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Asymmetric Hydrogenation of 2-Aryl-5,6-dihydropyrazine Derivatives with Chiral Cationic Ruthenium Diamine Catalysts†

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The first asymmetric hydrogenation of unfunctionalized 2-substituted and 2,3-disubstituted 5,6-dihydropyrazines catalyzed by chiral cationic Ru-diamine complex (*R*,*R*)-**1a** was developed, affording chiral piperazine derivatives with good enantioselectivities (up to 89% *ee*).

Keywords asymmetric hydrogenation, ruthenium, chiral diamines, piperazines

Introduction

Optically active chiral piperazines are an important class of building blocks for the asymmetric synthesis of biologically active and/or naturally occurring compounds which are important for pharmaceutical and agrochemical industries.[1] Some important representative examples include lomefloxacin, mirtazapine, *k*-receptor agonist, dragmacidin and piperazinomycin (Figure 1).[1] Furthermore, some chiral piperazine derivatives have proven to be useful chiral ligands in asymmetric catalysis.[2] To date, many methods have been developed to prepare such chiral heterocyclic compounds, mainly including chiral pool synthesis[3] and resolution of the corresponding racemic compounds.[4] Although the asymmetric hydrogenation offers a more straightforward and environmentally benign route to these optically active compounds,[5] much less attention has been directed toward the transition-metal-catalyzed reduction of pyrazines or partially reduced pyrazines.[6] For example, Fuchs reported the asymmetric hydrogenation of pyrazinecarboxylic acid derivatives catalyzed by $[Rh(COD)Cl]_2$/diphosphine with *ee* values up to 78%.[6b] Rossen and co-workers found that the Rh-BINAP complex was an efficient catalyst for the hydrogenation of 2-amide functionalized tetrahydropyrazines to give piperazines with up to 99% *ee*.[6c,6d] To the best of our knowledge, there are no reports on asymmetric hydrogenation of dihydropyrazine derivatives.

Recently, we have demonstrated that the cationic Ru- and Ir-complexes of chiral mono-tosylated diamines[7] are very efficient catalysts for the asymmetric hydrogenation of different types of *N*-containing heteroaromatic compounds[8] and various imines.[9] Most recently, the effectiveness of these Ru-catalysts was further proved in the asymmetric hydrogenation of a class of benzo-cyclic diimines, 2,4-disubstituted-3*H*-1,5-benzodiazepines, with excellent diastereoselectivity and excellent enantioselectivity.[10] Encouraged by these results and as a continuation of our ongoing endeavor to

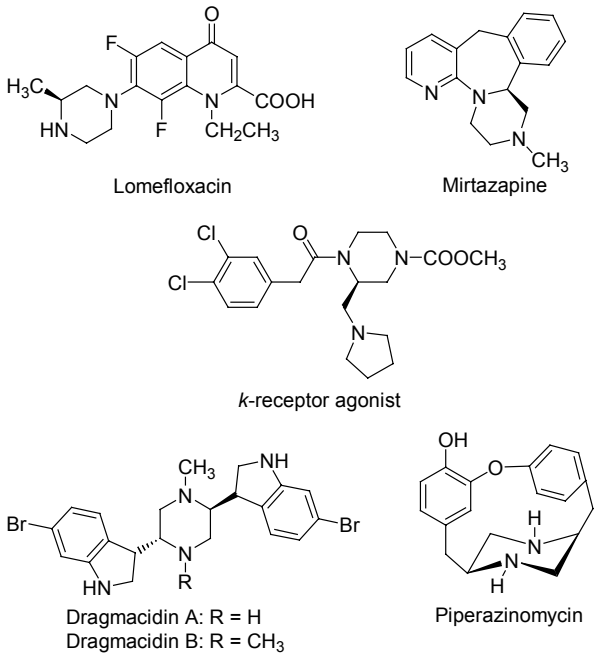

Figure 1 Selected bioactive compounds containing piperazine scaffold.

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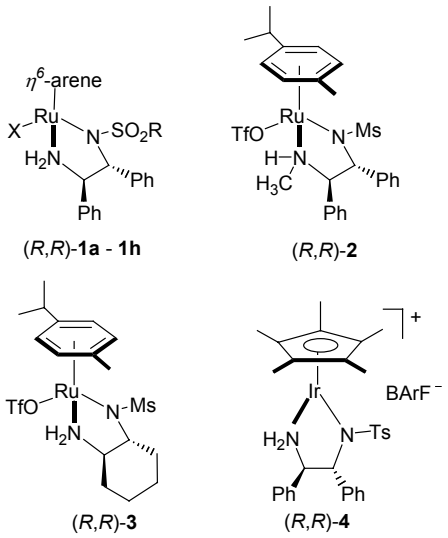
prepare enantiomerically pure *N*-containing heterocyclic compounds, herein, we report the first example of highly enantioselective hydrogenation of a range of readily available 2-aryl substituted 5,6-dihydropyrazine derivatives using chiral cationic Ru-diamine catalysts, thus providing an easy access to chiral 2-aryl substituted piperazine derivatives.



(*R*,*R*)-**1a**: R = CH_3, η^6-arene = *p*-cymene, X = OTf;
(*R*,*R*)-**1b**: R = CH_3, η^6-arene = benzene, X = OTf;
(*R*,*R*)-**1c**: R = CH_3, η^6-arene = 1,3,5-trimethylbenzene, X = OTf;
(*R*,*R*)-**1d**: R = 4-$CH_3C_6H_4$, η^6-arene = *p*-cymene, X = OTf;
(*R*,*R*)-**1e**: R = 4-$CH_3C_6H_4$, η^6-arene = hexamethylbenzene, X = OTf;
(*R*,*R*)-**1f**: R = 4-$CF_3C_6H_4$, η^6-arene = *p*-cymene, X = OTf;
(*R*,*R*)-**1g**: R = CH_3, η^6-arene = *p*-cymene, X = PF_6;
(*R*,*R*)-**1h**: R = CH_3, η^6-arene = *p*-cymene, X = BArF.

Figure 2 The catalysts used for the asymmetric hydrogenation of 2-aryl-5,6-dihydropyrazines.

Experimental

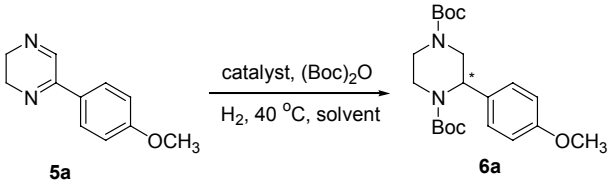
Typical procedure for asymmetric hydrogenation

In a 50 mL glass-lined stainless steel reactor with a magnetic stirring bar was charged with Ru-catalyst[8b] (0.008 mmol), substrate (0.2 mmol), 0.44 mmol $(Boc)_2O$ and solvent (2 mL). The hydrogenation was processed under 10 atm H_2 at 40 ℃ for 24 h. After carefully releasing the hydrogen, the mixture was concentrated. The residue was purified by column chromatography on silica eluted with petroleum ether/DCM (1/1, *V*/*V*) to give the pure product. The enantiomeric excess was determined by HPLC with a chiral AD-H column.

Results and Discussion

To evaluate the chiral Ru-diamine catalysts and optimize the reaction conditions, the hydrogenation of 2-(4-methoxyphenyl)-5,6-dihydropyrazine (**5a**) was selected as the standard reaction. The initial hydrogenation was carried out in the presence of 4 mol% (*R*,*R*)-**1a** in DCM with 2.2 equiv. $(Boc)_2O$ as additive. To our delight, the reaction proceeded smoothly, affording the piperazine product (**6a**) in 64% isolated yield with 81% *ee* (Table 1, Entry 1). Based on this promising result, other catalysts as shown in Figure 2 were then tested, and the results are listed in Table 1.

Table 1 Catalyst screening and optimization of the reaction conditions[a]



5a **6a**

Entry	Catalyst	Solvent	H_2/atm	Yield[b]/%	*ee*[c]/%
1	(*R*,*R*)-**1a**	DCM	40	64	81
2	(*R*,*R*)-**1b**	DCM	40	46	81
3	(*R*,*R*)-**1c**	DCM	40	58	77
4	(*R*,*R*)-**1d**	DCM	40	60	79
5	(*R*,*R*)-**1e**	DCM	40	55	21
6	(*R*,*R*)-**1f**	DCM	40	58	76
7	(*R*,*R*)-**1g**	DCM	40	65	81
8	(*R*,*R*)-**1h**	DCM	40	42	77
9	(*R*,*R*)-**2**	DCM	40	49	6
10	(*R*,*R*)-**3**	DCM	40	32	24
11	(*R*,*R*)-**4**	DCM	40	95	0
12	(*R*,*R*)-**1a**	DCE	40	62	81
13	(*R*,*R*)-**1a**	Toluene	40	46	80
14	(*R*,*R*)-**1a**	THF	40	52	69
15	(*R*,*R*)-**1a**	EA	40	63	60
16	(*R*,*R*)-**1a**	MeOH	40	35	52
17	(*R*,*R*)-**1a**	CF_3CH_2OH	40	31	69
18	(*R*,*R*)-**1a**	DCM	70	70	77
19	(*R*,*R*)-**1a**	DCM	20	62	85
20	(*R*,*R*)-**1a**	DCM	10	61	86
21[d]	(*R*,*R*)-**1a**	DCM	10	44	86
22[e]	(*R*,*R*)-**1a**	DCM	10	0	0
23[f]	(*R*,*R*)-**1a**	DCM	10	54	89

[a] Reaction conditions: 0.2 mmol substrate in 2 mL solvent, 4 mol% catalyst, 0.44 mmol $(Boc)_2O$, 40 ℃, 24 h. [b] Isolated yields. [c] Determined by HPLC with a chiral AD-H column. [d] Hydrogenation at 25 ℃. [e] Without the additive of $(Boc)_2O$. [f] 2 mol% catalyst was used.

Generally, the catalytic performance was significantly affected by both the substituent groups of the η^6-arene ligand and the *N*-sulfonate substituents (Table 1, Entries 1—6). Introduction of more alkyl substituents into the η^6-arene of the Ru catalyst led to significant

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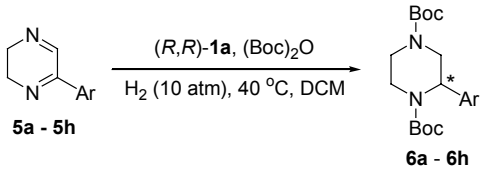
decrease in both yield and enantioselectivity (Table 1, Entry 2 vs. Entry 3, Entry 4 vs. Entry 5). Introducing electron-withdrawing *N*-sulfonate substituents into catalyst, for example (*R*,*R*)-**1f**, resulted in slightly lower enantioselectivity and reactivity (Table 1, Entries 6 vs. Entry 4). Moreover, it was observed that the weakly coordinating counteranion of Ru-complex had an obvious effect on enantioselectivity (Table 1, Entries 7 and 8). It is worth noting that the introduction of a methyl group into the primary amine of the diamine ligand in catalyst (*R*,*R*)-**2** greatly deteriorated the enantioselectivity of hydrogenation (Table 1, Entry 9). Replacement of the diamine ligand MsDpen with MsCydn led to much lower enantioselectivity and reactivity (Table 1, Entry 10). In addition, it is notable that the Ir-complex (*R*,*R*)-**4** exhibited the highest reactivity. The reduction of **5a** was very clean with quantitative isolated yield. Unfortunately, the product was found to be racemic (Table 1, Entry 11). Thus, the Ru-complex (*R*,*R*)-**1a** was chosen as the optimal catalyst.

With the Ru-complex (*R*,*R*)-**1a** as the catalyst, the reaction conditions were then optimized. It was found that the low-polarity solvents, especially the chlorinated solvents dichloromethane and dichloroethane, were suitable for obtaining high enantioselectivity (Table 1, Entries 1, 12—13). Decreased enantioselectivities were obtained in THF and EA, albeit with similar yields (Table 1, Entries 14—15). Moreover, low reactivities and enantioselectivities were also observed in alcoholic solvents (Table 1, Entries 16—17). Subsequently, the effect of hydrogen pressure and temperature were also tested. The results showed that slightly higher enantioselectivities could be obtained when the reaction was performed under lower hydrogen pressure (Table 1, Entries 18—20). Reducing the reaction temperature was favorable to obtain higher enantioselectivity, but a significant decrease in reactivity was also observed (Table 1, Entry 21). In addition, the additive of $(Boc)_2O$ was indispensable to the hydrogenation. When the reaction was carried out in the absence of $(Boc)_2O$, no hydrogenation product was found at all (Table 1, Entry 22). According to our previous studies,[9a,9b] the addition of $(Boc)_2O$ was to prevent deactivation of the catalyst, which might be poisoned by the amine product as well as the by-product due to the hydrolysis of substrate, through *in situ* protection of the corresponding amine poisons.[11] Notably, when the amount of catalyst (*R*,*R*)-**1a** was reduced from 4 mol% to 2 mol%, the highest enantioselectivity (89% *ee*) was obtained (Table 1, Entry 23). However, futher decreasing the catalyst loading to 1.0 mol% resulted in much low yield (18% yield and 89% *ee*). Considering both reactivity and enantioselectivity, the optimal reaction conditions were thus established: 0.2 mmol substrate in 2 mL DCM, 4 mol% catalyst, 0.44 mmol $(Boc)_2O$, 10 atm H_2, 40 ℃, 24 h.

With the optimal reaction conditions and catalyst (*R*,*R*)-**1a** in hand, we further explored the scope of the

Table 2 Asymmetric hydrogenation of 2-aryl-5,6-dihydropyrazines[a]



Entry	Ar/Substrate	Yield[b,d]/%	*ee*[c,d]/%
1	4-OCH_3-Ph (**5a**)	61 (54)	86 (89) (+)
2	Ph (**5b**)	70 (49)	79 (83) (+)
3	3-OCH_3-Ph (**5c**)	68 (48)	80 (82) (+)
4	3,4-$(OCH_3)_2$-Ph (**5d**)	64 (42)	84 (88) (+)
5	2-Nap (**5e**)	36 (42)	60 (88) (+)
6	4-Cl-Ph (**5f**)	67 (47)	74 (80) (+)
7	4-Br-Ph (**5g**)	70 (50)	75 (82) (+)
8	4-CF_3-Ph (**5h**)	63	75 (+)

[a] Reaction conditions: 0.2 mmol substrate in 2 mL DCM, 4 mol% catalyst, 0.44 mmol $(Boc)_2O$, 10 atm H_2, stirred at 40 ℃ for 24 h. [b] Isolated yields. [c] Determined by HPLC with a chiral AD-H column. [d] The data in brackets were obtained with 2 mol% catalyst.

Ru-catalyzed asymmetric hydrogenation of 2-aryl-5,6-dihydropyrazines (**5a**—**5h**). Generally, all the substrates could be efficiently hydrogenated to afford the corresponding chiral 2-arylpiperazine derivatives with good yields and enantioselectivities (Table 2). The electronic characteristic of substituents in the substrate has a significant influence on the enantioselectivity and reactivity. The substrates containing an electron-donating group gave higher enantioselectivities (Table 2, Entries 1, 3, 4). It was observed that the best results were obtained for the substrates bearing an electron-donating methoxyl group on the *para* position of the phenyl ring (Table 2, Entry 1 and Entry 4). In contrast, hydrogenation of substrates with electron-withdrawing groups offered much lower enantioselectivities (Table 2, Entries 6—8). For the 2-naphthyl-substituted substrate **5e**, the hydrogenation could be accomplished only with 60% *ee* in 36% yield. When the dosage of Ru-MsDpen catalyst was reduced from 4 mol% to 2 mol%, improved enantioselectivities were achieved, albeit the efficacy of the catalyst decreased obviously. Enantiomeric excesses up to 89% were afforded for the substrates screened in the presence of 2 mol% catalyst.

On the basis of our successful asymmetric hydrogenation of 2-aryl-5,6-dihydropyrazines, a disubstituted substrate of 2-methyl-3-phenyl-5,6-dihydropyrazine (**7**) was further subjected to the hydrogenation catalyzed by (*R*,*R*)-**1a** under 40 atm of H_2 (Scheme 1). The hydrogenation proceeded very well, a nearly quantitative isolated yield was achieved. Notably, a high diastereoselectivity (*cis*/*trans*=12) was observed, but with an extremely low enantioselectivity of 14% *ee*. In the subse-

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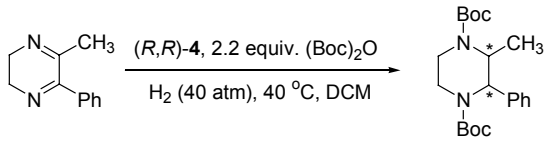
Scheme 1 Asymmetric hydrogenation of 2,3-disubstituted dihydropyrazine **7**



7 **8**

d.r. (*cis*/*trans*) = 16[a]

>95% yield, 29% *ee*[b]

[a] Determined by ^{1}H NMR spectroscopy;

[b] Determined by HPLC with a chiral AD-H column.

quent survey of different Ru-catalysts, no obvious enhancement of enantioselectivity was observed. When Ir-TsDpen (*R*,*R*)-**4** (Figure 2) was used as the catalyst, the reaction furnished the hydrogenation product with the highest enantioselectivity of 29% *ee*.

Conclusions

In summary, we have developed the first asymmetric hydrogenation of a range of 2-aryl-5,6-dihydropyrazines catalyzed by the chiral cationic Ru-diamine catalysts. Moderate to good isolated yields and high enantioselectivities (up to 89% *ee*) were achieved. Further work will be directed toward expanding the substrate scope of 2,3-disubstituted-5,6-dihydropyrazines and the mechanism study of this reaction.

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