



# Asymmetric transfer hydrogenation of aromatic ketones with chiral diamino-thiophene/iridium catalyst systems

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## ABSTRACT

The chiral diamino-bis(bithiophene) ligands were firstly employed in the iridium(I)-catalyzed asymmetric transfer hydrogenation of aromatic ketones. The new catalyst systems, generated in situ from chiral diamino-bis(bithiophene) ligands and  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  in  $^i\text{PrOH}$ , gave the corresponding optically active secondary alcohols with high yield and fair to good enantioselectivities (up to 90% ee). The chiral Ir(I)/diamino-bis(bithiophene) complexes were also synthesized and characterized. The XPS spectra showed that the potentially multidentate ligands coordinated to the Ir atom through the nitrogen atoms, while the thiophene pendants did not participate in coordination to the Ir atom.

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## 1. Introduction

Chiral ligands with mixed functional groups have been known to play an important role in transition metal complexes catalyzed asymmetric reactions [1]. In the past two decades, a large number of the chiral-mixed [PN], [NPN], [PNP], [PNNP], [ON] and [ONNO] ligands have been synthesized and served as excellent chiral auxiliaries for catalytic asymmetric synthesis [2–13]. Compared to the ligands with P, N or O as donor atoms, sulfur-containing based chiral mixed ligands have received much less attention. A plausible reason is that sulfur has a tendency to poison transition metal catalysts.

However, sulfur possesses a number of oxidation states available and can form some compounds that have different functional groups. Furthermore, its empty relatively low-energy d orbitals can accept back-donation of  $\pi$ -electron density from the metal, leading to stabilize the metal–S bond. Upon complexation of a metal, chirality can be induced at sulfur [14,15]. These promoting structural features exhibit very rich coordination chemistry towards transition metal and serve as powerful stereodirecting ligands in asymmetric synthesis [16–18]. Recently, sulfur-containing ligands have proved to be as excellent as other classical chiral ligands in the form of various groups, such as thioether [19,20], sulfoxide [14,21], sulfamide [22], thiocarbonyl [23], and aminosulfide [24].

Thiophene functional groups, as a type of extremely flexible coordination mode of the sulfur-containing five-membered ring,

can coordinate to metal centers through the sulfur, carbons or all five atoms in the thiophene ring [25]. The  $\pi$ -electron of the aromatic thiophene ring can involve in donor–acceptor interactions with metal atoms conveniently. More recently, the chiral thiophene derivatives as ligands have been successfully used as chiral auxiliaries for a wide range of reactions, such as asymmetric reduction [26–29], allylic alkylation [30–32], hydrosilylation [32], cyclopropanation [33], Diels–Alder reaction [34], and Heck reaction [35], while the use of thiophene ligands in asymmetric transfer hydrogenation (ATH) appears to be still rather underdeveloped [36].

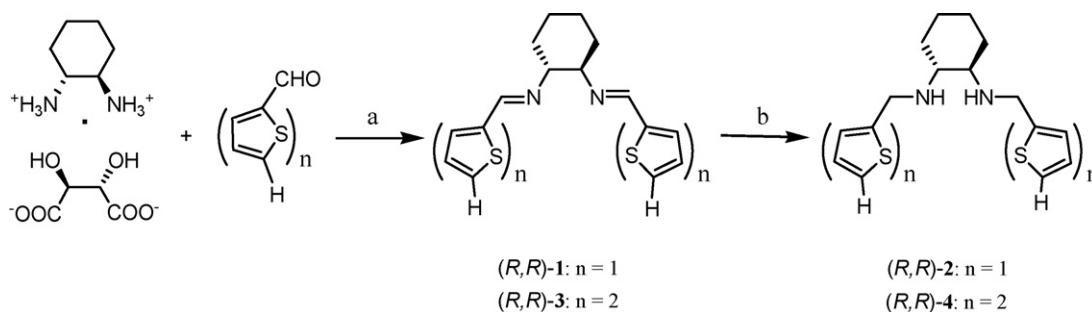
Previously, our lab has reported the application of chiral diamino-bis(thiophene) ligands **2** in ATH of aromatic ketones and the thiophene groups in the chiral sulfur-containing ligands enhanced chemical as well as optical yields in the final product [36]. In our present study, we further investigated the catalytic performance of chiral diamino-bis(bithiophene) ligands **4** bearing two thienyl units in each N-pendant and the coordination environment of the diamino-thiophene ligands.

## 2. Experimental

### 2.1. General methods

All experiments were carried out in 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. Conductance was determined by conducto metermodec DDS-11A.

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**Scheme 1.** Syntheses of chiral thiophene ligands. Reagents and conditions: (a)  $\text{K}_2\text{CO}_3$ ,  $\text{CH}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$ , reflux; (b)  $\text{NaBH}_4$ ,  $\text{CH}_3\text{CH}_2\text{OH}$ , reflux.

The XPS data were recorded on a Quantum 2000 spectrometer operating with Al  $\text{K}\alpha$  (1486.6 eV) radiation source and the binding energies were referred to the carbon C 1s peak ( $E_b = 284.7$  eV). Optical rotations were measured with a Perkin-Elmer 341 polarimeter. The yields and ee values were determined by GC analysis with a CP-Chirasil-Dex CB column. The solvents were dried and purified according to standard methods.

## 2.2. Preparation of chiral thiophene ligands

$\text{H}_2\text{O}$  (15 mL) and EtOH (30 mL) were added to a mixture of  $(R,R)$ -1,2-diammoniumcyclohexane mono-(+)-tartrate salt (1.32 g, 5 mmol) and  $\text{K}_2\text{CO}_3$  (1.28 g, 10 mmol), and then refluxed with stirring for 5 h. A solution of 5-(thiophen-2-yl)thiophene-2-carbaldehyde in EtOH (1.94 g, 10 mmol in 10 mL) was added. Afterwards the mixture continued stirring with reflux for 2 more days, followed by a  $\text{CH}_2\text{Cl}_2$  extraction. The combined extracts were washed with  $\text{H}_2\text{O}$  and dried over anhydrous  $\text{Na}_2\text{SO}_4$ , followed by filtration and concentration. The crude product was then recrystallised from hot ethanol to give diimino-bis(bithiophene) ligand  $(R,R)$ -3 as a white solid (2.12 g, 91% yield).

A solution of  $(R,R)$ -3 (2.00 g, 4.29 mmol) and  $\text{NaBH}_4$  (3.25 g, 85.8 mmol) in absolute ethanol (80 mL) was refluxed with stirring for 2 days. The solution was then cooled to room temperature.  $\text{H}_2\text{O}$  was added to destroy excess  $\text{NaBH}_4$ , followed by a  $\text{CH}_2\text{Cl}_2$  extraction. The combined extracts were washed with saturated  $\text{NH}_4\text{Cl}$  solution and  $\text{H}_2\text{O}$  successively. The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , followed by filtration, then concentrated to give diamino-bis(bithiophene) ligand  $(R,R)$ -4 as a white solid (1.90 g, 94% yield).

The ligands  $(S,S)$ -3 and  $(S,S)$ -4 were also synthesized via the similar procedure above.

## 2.3. Synthesis and characterization of chiral $\text{Ir(I)}$ /diamino-bis(bithiophene) complexes

$\text{CH}_2\text{Cl}_2$  (7 mL) was added to a mixture of  $(R,R)$ -4 (0.471 g, 1.0 mmol) and  $[\text{Ir}(\text{COD})\text{Cl}]_2$  (0.336 g, 0.5 mmol). The solution was stirred at room temperature and a yellow precipitate formed immediately. After stirring for 2.5 additional hours, a solid was collected by filtration, washed with a few milliliters of  $\text{CH}_2\text{Cl}_2$  and dried under vacuum to afford  $[\text{Ir}(\text{COD})-(R,R)\text{-4}]\text{Cl}$  (0.605 g, 75% yield).  $A_m = 56.23 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ .  $^1\text{H NMR}$  (400 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  0.93–1.12 (m, 4H), 1.32–1.42 (m, 2H), 1.67 (d,  $J = 8.4$  Hz, 2H), 2.24–2.32 (m, 4H), 2.33–2.44 (m, 4H), 2.90–3.03 (m, 2H), 3.53–3.61 (m, 2H), 3.94 (d,  $J = 15.2$  Hz, 2H), 4.56–4.63 (m, 4H), 7.13 (dd,  $J_1 = 3.6$  Hz,  $J_2 = 5.2$  Hz, 2H), 7.17–7.21 (m, 4H), 7.34 (dd,  $J_1 = 1.2$  Hz,  $J_2 = 3.6$  Hz, 2H), 7.43 (dd,  $J_1 = 0.8$  Hz,  $J_2 = 5.2$  Hz, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  26.5, 28.5, 30.3, 37.0, 46.8, 64.5, 67.6, 71.7, 124.4, 125.9, 127.0, 130.0, 132.4, 136.3, 129.0, 142.0. IR (KBr): 3432, 3105, 3068, 2935, 2852, 2832, 1629, 1467, 1383, 1202, 1046, 1007,

800, 723, and 695  $\text{cm}^{-1}$ . EIMS ( $m/z$ ): 771.2 ( $\text{M}-\text{Cl}$ ).  $[\alpha]_D^{20} = 36.1$  (c 1.0,  $\text{CH}_3\text{OH}$ ).

The complex  $[\text{Ir}(\text{COD})-(S,S)\text{-4}]\text{Cl}$  was also synthesized by the same procedure.  $[\alpha]_D^{20} = -36.8$  (c 1.0,  $\text{CH}_3\text{OH}$ ).

## 2.4. Typical procedure for ATH of ketones

A solution of  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  (3.9 mg, 0.005 mmol) and ligand  $(R,R)$ -4 (2.6 mg, 0.0055 mmol) in  $^i\text{PrOH}$  (5 mL) was stirred for 20 min. A solution of KOH in  $^i\text{PrOH}$  (0.06 mmol in 0.6 mL) and isobutyrophenone (0.5 mmol) were introduced, and then the solution was stirred at 45 °C for 16 h. The reaction mixture was then filtered through a pad of silica gel and analyzed by GC using a chiral CP-Chirasil-Dex CB column, giving 96% yield and 90% ee.

## 3. Results and discussion

Chiral thiophene ligands 1–4 were prepared according to literature procedure [31]. We used  $(R,R)$ -1,2-diammoniumcyclohexane mono-(+)-tartrate salt instead of  $(R,R)$ -1,2-cyclohexanediamine (Scheme 1). Ligands 3 and 4 were obtained with high chemical yield (91% and 94%, respectively).

Recently, Umani-Ronchi reported the application of chiral diamine ligands  $(R,R)$ -2 and 4 in asymmetric allylic alkylation and hydrosilylation, but the molar ratios of substrate to ligand were very low [31,32]. In our earlier studies, we used diamino-bis(thiophene) ligands 2 as chiral auxiliaries in ATH. In continuation with our findings, we decided to employ chiral diamino-bis(bithiophene) ligands 4 in ATH of aromatic ketones, giving the corresponding optically active alcohols with high yield and fair to good enantioselectivities.

**Table 1**

ATH of propiophenone with  $(R,R)$ -4 and various metal complexes as catalyst precursors<sup>a</sup>.

Entry	Metal complex	Alcohol	
		Yield <sup>b</sup> (%)	Ee <sup>b</sup> (%)
1	$\text{Ru}_3(\text{CO})_{12}$	29	61
2	$[\text{RuCl}_2(\text{COD})]_n$	94	22
3	$[\text{RuCl}_2(\text{cymene})]_2$	98	19
4	<i>trans</i> - $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$	34	47
5 <sup>c</sup>	$\text{RhH}(\text{CO})(\text{PPh}_3)_3$	20	47
6	$\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$	0	–
7	$\text{IrCl}(\text{COD})\text{PPh}_3$	97	56
8 <sup>c</sup>	$\text{IrH}(\text{CO})(\text{PPh}_3)_3$	96	68
9	$\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	97	76

<sup>a</sup> Reaction conditions: propiophenone, 0.5 mmol; Sub.: $[\text{M}]:\text{ligand}:\text{KOH} = 100:1:1.1:8$ ;  $^i\text{PrOH}$ , 5 mL; temp., 45 °C; time, 16 h.

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

<sup>c</sup> Temp., 60 °C.

In the initial experiment, the ATH of propiophenone was chosen as a model reaction. Some Ru, Rh, Pd and Ir complexes with ligand (*R,R*)-**4** have been tested. The catalyst systems generated in situ by mixing ligand (*R,R*)-**4** and metal complex in *i*PrOH, which were directly used for reduction of propiophenone. Typical results were listed in Table 1.

The trinuclear ruthenium cluster  $\text{Ru}_3(\text{CO})_{12}$  combined with ligand (*R,R*)-**4** showed low activity (Table 1, entry 1). While  $[\text{RuCl}_2(\text{COD})]_n$  and  $[\text{RuCl}_2(\text{cymene})]_2$  were used, the activity improved but enantioselectivities were still unsatisfactory (Table 1, entries 2 and 3). Low activity and fair enantioselectivities were observed when Rh complexes were employed in the reactions (Table 1, entries 4 and 5). Pd( $\text{CH}_3\text{CN}$ ) $_2\text{Cl}_2$  did not promote the reaction smoothly (Table 1, entry 6). Fortunately, when Ir complexes were employed as metallic precursors, good conversion and moderate enantioselectivities were obtained (Table 1, entries 7–9). The

catalytic system  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2/(\text{R,R})\text{-4}$  gave the best result (97% yield and 76% ee). Therefore  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  was chosen as metallic precursor for the further study.

Chiral diimine ligand (*R,R*)-**3** was also used as chiral auxiliary coupled with  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  in the reduction reaction. But the reaction proceeded very slowly, producing (*S*)-1-phenylpropan-1-ol with only 27% yield and 5% ee (45 °C, 17 h). The results were similar to chiral ligands **1** and **2** in our earlier studies [36], indicating that the NH functions in the ligands are responsible for the high activity and the NH linkage possibly can stabilize a catalytic transition state [37–40].

The catalytic systems  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2/(\text{R,R})\text{-4}$  or (*S,S*)-**4** have been further examined for the ATH of various aromatic ketones. The results were summarized in Table 2. A variety of aromatic ketones could be reduced to the corresponding optically active secondary alcohols with high chemical yield and fair to good enan-

**Table 2**  
ATH of various ketones catalyzed by  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2/\text{diamino-bis(bithiophene)}$  ligands **4**<sup>a</sup>.

Entry	Substrate	Ligand	Sub.: [M]:KOH	Time (h)	Alcohol		
					Yield <sup>b</sup> (%)	Ee <sup>b</sup> (%)	Config. <sup>c</sup>
1		( <i>R,R</i> )- <b>4</b>	100:1:8	12	95	71	<i>S</i>
2		( <i>R,R</i> )- <b>4</b>	100:1:8	16	97	76	<i>S</i>
3		( <i>S,S</i> )- <b>4</b>	100:1:12	16	96	75	<i>R</i>
4		( <i>S,S</i> )- <b>4</b>	100:1:12	16	95	74	<i>R</i>
5		( <i>R,R</i> )- <b>4</b>	100:1:12	16	96	90	<i>S</i>
6 <sup>d</sup>		( <i>S,S</i> )- <b>4</b>	100:1:12	20	93	90	<i>R</i>
7		( <i>S,S</i> )- <b>4</b>	100:1:8	12	96	89	<i>R</i>
8		( <i>R,R</i> )- <b>4</b>	100:1:12	14	94	64	<i>S</i>
9		( <i>R,R</i> )- <b>4</b>	100:1:12	16	96	62	<i>S</i>
10 <sup>d</sup>		( <i>R,R</i> )- <b>4</b>	100:1:12	20	90	34	<i>S</i>

<sup>a</sup> Reaction conditions: ketone, 0.5 mmol; [M]:ligand = 1:1.1; *i*PrOH, 5 mL; temp., 45 °C.

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

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

<sup>d</sup> Temp., 50 °C.

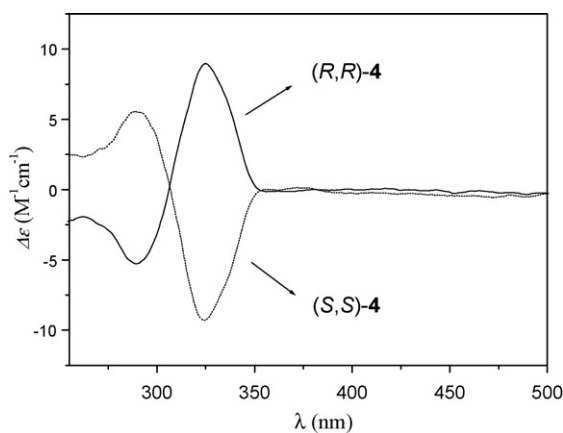


Fig. 1. The CD spectra of chiral diamino-bis(bithiophene) ligands.

tiomeric excesses under mild conditions. The steric property of the substrates in alkyl moiety affected the reactivity and enantioselectivity. The enantioselectivity of the reduction of propiophenone was higher than that of acetophenone (Table 2, entries 1 and 2). As the bulkiness of the alkyl group further increased to propyl or *n*-butyl, the reaction rate and enantioselectivities decreased slightly (Table 2, entries 3 and 4). Notably, the reductions of isobutyrophenone and cyclohexyl phenyl ketone proceeded with high chemical yield and 90% ee (Table 2, entries 5 and 6). For 1,1-diphenylacetone, the corresponding chiral alcohol could be obtained with 96% yield and 89% ee (Table 2, entry 7). The position of the groups in the ring substituent also affected the enantioselectivity of reduction reaction. With the position of methyl group shift from *ortho*-position to *meta*- and *para*-position, the reaction rates and enantioselectivities of the reductions were increased to a certain extent (Table 2, entries 8–10).

To gain further insights into the coordination mode of diamino-thiophene ligand to the Ir atom, we synthesized the chiral Ir/diamino-thiophene complexes. The interaction of  $[\text{Ir}(\text{COD})\text{Cl}]_2$  with two equivalents (*R,R*)-**4** or (*S,S*)-**4** in dichloromethane at room temperature gave chiral Ir(I)-diamino-bis(bithiophene) complexes  $[\text{Ir}(\text{COD})-(R,R)\text{-4}]\text{Cl}$  and  $[\text{Ir}(\text{COD})-(S,S)\text{-4}]\text{Cl}$ , respectively. Chiral Ir(I)/diamino-bis(thiophene) complex  $[\text{Ir}(\text{COD})-(R,R)\text{-2}]\text{Cl}$  was synthesized and characterized previously. These chiral iridium complexes have been fully characterized by IR, NMR, MS and CD. The CD spectra of ligands **4** and corresponding chiral iridium complexes have been measured in methanol (Figs. 1 and 2). The CD spectra of (*R,R*)-**4** and (*S,S*)-**4** bear a mirror-image relationship with  $\Delta\epsilon_{\text{max}}$  at 325 nm. Similarly, the CD spectra of chiral iridium

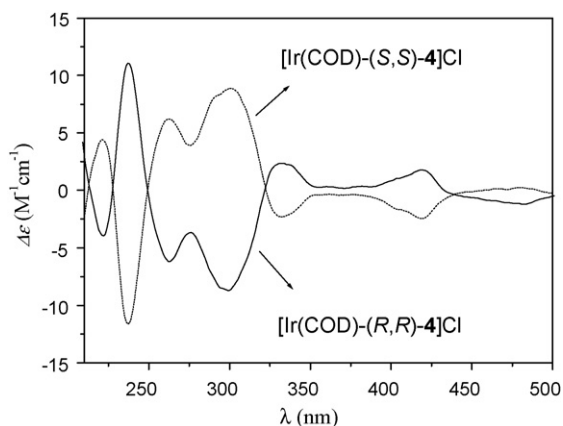


Fig. 2. The CD spectra of chiral Ir(I)/diamino-bis(bithiophene) complexes.

Table 3

Binding energies of the diamino-thiophene ligands and its chiral iridium complexes.

Entry	Compound	Ir 4f (eV)	N 1s (eV)	S 2p (eV)	C 12p (eV)
1	$[\text{IrCl}(\text{COD})]_2$	61.51	–	–	199.03
2	( <i>R,R</i> )- <b>2</b>	–	398.73	164.03	–
3	( <i>R,R</i> )- <b>4</b>	–	398.75	164.06	–
4	$[\text{Ir}(\text{COD})-(R,R)\text{-2}]\text{Cl}$	61.36	399.87	164.04	197.80
5	$[\text{Ir}(\text{COD})-(R,R)\text{-4}]\text{Cl}$	61.13	399.72	164.10	197.01

complexes also exhibit the mirror-image relationship, while the  $\Delta\epsilon_{\text{max}}$  is shifted toward about 237 nm, indicating the chiral ligands chelated with the center metal.

The XPS spectra of ligands (*R,R*)-**2**, **4** and their corresponding iridium complexes  $[\text{Ir}(\text{COD})-(R,R)\text{-2}]\text{Cl}$ , and  $[\text{Ir}(\text{COD})-(R,R)\text{-4}]\text{Cl}$  were tested (Table 3). The position of the spectrum line of the element to be determined allows one to distinguish not only the valency of the element, but also the coordination manner [41]. The shift of the N 1s signals of ligand (*R,R*)-**4** and  $[\text{Ir}(\text{COD})-(R,R)\text{-4}]\text{Cl}$  from 398.75 to 399.72 eV indicated that amine nitrogen atoms of the ligands were involved in donor-acceptor interactions with the central Ir atom. No notable change in the S 2p<sub>3/2</sub> electron binding energy of ligand (*R,R*)-**4** and  $[\text{Ir}(\text{COD})-(R,R)\text{-4}]\text{Cl}$  was deemed to have no coordination of sulfur atoms to the central Ir atom. The C 12p<sub>3/2</sub> signals shifted from 199.03 to 197.01 eV. Combining with mole conductance of  $[\text{Ir}(\text{COD})-(R,R)\text{-4}]\text{Cl}$  ( $\Lambda_m = 56.23 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ), the results indicated that the chlorine atoms changed from bridging ligands in  $[\text{IrCl}(\text{COD})]_2$  to outer sphere ion in  $[\text{Ir}(\text{COD})-(R,R)\text{-4}]\text{Cl}$ . The XPS spectra of ligand (*R,R*)-**2** and the related iridium complexes  $[\text{Ir}(\text{COD})-(R,R)\text{-2}]\text{Cl}$  have also been determined and the electron binding energy showed the similar results (Table 3, entries 2 and 4).

The above XPS analyses revealed that the potentially multidentate ligands coordinated to the Ir atom through the nitrogen atoms, while sulfur atoms did not participate in coordination to the Ir atom. For this coordination manner, the space orientation of the thiophene functional groups was uncertain. Therefore, the N-pendants of the ligands, especially the secondary thienyl ring in the diamino-bis(bithiophene) ligands, could not form a rigid three-dimensional architecture with substrate in catalytic transition state. This might be the reason for not obtaining very excellent enantioselectivity in the asymmetric catalytic reaction.

#### 4. Conclusion

Chiral diamino-thiophene ligands have proved to be efficient catalyst precursors in asymmetric transfer hydrogenation of aromatic ketones. The new catalytic systems, coupled with  $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$  and chiral diamino-bis(bithiophene) ligands **4**, catalyzed the ATH of a series of aromatic ketones efficiently with 96% yield and up to 90% ee. The related chiral iridium complexes  $[\text{Ir}(\text{COD})-(R,R)\text{-4}]\text{Cl}$  and  $[\text{Ir}(\text{COD})-(S,S)\text{-4}]\text{Cl}$  have been synthesized and fully characterized. The XPS spectra of the chiral diamino-thiophene ligands and the relevant Ir(I) complexes revealed that the potentially multidentate ligands coordinated to the central Ir atom through the nitrogen atoms, while sulfur atoms did not participate in coordination to the Ir atom. This work will provide a valuable index to develop the chemistry of sulfur-containing chiral ligands.

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