

Catalytic Enantioselective Amination of Alcohols by the Use of Borrowing Hydrogen Methodology: Cooperative Catalysis by Iridium and a Chiral Phosphoric Acid**

Yao Zhang, Ching-Si Lim, Derek Sui Boon Sim, Hui-Jie Pan, and Yu Zhao*

Dedicated to Professor Marc L. Snapper on the occasion of his 55th birthday

Abstract: The catalytic asymmetric reduction of ketimines has been explored extensively for the synthesis of chiral amines, with reductants ranging from Hantzsch esters, silanes, and formic acid to H_2 gas. Alternatively, the amination of alcohols by the use of borrowing hydrogen methodology has proven a highly atom economical and green method for the production of amines without an external reductant, as the alcohol substrate serves as the H_2 donor. A catalytic enantioselective variant of this process for the synthesis of chiral amines, however, was not known. We have examined various transition-metal complexes supported by chiral ligands known for asymmetric hydrogenation reactions, in combination with chiral Brønsted acids, which proved essential for the formation of the imine intermediate and the transfer-hydrogenation step. Our studies led to an asymmetric amination of alcohols to provide access to a wide range of chiral amines with good to excellent enantioselectivity.

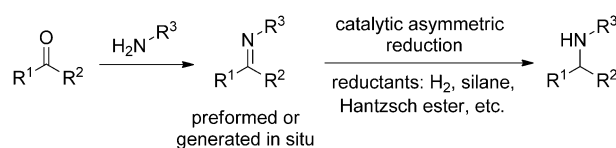
Owing to the widespread use of chiral amines in the pharmaceutical and fine-chemicals industries, the development of efficient methods to prepare these compounds in high enantiomeric purity has been an important goal in organic synthesis.^[1] One of the most explored reaction types for this purpose is the asymmetric hydrogenation of ketimines (or reductive amination of ketones; Scheme 1 a).^[2] Various systems based on transition-metal catalysis,^[3] organocatalysis,^[4] and cooperative catalysis involving both^[5] have been documented for imine hydrogenation, with reductants ranging from Hantzsch esters, silanes, and formic acid to H_2 gas.

In a related area of research, the amination of alcohols by the use of borrowing hydrogen methodology^[6] (also known as the hydrogen autotransfer process)^[6d] has long been recognized as a highly atom economical and green method for the production of amines. This approach involves the three steps of dehydrogenation of an alcohol to the corresponding

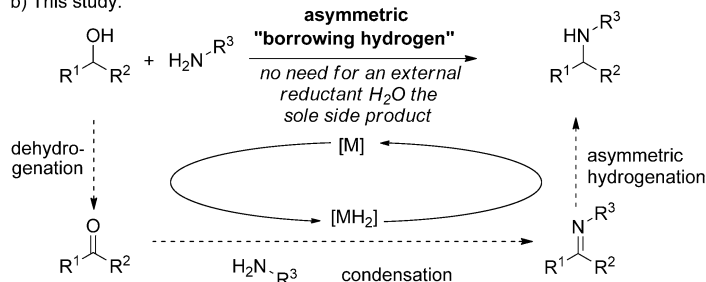
ketone, condensation to give an imine, and subsequent imine hydrogenation and utilizes the alcohol substrate as the H_2 donor (Scheme 1 b). Great progress has been made in the search for efficient catalytic processes for the reactions of various amines with primary and even secondary alcohols in the past decade, with state-of-the-art systems reported by the research groups of Beller, Williams, Fujita, Kempe, Crabtree, Yus, Peris, Martín-Matute, and others.^[7–9] A catalytic, enantioselective amination of alcohols by the use of borrowing hydrogen methodology would be a highly efficient way of preparing chiral amines from simple alcohol and amine starting materials without the need for an external reductant and with the generation of H_2O as the only side product. Such a process, to our surprise, has remained elusive until now.^[10] We report herein our recent studies towards the first such process.

We initiated our studies by examining the reaction of 2-octanol (**1a**) and *p*-anisidine (**2a**) to afford **3a**. As for the catalyst, we decided to start with metal complexes that have proven successful for asymmetric transfer-hydrogenation reactions,^[3] such as those supported by a privileged chiral monotosylated diamine^[11,3e–h] or various bisphosphine ligands. Despite extensive experimentation, however, no efficient conversion into the desired product **3a** was observed in the presence of iridium-, rhodium-, or ruthenium-based catalysts, even in refluxing toluene with the addition of 4 Å

a) Previous asymmetric reduction of imines to chiral amines:



b) This study:



Scheme 1. Different strategies for the synthesis of chiral amines.

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molecular sieves (MS; see examples in Table 1, entries 1 and 2).

Careful examination of the crude reaction mixture indicated the formation of a small amount of the corresponding ketone, which led us to speculate that the imine condensation was the problematic step. Inspired by previous studies on reductive amination by the research groups of MacMillan^[4g] and Xiao,^[5c] in which chiral phosphoric acids proved effective in promoting the condensation of ketones and anilines even at 35–50 °C, we decided to test the effect of

acid additives, even though all known amination reactions of alcohols on the basis of borrowing hydrogen methodology were carried out under basic or neutral conditions.^[6–9] As shown by the representative results listed in entries 3–5 of Table 1, whereas acid additives did not improve the reaction catalyzed by Ru complex **4** (entry 3), the combination of an acid (such as *p*-toluenesulfonic acid or phosphoric acid) and the Ir complex (*R,R*)-**5** successfully led to the formation of **3a**, although the level of efficiency and selectivity remained disappointingly low (entries 4,5). Chiral phosphoric acids were then tested. The identity of the 3,3'-substituents in the chiral backbone had a dramatic effect on the reaction outcome (Table 1, entries 6–9), whereby **10e** provided the highest level of enantioselectivity and promising efficiency. As two chiral sources were used, the combination of **10e** with the enantiomeric Ir complex (*S,S*)-**5** was tested. This pair provided significantly higher selectivity (87% *ee*), but with diminished 32% conversion (Table 1, entry 10). The matched/mismatched relationship of the two chiral sources is significant, whereby the chirality of the Ir complex is the determining factor.

We then switched our focus to the modification of the Ir complex. Variation of the substitution on the sulfonamide moiety as well as the chiral-diamine backbone led to the identification of complex (*S,S*)-**6** as the catalyst that provided the optimal combination of reactivity and selectivity (Table 1, entries 10–14). Mesylate (*S,S*)-**8** and cyclohexanediamine-derived (*S,S*)-**9** were surprisingly not effective at all. Further fine-tuning of various reaction parameters showed that a higher loading of the alcohol substrate (3 equiv or 5 equiv rather than 1.5 equiv; Table 1, entries 15 and 16 versus entry 11) led to an increase in enantioselectivity to >90% *ee*. In an effort to identify an alternative to this higher alcohol loading, which is detrimental to the overall efficiency of the process, we wondered whether the beneficial effect comes from a higher concentration of the hydrogen donor or simply an increase in the polarity of the reaction medium. *tert*-Amyl alcohol, which is not a hydrogen donor but a much more polar solvent, was then tested as the solvent. Gratifyingly, this change of solvent led to an increase in the *ee* value of the product to 89% (Table 1, entry 17 versus entry 11). Finally, a higher loading of **10e** proved beneficial. Under the optimal conditions, under which the alcohol was used in slight excess (1.5 equiv), **3a** was produced in 90% yield with 93% *ee* (Table 2, entry 1).

The same set of conditions can be applied to a wide range of alcohol substrates (Table 2). Alcohols bearing linear alkyl substituents (substrates **1a–c**) were transformed into **3** with high enantioselectivity (Table 2, entries 1–3). The reactions of substrates bearing α -branched substituents were particularly successful (up to 97% *ee*; Table 2, entries 4–6). Functionalities such as benzyl ether and silyl ether groups were well-tolerated (products **3i** and **3j**), even though the reaction involved reductive and acidic conditions (Table 2, entries 9 and 10). Aryl-alkyl-substituted products were also generally obtained with good to excellent enantioselectivity (Table 2, entries 11–17). The electronic properties of the substrates seemed to play a role, whereby products bearing electron-donating substituents were obtained with higher *ee* values

Table 1: Optimization of the enantioselective amination of **1a**.

Entry	[M]	Additive	Solvent	Conv. [%] ^[a]	<i>ee</i> [%] ^[b]
1	(<i>R,R</i>)- 4	–	toluene	< 5	N.D.
2	(<i>R,R</i>)- 5	–	toluene	< 5	N.D.
3	(<i>R,R</i>)- 4	TfOH (5 mol %)	toluene	< 5	N.D.
4	(<i>R,R</i>)- 5	TfOH (5 mol %)	toluene	32	7
5	(<i>R,R</i>)- 5	10a (5 mol %)	toluene	33	12
6	(<i>R,R</i>)- 5	10b (5 mol %)	toluene	60	9
7	(<i>R,R</i>)- 5	10c (5 mol %)	toluene	< 5	N.D.
8	(<i>R,R</i>)- 5	10d (5 mol %)	toluene	83	–17
9	(<i>R,R</i>)- 5	10e (5 mol %)	toluene	50	–46
10	(<i>S,S</i>)- 5	10e (5 mol %)	toluene	32	87
11	(<i>S,S</i>)- 6	10e (5 mol %)	toluene	> 99	81
12	(<i>S,S</i>)- 7	10e (5 mol %)	toluene	96	77
13	(<i>S,S</i>)- 8	10e (5 mol %)	toluene	< 5	N.D.
14	(<i>S,S</i>)- 9	10e (5 mol %)	toluene	< 5	N.D.
15 ^[c]	(<i>S,S</i>)- 6	10e (5 mol %)	toluene	> 99	90
16 ^[d]	(<i>S,S</i>)- 6	10e (5 mol %)	toluene	> 99	92
17	(<i>S,S</i>)- 6	10e (5 mol %)	<i>tert</i> -amyl alcohol	95	89
18	(<i>S,S</i>)- 6	10e (10 mol %)	<i>tert</i> -amyl alcohol	> 99	93

[a] Conversion was determined by NMR spectroscopy with 4,4'-*tert*-butylbiphenyl as an internal standard. [b] The *ee* value was determined by HPLC on a chiral stationary phase. [c] The reaction was carried out with 3 equivalents of the alcohol. [d] The reaction was carried out with 5 equivalents of the alcohol. N.D.: not determined; Tf = trifluoromethanesulfonfyl. See the Supporting Information for details.

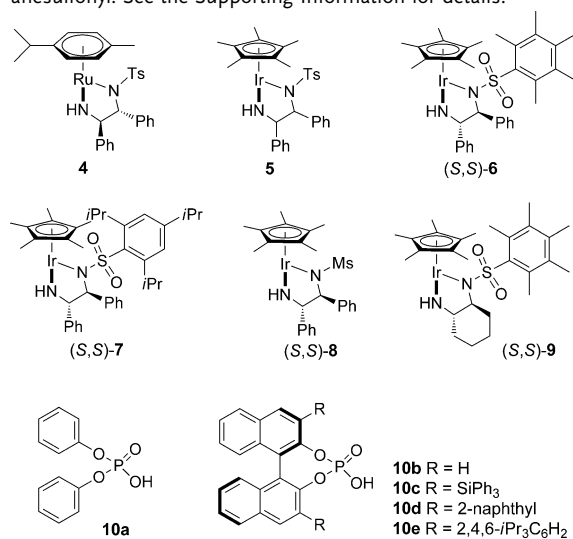


Table 2: Scope of the enantioselective amination with respect to the alcohol substrate.^[a]

Entry	R ¹	R ²	Product	Yield [%] ^[b]	ee [%]
1	<i>n</i> -hexyl	Me	3a	90	93
2 ^[c]	<i>n</i> Bu	Me	3b	90	92
3 ^[d]	<i>n</i> Pr	Me	3c	86	90
4	<i>i</i> Pr	Me	3d	88	96
5	cyclohexyl	Me	3e	92	97
6	cyclopropyl	Me	3f	93	91
7	<i>i</i> PrCH ₂	Me	3g	75	82
8	PhCH ₂ CH ₂	Me	3h	98	83
9	BnO(CH ₂) ₃	Me	3i	64	85
10	TBSO(CH ₂) ₃	Me	3j	95	91
11	Ph	Me	3k	81	91
12	4-MeC ₆ H ₄	Me	3l	97	91
13	4-MeOC ₆ H ₄	Me	3m	72	96
14	4-BrC ₆ H ₄	Me	3n	69	83
15	4-CF ₃ C ₆ H ₄	Me	3o	90 (40) ^[e]	70 (94) ^[e]
16	3-MeC ₆ H ₄	Me	3p	83	94
17	1-naphthyl	Me	3q	80	94
18	4-MeC ₆ H ₄	Et	3r	75	73
19	1-naphthyl	Et	3s	71	69
20 ^[f]	<i>i</i> Pr	Et	3t	80	75

[a] Unless stated otherwise, reactions were carried out in *tert*-amyl alcohol at reflux for 24 h. All reagents were used as received from the commercial supplier without purification. The absolute configuration of the products was determined by comparison of the optical rotation with reported data or by analogy (see the Supporting Information for details).

[b] Yield of the isolated product. [c] The reaction was carried out with 3 equivalents of the alcohol. [d] The reaction was carried out with 5 equivalents of the alcohol (see the Supporting Information for details).

[e] The values in parentheses refer to the corresponding reaction carried out at 80 °C for 48 h. [f] The reaction was carried out in refluxing toluene for 24 h. Bn = benzyl, PMP = *p*-methoxyphenyl, TBS = *tert*-butyldimethylsilyl.

(Table 2, entry 13 versus entries 14 and 15). For certain more reactive substrates, a lower reaction temperature could increase the *ee* value of the product dramatically, albeit at the cost of conversion (Table 2, entry 15). This catalytic system is not limited to methyl-substituted alcohols, although the enantioselectivity dropped to 69–75% *ee* for ethyl-containing substrates as a result of the diminished size difference of the two substituents (Table 2, entries 18–20). Use of the chiral phosphoric acid in excess with respect to the Ir complex proved essential for alcohols with aryl–alkyl substitution (but not for alkyl–alkyl-substituted alcohols, as shown in Table 1, entry 16). For example, for the reaction in Table 2, entry 11, if 5 mol % of **10e** was used (the same loading as that of (*S,S*)-**6**), **3k** was obtained with only 9% conversion.

Different types of amine substrates were also examined (Table 3). Various anilines, including those bearing substituents of an electron-donating or electron-withdrawing nature, were well-tolerated (Table 3, entries 1–5). It is particularly notable that heterocyclic amines, such as 5-aminoindole, can be successfully coupled with an alcohol to yield the chiral amine in good yield and enantioselectivity (Table 3, entry 6).

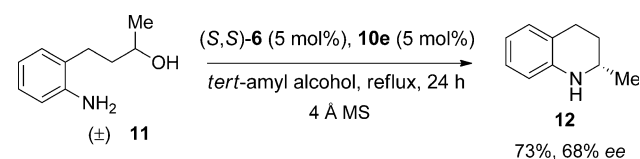
Table 3: Scope of the enantioselective amination with respect to the amine substrate.^[a]

Entry	R	Product	Yield [%] ^[b]	ee [%]
1	Ph	3u	91	88
2	4-MeC ₆ H ₄	3v	97	91
3	4-ClC ₆ H ₄	3w	81	83
4	4-PhC ₆ H ₄	3x	98	89
5	3-MeOC ₆ H ₄	3y	95	88
6		3z	84	81

[a,b] See Table 2.

However, despite extensive efforts to extend the scope of the reaction to other amines, such as benzylamine, tosylamide, or secondary amines, the current method failed to yield the product with good efficiency or selectivity. The effective condensation of the ketone intermediate with different amines and the asymmetric transfer hydrogenation of imines are challenges to be addressed.

The intramolecular amination of alcohols has been demonstrated by Fujita et al. as an efficient way to produce valuable heterocyclic compounds.^[7a] When we applied our optimal conditions to the reaction (Scheme 2), a good yield



Scheme 2. Example of the intramolecular amination of alcohols.

and promising enantioselectivity (68% *ee*) were observed for the quinoline product **12** bearing a simple methyl substituent. For this reaction, the higher loading of **10e** relative to **6** was not necessary. Thus, the intramolecular imine-condensation step is arguably efficient enough, even in the absence of the external acid cocatalyst.

Notably, to the best of our knowledge, our system represents the first highly enantioselective transfer hydrogenation of imines with an alcohol as the hydrogen donor, despite the great success of the use of related Ir and Ru complexes for the asymmetric transfer hydrogenation of imines with formic acid–Et₃N^[3e,f] as well as the asymmetric hydrogenation of imines with H₂.^[3g,h,5d–g] To better understand this cascade process, we examined the transfer hydrogenation of the corresponding imine **13** with **1k** as the hydrogen donor under similar conditions. As summarized in Table 4, in the absence of **10e**, very low efficiency and no stereoselectivity were observed with Ir complex **6** (entry 1). Even in the presence of **10e**, the *ee* value of the product was far from satisfactory (Table 4, entries 2 and 3). A higher loading of the alcohol resulted in a higher *ee* value, which led us to speculate

Table 4: Transfer hydrogenation of a preformed imine.

Entry	Amount of 1k [equiv]	10e [mol %]	Yield [%]	ee [%]
1	2.0	—	13	< 5
2	2.0	10	> 95	60
3	10.0	10	> 95	71

that the high enantioselectivity observed in our cascade amination reaction may be partly due to the slow formation of the imine intermediate (and thus a practically high proportion of the alcohol present).

We propose the catalytic cycle shown in Scheme 3 as a working hypothesis. Complex **I** formed between the Ir complex **6** and the chiral phosphoric acid **10e**^[5d-g] (as

to yield the amine with high enantioselectivity,^[12] and in this case, the chiral Ir complex is the determining factor in terms of the configuration of the chiral amine product.

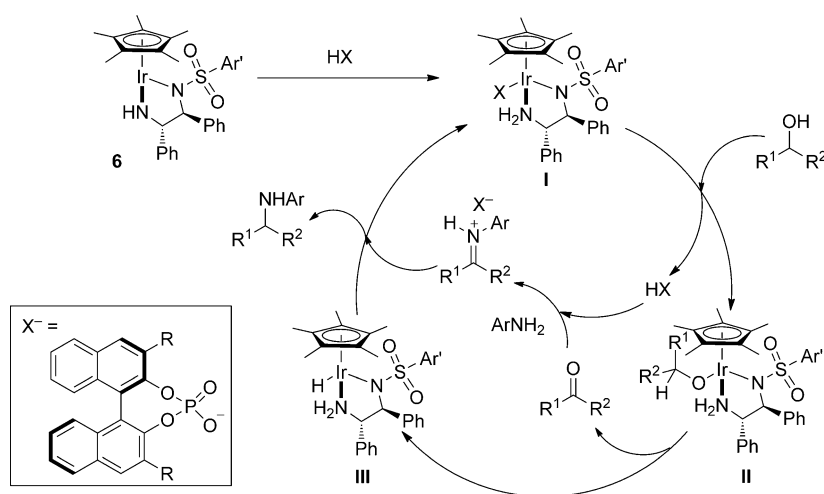
In conclusion, we have developed the first enantioselective amination of alcohols by the use of borrowing hydrogen methodology under the catalysis of a chiral Ir complex in cooperation with a chiral phosphoric acid. The identification of new and more efficient catalytic systems to access a wider range of chiral amines beyond anilines as well as N-containing heterocyclic compounds with high stereoselectivity is the focus of current efforts in our laboratories.

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Scheme 3. Proposed catalytic cycle.

supported by the loss of the amide NH peak of **6** and the formation of a new species identified by ³¹P NMR spectroscopy at $\delta = 6.14$ ppm) presumably reacts with the alcohol substrate to produce an iridium-alkoxide complex **II** as an intermediate towards the formation of the iridium hydride **III**. In situ ¹H NMR spectroscopic investigation of a mixture of (S,S)-**6**, **10e**, and 2-octanol (**1a**) in a 1:1:20 ratio at 110 °C in [D₈]toluene for 1 h showed the formation of an iridium hydride species (Ir–H at $\delta = -15.3$ ppm). Surprisingly, the Ir–H peak was not observed in the equivalent experiment without **10e**, even after 24 h. We speculate that the expected iridium hydride may be formed, but only in a tiny amount, which is consistent with the low efficiency of the transfer hydrogenation of **13** in the absence of **10e** (Table 4, entry 1). The acid cocatalyst HX is believed to be involved in promoting the imine condensation as well as activating the imine intermediate as the iminium species, which is then attacked by the chiral iridium hydride complex **III** to produce the desired product and regenerate the iridium phosphate **I**. The chiral acid and chiral Ir complex function cooperatively

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