

# Chiral sulfur-containing ligands for iridium(I)-catalyzed asymmetric transfer hydrogenation of aromatic ketones

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**Abstract**—New efficient catalyst systems, coupled with IrCl(COD)PPh<sub>3</sub> and chiral [SNNS]-type ligands, were employed in the asymmetric transfer hydrogenation of aromatic ketones under mild reaction conditions. The corresponding optically active alcohols were obtained in high yield and good to excellent enantioselectivities (up to 96% ee). The chiral Ir(I) complexes with the ligands of [SNNS]-type were also prepared and characterized, which showed good enantioselectivity and high activity. The reactions can be performed in air and the catalytic experiments are greatly simplified.

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## 1. Introduction

Transition metal complex catalysts based on ligands with mixed functional groups have great potential application in asymmetric catalysis.<sup>1</sup> Over the past two decades, a large number of the mixed chiral [PN], [NPN], [PNP], [PNNP], [ON], and [ONNO] ligands have been synthesized and serve as excellent chiral auxiliaries for catalytic asymmetric synthesis.<sup>2–13</sup> Compared to ligands with P, N or O as donor atoms, sulfur-containing chiral mixed ligands have received much less attention. A possible reason is that sulfur has a tendency to poison transition metal catalysts.

Indeed, sulfur possesses higher oxidation states available and can form some compounds that have different functional groups, such as thiol, sulfide, thioamide, sulfoxide, sulfinyl, thiocarbonyl, and thiocarbamide. Furthermore, its empty relatively low-energy d orbitals can accept back-donation of  $\pi$ -electron density from the metal, leading to stabilizing the metal–S bond. On complexation to a metal, chirality can be induced at sulfur.<sup>14,15</sup> These key structural features exemplify very rich coordination chemistry toward transition metals, and they serve as powerful stereodirecting ligands in asymmetric synthesis.<sup>16–18</sup> Over the last three decades, the study of sulfur-containing ligands has increased considerably. Several excellent review articles regarding

the synthesis and application of chiral sulfur-containing ligands in asymmetric catalysis have been published.<sup>19–22</sup> Recently, chiral sulfur-containing ligands have been successfully used as chiral auxiliaries for a wide range of reactions, such as allylic substitution,<sup>23</sup> vinylation of ketones,<sup>24</sup> asymmetric reduction,<sup>25</sup> enantioselective ring opening,<sup>26</sup> and asymmetric transfer hydrogenation (ATH).<sup>14,27</sup>

Over the past 10 years, the ATH of prochiral ketones has attracted considerable attention. Most research works in this area were carried out by using the chirally modified transition metals, such as Ru, Rh, and Ir, as catalyst precursors.<sup>28–34</sup>

In our earlier studies, we synthesized a family of excellent chiral [PNNP] ligands, and successfully employed them in ATH of aromatic ketones with up to 99% ee.<sup>35–40</sup> To extend our study, we developed the application of chiral tetradentate [SNNS] ligands in iridium(I)-catalyzed ATH of a series of aromatic ketones under mild reaction conditions, giving the corresponding optically active alcohols with high yield and up to 96% ee.

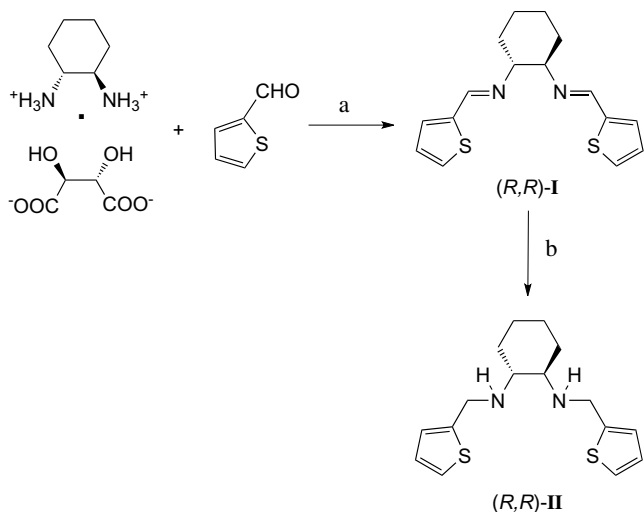
## 2. Results and discussion

### 2.1. Preparation of chiral [SNNS]-type ligands

Chiral ligand (1*R*,2*R*)-*N*<sup>1</sup>,*N*<sup>2</sup>-bis(thiophen-2-ylmethylene)-cyclohexane-1,2-diamine, (*R,R*)-**I**, was prepared by literature

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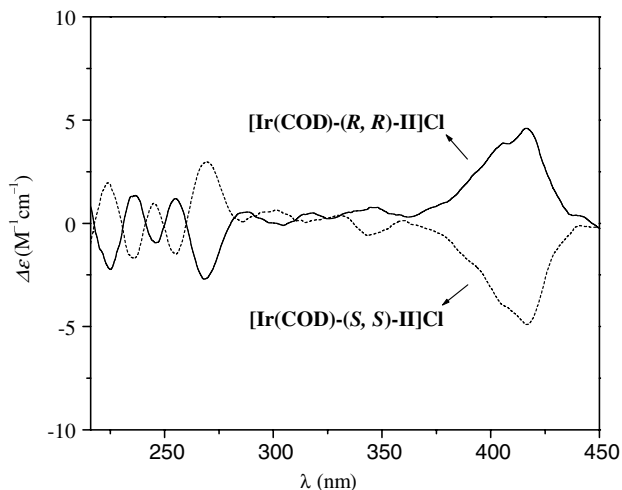
procedure,<sup>41</sup> except using (*R,R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt instead of (*R,R*)-1,2-cyclohexanediamine (Scheme 1). The reduction of ligand (*R,R*)-I with excess NaBH<sub>4</sub> was carried out in refluxing ethanol to afford (1*R*,2*R*)-*N*<sup>1</sup>,*N*<sup>2</sup>-bis(thiophen-2-ylmethyl)cyclohexane-1,2-diamine, (*R,R*)-II, in 99% yield.



**Scheme 1.** Synthesis of chiral [SNNS] ligands (*R,R*)-I and (*R,R*)-II. Reagents and conditions: (a) K<sub>2</sub>CO<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>OH/H<sub>2</sub>O, reflux; (b) NaBH<sub>4</sub>, CH<sub>3</sub>CH<sub>2</sub>OH, reflux.

## 2.2. Synthesis and characterization of chiral [SNNS]-iridium(I) complexes

The interaction of [Ir(COD)Cl]<sub>2</sub> with 2 equiv of (*R,R*)-II or (*S,S*)-II in CH<sub>2</sub>Cl<sub>2</sub> at room temperature gave chiral [SNNS]-Ir(I) complexes [Ir(COD)-(*R,R*)-II]Cl and [Ir(COD)-(*S,S*)-II]Cl, respectively. The CD spectra of chiral [SNNS] ligands and corresponding chiral iridium complexes have been measured in MeOH. Only weak absorbing peaks at 226 nm were found in the CD spectra of chiral [SNNS] ligands, while the CD spectra of [Ir(COD)-(*R,R*)-II]Cl and



**Figure 1.** The CD spectra of chiral iridium complexes.

[Ir(COD)-(*S,S*)-II]Cl bear a mirror-image relationship with  $\Delta\epsilon_{\text{max}}$  at 417 nm (Fig. 1), indicating that the metal center chelated with the chiral ligands.

## 2.3. ATH with [SNNS]-type ligands as chiral auxiliaries

Recently, König et al. employed chiral diimine ligand (*R,R*)-I to catalyze asymmetric addition of diethyl zinc to benzaldehyde, while Jacobsen et al. used ligand (*R,R*)-I as chiral auxiliary in asymmetric aziridination of alkenes, but the results were unsatisfactory.<sup>41,42</sup> Umani-Ronchi and Kim, respectively, reported the application of a chiral diamine ligand (*R,R*)-II in the asymmetric allylic alkylation, but the molar ratio of substrate to ligand was very low (S:L = 10:1).<sup>43,44</sup> In our study, we first employed chiral [SNNS]-type ligands in ATH of aromatic ketones under an air atmosphere, giving the corresponding optically active alcohols with high yield and enantioselectivity.

**2.3.1. ATH of propiophenone.** In the initial experiment, the ATH of propiophenone was chosen as a model reaction. Some Ru, Rh, and Ir complexes with ligand (*R,R*)-II have been tested. The catalyst systems were generated in situ by mixing ligand (*R,R*)-II and metal complexes in <sup>t</sup>PrOH under an air atmosphere. Typical results are listed in Table 1.

**Table 1.** ATH of propiophenone with (*R,R*)-II and various metal complexes as catalyst precursors<sup>a</sup>

Entry	Metal complex	Time (h)	Alcohol	
			Yield <sup>b</sup> (%)	ee <sup>b</sup> (%)
1	Ru(DMSO) <sub>4</sub> Cl <sub>2</sub>	8	15	5
2	CpRu(PPh <sub>3</sub> ) <sub>3</sub> Cl	8	25	22
3	Ru(PPh <sub>3</sub> ) <sub>3</sub> Cl <sub>2</sub>	8	14	52
4	<i>trans</i> -RhCl(CO)(PPh <sub>3</sub> ) <sub>3</sub>	8	3	—
5	[RhCl(COD)] <sub>2</sub>	8	71	45
6	[IrCl(COD)] <sub>2</sub>	5	97	75
7	[IrHCl <sub>2</sub> (COD)] <sub>2</sub>	5	92	61
8 <sup>c</sup>	IrH(CO)(PPh <sub>3</sub> ) <sub>3</sub>	4	95	77
9	IrCl(COD)PPh <sub>3</sub>	4.5	95	86

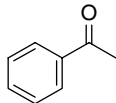
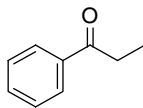
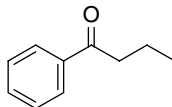
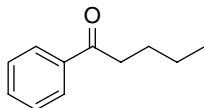
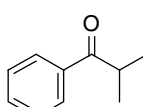
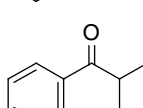
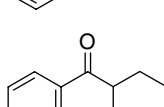
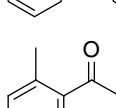
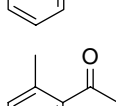
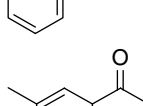
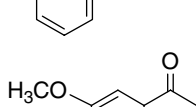
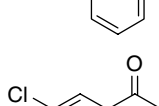
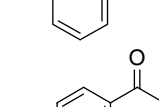
<sup>a</sup> Reaction conditions: L\* = (*R,R*)-II; propiophenone, 0.5 mmol; Sub.-[M]-Ligand-KOH = 100:1:1:4; <sup>t</sup>PrOH, 5 mL; temp, 45 °C; air atmosphere.

<sup>b</sup> Yield and ee were determined by GC analysis using a chiral G-TA column.

<sup>c</sup> Temp, 60 °C.

It could be seen that Ru complexes showed low activity and low to moderate enantioselectivities in the reactions (Table 1, entries 1–3). The *trans*-RhCl(CO)(PPh<sub>3</sub>)<sub>3</sub>/*(R,R)*-II system showed very low activity (Table 1, entry 4), while [RhCl(COD)]<sub>2</sub> was used, the activity improved but ee was still unsatisfactory (71% yield and 45% ee, Table 1, entry 5). When Ir complexes were employed as metallic precursors, good conversion and moderate to good enantioselectivities were obtained (Table 1, entries 6–9). The catalytic system IrCl(COD)PPh<sub>3</sub>/*(R,R)*-II gave the best result (95% yield and 86% ee). Therefore, IrCl(COD)PPh<sub>3</sub> was chosen as a metallic precursor for further study.

**Table 2.** ATH of various ketones catalyzed by IrCl(COD)PPh<sub>3</sub>/[SNNS]-type ligand **II**<sup>a</sup>

Entry	Substrate	Ligand	Time (h)	Alcohol		
				Yield <sup>b</sup> (%)	ee <sup>b</sup> (%)	Config <sup>d</sup>
1		( <i>R,R</i> )- <b>II</b>	6	96	83	( <i>S</i> )
2		( <i>R,R</i> )- <b>II</b>	8	94	87	( <i>S</i> )
3		( <i>R,R</i> )- <b>II</b>	10	94	88	( <i>S</i> )
4		( <i>R,R</i> )- <b>II</b>	12	97	90	( <i>S</i> )
5		( <i>R,R</i> )- <b>II</b>	48	92	95	( <i>S</i> )
6		( <i>S,S</i> )- <b>II</b>	46	92	94	( <i>R</i> )
7		( <i>S,S</i> )- <b>II</b>	22	97 <sup>c</sup>	96 <sup>c</sup>	( <i>R</i> )
8		( <i>R,R</i> )- <b>II</b>	9	96	91	( <i>S</i> )
9		( <i>S,S</i> )- <b>II</b>	9	92	90	( <i>R</i> )
10		( <i>R,R</i> )- <b>II</b>	7	94	82	( <i>S</i> )
11		( <i>S,S</i> )- <b>II</b>	7	94	89	( <i>R</i> )
12		( <i>R,R</i> )- <b>II</b>	5	99	71	( <i>S</i> )
13		( <i>R,R</i> )- <b>II</b>	5	94	58	( <i>S</i> )

<sup>a</sup> Reaction conditions: ketone, 0.5 mmol; Sub.-[M]-Ligand-KOH = 100:1:1:8; <sup>t</sup>PrOH, 5 mL; temp, 25 °C; air atmosphere.

<sup>b</sup> Yield and ee were determined by GC analysis using chiral G-TA column unless otherwise specified.

<sup>c</sup> Yield and ee were determined by GC analysis using chiral CP-Chirasil-Dex CB column.

<sup>d</sup> The configurations were determined by comparison of the retention times of the enantiomers on the GC traces with literature values.

Chiral diimine ligand (*R,R*)-**I** was also used as a ligand with IrCl(COD)PPh<sub>3</sub> in the reduction reaction. But the reaction proceeded very slowly, producing (*S*)-1-phenylpropan-1-ol in only 27% yield and 5% ee (45 °C, 17 h). These results are similar to those of earlier studies,<sup>35,45</sup> indicating that the NH functions in the ligands are responsible for the high activity and the NH linkage can possibly stabilize a catalytic transition state.<sup>46–48</sup>

**2.3.2. ATH of various aromatic ketones.** The catalytic systems IrCl(COD)PPh<sub>3</sub>/**II**, which were generated in situ by mixing chiral ligand **II** and IrCl(COD)PPh<sub>3</sub> in <sup>t</sup>PrOH under an air atmosphere, have been further examined for the ATH of various aromatic ketones. The results are summarized in Table 2. A variety of aromatic ketones could be reduced to the corresponding optically active secondary alcohols with high chemical yield and good enantiomeric excesses under mild reaction conditions. The reactivity and enantioselectivity were affected by the steric property of the substrates in the alkyl moiety. As the bulkiness of the alkyl group increased from methyl, ethyl, propyl to *n*-butyl, the enantioselectivity increased gradually, while the reaction rate slowed down (Table 2, entries 1–4). The reduction of isobutyrophenone proceeded smoothly with 95% ee (Table 2, entry 5). Notably, for cyclohexyl phenyl ketone the corresponding chiral alcohols could be obtained with 97% yield and 96% ee (Table 2, entry 7). The electronic properties and position of the groups in the ring substituent also affected the enantioselectivity of reduction reaction. *ortho*-Methyl acetophenone was reduced with 91% ee (Table 2, entry 8), while a lower ee was obtained for *meta*-methyl acetophenone (Table 2, entry 10). The ketone having an electron-donating substituent, *meta*-methoxyl acetophenone, achieved 94% chemical yield with 89% ee (Table 2, entry 11). Introduction of an electron-withdrawing group such as a chloro substituent onto the aromatic ring would decrease the enantioselectivity (Table 2, entries 12 and 13).

To determine the role of sulfur in the thiophene group of ligand **II**, we synthesized the chiral ligand, (1*R*, 2*R*)-*N*<sup>1</sup>,*N*<sup>2</sup>-bis(furan-2-ylmethyl)cyclohexane-1,2-diamine, which used oxygen instead of sulfur. This ligand has also been examined in the ATH of propiophenone, with lower conversion and ee achieved (25% conv., 75% ee). This result indicated that the sulfur in the thiophene group of ligand **II** played an important role in ATH.

#### 2.4. ATH with chiral [SNNS]-iridium(I) complexes as catalysts

The above results indicated that the chiral [SNNS]/Ir(I) mixed systems were very effective for the ATH of aromatic ketones under mild conditions. Although the nature of the active catalyst remained unknown, the relevant Ir(I) complexes [Ir(COD)-(*R,R*)-**II**]Cl and [Ir(COD)-(*S,S*)-**II**]Cl have been synthesized and fully characterized by IR, NMR, MS, and CD. These chiral iridium complexes served as a catalyst for the ATH of propiophenone, giving 98% yield and 82% ee (45 °C, 4 h). When *ortho*-methyl acetophenone was used as a substrate, 99% yield and 87% ee were obtained (45 °C, 8 h). These results suggest that the

preformed complex probably exists as the catalytically active species in the course of the catalytic reaction.

### 3. Conclusion

We have found the new catalytic systems, coupled with IrCl(COD)PPh<sub>3</sub> and chiral [SNNS]-type ligands, which efficiently catalyzed the ATH of a series of aromatic ketones with <sup>t</sup>PrOH in air, giving the corresponding optically active alcohols with up to 99% yield and up to 96% ee. The related chiral iridium complexes [Ir(COD)-(*R,R*)-**II**]Cl and [Ir(COD)-(*S,S*)-**II**]Cl have been synthesized and fully characterized. These complexes act as a catalytic precursor and catalyze the ATH with good results. In order to reveal the exact reaction mechanism, isolation, and characterization of the catalytic active species is under further investigation. This work will provide a valuable index to develop the chemistry of chiral sulfur-containing ligands.

### 4. Experimental

#### 4.1. General methods

The preparation of ligands and chiral iridium complexes was carried out under a nitrogen atmosphere. NMR spectra were recorded on a Bruker AV 400 instrument. Mass spectra were carried out on a Finnigan LCQ mass spectrometer. IR spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer. CD spectra were measured with a JASCO J-810 spectrophotometer. The yields and ee values were determined by GC analysis with a chiral G-TA column or CP-Chirasil-Dex CB column. Melting points were measured using an X-4 digital apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer 341 polarimeter. Conductance was determined by conducto metermodex DDS-11A. The solvents were dried and purified according to standard methods.

#### 4.2. Preparation of chiral [SNNS]-type ligands

To a mixture of (*R,R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt (5.29 g, 20 mmol) and K<sub>2</sub>CO<sub>3</sub> (5.54 g, 40 mmol) were added H<sub>2</sub>O (60 mL) and EtOH (120 mL). The solution was refluxed with stirring for 5 h before thiophene-2-carbaldehyde (3.82 mL, 40 mmol) was added. Then the mixture was refluxed with stirring overnight. The mixture solution was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined extracts were washed with H<sub>2</sub>O and the organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, followed by filtration and concentration. The crude product was recrystallised from hot ethanol to give (*R,R*)-**I** as a white solid (5.08 g, 84% yield).

A solution of (*R,R*)-**I** (2.70 g, 8.94 mmol) and NaBH<sub>4</sub> (7.05 g, 178.8 mmol) in absolute ethanol (140 mL) was refluxed with stirring for 2 days. The solution was cooled to room temperature and H<sub>2</sub>O was added to destroy excess NaBH<sub>4</sub>. The mixture solution was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined extracts were washed with saturated NH<sub>4</sub>Cl solution and H<sub>2</sub>O. The organic layer was dried over anhy-

drous Na<sub>2</sub>SO<sub>4</sub>, followed by filtration, then concentrated to give ligand (*R,R*)-**II** as a white solid (2.70 g, 99 % yield).  $[\alpha]_{\text{D}}^{20} = -102.0$  (*c* 0.5, CH<sub>3</sub>OH).

The ligands (*S,S*)-**I** and (*S,S*)-**II** were also synthesized by a procedure similar to the one mentioned above.

#### 4.3. Synthesis and characterization of chiral [SNNS]-iridium(I) complexes

CH<sub>2</sub>Cl<sub>2</sub> (3.5 mL) was added to a mixture of (*R,R*)-**II** (0.153 g, 0.5 mmol) and [Ir(COD)Cl]<sub>2</sub> (0.168 g, 0.25 mmol). The solution was stirred at room temperature and a yellow precipitate was immediately formed. After stirring for 3.5 additional hours, the solid was collected by filtration, washed with a few milliliters of CH<sub>2</sub>Cl<sub>2</sub> and dried under vacuum to afford [Ir(COD)-(*R,R*)-**II**]Cl (0.304 g, 60% yield). Mp 107 °C (dec).  $A_{\text{m}} = 61.86 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD):  $\delta$  0.86–0.94 (m, 2H), 0.98–1.07 (m, 2H), 1.26–1.38 (m, 2H), 1.64 (d, *J* = 8.8 Hz, 2H), 2.12–2.24 (m, 4H), 2.30–2.36 (m, 4H), 2.81–2.92 (m, 2H), 3.53–3.60 (m, 2H), 3.94 (d, *J* = 15.0 Hz, 2H), 4.49 (t, *J* = 7.0 Hz, 2H), 4.64 (d, *J* = 15.0 Hz, 2H), 7.09 (dd, *J* = 3.5 Hz, *J* = 5.3 Hz, 2H), 7.34 (d, *J* = 13.0 Hz, 2H), 7.61 (d, *J* = 12.8 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD):  $\delta$  25.65, 27.70, 29.61, 35.88, 45.47, 63.47, 66.54, 70.55, 127.66, 129.00, 130.66, 136.54. IR (KBr): 3426, 2935, 2858, 2832, 1626, 1466, 1383, 1229, 1108, 1050, 1005, 937, 894, 850, 702 cm<sup>-1</sup>. EIMS (*m/z*): 607.1 (M–Cl).

The complex [Ir(COD)-(*S,S*)-**II**]Cl was also synthesized by the same procedure.

#### 4.4. General procedure for ATH of ketones

A solution of catalyst (0.005 mmol) in <sup>i</sup>PrOH (5 mL) was stirred for 15 min under air atmosphere. KOH/<sup>i</sup>PrOH solution and aromatic ketone (0.5 mmol) were introduced, and then the solution was stirred at the desired temperature for the required reaction time. At the end of the experiment, the reaction mixture was filtered through a pad of silica gel and analyzed by GC using a chiral G-TA column.

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