v(Si-O)and $\delta(Si-O)$ in magnetic nanoparticles. Weak bands of **5** and **6** at 3100–2800 cm⁻¹ were assigned to asymmetric and symmetric stretching vibrations of C–H bonds while the bands at 1557–1451 cm⁻¹ were attributed to breathing vibrations of C=C bo nds in aromatic ring.^[16] Furthermore, the bands indicative of v(Si-C)around 1145 cm⁻¹ were overlapped partly by the absorbance from v(Si-O) in the magnetic nanoparticles.^[16a,b]All these relatively weak bands derived from the organometallic complexes demonstrated their successful incorporation onto the magnetic nanoparticles.

Figure 2 show the wide-angle X-ray powder diffraction (XRD) patterns of **4-6**. Obviously, several typical peaks of $SiO_2@Fe_3O_4$ (**4**) were observed in **5** and **6**, suggesting that there were no obvious changes after the subsequent surface modifications. The scanning



Figure 1. The FT-IR spectra of 4–6.

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Figure 2. The wide-angle powder XRD patterns of 4-6.

electron microscopy (SEM) images exhibited clearly that the average sizes of 5 and 6 were about 380 and 430 nm, forming a stable dispersed state and showing no tendency to self-aggregation due to the protective silica coating as shown in Figure 3 (a). The transmission electron microscopy (TEM) images further confirmed that these core-shell catalysts 5 and 6 were encapsulated by thin silica layer of 35 nm thickness [Figure 3 (b)]. Such a kind of silica coatings did not only prevent the exposure of magnetite nanoparticles on the surface and avoid the anisotropic magnetic dipolar attraction among nanoparticles but also did retain enough superparamagnetic property to separate the magnetic catalysts. As shown in Figure 4 (a), the magnetization curves measured at 300 K showed that 4 and 6 were superparamagnetic and had magnetization saturation values of 132.8, 56.3 and 37.7 emug,⁻¹ respectively. As could be seen from Figure 4 (b), the catalysts 5 and 6 were readily dispersible in reactive system and could be easily separated with a small magnet near the bottle.

Catalytic Properties of the Magnetic Nanoparticles-Supported Chiral Catalysts

With the magnetic catalysts in hand, we examined their catalytic activity and enantioselectivity in the asymmetric transfer hydrogenation of aromatic ketones in aqueous medium according to the reported literature,^[11] in which the catalytic reaction was carried out using HCO₂Na as a hydrogen source and 1.0 mol% amount of **5** or **6** as catalyst. Because a certaibn reaction time was required to render efficiently catalytic reaction in a heterogeneous catalytic system, the reaction time was prolonged to 8 h. When acetophenone was chosen as a substrate, the catalyst **5** gave (*S*)-1-phenyl-1-ethanol with 98.6% conversion



Figure 3. The SEM images (a) and the TEM images (b) of 5 and 6.



Figure 4. (a) The magnetization curves of 4–6 at 300 K. (b) The separation-redispersion process of the catalyst 5.

and an 89.6% ee value (Table 1, entry 2). Such an enantioselectivity was comparable to that of Cp*IrTsDPEN (entry 2 versus 1^[11]) and obviously higher than that of the parent catalyst (entry 2 versus 3). Similarly, the catalyst 6 did also show the nearly same enantioselectivity as Cp*RhTsDACH (entry 12 versus 11) and gave obviously a higher enantioselectivity than the parent catalyst (entry 12 versus 13). A low enantioselectivity in both parent catalysts should be due to the hydrolysis of organic silicas 2 and 3 during the catalysis process, in which the change of the chiral microenvironment derived from hydrolysis was responsible for a low enantioselectivity. Such a phenomenon had been observed in our previous report.^[12e] In contrast, it was found easily that the (S,S)configuration of catalyst 5 offered the (S)-configuration product while the (R,R)-configuration of catalyst

6 gave the (R)-configuration product, in which the absolute configuration did not affect their ee values. In a comparison of the enantioselectivities of 5 and 6 with those of the homogeneous Cp*IrTsDPEN and Cp*RhTsDACH, the nearly identical enantioselectivities indicate that the modified homogeneous catalysts on the magnetic nanoparticles could not result in a change of the chiral microenvironment, which could be further proved by the XPS spectra. As shown in Figure 5, the same binding energy of 5 as Cp*IrTsDP-EN or of 6 as Cp*RhTsDACH was observed, whereby these values obviously deviated from the values of [Cp*IrCl₂]₂ or [Cp*RhCl₂]₂ (see Figure S3 in Supporting Information). On the basis of these results, the catalysts 5 and 6 were further investigated using a series of aromatic ketones as substrates (entries 6-10, 16-20). In general, high conversions and no side products, and high enantioselectivities were obtained under similar conditions.

To investigate the nature of **5** and **6** prepared by a chemical-bonding method and those via an in situ post-modification method, and to eliminate the effect of non-covalent adsorption on the catalytic process, two control experiments were carried out using (S,S)plus TsDPEN-MNPs $[Cp*IrCl_2]_2$ and **4** plus Cp*IrTsDPEN as catalysts under similar reaction conditions. It was found that the former afforded the corresponding alcohol with 78.9% conversion and 77.2% ee value (entry 4), while the latter gave the corresponding alcohol with 84.3% conversion and 88.1% ee value (entry 5). The former result suggested that the catalyst synthesized by an in situ post-modification method could also result in a catalytic performance. However, the lower catalytic activity and enantioselectivity than 5 should be due to the fact that a small part of the post-modified $[Cp*IrCl_2]_2$ had not been coordinated on the catalytic process.^[12a-c] A similar result was also obtained using (R,R)-TsDACH-MNPs plus [Cp*RhCl2]2 as a catalyst



Figure 5. The XPS spectra: (left) Cp*IrTsDPEN and 5; (right) Cp*RhTsDACH and 6.

Table 1. Asymmetric transfer hydrogenation of	f aromatic ketones. ^[a]
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Entry	Catalyst	Substrate	Conversion [%] ^[b]	<i>ee</i> [%] ^[b] 90.0	
1	Cp*IrTsDPEN	7	99.2		
2	5	7	98.6	89.6	
3	$2 + [Cp*IrCl_2]_2$	7	91.5	76.2	
4	(S,S) -TsDPEN-MNPs + $[Cp*IrCl_2]_2$	7	78.9	77.2	
5	4+Cp*IrTsDPEN	7	84.3	88.1	
6	5	8	99.6	88.7	
7	5	9	98.4	92.5	
8	5	10	96.7	87.2	
9	5	11	96.4	81.6	
10	5	12	99.5	79.0	
11	Cp*RhTsDACH	7	>99.9	87.9	
12	6	7	99.9	87.6	
13	$3 + [Cp*RhCl_2]_2$	7	96.8	74.2	
14	(R,R)-TsDACH-MNPs+[Cp*RhCl ₂] ₂	7	77.7	77.2	
15	4+Cp*RhTsDACH	7	96.5	86.6	
16	6	8	98.2	84.0	
17	6	9	99.5	86.7	
18	6	10	99.4	85.9	
19	6	11	>99.9	85.0	
20	6	12	99.1	85.6	

[a] Reactions were carried out in water. *Reaction conditions:* catalysts (4.0 μmol of Ir or Rh, based on the ICP analysis), HCO₂Na (0.68 g, 10.0 mmol), Bu₄NBr (0.29 g, 0.80 mmol), ketone (2.0 mmol) and 2.0 mL water, reaction temperature (40 °C), reaction time (8.0 h).

^[b] Determined by chiral GC or HPLC analysis (see Figure S4 in Supporting Information).

(entry 14). The latter showed that the catalyst prepared *via* non-covalent adsorption on the catalytic process gave nearly the same enantioselectivity as Cp*IrTsDPEN, which was further confirmed using **4** plus Cp*RhTsDACH as a catalyst (entry 15). However, both catalytic activity and enantioselectivity disappeared completely when the catalysts that had undergone a Soxlet extraction process were employed

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Catalyst	Recycle	1	2	3	4	5	6	7	8	9	10
5	Conv. [%]	98.6	99.0	99.2	99.1	98.1	97.6	96.3	98.0	98.5	95.9
	ee [%]	89.6	89.0	88.9	88.8	87.4	87.2	86.6	86.3	86.1	86.0
6	Conv. [%]	99.9	99.3	99.4	99.7	99.2	97.8	98.0	96.9	98.6	98.6
	ee [%]	87.6	86.5	85.7	85.2	85.2	85.7	85.4	84.8	84.2	83.8

 Table 2. Reusabilities of 5 and 6 for asymmetric transfer hydrogenation of acetophenone.^[a]

^[a] Reactions were carried out in water. *Reaction conditions:* catalysts (4.0 µmol of Ir or Rh, based on the ICP analysis), HCO₂Na (0.68 g, 10.0 mmol), Bu₄NBr (0.29 g, 0.80 mmol), ketone (2.0 mmol) and 2.0 mL water, reaction temperature (40 °C), reaction time (8.0 h).

(Soxlet extracting 4 plus Cp*IrTsDPEN or 4 plus Cp*RhTsDACH in toluene), indicating that the noncovalent adsorption on the catalytic process could be eliminated completely through the Soxlet extraction. This was also further proved by ICP analyses (nearly same loading amounts of Rh or Ir were detected in solution after Soxlet extraction). In other words, catalysts 5 and 6 prepared *via* a chemical-bonding method did not only give a higher catalytic efficiency than those made *via* an *in situ* post-modification method, but also could overcome the loss of catalyst from non-covalent adsorption, resulting in a high catalyst reusability.

An important feature of the design of the catalysts **5** and **6** was the easy and reliable separation *via* an appropriate magnetic field. For example, upon completion of the reaction, the heterogeneous catalysts **5** and **6** were quantitatively recovered *via* a small magnet held near the bottle [Figure 4 (b)]. As shown in Table 2, when acetophenone was used as a substrate, in ten consecutive reactions, the recycled catalyst **5** still afforded 95.9% conversion and 86.0% *ee* while the recycled catalyst **6** gave 98.6% conversion and 83.8% *ee*. The slight decrease of catalytic activity and tiny change of enantioselectivity should be due to the normal loss of the catalysts during the work-up stage.

Conclusions

In conclusion, we have supplied a facile approach to prepare two magnetic nanoparticles-supported chiral iridium and rhodium catalysts **5** and **6**. Both catalysts exhibited highly catalytic activities (up to 99%) and high enantioselectivities (up to 92% *ee*) in the asymmetric transfer hydrogenation of aromatic ketones in aqueous medium. In particular, both heterogeneous catalysts could be recovered easily by using a magnet. Neither filtration nor extraction was necessary. The recycled catalysts **5** and **6** were reused 10 times and still showed high catalytic efficiency without affecting obviously their enantioselectivities, showing their good potential for industry applications.

Experimental Section

General Remarks

All experiments, which were sensitive to moisture or air, were carried out under an Ar atmosphere using standard Schlenk techniques. 2-(4-Chlorosulfonylphenyl)ethyltrime-thoxysilane, (1*S*,2*S*)-1,2-diphenylethylenediamine, (1*R*,1*R*)-1,2-cyclohexanediamine, [Cp*IrCl₂]₂ and [Cp*RhCl₂]₂ were purchased from Sigma–Aldrich Company Ltd. and used as received. Compound **2** was synthesized according to the reported procedure.^[15] The products were analyzed by GC using a Supelco β -Dex 120 chiral column (30 m×0.25 mm i.d., 0.25 µm film) or HPLC with a UV-Vis detector using a Daicel OJ-H chiralcel columns(\emptyset 0.46×25 cm).

Characterization

Rh and Ir loading amounts in the catalysts were analyzed using an inductively coupled plasma optical emission spectrometer (ICP, Varian VISTA-MPX). Fourier transform infrared (FT-IR) spectra were collected on a Nicolet Magna 550 spectrometer using the KBr method. X-ray powder diffraction (XRD) studies were carried out on a Rigaku D/ Max-RB diffractometer with Cu-Ka radiation. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6380LV microscope operating at 20 kV. Transmission electron microscopy (TEM) images were performed on a JEOL JEM2010 electron microscope at an acceleration voltage of 220 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Perkin-Elmer PHI 5000C ESCA system. All the binding energies were calibrated by using the contaminant carbon ($C_{1s} = 284.6 \text{ eV}$) as a reference. The magnetic measurements were performed with a Lake Shore VSM 736 at room temperature. Liquid ¹H NMR, ¹³C NMR spectra were recorded using a Bruker AV-400 spectrometer. Elemental analyses were performed with a Carlo Erba 1106 Elemental Analyzer.

Catalyst Preparation

Synthesis of 3: Under an argon atmosphere, to a stirred solution of (R,R)-DACH (1.00 g, 8.77 mmol) and triethylamine (1.06 mL, 17.54 mmol) in 20 mL dry dichloromethane was added a solution of 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane 1 (0.71 g, 2.19 mmol) in 2 mL dry dichloromethane at 0 °C. The resulting mixture was then allowed to warm to room temperature slowly and was stirred for another 3 h. After the solvent had been removed under vacuum, the residue was rapidly passed through a short column

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(silica gel, eluent: Et₃N:CH₃OH:CH₂Cl₂=1:10:100) and concentrated under vacuum to afford **3** as a beige glass; yield: 0.67 g (1.67 mmol, 76.3%). For NMR and IR spectra see Figure S2 in Supporting Information. $[\alpha]_{D}^{20}$: -243.7 (c 0.002, CH₃OH); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.84-7.82$ (d, J = 8.40 Hz, 2H), 7.33–7.31 (d, J = 8.40 Hz, 2H), 4.46 (s, NH, 3H), 3.56 (s, 9H), 2.80- 2.76 (t, J=8.40 Hz, 2H), 2.76-2.73 (m, 1H), 2.58-2.54 (m, 1H), 1.99-1.96 (m, 1H), 1.68-1.54(m, 3H), 1.06–1.28 (m, 4H), 1.01–0.96 (t, J=8.40 Hz, 2H); ¹³C NMR (126 MHz, CDCl₃): $\delta = 11.1$, 24.8, 28.9, 32.5, 34.9, 50.8, 54.9, 59.9, 127.4, 128.7, 138.7, 149.6; IR (KBr): v = 3424 (s), 2981 (m), 2943 (m), 1640 (m), 1565 (s), 1473 (m), 1445 (m), 1400 (m), 1149 (s), 1067 (s), 1039 (s), 945 (m), 853 (m), 548 cm⁻¹ (m); HPLC-MS (100 eV): m/z (%)=402.16 $[M]^+$, 403.20 $[M+H]^+$; elemental analysis (%) calcd. for C₁₇H₃₀N₂O₅SSi: C 50.72, H 7.51, N 6.96; S, 7.96; found: C 50.68, H 7.63, N 6.91, S 7.89.

Preparation of Cp*IrTsDPEN-MNPs (5): To a stirred suspension of $SiO_2@Fe_3O_4$ (4) (1.0 g) in 15 mL dry toluene was added a solution of 2 (0.15 g, 0.30 mmol) in 5 mL dry toluene. The resulting mixture was refluxed for 24 h under an argon atmosphere. After magnetic separation, the red crude solid (S,S)-TsDPEN-MNPs was suspended in 20 mL dry CH₂Cl₂ again and [Cp*IrCl₂]₂ (0.12 g, 0.15 mmol) was added at room temperature. The resulting mixture was stirred at room temperature for 2 h. After magnetic separation, the red crude product was extracted thoroughly in toluene solvent using a Soxlet apparatus to remove homogeneous and unreacted start materials. The solid was dried at 60 °C under vacuum for 24 h to afford Cp*IrTsDPEN-MNPs (5) as a red powder; yield: 1.12 g (48.1% relative to 4). IR (KBr): v =3448 (s), 3066 (w), 2923 (w), 2821 (w), 1618 (m), 1451 (m), 1354 (m), 1154 (s), 1093 (s), 810 (w), 694 (w), 572 (m), 469 cm⁻¹ (m); elemental analysis (%) found: C 5.56, H 0.78, N 0.40, S 0.46.

Preparation of Cp*RhTsDACH-MNPs (6): To a stirred suspension of SiO₂@Fe₃O₄ (4) (1.0 g) in 15 mL dry toluene was added a solution of 3 (0.10 g, 0.25 mmol) in 5 mL dry toluene. The resulting mixture was refluxed for 24 h under argon atmosphere. After magnetic separation, the red crude solid (R,R)-TsDACH-MNPs was suspended in 20 mL dry CH₂Cl₂ again and [Cp*RhCl₂]₂ (0.077 g, 0.12 mmol) was added at room temperature. The resulting mixture was stirred at room temperature for 2 h. After magnetic separation, the red crude product was extracted thoroughly in toluene solvent using a Soxlet apparatus to remove homogeneous and unreacted starting materials. The solid was dried at 60°C under vacuum for 24 h to afford Cp*RhTsDACH-MNPs (6) as a red powder; yield: 1.08 g (45.2% relative to 4). IR (KBr): v = 3435 (s), 2958 (w), 2931 (w), 1641 (m), 1557 (m), 1420 (w), 1142 (s), 1088 (s), 998 (w), 947 (w), 855 (m), 545 (m), 516 cm⁻¹ (m); elemental analysis (%) found: C 3.56, H 0.67, N 0.34, S 0.39.

General Procedure for Asymmetric Transfer Hydrogenation of Ketones in Aqueous Medium

A typical procedure is as follows: The magnetic catalyst Cp*IrTsDPEN-MNPs (5) (27.8 mg, 4.00 μ mol based on Ir from ICP), HCO₂Na (0.68 g, 10.0 mmol), Bu₄NBr (0.29 g, 0.80 mmol), ketone (2.0 mmol) and 4.0 mL water were added in a 10-mL round-bottom flask in turn. The mixture

was allowed to react at 40 °C for 8 h. During that time, the reaction was monitored constantly by TLC. After completion of the reaction, the magnetic catalyst was separated by a small magnet near the bottle for the recycle experiment. The aqueous solution was extracted by Et₂O (3×3.0 mL). The combined Et₂O extract was washed with brine twice and dehydrated with Na₂SO₄. After the evaporation of Et₂O, the residue was purified by silica gel flash column chromatography to afford the desired product. The conversion and the *ee* value could be determined by chiral GC using a Supelco β -Dex 120 chiral column (30 m×0.25 mm i.d., 0.25 µm film) or HPLC analysis with a UV-Vis detector using a Daicel OJ-H chiralcel columns (Φ 0.46×25 cm).

Supporting Information

Experimental procedures and analytical data for the obtained chiral aromatic alcohols are available as Supporting Information.

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