Efficient Heterogeneous Asymmetric Transfer Hydrogenation Catalyzed by Recyclable Silica-Supported Ruthenium Complexes

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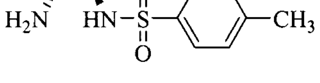
Easily accessible *N*-(*p*-tolylsulfonyl)-1,2-diphenylethylenediamine-(TsDPEN-)derived organic–inorganic hybrid ligands were prepared and applied to the heterogeneous asymmetric transfer hydrogenation in traditional HCO_2H/NEt_3 and in water with HCO_2Na as the hydrogen source and sodium dodecyl sulfate (SDS) as the phase-transfer catalyst. The reactions demonstrated high catalytic activities and excellent enantioselectivities for most aromatic ketones and the imine tested, with results similar to those in homogeneous catalysis. In particular, this heterogeneous catalyst can be readily recovered and used in multiple consecutive catalytic runs with the high enantioselectivity maintained both in HCO_2H/NEt_3 and in water.

Introduction

During the last decades thousands of chiral homogeneous catalysts have been developed for a great variety of enantioselective transformations, and many of them are known to be highly effective.[1] However, the application of such catalysts in industry is greatly limited, partly due to the problems of separation and recycling of the often expensive or toxic catalysts. To overcome such drawbacks, covalent immobilization of homogeneous chiral catalysts on insoluble supports has received very fast growing interest in recent years as it greatly simplifies the separation of the catalysts from the reaction mixtures and allows the efficient recovery and reuse of the expensive catalysts.[2–4] Moreover, if the heterogeneous asymmetric catalytic reactions using the supported catalysts can be performed in water,[5] they meet the requirement of green chemistry very well and are therefore very attractive for industry because they combine the advantages of both aqueous and heterogeneous switching in one system and provide risk-free and environmentally friendly processes, as well as easy work-up and efficient catalyst recycling.[6]

Asymmetric transfer hydrogenation, which affords important chiral secondary alcohols or amines, is one of the most important enantioselective catalytic transformations because of its high enantioselectivity, high product yield and operational simplicity. Among the great progress achieved in this area,[7] the most significant to date is perhaps the discovery of the catalyst consisting of a ruthenium(II) complex with (*R*,*R*)- or (*S*,*S*)-*N*-(*p*-tolylsulfonyl)-1,2-diphenylethylenediamine (TsDPEN, Figure 1) reported by Noyori et al.[8] Although some reports have appeared concerning heterogeneous asymmetric transfer hydrogenation with polymer- or dendrimer-supported catalysts,[3,9] examples of catalysts supported on inorganic supports are still rare.[4,10] Moreover, the catalytic activities or enantioselectivities, especially the recycling of these supported catalysts, are not ideal. In a recent preliminary communication[11] we reported studies of the highly recyclable silica-supported Ru-TsDPEN for asymmetric transfer hydrogenation of ketones in HCO_2H/NEt_3 (formic acid-triethylamine azeotrope), which demonstrates high reactivity and excellent enantioselectivity. In this paper we wish to present the details of the preparation and further expanded use of the supported Ru-TsDPEN catalyst for asymmetric transfer hydrogenation in HCO_2H/NEt_3, as well as in water with HCO_2Na as the hydrogen source and sodium dodecyl sulfate (SDS) as the phase-transfer catalyst (PTC).



(*R*,*R*)-TsDPEN (**1**)

Figure 1. The structure of ligand TsDPEN (**1**).

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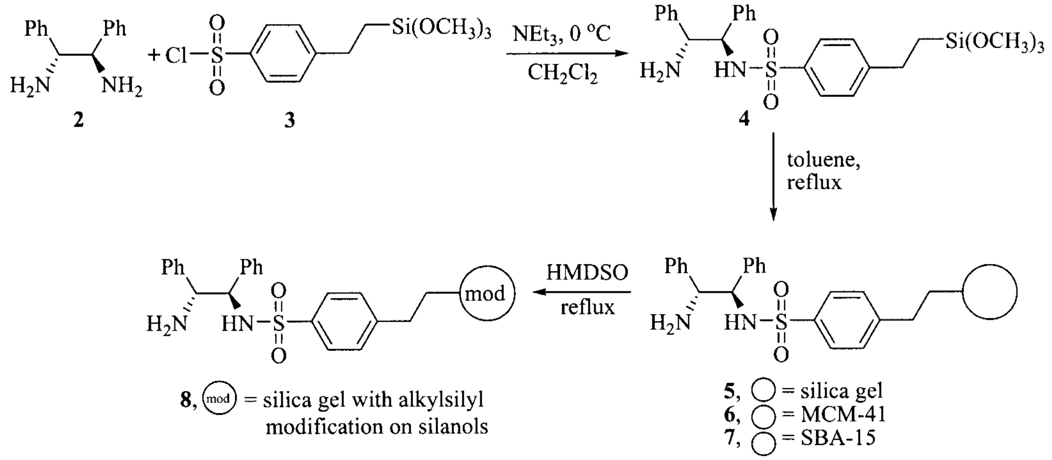


Scheme 1. Synthesis of the supported ligands **5**–**8**.

Results and Discussion

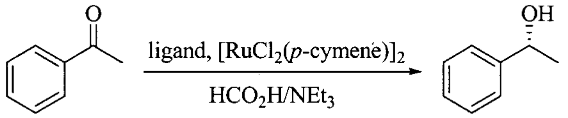
Preparation of Supported Ligands 5–8

As shown in Scheme 1,[11] the reaction of (*R*,*R*)-DPEN (1,2-diphenylethylenediamine) (**2**) with **3** in CH_2Cl_2, with triethylamine as base, smoothly gave the TsDPEN-derived ligand **4**, which was then immobilized onto amorphous silica gel and mesopores of MCM-41 and SBA-15 by refluxing in toluene for 24 h to afford the supported ligands **5**–**7**, respectively. We also modified the remaining free silanol sites on ligand **5** to alkylsilanes by treating **5** with a large excess of hexamethyldisiloxane (HMDSO) at reflux temperature for 18 h to afford the ligand **8**. Subsequent elemental analysis of ligands **5**–**8** based on the wt.-% of N demonstrated that the loading ratios of the chiral ligands were 0.15, 0.14, 0.10 and 0.12 mmol g^{-1}, respectively. Although the amounts of organic moieties contained in the organic–inorganic hybrid materials are rather low, the FT-IR spectra of the ligands still show some small new peaks at 2960, 2860, 1464, 702 cm^{-1} in comparison with the inorganic supports before grafting, which indicate the formation of the organic–inorganic hybrid ligands.

The Asymmetric Transfer Hydrogenation of Acetophenone Catalyzed by Ru-*n* in HCO_2H/NEt_3

With the supported ligands **5**–**8** in hand, the ruthenium complexes Ru-**5**–Ru-**8** were prepared in situ by mixing the corresponding ligands and $[RuCl_2(p\text{-cymene})]_2$ in CH_2Cl_2 at 28 °C for 1 h with triethylamine as the base. Subsequently, Ru-**5**–Ru-**8** (1 mol-%) were examined in the traditional HCO_2H/NEt_3 solvent mixture for the asymmetric transfer hydrogenation of the model substrate acetophenone at 40 °C; the results are listed in Table 1.[11] We were very pleased to find that the cheapest amorphous silica gel gave the best results, 99% yield and 97% *ee* after just 6 h, which is as good as the results obtained with the non-immobilized homogeneous catalysts Ru-**1** and Ru-**4** (entries 1, 6 and 7). Moreover, Ru-**5** can be readily recovered by centrifugation and can be reused up to five times with the same high enantioselectivity and without recharging the Ru metal, although the reactivity decreases slightly in subsequent reactions. We presume that the excellent performance of the amorphous silica gel-supported Ru-**5** might be due to the comparably large pore size and the amorphous structure of silica gel, which allows better accessibility of substrates and reactants.

Table 1. Supported ruthenium(II) complexes (Ru-***n***)-catalyzed asymmetric transfer hydrogenation of acetophenone in HCO_2H/NEt_3.[a]



Entry	Ligand	Run	Time [h]	Conv. [%][b]	*ee* [%][c]
1	**5**	1	6	99	97
2	**5**	2	8	>99	97
3	**5**	3	9	97	97
4	**5**	4	22	99	97
5	**5**	5	44	94	97
6	**1**	1	5.5	>99	97
7	**4**	1	5.5	>99	97
8	**6**	1	8	99	96
9	**6**	2	24	99	96
10	**6**	3	88	44	96
11	**7**	1	8	>99	97
12	**7**	2	11	99	97
13	**7**	3	24	92	97
14	**7**	4	72	45	96
15	**8**	1	9	98	96
16	**8**	2	60	5	–

[a] The reactions were carried out at 40 °C with 0.4 mmol of acetophenone in 0.2 mL of HCO_2H/NEt_3 with an Ru/ligand/acetophenone ratio of 1:1.7:100. [b] Based on GC analysis. [c] Determined by GC with a CP-Chirasil-DEX CB column (25 m × 0.32 mm); the (*R*)-configuration was determined from the optical rotation value.

To investigate the reasons for the decrease of the catalytic activity after five recycling runs we measured the leaching of Ru metal by inductively coupled plasma atomic emission spectrometry (ICP-AES). The results demonstrated that the amount of Ru metal contained in Ru-**5** before reaction and after five runs was 0.54% and 0.35%, which means that 30–40% of the Ru has leached from the catalyst after five uses. The amount of Ru metal leached in the five reaction batches (including the workup procedures) was measured to be 0.011 mg, 0.015 mg, 0.017 mg, 0.024 mg and 0.034 mg, respectively, which matches with the trend of reactivity decrease of the catalyst in the recycling reactions. Moreover, a colour change of the catalyst from yellow to red could be observed in the recycling routine and the FT-IR spectrum of Ru-**5** after five uses shows new strong peaks at 1660 and 1609 cm^{-1}. In addition, the addition of further $[RuCl_2(p\text{-cymene})]_2$ to the catalytic system does not regain the catalytic activity. Such phenomena indicate that decomposition or deactivation of the active species in the catalyst occurs irreversibly in the recycling routine, which causes a gradual decrease of the activity of the catalyst.

For the further examination of the reaction rates a comparative experiment between Ru-**5** and the non-immobilized catalysts Ru-**1** and Ru-**4** was conducted. The results (Figure 2) reveal that the heterogeneous reaction containing immobilized catalyst Ru-**5** possesses a very similar reaction rate at 40 °C to the homogeneous reactions containing the non-immobilized ones. In fact, this supported catalyst with a similar catalytic activity and enantioselectivity as the homogeneous catalysts is distinguished because the immobilization of chiral catalysts often results in lower reactivities and enantioselectivities.

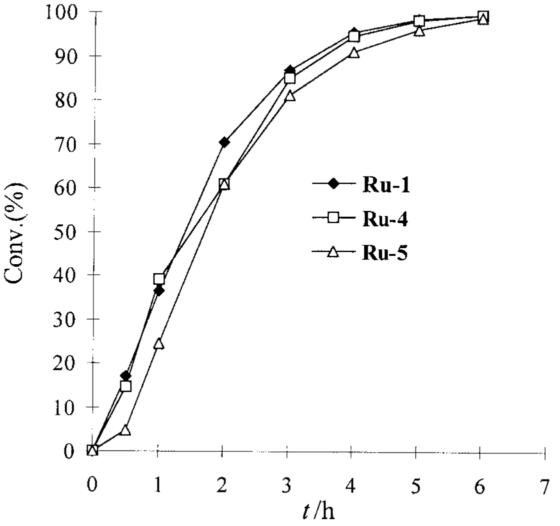
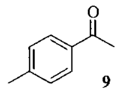
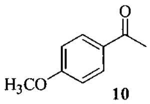
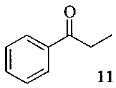
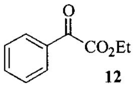
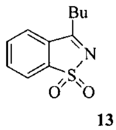


Figure 2. Reaction rates of the asymmetric transfer hydrogenation of acetophenone catalyzed by Ru-**1**, Ru-**4** and Ru-**5**.

The Asymmetric Transfer Hydrogenation of Ketones and Imine Catalyzed by Ru-5 in HCO_2H/NEt_3

As shown in Table 2, a variety of aromatic ketones **9**–**12** and imine **13** could be reduced to the corresponding chiral alcohols or sultam in the presence of the amorphous silica gel-supported complex Ru-**5**. The asymmetric transfer hydrogenation of 4-methylacetophenone (**9**) occurs with an excellent 95% *ee* and quantitative yield after 14 h, and in the third run 94% *ee* and 98% yield could still be observed (entries 1–3). For 4-methoxyacetophenone (**10**), the asymmetric reduction gives an excellent enantiomeric excess (96% *ee*) with a shorter reaction time than for the homogeneous reaction,[8b] and three uses of Ru-**5** (entries 4–6). In the asymmetric reaction of propiophenone (**11**), a high *ee* value (94% *ee*) and fairly low reactivity were obtained, and the catalyst could be used one more time with 94% *ee* and 94% yield (entries 7 and 8). We also investigated the heterogeneous transfer hydrogenation of ethyl benzoylformate (**12**), which shows that the strong electron-with-

Table 2. Supported ruthenium(II) complex (Ru-**5**)-catalyzed asymmetric transfer hydrogenation of ketones and imine in HCO_2H/NEt_3.[a]

Entry	Substrate	Run	Time [h]	Conv. [%][b]	*ee* [%][c]
1	 **9**	1	14	>99	95
2		2	29	>99	95
3		3	48	98	94
4	 **10**	1	17	99	96
5		2	30	>99	96
6		3	47	56	96
7	 **11**	1	21	98	94
8		2	48	94	94
9	 **12**	1	1	>99	70[d]
10		2	1	>99	72[d]
11		3	2	97	74[d]
12		4	2	98	73[d]
13		5	3	99	71[d]
14		6	37	50	72[d]
15	 **13**	1	1.5	>99[f]	93[e]
16		2	1	>99[f]	92[e]
17		3	1	>99[f]	92[e]
18		4	2	>99[f]	92[e]
19		5	3	>99[f]	92[e]
20		6	7	>99[f]	91[e]
21		7	7	96[f]	90[e]

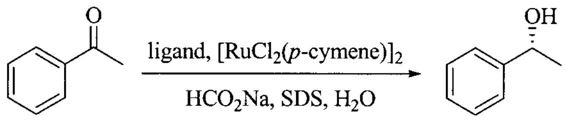
[a] The reactions were carried out at 40 °C with 0.4 mmol substrate in 0.2 mL of HCO_2H/NEt_3 with a Ru/**5**/substrate ratio of 1:1.7:100. [b] Based on GC analysis. [c] Determined by GC with a CP-Chirasil-DEX CB column (25 m × 0.32 mm) unless noted; the configurations of the products were determined as *R* from the optical rotation values, unless noted. [d] The configuration was determined as *S* from the optical rotation value. [e] Determined by HPLC on a Chiralcel OD column. [f] Isolated yield.

drawing ester group linked directly to the carbonyl carbon atom of the ketone reduces the enantioselectivity greatly to 70–74% *ee*, although the reaction activity was remarkably high (>99% yield after 1 h) and the same high reactivity could even be observed in the fifth run (entries 9–14). We also prepared the imine **13** from saccharin and applied it to the transfer hydrogenation catalyzed by Ru-**5** to give the useful chiral sultam auxiliary.[12] The results showed the reaction could achieve good enantioselectivity (92% *ee*) and very high reactivity. The recycling use of the catalyst for this imine was very good (seven runs), although the *ee* values decreased a little in the sixth and seventh runs (entries 15–21).

The Asymmetric Transfer Hydrogenation of Acetophenone Catalyzed by Ru-*n* in Water

Recently, asymmetric transfer hydrogenation in water has been attracting increasing interest as it meets the requirements of green chemistry.[13] As the silica would be effective as an organic reaction medium in water based on its adsorptive nature,[14] we tried to apply our silica-supported catalysts in water (Table 3). The ligands **5**–**8** were respectively stirred with [RuCl$_2$(*p*-cymene)]$_2$ in CH$_2$Cl$_2$ at 28 °C for 1 h with triethylamine as the base to afford the complexes Ru-**5**–Ru-**8** after the removal of CH$_2$Cl$_2$ and triethylamine by evaporation. The catalysts were then used in the transfer hydrogenation of acetophenone in water with HCO$_2$Na (5 equiv.) as the hydrogen source. We were very pleased to find that the organic-solvent-free catalytic reaction in water (Table 4) catalyzed by **Ru-5** proceeded smoothly with >99% yield and 91% *ee* after 9 h. Moreover, the catalyst could be recovered readily and used in two more runs with a slightly enhanced enantioselectivity (92% *ee*) and high yields (entries 1–3). We then added the surfactant SDS (4% mol) to the reaction mixture and achieved better enantioselectivity (94% *ee*). The catalyst could be used in three runs with the same 94% *ee*, although the catalytic activity in the third run was rather low (entries 4–6). When the catalyst was prepared in water, the transfer hydro-

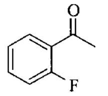
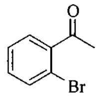
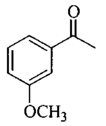
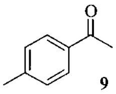
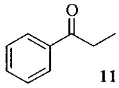
Table 3. Supported ruthenium(II) complex (Ru-***n***)-catalyzed asymmetric transfer hydrogenation of acetophenone in water.[a]



Entry	Ligand	Temp. [°C]	Run	Time [h]	Conv. [%][b]	*ee* [%][c]
1[d,e]	**5**	40	1	9	>99	91
2[d,e]	**5**	40	2	21	>99	92
3[d,e]	**5**	40	3	79	98	92
4	**5**	40	1	9	>99	94
5	**5**	40	2	21	>99	95
6	**5**	40	3	72	70	94
7[f]	**5**	40	1	9	>99	94
8[f]	**5**	40	2	36	97	94
9[f]	**5**	40	3	72	36	94
10	**6**	40	1	22	>99	87
11	**7**	40	1	8	>99	92
12	**7**	40	2	11	>99	93
13	**7**	40	3	22	99	94
14	**7**	40	4	47	43	94
15	**8**	40	1	13	>99	95
16	**8**	40	2	53	77	95
17	**5**	28	1	11	>99	95
18	**5**	28	2	50	89	95
19	**5**	28	3	77	8	95
20	**5**	20	1	35	>99	95
21	**5**	20	2	53	55	95

[a] The reactions were carried out with 0.4 mmol of acetophenone in 0.4 mL of water with 2.0 mmol of HCO$_2$Na·2H$_2$O, 0.016 mmol of SDS and a Ru/ligand/acetophenone ratio of 1:1.7:100. [b] Based on GC analysis. [c] Determined by GC with a CP-Chirasil-DEX CB column (25 m × 0.32 mm); the (*R*)-configuration was determined from the optical rotation value. [d] Without SDS. [e] The catalyst was prepared by stirring ligand and [RuCl$_2$(*p*-cymene)]$_2$ in H$_2$O at 80 °C for 1 h. [f] The catalyst was prepared by stirring ligand and [RuCl$_2$(*p*-cymene)]$_2$ in H$_2$O at 40 °C for 1 h.

Table 4. Supported ruthenium(II) complex (Ru-**5**)-catalyzed asymmetric transfer hydrogenation of ketones in water.[a]

Entry	Substrates	Run	Time [h]	Conv. [%] [b]	*ee* [%] [c]
1		1	5	>99	83
2		2	13	>99	84
3	**14**	3	8	>99	83
4		4	14	>99	83
5		5	10	87	84
6		6	36	78	84
7		1	7	99	93
8		2	11	>99	93
9	**15**	3	10	>99	93
10		4	18	>99	93
11		1	7	>99	93
12		2	12	>99	93
13		3	22	99	93
14	**16**	4	72	19	92
15		1	20	>99	92
16	**9**	2	54	67	91
17	 **11**	1	27	99	87

[a] The reactions were carried out at 40 °C with 0.4 mmol of acetophenone in 0.4 mL of water with 2.0 mmol of HCO$_2$Na·2H$_2$O, 0.016 mmol of SDS and a Ru/**5**/ketone ratio of 1:1.7:100. [b] Based on GC analysis. [c] Determined by GC with a CP-Chirasil-DEX CB column (25 m × 0.32 mm); the configurations of all the products were determined as *R* from the optical rotation values.

genation gave worse results with regards to the catalytic recycling (entries 7–9). Similar to the reactions in HCO_2H/NEt_3, the application of the mesoporous-material-supported Ru-**6** and Ru-**7** for the heterogeneous asymmetric transfer hydrogenation in water with SDS gave worse enantioselectivities than Ru-**5** (entries 10–14), although Ru-**7** supported on mesopores of SBA-15 exhibited a better recycling performance (4 runs). Ru-**8**, whose silanol sites have been capped, gave high enantioselectivity (95% *ee*) in this aqueous reaction, but with only 77% yield in the second run (entries 15 and 16). When the temperature was lowered to 28 °C the enantioselectivity of Ru-**5** increased to 95% *ee*, but the catalytic activity and recycling use were affected negatively (entries 17–19). A further decrease of the temperature to 20 °C had no further effect on the enantioselectivity but the catalytic activity and recovery performance of the catalyst became worse (entries 20 and 21).

The Asymmetric Transfer Hydrogenation of Ketones Catalyzed by Ru-5 in Water

The ketones **9**, **11** and **14**–**16** were applied to the organic-solvent-free heterogeneous asymmetric transfer hydrogenation in water in the presence of Ru-**5** and SDS. The aqueous reduction of 2-fluoroacetophenone (**14**) occurred with lower enantioselectivity (83–84% *ee*) than the reaction in HCO_2H/NEt_3,[11] but its reactivity and recycling performance (six runs with the same enantioselectivity) were both the best amongst the substrates tested in this aqueous reaction. In the investigation of 2-bromoacetophenone (**15**) we were pleased to find that the reaction in water possesses high reactivity and excellent enantioselectivity (93% *ee*) that are just as good as the results obtained in HCO_2H/NEt_3.[11] With this substrate Ru-**5** could be used in four runs with the same *ee* values and quantitative yields. For 3-methoxyacetophenone (**16**), 93% *ee* and >99% yield were obtained after 7 h and the catalyst could be used for four runs in water. As for the transfer hydrogenation of 4-methylacetophenone (**9**), good enantioselectivity (92% *ee*) and fairly low reactivity (>99% yield after 20 h) were observed. For propiophenone (**11**), the asymmetric reaction gave relatively poor results (87% *ee* and 99% yield after 27 h), while a much worse result (80% *ee* and 19% yield after 20 h) was observed in the transfer hydrogenation in water catalyzed by the water-soluble Ru-TsDPEN-derived catalyst.[13e]

Conclusions

In summary, we have synthesized easily accessible TsDPEN-derived organic–inorganic hybrid ligands by attaching the homogeneous chiral ligand covalently onto silica gel and mesopores of MCM-41 and SBA-15. The ruthenium complex of ligand **5** supported on cheap amorphous silica gel has proved to be the most effective catalyst for asymmetric transfer hydrogenation not only in traditional HCO_2H/NEt_3, but also in water with HCO_2Na as the hydrogen source and SDS as PTC. The heterogeneous asymmetric transfer hydrogenation in HCO_2H/NEt_3 or in water catalyzed by Ru-**5** demonstrates high catalytic activities and excellent enantioselectivities for most aromatic ketones and the imine tested, which were comparable with the results obtained in homogeneous catalysis. Furthermore, this heterogeneous catalyst can be readily recovered and used in multiple consecutive catalytic runs with the high enantioselectivity maintained both in HCO_2H/NEt_3 and in water, which is beneficial for possible industrial applications. Further exploration of this green and recyclable heterogeneous asymmetric transfer hydrogenation in water are in progress in our laboratory.[15]

Experimental Section

General: (1*R*,2*R*)-TsDPEN (**1**) and HCO_2H/NEt_3 were prepared by standard methods. Acetophenone was distilled from $KMnO_4$ and CH_2Cl_2 was distilled from CaH_2. Triethylamine and H_2O were distilled before use. $[RuCl_2(p\text{-cymene})]_2$ and imine **13** were prepared according to literature procedures.[16] Amorphous silica gel (60–100 mesh, purchased from Qingdao Haiyang Chemical Co., Ltd.), mesoporous silicas of MCM-41 and SBA-15 (provided by Prof. D.-Y. Zhao of the Chemistry Department of Fudan University) were heated at 150 °C for 3 h and cooled under argon before use. Toluene was freshly distilled from a deep-blue solution of sodium-benzophenone under argon. Other reagents and chemicals were used as received. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury-plus 300 BB with TMS as internal standard. HRMS data were measured with ESI techniques (Bruker Apex II). Elemental analysis was performed with an elementar vario EL and FT-IR spectra were recorded with a Nicolet NEXUS 670. The pore sizes and surface areas were determined with a Micromeritics ASAP 2010 Accelerated Surface Area and Porosimetry System. Optical rotation values were measured with a Perkin–Elmer 341 polarimeter.

Synthesis of (1*R*,2*R*)-4: (1*R*,2*R*)-DPEN (**2**; 0.64 g, 3.0 mmol) and triethylamine (0.6 mL) were dissolved in CH_2Cl_2 (30 mL), and 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane (**3**; 0.75 g, 2.3 mmol) in CH_2Cl_2 (30 mL) was then added dropwise at 0 °C. The reaction mixture was then allowed to warm to room temperature slowly and stirred for 3 h. After removal of the solvent in vacuo, the residue was passed quickly through a short column (silica gel; eluent: $Et_3N/CH_3OH/CH_2Cl_2$ = 1:10:100) and concentrated in vacuo to afford (*R*,*R*)-**4** as **a** beige glass. Yield: 86%. $[\alpha]_D^{20} = -36$ ($c = 0.8$, CH_2Cl_2). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.89–0.95 (m, 2 H), 1.50 (s, 2 H, NH_2), 2.65–2.70 (m, 2 H), 3.59 (s, 9 H), 4.12 (d, J = 5.4 Hz, 1 H), 4.37 (d, J = 5.4 Hz, 1 H), 6.99–7.34 (m, 14 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.0, 28.5, 50.6, 60.4, 63.2, 126.5, 126.9, 127.3, 127.4, 127.8, 128.2, 128.3, 137.3, 139.1, 141.3, 148.8. IR: $\tilde{\nu}$ = 3352, 3296, 3171, 3060, 3028, 2941, 2841, 1902, 1691, 1600, 1495, 1454, 1410, 1343, 1322, 1265, 1191, 1157, 1088, 1013 cm^{-1}. ESI-HRMS calcd. for $C_{25}H_{32}N_2O_5SSi + H^+$ 501.1874; found 501.1881.

General Procedure for the Synthesis of Supported Ligands 5–7: The predried silica (3 g) and ligand (*R*,*R*)-**4** (0.25 g) were added to dry toluene (40 mL) and the mixture was refluxed for 24 h under argon. After filtration, the white solid was washed with toluene (60 mL) and a mixture of CH_2Cl_2 and CH_3OH (1:1, 100 mL). The solid was then suspended in a mixture of CH_2Cl_2 and CH_3OH (1:1, 50 mL) and stirred overnight. After filtration and thorough washing (CH_2Cl_2/CH_3OH = 1:1, 50 mL and CH_3OH, 50 mL), the solid was dried at 60 °C in vacuo for 24 h to give the supported ligand.

Ligand 5: IR: $\tilde{\nu}$ = 3440, 2960, 2856, 1642, 1509, 1464, 1097, 801, 702, 559, 469 cm^{-1}. Elemental analysis: C 4.71, H 0.59, N 0.41, S 0.48. Average pore size: 90.2 Å. S_{BET}: 324 $m^2 g^{-1}$.

Ligand 6: IR: $\tilde{\nu}$ = 3442, 2962, 2860, 1627, 1461, 1081, 812, 698, 455 cm^{-1}. Elemental analysis: C 6.52, H 1.04, N 0.38, S 0.47. Average pore size: 18.7 Å. S_{BET}: 1150 $m^2 g^{-1}$.

Ligand 7: IR: $\tilde{\nu}$ = 3438, 2958, 2856, 1635, 1462, 1084, 811, 701, 462 cm^{-1}. Elemental analysis: C 5.74, H 0.54, N 0.28, S 0.31. Average pore size: 61.8 Å. S_{BET}: 497 $m^2 g^{-1}$.

Synthesis of the Modified Ligand 8: Supported ligand **5** (0.3 g) was added to hexamethyldisiloxane (HMDSO, 10 mL) and the mixture was refluxed for 18 h under argon. After filtration and thorough washing with CH_3OH (30 mL), the solid was dried at 60 °C in vacuo for 24 h to give ligand **8**. IR: $\tilde{\nu}$ = 3439, 2970, 2845, 1637, 1460, 1095, 965, 802, 700, 467 cm^{-1}. Elemental analysis: C 5.55, H 1.10, N 0.33, S 0.41. Average pore size: 87.4 Å. S_{BET}: 313 $m^2 g^{-1}$.

General Procedure for the Transfer Hydrogenation in HCO_2H/NEt_3 Using the Supported Catalysts: Supported ligand (0.0068 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.002 mmol) and triethylamine (0.016 mmol) were stirred in dry CH_2Cl_2 (0.4 mL) for 1 h under argon at 28 °C. Then, HCO_2H/NEt_3 (0.2 mL) and the ketone (or imine, 0.4 mmol) were added and the mixture was stirred at 40 °C and monitored by TLC. After the completion of the reaction, dry CH_2Cl_2 (1 mL) was added and the mixture was stirred for 1–2 min, then the reactor was centrifuged (3000 min^{-1}) for 2–3 min and the solution was removed with a syringe. The catalyst was then washed with CH_2Cl_2 (1 mL) twice and the CH_2Cl_2 was removed; a new reaction could be conducted by adding HCO_2H/NEt_3 (0.2 mL) and ketone (or imine, 0.4 mmol) in turn to the recovered catalyst. The solution containing the product was passed rapidly through a short column (silica gel, eluent: Et_2O) and the conversion and the *ee* value were then determined by chiral GC on a CP-Chirasil-DEX CB column (25 m × 0.32 mm) or by HPLC with a Chiralcel OD column on Agilent 1100 Series.

General Procedure for the Transfer Hydrogenation of Ketones in Water Using the Supported Catalysts: Supported ligand (0.0068 mmol), $[RuCl_2(p\text{-cymene})]_2$ (0.002 mmol) and triethylamine (0.016 mmol) were stirred in dry CH_2Cl_2 (0.4 mL) for 1 h under argon at 28 °C and then CH_2Cl_2 and triethylamine were evaporated under reduced pressure. $HCO_2Na \cdot 2H_2O$ (2.0 mmol), SDS (0.016 mmol), H_2O (0.4 mL) and ketone (0.4 mmol) were added subsequently and the mixture was stirred at 40 °C and monitored by TLC. After completion of the reaction, H_2O (1 mL) was added and the mixture was stirred for 1 min, then the reactor was centrifuged (4000 min^{-1}) for 3–5 min and the solution was removed with a syringe. The catalyst was washed with CH_3OH (1 mL, twice) and H_2O (1 mL, twice) and the solutions were removed with a syringe. A new reaction could be conducted by adding $HCO_2Na \cdot 2H_2O$ (2.0 mmol), SDS (0.016 mmol), H_2O (0.4 mL) and ketone (0.4 mmol) in turn to the recovered catalyst. The solvent CH_3OH was removed in vacuo, the residue was dissolved in Et_2O and the aqueous solution was extracted with Et_2O. The combined Et_2O fractions were washed twice with brine and dehydrated with Na_2SO_4. After the evaporation of Et_2O, the conversion and the *ee* value could be determined directly by chiral GC on a CP-Chirasil-DEX CB column (25 m × 0.32 mm).

Supporting Information Available (see also footnote on the first page of this article)**:** $[\alpha]_D$, ^1H and ^{13}C NMR spectra, analytical conditions and retention times of GC or HPLC of the obtained chiral aromatic alcohols.

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