

Highly Enantioselective Synthesis of Heteroaromatic Alcohols Catalyzed by Chiral Diaminodiphosphine–Ruthenium(II) Complexes

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Abstract: Chiral diaminodiphosphine–ruthenium(II) complexes were found to be excellent catalysts for the asymmetric transfer hydrogenation of heteroaromatic ketones in propan-2-ol. In the presence of potassium hydroxide, the enantioselective reduction of heteroaromatic ketones proceeded smoothly to give chiral alcohols with excellent enantiomeric excess (up to 97% ee) under mild conditions without reduction of the heterocycle.

Key words: asymmetric, transfer hydrogenation, catalysis, heteroaromatic ketones, heteroaromatic alcohols

Chiral heteroaromatic alcohols are valuable intermediates and building blocks for a variety of biologically active compounds and chiral auxiliaries.¹ Hitherto the preparation of these compounds involved resolution of racemic alcohols,² enantioselective addition of dialkylzinc to aldehydes,³ catalytic asymmetric reduction of prochiral ketones, etc.⁴ The inherent disadvantage of resolution of racemic alcohols is that the maximum yield will be only 50% and the separation of the product is often problematic. The enantioselective alkylation is limited to only a few dialkylzinc derivatives. However, enantioselective reduction of prochiral ketones represents one of the simplest routes. In recent years, several highly efficient catalytic systems consisting of a chiral diphosphine–ruthenium–diamine complex and an inorganic base, which were developed by Noyori and others, have been used for the asymmetric hydrogenation of heteroaromatic ketones.^{4j–r} Using these catalytic systems, a wide range of heteroaromatic alcohols were obtained in high yields with excellent enantioselectivities. Compared with asymmetric hydrogenation, asymmetric transfer hydrogenation (ATH) using nonhazardous organic molecules such as propan-2-ol, provides a useful complement to catalytic reduction using molecular hydrogen, particularly for small-to-medium-scale reactions. It also produces alcohols with high enantiomeric excess and the operation is simpler.^{5–8} Some research groups have achieved success in obtaining enantiopure heteroaromatic alcohols by ATH of the corresponding ketones.^{4b,d,f–h,j}

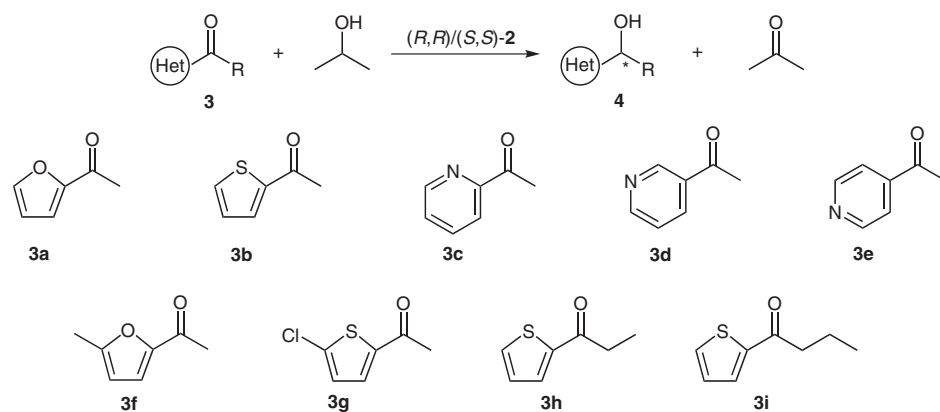
In the past decade, we have successfully prepared a class of chiral $C_6P_2(NH)_2$ –Ru(II), –Rh(I), –Ir(I), or –Ir(III) complexes, which were used as catalysts in the ATH of ar-

omatic ketones and in the kinetic resolution of racemic secondary alcohols.⁹ These catalytic systems have been found to be excellent for the enantioselective reduction of a series of aromatic ketones, leading to the corresponding chiral alcohols with up to 99% ee and the molar ratio of ketone to catalyst up to 10000:1. These systems were also used for oxidative kinetic resolution of the alcohols with excellent enantioselectivity of up to 98% ee. These good results prompt us to explore their applications in the ATH of heteroaromatic ketones.

In an initial experiment, the ATH of 4-acetylpyridine (**3e**) was chosen as a model reaction. Various chiral diamino-diphosphine–Ru, –Rh, or –Ir catalysts were tested for the ATH of 4-acetylpyridine (**3e**). Typical results are listed in Table 1.

As shown in Table 1 (see also Figure 1 for the structures of **1** and **2**), for the rhodium catalysts, the $RhH(CO)(PPh_3)_3/(R,R)$ -**1** system showed low activity and moderate enantioselectivity (Table 1, entry 1), while $[RhCl(COD)]_2$ exhibited higher activity but even lower enantiomeric excess (Table 1, entry 2). As for iridium catalysts, both $[IrCl(COD)]_2/(R,R)$ -**1** and $[IrHCl_2(COD)]_2/(R,R)$ -**1** systems gave good activity but poor enantioselectivity (Table 1, entries 3 and 4). Fortunately, the (R,R) -**2** system displayed excellent enantioselectivity giving (*S*)-1-(pyridin-4-yl)ethanol (**4e**) in high yield (97% ee, 99% conversion, Table 1, entry 5). Without the addition of base, no reaction occurred (Table 1, entry 6), but when the ratio of potassium hydroxide to catalyst varied from 5:1 to 10:1, the enantiomeric excess values of the desired product were essentially identical, while the lower ratio of potassium hydroxide to catalyst resulted in a somewhat slower rate (Table 1, entry 5 vs 7). Increasing the reaction temperature from 40–55 °C caused deterioration in the performance of the catalyst. This indicates that an appropriate reaction temperature is crucial for obtaining high enantioselectivity of the catalytic system (Table 1, entry 5 vs 8).

The preliminary results encouraged us to apply the chiral $C_6P_2(NH)_2$ –Ru(II) catalyst **2** (Figure 1) to the ATH of a wide range of heteroaromatic ketones. The results are summarized in Table 2. We found that the reactivity and enantioselectivity were affected by the kind of heteroatom in the heterocycle of the ketones. The furan-2-yl ketone **3a** and thiophen-2-yl ketone **3b** were reduced smoothly with 87% ee and 95% ee, respectively, but hydrogenation of

Table 2 ATH of Various Heteroaromatic Ketones Catalyzed by (*R,R*)/(*S,S*)-**2**^a

Entry	Substrate	Catalyst	Temp. (°C)	Time (h)	Product	Conv. ^b (%) [Yield ^c (%)]	ee ^b (%)
1	3a	(<i>R,R</i>)- 2	40	12	4a	90 [82]	87 (<i>S</i>)
2	3b	(<i>R,R</i>)- 2	40	12	4b	86 [79]	95 (<i>S</i>)
3	3c	(<i>R,R</i>)- 2	40	6	4c	96 [92]	78 (<i>S</i>) ^d
4	3d	(<i>R,R</i>)- 2	40	6	4d	99 [94]	90 (<i>S</i>)
5	3e	(<i>R,R</i>)- 2	40	4	4e	99 [93]	97 (<i>S</i>)
6	3e	(<i>S,S</i>)- 2	45	4	4f	99 [94]	96 (<i>R</i>)
7	3f	(<i>R,R</i>)- 2	40	20	4g	80 [71]	82 (<i>S</i>)
8	3g	(<i>S,S</i>)- 2	40	7	4h	92 [83]	90 (<i>R</i>)
9	3h	(<i>R,R</i>)- 2	40	20	4i	90 [81]	96 (<i>S</i>)
10	3i	(<i>S,S</i>)- 2	40	12	4j	81 [68]	97 (<i>R</i>)

^a Reaction conditions: substrate **3** (1.0 mmol), *i*-PrOH (10 mL, ratio substrate/catalyst/KOH, 100:1:5).

^b Conversions and enantiomeric excesses were determined by GC analysis using a chiral CP-Chirasil-Dex CB column. The absolute configuration was determined by the sign of the specific rotation and comparison of the retention time with literature data.

^c Isolated yield.

^d The ee value was determined by HPLC analysis with a Daicel Chiralcel OD column.

(*S*)-1-(Furan-2-yl)ethanol [(*S*)-**4a**]^{4e,j}

GC [chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m; column temperature = 80 °C (isothermal); inject temperature = 250 °C; detector temperature = 250 °C; inlet pressure = 0.12 MPa]; *t*_R = 4.47 (substrate), 10.24 (*R*-isomer), 10.69 min (*S*-isomer); 90% conversion, 87% ee (*S*). The residue was purified by column chromatography (silica gel, EtOAc–hexane, 1:5) to give (*S*)-**4a** (92 mg, 82%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 1.54 (d, *J* = 6.8 Hz, 3 H, CH₃), 2.01 (s, 1 H, OH), 4.88 (q, *J* = 6.8 Hz, 1 H, CH), 6.22–6.24 (m, 1 H), 6.32 (dd, *J* = 3.2, 2.0 Hz, 1 H), 7.37 (dd, *J* = 2.0, 0.8 Hz, 1 H).

(*S*)-1-(Thiophen-2-yl)ethanol [(*S*)-**4b**]^{4e}

GC [chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m, column temperature = 110 °C (isothermal), inject temperature = 250 °C, detector temperature = 250 °C, inlet pressure = 0.12 MPa]; *t*_R = 4.57 (substrate), 8.95 (*R*-isomer), 9.49 min (*S*-isomer); 86% conversion, 95% ee (*S*). The residue was purified by column chromatography (silica gel, EtOAc–hexane, 1:15) to give (*S*)-**4b** (101 mg, 79%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 1.59 (d, *J* = 6.4 Hz, 3 H, CH₃), 2.14 (s, 1 H, OH), 5.12 (q, *J* = 6.4 Hz, 1 H, CH), 6.94–6.98 (m, 2 H), 7.22–7.24 (m, 1 H).

(*S*)-1-(Pyridin-2-yl)ethanol [(*S*)-**4c**]^{4e}

HPLC [Daicel Chiralcel OD column, 4.6 mm i.d. × 250 mm; eluent = *i*-PrOH–hexane, 5:95; *T* = 25 °C; flow rate = 0.9 mL/min; λ = 254 nm]; *t*_R = 10.73 (*R*-isomer), 11.81 min (*S*-isomer); 78% ee (*S*).

Conversion was determined by GC [chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m; column temperature = 110 °C (isothermal); inject temperature = 250 °C; detector temperature = 250 °C; inlet pressure = 0.12 MPa]; *t*_R = 2.87 (substrate), 6.95 min (alcohol); 96% conversion. The residue was purified by column chromatography (silica gel, EtOAc–hexane, 4:1) to give (*S*)-**4c** (113 mg, 92%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 1.51 (d, *J* = 6.4 Hz, 3 H, CH₃), 4.40 (s, 1 H, OH), 4.90 (q, *J* = 6.4 Hz, 1 H, CH), 7.18–7.22 (m, 1 H), 7.29 (d, *J* = 8.4 Hz, 1 H), 7.66–7.71 (m, 1 H), 8.53 (d, *J* = 4.0 Hz, 1 H).

(*S*)-1-(Pyridin-3-yl)ethanol [(*S*)-**4d**]^{4e,j}

GC [chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m; column temperature = 110 °C (isothermal); inject temperature = 250 °C; detector temperature = 250 °C; inlet pressure = 0.12 MPa]; *t*_R = 2.87 (substrate), 7.67 (*R*-isomer), 8.00 min (*S*-isomer); 99% conversion, 90% ee (*S*). The residue was purified by column chro-

matography (silica gel, EtOAc–hexane, 4:1) to give (*S*)-**4d** (116 mg, 94%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 1.50 (d, *J* = 5.6 Hz, 3 H, CH₃), 4.21 (br, s, 1 H, OH), 4.91 (q, *J* = 5.6 Hz, 1 H, CH), 7.26 (dd, *J* = 11.2, 6.8 Hz, 1 H), 7.74 (d, *J* = 6.8 Hz, 1 H), 8.36–8.45 (m, 2 H).

(*S*)-1-(Pyridin-4-yl)ethanol [(*S*)-4e**] and (*R*)-1-(Pyridin-4-yl)ethanol [(*R*)-**4e**]^{4c}**

GC [chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m; column temperature = 120 °C (isothermal); inject temperature = 250 °C; detector temperature = 250 °C; inlet pressure = 0.12 MPa]: *t*_R = 14.71 (*R*-isomer), 15.31 min (*S*-isomer); >99% conversion, 97% ee (*S*); *t*_R = 3.95 (substrate), 14.85 (*R*-isomer), 16.97 (*S*-isomer), 99% conversion, 96% ee (*R*). The residue was purified by column chromatography (silica gel, EtOAc–hexane, 4:1) to give **4e** as a white solid [(*S*)-**4e**: 115 mg, 93%; (*R*)-**4e**: 116 mg, 94%).

¹H NMR (400 MHz, CDCl₃): δ = 1.50 (d, *J* = 6.4 Hz, 3 H, CH₃), 3.07 (br, s, 1 H, OH), 4.90 (q, *J* = 6.4 Hz, 1 H, CH), 7.30 (d, *J* = 4.0 Hz, 2 H), 8.50 (d, *J* = 4.0 Hz, 2 H).

(*S*)-1-(5-Methylfuran-2-yl)ethanol [(*S*)-4f**]^{2d}**

GC [chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m; column temperature = 80 °C (isothermal); inject temperature = 250 °C; detector temperature = 250 °C; inlet pressure = 0.12 MPa]: *t*_R = 7.92 (substrate), 15.00 (*R*-isomer), 15.29 min (*S*-isomer); 80% conversion, 82% ee (*S*). The residue was purified by column chromatography (silica gel, EtOAc–hexane, 1:15) to give (*S*)-**4f** (90 mg, 71%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 1.52 (d, *J* = 6.8 Hz, 3 H, CHCH₃), 2.00 (s, 1 H OH), 2.28 (s, 3 H, CH₃), 4.82 (q, *J* = 6.8 Hz, 1 H, CH), 5.89 (d, *J* = 2.4 Hz, 1 H), 6.09 (d, *J* = 2.4 Hz, 1 H).

(*R*)-1-(5-Chlorothiophen-2-yl)ethanol [(*R*)-4g**]**

GC [chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m; column temperature = 120 °C (isothermal); inject temperature = 250 °C; detector temperature = 250 °C; inlet pressure = 0.12 MPa]: *t*_R = 5.48 (substrate), 13.56 (*R*-isomer), 16.07 (*S*-isomer); 92% conversion, 90% ee (*R*). The residue was purified by column chromatography (silica gel, EtOAc–hexane, 1:15) to give (*R*)-**4g** (135 mg, 83%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 1.55 (d, *J* = 6.4 Hz, 3 H, CH₃), 2.13 (s, 1 H, OH), 5.01 (q, *J* = 6.4 Hz, 1 H, CH), 6.72 (d, *J* = 4.0 Hz, 1 H), 6.76 (d, *J* = 4.0 Hz, 1 H).

(*S*)-1-(Thiophen-2-yl)propan-1-ol [(*S*)-4h**]^{4a}**

GC [chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m; column temperature = 110 °C (isothermal); inject temperature = 250 °C; detector temperature = 250 °C; inlet pressure = 0.12 MPa]: *t*_R = 6.81 (substrate), 15.12 (*R*-isomer), 15.81 min (*S*-isomer); 90% conversion, 96% ee (*S*). The residue was purified by column chromatography (silica gel, EtOAc–hexane, 1:15) to give (*S*)-**4h** (115 mg, 81%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 0.97 (t, *J* = 7.2 Hz, 3 H, CH₃), 1.79–1.96 (m, 2 H, CH₂), 2.05 (s, 1 H, OH), 4.84 (t, *J* = 6.4 Hz, 1 H, CH), 6.95–6.99 (m, 2 H), 7.24–7.26 (m, 1 H).

(*R*)-1-(Thiophen-2-yl)butan-1-ol [(*R*)-4i**]**

GC [chiral CP-Chirasil-Dex CB column, 0.25 mm × 25 m; column temperature = 110 °C (isothermal); inject temperature = 250 °C; detector temperature = 250 °C; inlet pressure = 0.12 MPa]: *t*_R = 10.56 (substrate), 24.07 (*S*-isomer), 24.31 min (*R*-isomer); 81% conversion, 97% ee (*R*). The residue was purified by column chromatography (silica gel, EtOAc–hexane, 1:15) to give (*R*)-**4i** (106 mg, 68%) as a colorless oil.

¹H NMR (400 MHz, CDCl₃): δ = 0.95 (t, *J* = 7.2 Hz, 3 H, CH₃), 1.29–1.54 (m, 2 H, CH₂CH₃), 1.74–1.92 (m, 2 H, CHCH₂), 2.05 (br, s, 1 H, OH), 4.92 (t, *J* = 6.8 Hz, 1 H, CH), 6.94–6.97 (m, 2 H), 7.24 (dd, *J* = 4.4, 2.0 Hz, 1 H).

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