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# Efficient asymmetric hydrogenation of quinolines in neat water catalyzed by chiral cationic Ru-diamine complexes†

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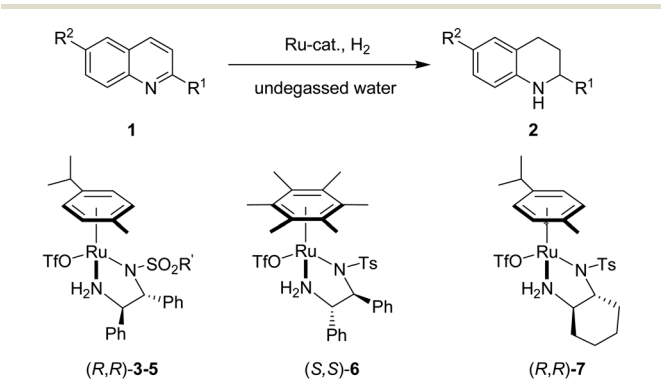
We describe herein highly effective asymmetric hydrogenation of quinolines in undegassed water catalyzed by chiral cationic Ru-diamine complexes for the first time. This facile and green protocol is applicable to the scaled-up synthesis of 6-fluoro-2-methyl-1,2,3,4-tetrahydroquinoline, a key intermediate for the preparation of the antibacterial agent (*S*)-flumequine, with 98% ee.

Water has been considered as the most preferred reaction media from the economical and environmental point of view.[1] Due to its unique physical and chemical properties, water has emerged as a powerful solvent for the catalytic reactions by accelerating the rate and/or increasing the selectivity (chemo-, regio-, stereo-, and even enantioselectivity).[2,3] Despite considerable progress made in this field, only limited success has been achieved in the highly effective asymmetric hydrogenation in neat water.[4] Because of the low solubility of organic substrates and catalysts in the aqueous phase, lower activity and/or enantioselectivity are often observed as compared to those obtained in organic solvents.[4a–c] To overcome these drawbacks, the use of amphiphilic chiral ligands and/or the addition of co-solvents such as alcoholic solvents, as well as surfactants are necessary.[3f,4] Therefore, it is still a big challenge to realize highly effective asymmetric hydrogenation in neat water by using the unmodified chiral catalysts.

Optically pure tetrahydroquinoline derivatives are an important class of building blocks for the preparation of biologically active compounds.[5] The transition-metal-catalyzed asymmetric hydrogenation of readily available quinolines is one of the most straightforward, efficient and atom-economic methods for attaining these optically active heterocycles.[6] Since the pioneering work reported by Zhou and co-workers,[7] a number of iridium complexes containing different types of chiral phosphorus ligands have been developed to catalyze the enantioselective hydrogenation of quinoline derivatives in organic solvents.[7] To the best of our knowledge, none of these catalyst systems was reported to be efficient for such a transformation in water.[8]

Recently, we have reported that the cationic ruthenium complexes of chiral monotosylated diamines, which are powerful catalysts for asymmetric transfer hydrogenation of aromatic ketones and imines,[9,10] are effective catalysts for the asymmetric hydrogenation of quinolines with unprecedented enantioselectivity and reactivity.[11] In addition, these phosphine-free ruthenium complexes could catalyze this reaction in ionic liquids or even under solvent-free conditions.[11a,c] Encouraged by these results, we hope to carry out the asymmetric hydrogenation of quinoline in neat water with the ruthenium catalysts (Scheme 1). Most recently, Xiao and co-workers demonstrated that the analogous Rh-diamine complexes could efficiently catalyze the asymmetric transfer hydrogenation of quinolines in HOAc–NaOAc buffer solution employing HCOONa as the hydrogen source.[12] However, the Ru-diamine complex exhibited much




**Scheme 1** Asymmetric hydrogenation of quinolines in undegassed water catalyzed by chiral cationic ruthenium-diamine complexes.

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lower reactivity and enantioselectivity under otherwise identical conditions. Herein, we report the details of the asymmetric hydrogenation of various quinoline derivatives with Ru-catalysts in neat undegassed water, including a scaled-up synthesis of 6-fluoro-2-methyl-1,2,3,4-tetrahydroquinoline.

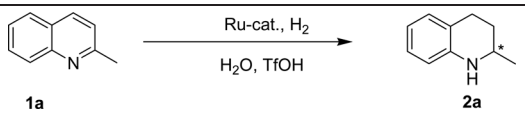
We started our study with 2-methylquinoline (**1a**) as a standard substrate. With 1.0 mol% of (*R*,*R*)-**3**, the hydrogenation was carried out under 50 atm of $H_2$ at 30 °C in degassed deionized water. As shown in Table 1, to our delight, 26% conversion and 95% ee were obtained in 3 h (entry 1). The enantioselectivity is comparable to that obtained in methanol (95% ee *vs.* 94% ee).[11a] Considering that quinoline is reduced *via* an ionic and cascade reaction pathway,[11b] $CF_3SO_2OH$ (TfOH) was added to activate the substrate. As expected, the reaction rate increased significantly upon the addition of TfOH. Full conversion and the same enantioselectivity were observed in the presence of 10 mol% of TfOH (entry 2). Notably, without the use of a glovebox and undegassed water, the reaction gave the same conversion and enantioselectivity (entry 3 *vs.* entry 2). Even when the hydrogenation was carried out in the presence of air, almost identical enantioselectivity was observed (entry 4). These results indicate that both the ruthenium precatalyst and the catalytically active species are air-stable under aqueous conditions. Interestingly, when undegassed tap water was used as solvent, the enantioselectivity is comparable to that obtained in deionized water (entry 5 *vs.* entry 3).

Next, the effects of $H_2$ pressure, reaction temperature and chiral ligands on catalytic activity and enantioselectivity were examined. It was found that the enantioselectivity is insensitive to hydrogen pressure and temperature (entries 6–10). The hydrogenation of **1a** could also be carried out under 10 atm of hydrogen, giving the same ee value but a lower conversion (entry 6). Remarkably, even if the reaction proceeded at low catalyst loading (0.2 mol%), full conversion and 94% ee were also obtained upon prolonged reaction time (entry 11). On the other hand, the catalytic performance was significantly affected by both the *N*-sulfonate substituents and the $\eta^6$-arene ligand (entries 12–14). The use of the Ru-catalyst, (*S*,*S*)-**6**, with sterically demanding hexamethylbenzene led to a significant increase in enantioselectivity, albeit at a low conversion (entry 14). In addition, increasing the reaction temperature resulted in a remarkable increase in reactivity while maintaining the enantioselectivity (entry 15). It was noted that replacement of diamine ligand TsDpen (*N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine) with TsCydn (*N*-(*p*-toluenesulfonyl)-1,2-cyclohexanediamine) led to a much lower enantioselectivity (entry 16).

With optimal catalysts (*S*,*S*)-**6** and (*R*,*R*)-**3** in hand, a series of quinoline derivatives were then hydrogenated in undegassed deionized water (Table 2). For substrates **1a**–**e**, by increasing the length of the 2-substituted side chain from methyl to ethyl and *n*-penthyl, the reactivities and enantioselectivities dropped gradually when (*S*,*S*)-**6** was used as the catalyst (entries 1–3). On the basis of better reactivity obtained by catalyst (*R*,*R*)-**3** (Table 1, entry 3 *vs.* entry 13), the substrates bearing alkyl chains were further hydrogenated under the following conditions: 1.0 mol% (*R*,*R*)-**3**, 50 atm of $H_2$ and 30 °C. Despite slightly low enantioselectivities, full conversions were achieved in all cases, and the enantioselectivities were relatively insensitive to the length of the side chain (entries 4–9). However, the quinoline derivative with a hydroxyl group at the side chain exhibited much low reactivity (entry 9). Interestingly, substrates **1h**–**j** were hydrogenated efficiently with (*S*,*S*)-**6** as a catalyst, and the presence of a substituted group on the 6-position had no obvious effect on either yield or enantioselectivity (entries 10–12). Notably, when asymmetric hydrogenation of **1a** and **1h** was carried out at a substrate/catalyst ratio of 500 : 1, high conversions were observed in both cases, albeit with slightly low enantioselectivities (entries 13 and 14). Unfortunately, the hydrogenation of 2-phenyl-substituted quinoline exhibited much lower enantioselectivity and reactivity than those of 2-alkylated quinolines catalyzed by (*R*,*R*)-**3** (entry 15).

The usefulness of the present work was exemplified in the scaled-up synthesis of 6-fluoro-2-methyl-1,2,3,4-tetrahydroquinoline, which is a key intermediate for the synthesis of the antibacterial agent (*S*)-flumequine.[13] Hydrogenation of the easily available substrate, **1j**, was carried out on a 0.5 g scale in the presence of

**Table 1** Optimization of reaction conditions for the asymmetric hydrogenation of **1a** in undegassed deionized water[a]



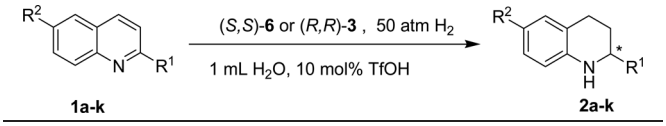

**1a** **2a**

| Entry | Catalyst | $H_2$ (atm); $T$ (°C) | TfOH (%) | Conv.[b] (%) | Ee[c] (%) |
|---|---|---|---|---|---|
| 1[d] | (*R*,*R*)-**3** | 50; 30 | 0 | 26 | 95 |
| 2[d] | (*R*,*R*)-**3** | 50; 30 | 10 | >99 | 95 |
| 3 | (*R*,*R*)-**3** | 50; 30 | 10 | >99 | 95 |
| 4[e] | (*R*,*R*)-**3** | 50; 30 | 10 | >99 | 94 |
| 5[f] | (*R*,*R*)-**3** | 50; 30 | 10 | >99 | 95 |
| 6 | (*R*,*R*)-**3** | 10; 30 | 10 | 64 | 95 |
| 7 | (*R*,*R*)-**3** | 30; 30 | 10 | >99 | 95 |
| 8 | (*R*,*R*)-**3** | 80; 30 | 10 | >99 | 96 |
| 9 | (*R*,*R*)-**3** | 50; 20 | 10 | 95 | 96 |
| 10 | (*R*,*R*)-**3** | 50; 50 | 10 | >99 | 95 |
| 11[g] | (*R*,*R*)-**3** | 50; 50 | 10 | >99 | 94 |
| 12 | (*R*,*R*)-**4** | 50; 30 | 10 | >99 | 92 |
| 13 | (*R*,*R*)-**5** | 50; 30 | 10 | >99 | 94 |
| 14 | (*S*,*S*)-**6** | 50; 30 | 10 | 71 | 99 |
| 15 | (*S*,*S*)-**6** | 50; 50 | 10 | >99 | 99 |
| 16 | (*R*,*R*)-**7** | 50; 30 | 10 | >99 | 82 |

[a] Reaction conditions: **1a** (0.2 mmol) in undegassed deionized water (1 mL), Ru-catalyst (1.0 mol%), stirred for 3 h. All manipulations were conducted in air, and the autoclave was purged with $H_2$ three times before reaction.
[b] The conversions were determined by $^1$H NMR.
[c] The enantiomeric excesses were determined by HPLC with a chiral OJ-H column.
[d] All manipulations were conducted under anaerobic conditions (with the use of degassed water and a glovebox).
[e] All manipulations were conducted in air, without purging the autoclave with $H_2$ before reaction.
[f] Undegassed tap water was used as solvent.
[g] Substrate/catalyst = 500 (143 mg of substrate in 5 mL of $H_2O$), stirred for 12 h.

**Table 2** Asymmetric hydrogenation of quinoline derivatives in undegassed deionized water[a]



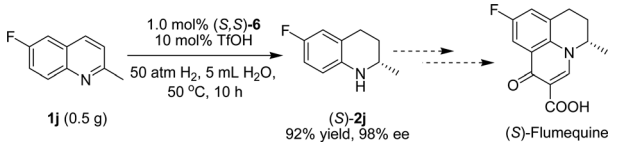

| Entry | $R^2/R^1$ | Catalyst | Temp (°C); time (h) | Yield[b] (%) | Ee[c,d] (%) |
|---|---|---|---|---|---|
| 1 | H/Me | (*S*,*S*)-**6** | 50; 3 | 95 | 99 (*S*) |
| 2 | H/Et | (*S*,*S*)-**6** | 50; 3 | 89[e] | 97 (*S*) |
| 3 | H/*n*-Pen | (*S*,*S*)-**6** | 50; 3 | 55[e] | 94 (*S*) |
| 4 | H/Et | (*R*,*R*)-**3** | 30; 3 | 95 | 94 (*R*) |
| 5 | H/*n*-Pr | (*R*,*R*)-**3** | 30; 3 | 93 | 94 (*R*) |
| 6 | H/*n*-Bu | (*R*,*R*)-**3** | 30; 3 | 96 | 93 (*R*) |
| 7 | H/*n*-Pen | (*R*,*R*)-**3** | 30; 3 | 91 | 95 (*R*) |
| 8 | H/Ph | (*R*,*R*)-**3** | 30; 3 | 95 | 93 (*R*) |
| 9 | H/OH | (*R*,*R*)-**3** | 30; 12 | 92 | 93 (*S*) |
| 10 | Me/Me | (*S*,*S*)-**6** | 50; 3 | 96 | 99 (*S*) |
| 11 | MeO/Me | (*S*,*S*)-**6** | 50; 3 | 94 | 99 (*S*) |
| 12 | F/Me | (*S*,*S*)-**6** | 50; 3 | 94 | 98 (*S*) |
| 13[f] | H/Me | (*S*,*S*)-**6** | 50; 12 | 87[e] | 98 (*S*) |
| 14[f] | Me/Me | (*S*,*S*)-**6** | 50; 12 | 91[e] | 96 (*S*) |
| 15 | H/Ph | (*R*,*R*)-**3** | 30; 12 | 92 | 63 (*S*) |

[a] Reaction conditions: quinolines **1a**–**k** (0.2 mmol) in undegassed deionized water (1 mL), (*R*,*R*)-**3** or (*S*,*S*)-**6** (1.0 mol%), undegassed TfOH (10 mol%), $H_2$ (50 atm).
[b] Isolated yield.
[c] The enantiomeric excesses were determined by HPLC with a chiral column.
[d] The absolute configurations for the products were assigned by comparison with the optical rotations in the published literature.[11b]
[e] The conversions were determined by $^1$H NMR.
[f] Substrate/catalyst = 500 (1 mmol of substrate in 5 mL of $H_2O$).

(*S*,*S*)-**6** (1.0 mol%), giving tetrahydroquinoline (*S*)-**2j** in 92% yield with 98% ee (Scheme 2).

### Conclusions

In summary, we have developed the first highly effective asymmetric hydrogenation of quinolines in neat undegassed water catalyzed by phosphine-free Ru-diamine catalysts. Excellent enantioselectivities were obtained, which are comparable to those obtained in organic solvents. On the basis of the fact that inert gas protection is not needed throughout the entire operation, it thus provides a more practical and greener synthetic approach for the synthesis of a variety of optically active 1,2,3,4-tetrahydroquinoline derivatives.




**Scheme 2** Scaled-up synthesis of 6-fluoro-2-methyl-1,2,3,4-tetrahydroquinoline.

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