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New chiral amino alcohol ligands derived from 1-phenylethylamine for efficient Ru-catalyzed asymmetric transfer hydrogenation

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ABSTRACT

A series of chiral amino alcohols have been prepared from cheap and readily available (*S*)-1-phenylethylamine through a one-step transformation. The ability of these newly developed amino alcohols as chiral ligands was evaluated in the Ru-catalyzed asymmetric transfer hydrogenation of aromatic alkyl ketones, providing chiral secondary alcohols with good to excellent conversions (71–100%) and moderate to good enantioselectivities (67–95% ee). The results also showed that the structure of these amino alcohols has a significant influence on the conversion and enantioselectivity.

1. Introduction

Enantioselective reduction of prochiral ketones is an important organic transformation since the enantiopure secondary alcohols obtained are often employed as intermediates in the production of pharmaceuticals, argochemicals and advanced materials.[1] Among the different catalytic methods, the asymmetric transfer hydrogenation is of great interest. It avoids the use of flammable hydrogen as a reducing agent, representing a mild, practical, and safe alternative to catalytic hydrogenation.[2] In 1990s, Noyori et al. found that a ruthenium η^6-arene complex in combination with monotosylated diamines could serve as efficient catalysts for the asymmetric transfer hydrogenation of ketones.[3] This significant development has led to the intense exploration of the Ru-catalyzed asymmetric transfer hydrogenation with substantial emphasis on the use of new chiral ligand scaffolds, of which chiral amino alcohols are arguably among those with the greatest utility. Noyori et al. reported that a Ru-catalyst bearing some simple amino alcohols such as ephedrine **1** showed high catalytic activity and enantioselectivity (95% yield and 91% ee) in the reduction of ketones.[4] Andersson et al. have developed 2-azanorboronyl based amino alcohol **2**, which displayed good to excellent enantioselectivities (85–99% ee) in the Ru-catalyzed transfer hydrogenation.[5] Wills et al. used (1*R*,2*S*)-*cis*-1-aminoindan-2-ol **3** as a ligand in the Ru-catalyzed asymmetric transfer hydrogenation, achieving good to excellent enantioselectivities (see Fig. 1).[6]

Besides these representative ligands, there are a number of chiral amino alcohol ligands that were reported to be efficient for the Ru-catalyzed asymmetric transfer hydrogenation.[1,7] A structural analysis disclosed that most of these ligands belong to 1,2-amino alcohols in nature, and few other types of amino alcohols, such as 1,3- or 1,4-amino alcohols have been used in the Ru-catalyzed asymmetric transfer hydrogenation. With this background, we report herein the rapid synthesis of a new type of amino alcohols **4** having a 1,4-amino alcohol structural feature from readily available (*S*)-1-phenylethylamine (Scheme 1) along with results concerning their use as ligands for the Ru-catalyzed asymmetric transfer hydrogenation. It has been demonstrated that these new amino alcohol ligands were efficient for this transformation, displaying good to excellent conversions (71–100%) and moderate to good enantioselectivities (67–95% ee) for a variety of aromatic alkyl ketones.

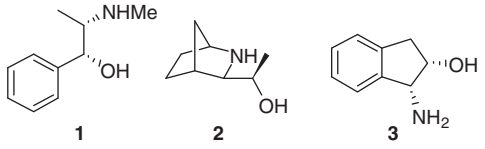

Figure 1. Representative examples of chiral amino alcohols reported with high enantioselectivity in Ru-catalyzed asymmetric transfer hydrogenation.

2. Results and discussion

2.1. Synthesis of chiral amino alcohols 4a–d from (*S*)-1-phenylethylamine

These chiral amino alcohols can be prepared from commercially available (*S*)-1-phenylethylamine through a one-step transformation as outlined in Scheme 1.[8] The treatment of (*S*)-1-phenylethylamine with *n*-BuLi at −35 °C, followed by a slow addition of neat

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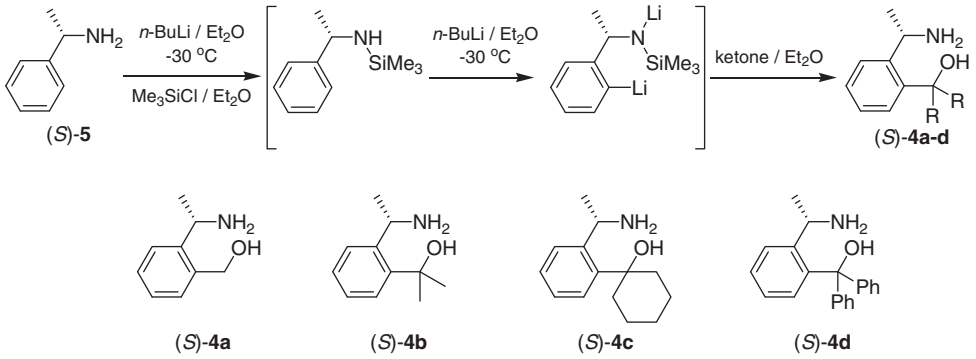


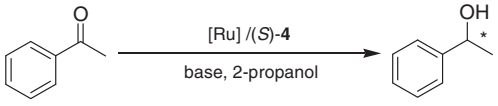
Scheme 1. Synthesis of chiral 1-phenylethylamine-derived amino alcohols.

Me_3SiCl, generated the monosilylated product, *N*-(trimethylsilyl)-1-phenylethylamine in situ.[9] The latter was dilithiated by further addition of 3 equiv of *n*-BuLi at −35 °C and then quenched with a variety of carbonyl compounds including formaldehyde, acetone, cyclohexanone, and benzophenone. Following work-up and crystallization, amino alcohols **4a–d** were produced in 11.9–37.9% yields. Although relatively low yields were obtained in this transformation, few by-products besides the starting material, (*S*)-1-phenylethylamine **5**, were detected. Most of the unreacted (*S*)-1-phenylethylamine **5** can be recovered by column chromatography.

2.2. Ru-catalyzed asymmetric transfer hydrogenation of aromatic alkyl ketones

With these newly developed amino alcohol ligands in hand, we then investigated their efficiency in the Ru-catalyzed asymmetric transfer hydrogenation of acetophenone, and the results are summarized in Table 1. In a typical experiment, ruthenium complexes were prepared in situ by refluxing 0.5 mol % of $[RuCl_2(p\text{-cymene})]_2$ in combination with an appropriate amount of ligand (*S*)-**4a–d** in 2-propanol for 0.5 h. The resulting solution was then used for the transfer hydrogenation of acetophenone in the presence of 10 mol % of KOH in 2-propanol at ambient temperature for 1 h, using a substrate/catalyst ratio of 100. Initially, the ratio of ligand to [Ru] was examined. The results indicated that the ratio of ligand to [Ru] had some influence on the enantioselectivity, and increasing the ratio of ligand to [Ru] tended to promote the enantioselectivity (entries 1–3). We next evaluated the effect of the ligand structure on catalytic activity and enantioselectivity. As presented in Table 1, the asymmetric transfer hydrogenation proceeded smoothly with all amino alcohol ligands **4a–d**, giving conversions of 98% (entries 3–6). However, the enantioselectivity dramatically changed with these ligands, ranging between 54% and 86% ee. Among these amino alcohol ligands, the simplest member, **4a** bearing a primary hydroxyl moiety gave the best ee-value of 86% (entry 3). These results suggested that the structure of these newly developed amino alcohols significantly affects the enantioselectivity, and that less sterically demanding ligands seem to be more favorable for achieving high enantioselectivity. The reduction proved to be highly sensitive to the catalyst precursors (entries 3, 7 and 8). Comparison of the results obtained with various catalyst precursors clearly showed that high conversion and good enantioselectivity were obtained only when $[RuCl_2(p\text{-cymene})]_2$ was used (entries 3, 7 and 8). Further work on the screening of various bases indicated that KOH was a better choice (entries 3, 9 and 10). The reduction can be completed in 5 min when it was performed at reflux temperature (entry 11). However, the enantioselectivity was

Table 1
Ru-catalyzed asymmetric transfer hydrogenation of acetophenone **6a**[a]



Entry	Ligand	[Ru]	L/[Ru]	Base	Temperature	Time (h)	Conversion[b] (%)	Ee[b] (%) (config.)[c]
1	**4a**	$[RuCl_2(p\text{-cymene})]_2$	1:1	KOH	rt	1	50	86 (*R*)
2	**4a**	$[RuCl_2(p\text{-cymene})]_2$	2:1	KOH	rt	1	96	85 (*R*)
3	**4a**	$[RuCl_2(p\text{-cymene})]_2$	4:1	KOH	rt	1	98	86 (*R*)
4	**4b**	$[RuCl_2(p\text{-cymene})]_2$	4:1	KOH	rt	1	98	55 (*R*)
5	**4c**	$[RuCl_2(p\text{-cymene})]_2$	4:1	KOH	rt	1	98	69 (*R*)
6	**4d**	$[RuCl_2(p\text{-cymene})]_2$	4:1	KOH	rt	1	98	54 (*R*)
7	**4a**	$[RuCl_2(benzene)]_2$	4:1	KOH	rt	5	12	74 (*R*)
8	**4a**	$RuCl_2(DMSO)_4$	4:1	KOH	rt	1	26	—[d]
9	**4a**	$[RuCl_2(p\text{-cymene})]_2$	4:1	*t*-BuOK	rt	1	96	85 (*R*)
10	**4a**	$[RuCl_2(p\text{-cymene})]_2$	4:1	NaOMe	rt	1	96	86 (*R*)
11	**4a**	$[RuCl_2(p\text{-cymene})]_2$	4:1	KOH	Reflux	5 (min)	100	76 (*R*)
12	**4a**	$[RuCl_2(p\text{-cymene})]_2$	4:1	KOH	−10 °C	3	98	92 (*R*)

[a] Reaction conditions: acetophentone (0.5 mmol), [Ru] (1 mol %), (*S*)-**4** (4 mol %), base (10 mol %), 2-propanol (20 mL).
[b] Conversions and ee (%) were determined by GC analysis using a chiral column.
[c] Absolute configurations were assigned by comparing specific rotations with literature values.
[d] Not determined because of low conversion.

reduced to 76% ee. Lowering the reaction temperature to −10 °C resulted in decreased reaction rate but increased enantioselectivity (92% ee) (entry 12).

Having identified the best amino alcohol ligand and established the optimal reduction conditions ([$RuCl_2$(*p*-cymene)]$_2$ as the catalyst precursor, **4a** as chiral ligand, KOH as base, performed at −10 °C), we then undertook studies on different aromatic alkyl ketone substrates (Fig. 2). The results are summarized in Table 2. As

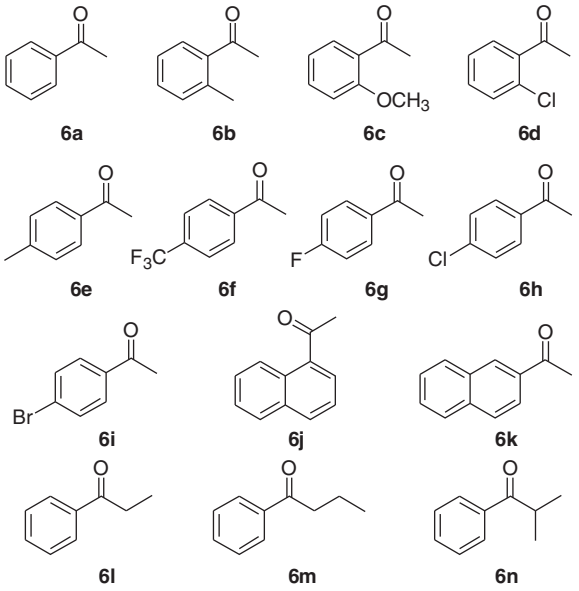
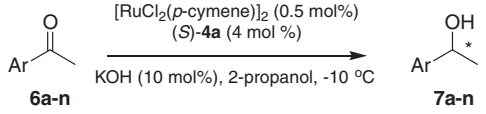


Figure 2. Aryl alkyl ketones **6a–n** screened in the asymmetric transfer hydrogenation catalyzed by Ru/(*S*)-**4a** complex.

Table 2
Ruthenium-catalyzed asymmetric transfer hydrogenation of aryl alkyl ketones[a]



Entry	Substrate	*t* (h)	Conv.[b] (%)	Ee[b] (%) (config.)[c]
1	**6a**	3	98	92 (*R*)
2	**6b**	2	94	94 (*R*)
3	**6c**	3	96	91 (*R*)
4	**6d**	2	100	84 (*R*)
5	**6e**	5	93	86 (*R*)
6	**6f**	5	91	69 (*R*)
7	**6g**	2	94	73 (*R*)
8	**6h**	2	99	77 (*R*)
9	**6i**	2	99	75 (*R*)
10	**6j**	3	99	95 (*R*)
11	**6k**	3	97	84 (*R*)
12	**6l**	3	98	88 (*R*)
13	**6m**	5	84	88 (*R*)
14	**6n**	10	71	67 (*R*)

[a] Reaction conditions: ketone (0.5 mmol), [$RuCl_2$(*p*-cymene)]$_2$ (0.0025 mmol, 0.5 mol %), (*S*)-**4a** (0.02 mmol, 4 mol %), KOH (0.05 mmol, 10 mol %), 2-propanol (20 mL) at −10 °C.
[b] Conversions and ee (%) were determined by GC analysis using a chiral column.
[c] Absolute configurations were assigned by comparing specific rotations with literature values.

in the reduction of acetophenone **6a**, all of the substituted acetophenones **6b–6i** were also reduced smoothly in high conversions (91–100%) and moderate to good enantioselectivities (69–94% ee) (entries 1–9). The substrates can be grouped based on their electronic and steric properties. Substrates bearing electron-donating substituents generally gave better enantioselectivities, but a lower reaction rate in comparison with their counterparts. For example, substrate **6e** with a 4-methyl group on the phenyl ring was reduced in 86% ee and 93% conversion after 5 h (entry 5); while the reduction of **6h** with a 4-Cl group on the phenyl ring gave only 77% ee but 99% conversion in a shorter reaction time (2 h) (entry 8). On the other hand, the substrates with an *ortho*-group on the phenyl ring gave substantially higher enantioselectivity and activity than those bearing a *para*-substituent. Thus, the substrate **4b** bearing a methyl group on the *ortho*-position was reduced in 94% ee rapidly (entry 2), in contrast to 86% ee with its *para*-substituted analogue (entry 5). The reduction of 1-acetonaphthone and 2-acetonaphthone was also performed, and both of them gave high conversions and good enantioselectivities (entries 10 and 11). In particular, the best performance (99% conversion and 95% ee) was obtained in the reduction of 1-acetonaphthone (entry 10). The reduction of linear aromatic alkyl ketones **6l–m** proceeded smoothly to give the corresponding chiral alcohols with good enantioselectivity (88% ee) (entries 12–13). However, the reduction of aromatic ketones with a branched alkyl group such as an isopropyl tended to give lower conversion and enantioselectivity with a longer reaction time (entry 14).

3. Conclusion

In conclusion, we have prepared a new family of chiral amino alcohol ligands from commercially available and inexpensive (*S*)-α-phenylethylamine through a one-step transformation. These amino alcohols have been successfully employed in the Ru-catalyzed asymmetric transfer hydrogenation of various aromatic alkyl ketones, providing optically active secondary alcohol with 71–100% conversions and 67–95% ee. Ligand-screening disclosed that less sterically demanding ligand **4a** tended to give higher enantioselectivity Furthermore, in comparison with the traditionally used 1,2-amino alcohol ligands in the Ru-catalyzed asymmetric transfer hydrogenation, these newly developed amino alcohols had a 1,4-amino alcohol structural feature. Further application of these new amino alcohols in asymmetric synthesis is in progress.

4. Experimental

4.1. General

All reactions were carried out under nitrogen atmosphere. All solvents were purified by a standard procedure, and commercially obtained reagents were used without further purification. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer in chloroform-*d*[1]. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. ^{13}C NMR spectra were recorded on a Bruker 100 MHz spectrometer in chloroform-*d*[1]. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. GC analyses were performed on a HP4890D equipped with a chiral column (Supelco Astec Chiral Dex™ G-TA column, 30 m × 0.25 mm × 0.12 μm, HP-Chiral column or a Supelco β-DEX 120 column, 30 m × 0.25 mm × 0.12 μm) using hydrogen and nitrogen as the carrier gas, respectively. HPLC analyses were performed on an Agilent 1100 series instrument with a chiral column (Chiralcel OJ-H) with hexanes and 2-propanol as solvents. Optical rotations were recorded on a Jasco P-1020 polarimeter. The absolute configurations of the known products were determined by comparing the specific rotation with the reported data.

4.2. General procedure for the preparation of chiral amino alcohol ligands 4a–d

To a solution of (*S*)-1-phenylethylamine **5** (6.06 g, 50 mmol) in 120 mL of ether at −35 °C was added dropwise 22 mL (55 mmol)

of a 2.5 M solution of *n*-BuLi in hexane. The resulting solution was stirred at −35 °C for 30 min, and then 7.0 mL (55.0 mmol, 1.1 equiv) of Me_3SiCl was added slowly at the same temperature. The reaction mixture was stirred for 1 h and then 60 mL (150 mmol, 3 equiv) of a 2.5 M solution of *n*-BuLi was added dropwise. After the addition was completed, the reaction mixture was stirred at −35 °C for 4 h. The reaction mixture was slowly warmed to room temperature and stirred overnight. The reaction mixture was cooled to −35 °C again, and an appropriate carbonyl compound (55 mmol, 1.1 equiv) was added slowly over 0.5 h. The reaction mixture was stirred for another 3 h at the same temperature, and then warmed to room temperature. After stirring for another 10 h, a solution of 1 M aqueous HCl was added slowly until the reaction mixture became clear in both phases. The aqueous phase was extracted with ether (3 × 50 mL). Combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/acetate/triethylamine, 4/1/0.4) to give the targeted amino alcohols **4a–d** and recover the unreacted (*S*)-1-phenylethylamine **5.**

4.2.1. {2-[(*S*)-1-Aminoethyl]phenyl}methanol 4a

Prepared as a white solid from paraformaldehyde in 16.1% yield. $[\alpha]_D^{20} = -18.3$ (*c* 0.38, ethanol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.59–1.61 (d, *J* = 8 Hz, 3H), 3.48 (s, 3H), 4.40–4.45 (m, 1H), 4.52–4.55 (d, *J* = 12 Hz, 1H), 4.83–4.86 (d, *J* = 12 Hz, 1H), 7.25–7.39 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.7, 48.4, 64.4, 125.9, 127.8, 128.0, 130.4, 140.6, 143.0; HRMS (*m/z*) calcd for $C_9H_{13}NO$: 151.0997, found: 151.1000.

4.2.2. 2-{2-[(*S*)-1-Aminoethyl]phenyl}propan-2-ol 4b

Prepared as colorless oil from acetone in 14.6% yield. $[\alpha]_D^{20} = -3.3$ (*c* 0.38, ethanol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.55–1.68 (m, 9H), 3.51 (s, 3H), 4.85–4.87 (m, 1H), 7.21–7.44 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.6, 32.8, 33.0, 48.1, 73.3, 126.5, 126.9, 127.0, 127.3, 143.5, 146.5; HRMS (*m/z*) calcd for $C_{11}H_{17}NO$: 179.1310, found: 179.1310.

4.2.3. 1-{2-[(*S*)-1-Aminoethyl]phenyl}cyclohexanol 4c

Prepared as colorless oil from cyclohexanone in 11.9% yield. $[\alpha]_D^{20} = +10.2$ (*c* 0.35, ethanol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.24–1.99 (m, 13H), 3.24 (m, 1H), 7.22–7.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.1, 22.3, 24.0, 25.8, 39.2, 40.0, 47.9, 73.9, 126.4, 126.9, 127.0, 127.5, 143.2, 147.2; HRMS (*m/z*) calcd for $C_{14}H_{21}NO$: 219.1623, found: 219.1626.

4.2.4. {2-[(*S*)-1-Aminoethyl]phenyl}diphenylmethanol 4d

Prepared as a white solid from benzophenone in 37.9% yield. $[\alpha]_D^{20} = -73.2$ (*c* 0.38, ethanol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (d, *J* = 6.4 Hz, 3H), 4.18 (m, 1H), 6.63–6.65 (m, 1H), 7.06–7.10 (m, 1H), 7.26–7.28 (m, 10H), 7.50–7.51 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.8, 47.1, 82.4, 126.4, 126.7, 126.8, 126.9, 127.3, 127.7, 127.8, 128.6, 130.7, 142.3, 146.9, 147.9, 149.1; HRMS (*m/z*) calcd for $C_{21}H_{21}NO$: 303.1623, found: 303.1626.

4.3. General procedure for the transfer hydrogenation of aromatic ketones

A mixture of $[RuCl_2(p\text{-cymene})]_2$ (1.5 mg, 0.0025 mmol) and (*S*)-**4a** (3.0 mg, 0.02 mmol) in 2 mL of 2-propanol was stirred at 80 °C for 30 min under argon atmosphere. After cooling to room temperature, 2-propanol (15 mL), KOH (0.6 mL, 0.1 M in 2-propanol), acetophenone (0.5 mmol, dissolved in 5 mL of 2-propanol) were added. The resulting solution was stirred at −10 °C, and the reaction was monitored by GC or HPLC. The mixture was neutralized with dilute HCl and 2-propanol was removed under reduced pressure. The residue was diluted with ethyl acetate (25 mL) and the organic solution was washed with brine (3 × 20 mL) and dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was subjected to short column chromatography on silica gel (hexane/ethyl acetate as eluent) for ee and conversion determination.

Acknowledgments

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