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Asymmetric hydrogenation of aromatic ketones catalyzed by achiral monophosphine TPPTS-stabilized Ru in ionic liquids

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Abstract—Achiral monophosphine TPPTS [TPPTS: P(*m*-$C_6H_4SO_3Na)_3$]-stabilized Ru was synthesized by reduction of $RuCl_3{\cdot}3H_2O$ with hydrogen in ethanol using TPPTS as the stabilizer. The catalytic asymmetric hydrogenation of aromatic ketones using TPPTS-stabilized Ru modified by a chiral diamine (1*R*,2*R*)-DPENDS [disodium salt of sulfonated (1*R*,2*R*)-1,2-diphenyl-1,2-ethylene-diamine] was investigated in hydrophilic ionic liquid [RMIM]Ts (1-alkyl-3-methylimidazolium *p*-methylphenylsulfonates, R = ethyl, butyl, octyl, dodecyl, hexadecyl). Hundred percent conversion and 85.1% ee were obtained for acetophenone under optimized conditions. The resulting products can be easily separated from the catalyst immobilized in ionic liquid by simple extraction with *n*-hexane, and the catalyst can be reused several times without a significant loss of ee value or conversion. In particular, the addition of water can improve the catalyst performance.

1. Introduction

Homogeneous catalysts show distinguished catalytic properties in asymmetric hydrogenation of simple ketones,[1] but these catalysts are very expensive and are difficult to recycle and reuse.[2] Ionic liquids (ILs) have attracted a great deal of interest because of their capability to immobilize homogeneous catalysts and to facilitate catalysts recycling.[2,3] In recent years, the asymmetric hydrogenation of enamides, arylacrylic acids, aromatic ketones, imines, and β-ketoesters in ionic liquids have been reported.[4] The results indicate that the products can be easily separated by extraction with organic solvent while ionic liquids containing homogeneous catalysts could be reused several times without the loss of catalytic activity or enantioselectivity.

Furthermore, ligand-stabilized metal nanoparticles have been reported in enantioselective reactions,[5,6] and the introduction of ligands as nanoparticle stabilizers is of special interest.[7]

Herein we report that newly formed achiral monophosphine TPPTS-stabilized Ru modified by (1*R*,2*R*)-DPENDS (see Fig. 1) can asymmetrically hydrogenate aromatic ketones in an ionic liquids [RMIM]Ts (see Fig. 2) and water mixed solvent under mild reaction conditions (see Fig. 3), and that the resulting products can be easily separated from the catalyst by extraction with *n*-hexane.

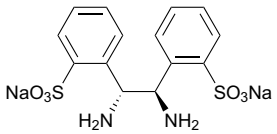

Figure 1. (1*R*,2*R*)-DPENDS.

The TPPTS-stabilized Ru catalyst not only exhibits excellent activity and enantioselectivity in asymmetric hydrogenation of aromatic ketones, but also simplifies its recycling and reuse.

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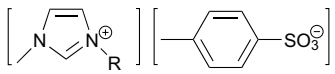

Figure 2. Ionic liquids [RMIM]Ts.

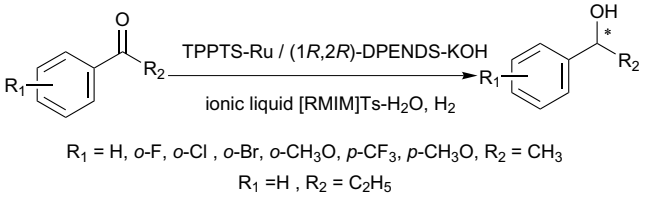

Figure 3. Asymmetric hydrogenation of aromatic ketones.

2. Results and discussion

2.1. Determination of TPPTS-stabilized Ru

The morphology of TPPTS-stabilized Ru was investigated with a transmission electron microscope (JEM-1200) at an accelerating voltage of 100 kV. It can be seen that the size of TPPTS-stabilized Ru is about 5 nm (see Fig. 4).

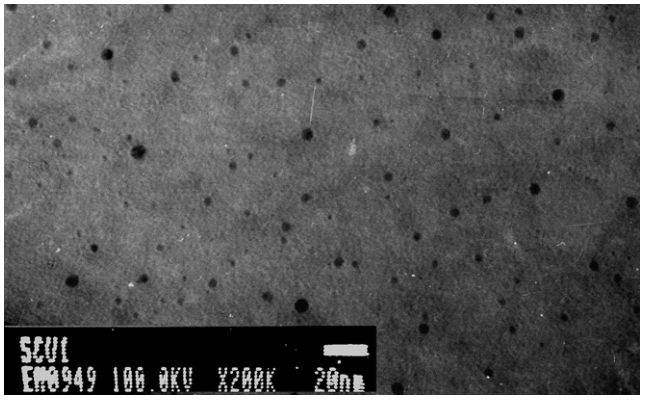

Figure 4. TEM photography of TPPTS-stabilized Ru.

The X-ray photoelectron spectroscopy (XPS) spectrum of TPPTS-Ru showed the Ru 3d binding energies at 280.6 eV and 284.8 eV, indicating that Ru has been reducted to the low oxidation state.

2.2. Influence of water on the asymmetric hydrogenation of acetophenone

Literature information indicates that water affects the reaction when ILs are used as a solvent.[8] In order to improve the catalytic performance of TPPTS-stabilized Ru-(1*R*,2*R*)-DPENDS–KOH catalyst, we added some water to evaluate its effect on the asymmetric hydrogenation of aromatic ketones. The results, as shown in Table 1, suggest that the addition of appropriate amounts of water can increase the ee value from 45.1% to 80.3%. The increase in the ee values can be attributed to the enhancement of the solubility of the water-soluble catalyst in ionic liquid. However, a lower activity and enantioselectivity are observed when only water is used as a solvent. A similar phenomenon was observed in the asymmetric hydrogenation of α,β-unsaturated ketones in our previous work.[9]

Table 1. Effect of water on the asymmetric hydrogenation of acetophenone[a]

V_{Ils}/V_{H_2O}	Conversion (%)	ee (%)	Configuration
No water	94.6	45.1	(*S*)
1:0.5	100	80.3	(*S*)
1:1	100	74.9	(*S*)
1:1.5	94.1	74.5	(*S*)
No IL	76.8	35.9	(*S*)

[a] Reaction conditions: acetophenone: 0.85 mmol; Ru/acetophenone/(1*R*,2*R*)-DPENDS = 1:112:9; ionic liquid: 0.5 mL; KOH: 0.7 mol/L; P_{H_2}: 5.0 MPa; *T*: 30 °C; *t*: 80 min.

2.3. Influence of different ionic liquids and temperatures on the asymmetric hydrogenation of acetophenone

The results listed in Table 2 show that the conversions and ee values of asymmetric hydrogenation are sensitive to the nature of the ionic liquids. The ethyl group in [RMIM]Ts was substituted by another alkyl group, the conversion and enantioselectivity decreased gradually with an increase of the alkyl chain length. An increase of the alkyl chain length in [RMIM]Ts is not favorable, due to the solubility of the water-soluble chiral ligand (1*R*,2*R*)-DPENDS in ionic liquids and the chiral modification of (1*R*,2*R*)-DPENDS to Ru catalyst is reduced, therefore, the enantioselectivity decreases. In our previous work, similar phenomena were also observed.[9,10]

Table 2. Effect of different ionic liquids on the asymmetric hydrogenation of acetophenone[a]

Ionic liquids	Conversion (%)	ee (%)	Configuration
[EMIM]Ts	100	80.3	(*S*)
[BMIM]Ts	100	77.1	(*S*)
[OMIM]Ts	84.3	58.7	(*S*)
[DoMIM]Ts	18.6	46.7	(*S*)
[HeMIM]Ts	7.0	7.7	(*S*)

[a] Ionic liquid/H_2O (v/v) = 1:0.5, other reaction conditions were the same as those in Table 1.

The data listed in Table 3 indicate that the enantioselectivity increases with the decrease of temperature; 85.1% ee

Table 3. The effect of temperature on the asymmetric hydrogenation of acetophenone[a]

Temperature (°C)	Conversion (%)	ee (%)	Configuration
5	69.6	85.1	(*S*)
15	98.2	83.3	(*S*)
30	100	80.3	(*S*)
45	100	80.2	(*S*)

[a] Reaction conditions were the same as those in Table 2.

Table 4. Comparison of TPPTS-stabilized Ru with $RuCl_2(TPPTS)_2$ in the asymmetric hydrogenation of aromatic ketones

Substrates	TPPTS-stabilized Ru[a]		$RuCl_2(TPPTS)_2$[b]	
	Conversion (%)	ee (%)	Conversion (%)	ee (%)
Acetophenone	100	80.3	50.3	80.3
2′-Bromo-acetophenone	99.6	82.7	9.2	82.9
4′-Methoxy-acetophenone	96.0	76.5	3.6	57.7

[a] Ionic liquid/H_2O (v/v) = 1:0.5, other reaction conditions were the same as those in Table 1.
[b] Reaction conditions were the same as those of TPPTS-stabilized Ru.

was obtained at 5 °C, which is the highest value using TPPTS as the stabilizer.

2.4. Comparison of TPPTS-stabilized Ru with $RuCl_2(TPPTS)_2$ in the asymmetric hydrogenation of aromatic ketones

As seen in Table 4, asymmetric hydrogenation of acetophenone, 2′-bromo-acetophenone and 4′-methoxy-acetophenone catalyzed by TPPTS-stabilized Ru catalyst, all afforded high activities (>96.0% conversion) and good enantioselectivities. Although similar high ee values were obtained by $RuCl_2(TPPTS)_2$, the TPPTS-stabilized Ru catalyst is definitely more active under the same reaction conditions. With respect to the catalyst precursor $RuCl_2(TPPTS)_2$, there was a long induction period before conversion to the active species $RuHCl(TPPTS)_2$, which resulted in a lower activity.

2.5. Influence of the mole ratio of ruthenium to (*R*,*R*)-DPENDS and KOH concentration on asymmetric hydrogenation of acetophenone

As shown in Tables 5 and 6, the influence of (1*R*,2*R*)-DPENDS and KOH on the asymmetric hydrogenation of acetophenone is very significant. The conversion was only 9.0% and no ee value was obtained in the absence of (1*R*,2*R*)-DPENDS. The addition of (1*R*,2*R*)-DPENDS could apparently increase the catalytic activity and enantioselectivity. When the molar ratio of ruthenium to (1*R*,2*R*)-DPENDS was 1:9, the conversion and ee value could reach up to 100% and 80.3%, respectively. Similarly, if no KOH was added, the conversion and ee value were only 0.5% and 45.3%, respectively. With an increase of KOH concentration, the conversion and ee value obviously increased. When the concentration of KOH was 0.92 mol/L, 100% conversion and 80.3% ee were obtained. However, increasing the KOH amount resulted in no increase in the conversions and ee values. The results shown in Tables 5 and 6 indicate that there was a synergistic effect between (1*R*,2*R*)-DPENDS and KOH. A similar phenomenon was observed in our previous work.[10]

Table 5. The effect of the mole ratio of ruthenium to (1*R*,2*R*)-DPENDS on the asymmetric hydrogenation of acetophenone[a]

Mole ratio	Conversion (%)	ee (%)	Configuration
No (*R*,*R*)-DPENDS	9.0	0	—
1:3	95.0	80.3	(*S*)
1:6	99.5	79.9	(*S*)
1:9	99.6	80.3	(*S*)

[a] Reaction conditions were the same as those in Table 2.

Table 6. The effect of KOH concentration on the asymmetric hydrogenation of acetophenone[a]

Concentration (mol/L)	Conversion (%)	ee (%)	Configuration
0	0.5	45.3	(*S*)
0.23	37.2	77.3	(*S*)
0.46	99.3	79.3	(*S*)
0.70	100	77.7	(*S*)
0.92	100	80.3	(*S*)
1.15	98.6	80.1	(*S*)

[a] Reaction conditions were the same as those in Table 2.

2.6. Asymmetric hydrogenation of different aromatic ketones

Various aromatic ketones were hydrogenated with TPPTS-stabilized Ru-(1*R*,2*R*)-DPENDS–KOH catalyst in an ionic liquid-water mixed solvent and the results are summarized in Table 7. The results indicate that this novel catalyst shows high reactivities except with 2′-methoxyacetophenone; high enantioselectivities were obtained in the asymmetric hydrogenation of acetophenone, propiophenone, and 2′-bromoacetophenone. The substituent on the phenyl ring, whether it was an electron-withdrawing group or electron-donating group, obviously influences the enantioselectivity of aromatic ketones. Furthermore, the steric effect, which influences the reactant–modifier interaction, markedly affects the activity and enantioselectivity.

Table 7. Asymmetric hydrogenation of acetophenone and its derivatives[a]

Substrates	Conversion (%)	ee (%)	Configuration
Acetophenone	99.6	80.3	(*S*)
Propiophenone	99.3	80.0	(*S*)
2′-Bromoacetophenone	99.6	82.7	(*S*)
2′-Chloroacetophenone	99.8	77.3	(*S*)
2′-Fluoroacetophenone	99.7	54.3	(*S*)
2′-Methoxyacetophenone	47.6	45.4	(*R*)
4′-(Trifluoromethyl)acetophenone	99.5	58.7	(*S*)
4′-Methoxyacetophenone	96.0	76.5	(*S*)

[a] Reaction conditions were the same as those in Table 2.

2.7. Catalyst recycling

For the catalyst used in this study, we have also demonstrated that the chiral alcohol products could be easily separated by extraction with *n*-hexane, while the catalyst and modifiers immobilized in ionic liquid and water could

be recycled and reused several times. As shown in Table 8, although the reactivities of the TPPTS-stabilized Ru catalyst started to drop from the fifth run, the ee value could still be maintained at above 75%. When 0.18 mmol KOH was added into the reaction system in the seventh run, the conversion slightly increased from 63.8% (run 6) to 73.2% (run 7), which proved the novel influence of the base on catalytic activity. Similar phenomena were observed in the asymmetric hydrogenation of α,β-unsaturated ketones in ionic liquids-water in our previous work.[9] Inductively coupled plasma (ICP) spectroscopy further showed that no appreciable leaching of Ru occurred during the extraction of organic products. We estimated from ICP experiments that less than 0.06% of the Ru catalyst had leached into the chiral alcohol phase from the ionic liquid phase.

Table 8. Recycling and reuse of TPPTS-stabilized Ru-(1*R*,2*R*)-DPENDS–KOH catalyst in ionic liquid [EMIM]Ts/H_2O[a]

Run	Conversion (%)	ee (%)	Configuration
1	99.8	80.3	(*S*)
2	92.1	78.7	(*S*)
3	91.0	78.7	(*S*)
4	92.1	77.4	(*S*)
5	70.0	76.5	(*S*)
6	63.8	75.9	(*S*)
7[b]	73.2	77.5	(*S*)

[a] Reaction conditions were the same as those in Table 2.
[b] 0.18 mmol of KOH was added.

3. Conclusions

In conclusion, we have prepared the TPPTS-stabilized Ru catalyst, and successfully applied it to the asymmetric hydrogenation of aromatic ketones in an ionic liquid-water mixed solvent, which gave high activity and good enantioselectivity. The resulting products can be easily separated from the catalyst system by extraction with *n*-hexane. The catalyst immobilized in ionic liquids can be reused several times without any significant loss of the ee value and conversion.

4. Experimental

4.1. Materials

1-Methylimidazole (Fluka, >99%) and 1-butylbromide (Lancaster, >99%) were distilled before use. Aromatic ketones (>98% Acros) and hydrogen (99.99%) were used as received. $RuCl_3{\cdot}3H_2O$ and other reagents were all of analytical grade. TPPTS, ionic liquids [RMIM]Ts, $RuCl_2(TPPTS)_2$ and chiral modifier (1*R*,2*R*)-DPENDS were synthesized according to known methods in our laboratory.[11]

4.2. Synthesis and determination of TPPTS-stabilized Ru

To a 60 mL stainless steel autoclave with a glass linear and magnetic stirrer were added ethanol, $RuCl_3{\cdot}3H_2O$ and stabilizer TPPTS. After purging with H_2 five times, the final H_2 pressure was adjusted to 50 atm. After stirring at 120 °C for 4 h, a black 'solution' was obtained. After removal of the solvent, the TPPTS-stabilized Ru was yielded. The TEM of TPPTS-stabilized Ru was examined using a JEM-1200 microscope operating at an accelerating voltage of 100 kV.

4.3. Asymmetric hydrogenation of aromatic ketones

To a 60 mL stainless steel autoclave with a glass linear and magnetic stirrer were added the ionic liquid [EMIM]Ts, TPPTS-stabilized Ru, (1*R*,2*R*)-DPENDS, KOH, H_2O, and substrate. Hydrogen was introduced to the desired pressure after the reaction mixture had been purged with H_2 five times. The mixture was stirred at 30 °C for a predetermined period of time. After hydrogen was vented, *n*-hexane (5 mL) was added to extract the organic product. The resulting two layers were mixed thoroughly by vigorous stirring for 5 min. The upper solution layer was separated by decantation. This manipulation was repeated one more time. The combined extracts containing the product were purified by silica gel (yield 98%). The products were analyzed by GC-960 with a FID detector and β-DEX™120 capillary column (30 m × 0.25 mm, 0.25 μm film). The enantiomeric excess (ee value) was calculated from the equation: ee (%) = $100 \times (S - R)/(S + R)$. The recovered catalyst in ionic liquids was reused in the next batch of the catalytic reaction under identical conditions.

(*S*)-(−)-1-Phenylethanol: $[\alpha]_D^{28} = -23.2$ (*c* 1.08, CH_2Cl_2), 80.3% ee, (*S*); column temperature: 115 °C, $t_R(R) =$ 12.6 min, $t_R(S) = 13.3$ min.

(*S*)-(−)-1-Phenylpropanol: $[\alpha]_D^{28} = -39.5$ (*c* 1.52, C_2H_5OH), 80.0% ee, (*S*); column temperature: 120 °C, $t_R(R) =$ 16.3 min, $t_R(S) = 16.8$ min.

(*S*)-(−)-1-(2′-Fluorophenyl)ethanol: $[\alpha]_D^{28} = -35.7$ (*c* 1.26, $CHCl_3$), 54.3% ee, (*S*); column temperature: 110 °C, $t_R(R) = 15.7$ min, $t_R(S) = 17.4$ min.

(*S*)-(−)-1-(2′-Chlorophenyl)ethanol: $[\alpha]_D^{28} = -29.5$ (*c* 1.76, $CHCl_3$), 77.3% ee (*S*); column temperature: 140 °C, $t_R(R) = 12.8$ min, $t_R(S) = 14.8$ min.

(*S*)-(−)-1-(2′-Bromophenyl)ethanol: $[\alpha]_D^{28} = -31.3$ (*c* 1.60, $CHCl_3$), 82.7% ee, (*S*); column temperature: 140 °C, $t_R(R) = 21.2$ min, $t_R(S) = 26.5$ min.

(*R*)-(+)-1-(2′-Methoxyphenyl)ethanol: $[\alpha]_D^{28} = +33.3$ (*c* 1.05, $CHCl_3$), 45.4% ee, (*R*); column temperature: 135 °C, $t_R(R) = 15.9$ min, $t_R(S) = 16.8$ min.

(*S*)-(−)-1-(4′-Methoxyphenyl)ethanol: $[\alpha]_D^{28} = -29.1$ (*c* 1.03, $CHCl_3$), 76.5% ee, (*S*); column temperature: 115 °C, $t_R(R) = 20.6$ min, $t_R(S) = 21.5$ min.

(*S*)-(−)-1-(4′-Trifluoromethylphenyl)ethanol: $[\alpha]_D^{28} = -39.0$ (*c* 1.41, CH_3OH), 58.7% ee, (*S*); column temperature: 120 °C, $t_R(R) = 13.0$ min, $t_R(S) = 14.6$ min.

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References

1. (a) Ohkuma, T.; Koizumi, M.; Doucet, H.; Pham, T.; Kozawa, M.; Murata, K.; Katayama, E.; Yokozawa, T.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1998**, *120*, 13529; (b) Ohkuma, T.; Ishii, D.; Takeno, H.; Noyori, R. *J. Am. Chem. Soc.* **2000**, *122*, 6510–6511; (c) Ohkuma, T.; Koizumi, M.; Muniz, K.; Hilt, G.; Kabuto, C.; Noyori, R. *J. Am. Chem. Soc.* **2002**, *124*, 6508; (d) Doucet, H.; Okhuma, T.; Murata, K.; Yokozawa, T.; Kozawa, M.; Katayama, E.; England, A. F.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1703.
2. Ngo, H. L.; Hu, A.; Lin, W. *Tetrahedron Lett.* **2005**, *46*, 595–597.
3. (a) Pu, L. *Chem. Rev.* **1998**, *98*, 2405–2409; (b) Fan, Q.-H.; Li, Y.-M.; Chan, A. S. C. *Chem. Rev.* **2002**, *102*, 3385.
4. (a) Guernik, S.; Wolfson, A.; Herskowitz, M.; Greenspoon, N.; Geresh, S. *Chem. Commun.* **2001**, 2314; (b) Berger, A.; de Souza, R. F.; Delgado, M. R.; Dupont, J. *Tetrahedron: Asymmetry* **2001**, *12*, 1825; (c) Brown, R. A.; Pollet, P.; Mckoon, E.; Liotta, C. L.; Jessop, P. G. *J. Am. Chem. Soc.* **2001**, *123*, 1254; (d) Giernoth, R.; Krumm, M. S. *Adv. Synth. Catal.* **2004**, *346*, 989; (e) Zhu, Y. H.; Carpenter, K.; Ching, C. B.; Bahnmueller, S.; Chan, P. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 3792; (f) Ngo, H. L.; Hu, A.; Lin, W. *Chem. Commun.* **2003**, 1912; (g) Hu, A.; Ngo, H. L.; Lin, W. *Angew. Chem., Int. Ed.* **2004**, *43*, 2501; (h) Berthod, M.; Joerger, J. M.; Mignani, G.; Vaultier, M.; Lemaire, M. *Tetrahedron: Asymmetry* **2004**, *15*, 2219; (i) Lam, K. H.; Xu, L.-J.; Feng, L.-C.; Ruan, J.-W.; Fan, Q.-H.; Chan, A. S. C. *Can. J. Chem.* **2005**, *83*, 903.
5. Nasar, K.; Fache, F.; Lemaire, M.; Draye, M.; Buziat, J. C.; Besson, M.; Galez, P. *J. Mol. Catal.* **1994**, *87*, 107.
6. (a) Bönnemann, H.; Braun, G. A. *Chem. Eur. J.* **1997**, *3*, 1200; (b) Zuo, X.; Liu, H.; Guo, D.; Yang, X. *Tetrahedron* **1999**, *55*, 203; (c) Studer, M.; Blaser, H.-U.; Exner, C. *Adv. Synth. Catal.* **2003**, *345*, 45; (d) Tamura, M.; Fujihara, H. *J. Am. Chem. Soc.* **2003**, *125*, 15742; (e) Jansat, S.; Gomez, M.; Philippot, K.; Muller, G.; Guiu, E.; Claver, C.; Castillon, S.; Chaudret, B. *J. Am. Chem. Soc.* **2004**, *126*, 1592.
7. Astruc, D.; Lu, F.; Aranzaes, J. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 7852–7872.
8. (a) Brown, R. A.; Pollet, P.; McKoon, E.; Eckert, Ch. A.; Liotta, Ch. L.; Jessop, P. G. *J. Am. Chem. Soc.* **2001**, *123*, 1254–1255; (b) Pugin, B.; Studer, M.; Kuesters, E.; Sedelmeier, G.; Feng, X. *Adv. Synth. Catal.* **2004**, *346*, 1481–1486; (c) Wolfson, A.; Vankelecom, I. F. J.; Jacobs, P. A. *Tetrahedron Lett.* **2005**, *46*, 2513–2516; (d) Berthod, M.; Joerger, J. M.; Mignani, G.; Vaultier, M.; Lemaire, M. *Tetrahedron: Asymmetry* **2004**, *15*, 2219–2221; (e) Baudequin, C.; Baudoux, J.; Levillain, J.; Cahard, D.; Gaumont, A. C.; Plaquevent, J. C. *Tetrahedron: Asymmetry* **2003**, *14*, 3081–3093.
9. Wang, J.-B.; Qin, R.-X.; Fu, H.-Y.; Chen, J.; Feng, J.; Chen, H.; Li, X.-J. *Tetrahedron: Asymmetry* **2007**, *18*, 847.
10. Xiong, W.; Lin, Q.; Ma, H.-X.; Zheng, H.-J.; Chen, H.; Li, X.-J. *Tetrahedron: Asymmetry* **2005**, *16*, 1959.
11. (a) Chen, H. Ph.D. Thesis, Sichuan University, 1999; (b) Tim, T.; Stephen, M. B.; John, C. *Tetrahedron Lett.* **2000**, *41*, 4503; (c) Herrmann, W. A.; Kohlpaintner, C. W.; Bahrmann, H.; Konkol, W. *J. Mol. Catal.* **1992**, *73*, 191; (d) Fuller, J.; Carlin, R. T.; Delong, H. C.; Haworth, D. *Chem. Commun.* **1994**, 299; (e) Wilkes, J. S.; Zaworotko, M. *J. Chem. Commun.* **1992**, 965; (f) Bonbote, P.; Dias, A.; Papageorgiou, N.; Kalyansundaram, K.; Gratzel, M. *Inorg. Chem.* **1996**, *35*, 1168; (g) Ma, Y.-P.; Liu, H.; Chen, L.; Cui, X.; Zhu, J.; Deng, J.-G. *Org. Lett.* **2003**, *5*, 2103; (h) Face, E.; Santini, C.; Senocq, F.; Basset, J. M. *J. Mol. Catal.* **1992**, *72*, 331.