Asymmetric Catalysis

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Consecutive Intermolecular Reductive Amination/Asymmetric Hydrogenation: Facile Access to Sterically Tunable Chiral Vicinal Diamines and N-Heterocyclic Carbenes

Ya Chen, Yixiao Pan, Yan-Mei He, and Qing-Hua Fan**

Abstract: *A highly enantioselective iridium- or ruthenium-catalyzed intermolecular reductive amination/asymmetric hydrogenation relay with 2-quinoline aldehydes and aromatic amines has been developed. A broad range of sterically tunable chiral N,N′-diaryl vicinal diamines were obtained in high yields (up to 95 %) with excellent enantioselectivity (up to > 99 % ee). The resulting chiral diamines could be readily transformed into sterically hindered chiral N-heterocyclic carbene (NHC) precursors, which are otherwise difficult to access. The usefulness of this synthetic approach was further demonstrated by the successful application of one of the chiral vicinal diamines and chiral NHC ligands in a transition-metal-catalyzed asymmetric Suzuki–Miyaura cross-coupling reaction and asymmetric ring-opening cross-metathesis, respectively.*

Chiral vicinal diamines are important structural moieties found in a variety of biologically active natural products and pharmaceuticals (**A1**–**A4**, Figure 1), as well as in chiral ligands and catalysts for transition-metal-catalyzed asymmetric reactions and organocatalysis (**A5**–**A8**, Figure 1).[1] Accordingly, the development of efficient synthetic routes to chiral vicinal diamines has attracted great interest over the past decades. To date, a number of elegant synthetic methods based on asymmetric catalysis have been reported.[2–7] However, most of these methods still suffer from narrow substrate scope, the requirement of electron-withdrawing protecting groups and subsequent transformation to form the free amines, and/or the inability to differentiate the two amino groups in the product. Therefore, it is highly desirable to develop direct and atom-economical approaches to the catalytic asymmetric synthesis of unprotected chiral vicinal diamines with structural diversity from simple starting materials.

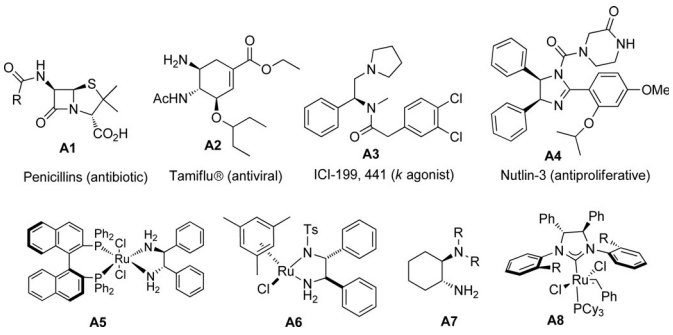
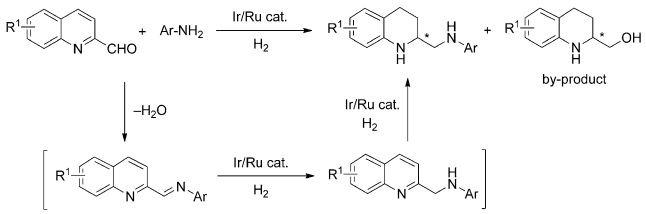


Figure 1. Selected examples of chiral 1,2-diamine-based biologically active compounds and chiral ligands and catalysts. Cy = cyclohexyl, Ts = *p*-toluenesulfonyl.

N-Heterocyclic carbenes (NHCs) have emerged as a unique class of ligands and organocatalysts for a huge number of catalytic transformations over the last two decades.[1g,8] Among them, imidazolium-derived NHCs, such as 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes),[9] have been widely used for transition-metal catalysis. However, only a few chiral variants of IMes have been reported so far.[10] Such chiral NHCs could be readily accessed through the direct derivatization of vicinal diamines.[10a–f] However, to the best of our knowledge, the direct catalytic asymmetric synthesis of sterically hindered *N,N′*-diaryl vicinal diamines has not been achieved.[11,12]

Asymmetric hydrogenation has proven to be one of the most powerful methods for the preparation of various chiral amines.[13] However, examples of the direct synthesis of chiral vicinal diamines by catalytic asymmetric hydrogenation are extremely rare.[12,14] Previously, we demonstrated that the cationic ruthenium or iridium complexes of chiral monosulfonated diamines[1e] are excellent catalysts in the asymmetric hydrogenation of quinoline derivatives and ketimines.[15] Later, this catalytic system was successfully applied to the asymmetric hydrogenation of 2,2′-bisquinoline derivatives, affording direct access to chiral endocyclic vicinal diamines.[12] However, this method suffered from difficulties in substrate synthesis and low stereoselectivity for sterically hindered substrates. More recently, an asymmetric tandem reaction of quinolinyl- and quinoxalinyl-containing ketones was realized with this catalytic system, providing access to chiral benzo-fused N-heterocyclic compounds.[16] Encouraged by these results, we envisioned that readily available 2-quinoline aldehydes and aromatic amines could be utilized to prepare chiral *N,N′*-diaryl vicinal diamines through a relay sequence of intermolecular reductive amination and asymmetric hydrogenation of quinolines (Scheme 1). In this

[*] Y. Chen, Y. Pan, Y.-M. He, Prof. Dr. Q.-H. Fan
Beijing National Laboratory for Molecular Sciences
CAS Key Laboratory of Molecular Recognition and Function
Institute of Chemistry, Chinese Academy of Sciences (ICCAS)
University of Chinese Academy of Sciences
Beijing 100190 (P. R. China)
E-mail: heym@iccas.ac.cn
fanqh@iccas.ac.cn
Prof. Dr. Q.-H. Fan
Collaborative Innovation Center of Chemical Science and Engineering
Tianjin 300072 (P. R. China)
Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.201909919.



Scheme 1. Synthesis of chiral vicinal diamines through a intermolecular reductive amination/asymmetric hydrogenation relay sequence.

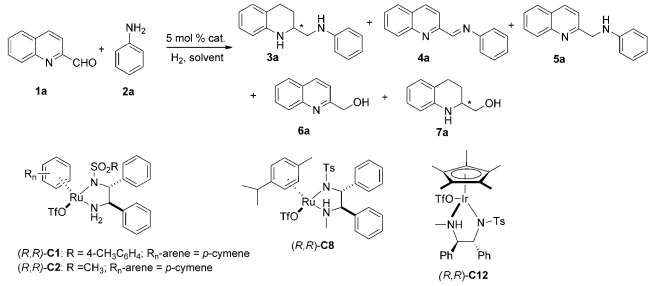
tandem reaction, three major challenges are encountered: 1) the strong ligating diamine product might deactivate the Ir or Ru catalyst; 2) the direct reduction of 2-quinoline aldehydes might occur; 3) the precise control of enantioselectivity is more difficult when using sterically hindered starting materials.[17] Herein, we report the iridium- or ruthenium-catalyzed intermolecular reductive amination/asymmetric hydrogenation tandem reaction with readily available quinoline aldehydes and aromatic amines to afford direct, atom-economical, and powerful access to a variety of sterically and electronically tunable chiral *N*,*N*′-diaryl vicinal diamines under mild conditions. Furthermore, several sterically hindered NHC precursors were readily prepared on a gram scale from these chiral *N*,*N*′-diaryl vicinal diamines.

Initially, the asymmetric tandem reaction between commercially available quinoline-2-carbaldehyde (**1a**) and aniline (**2a**) catalyzed by Ru complex (*R*,*R*)-**C1** was studied. The reaction in methanol (Table 1, entry 1) gave the desired product **3a** in only 36% yield with 83% *ee*, while intermediate **5a** from reductive amination was found to be the main product.[18] Pleasingly, by screening various organic solvents, we found that **3a** was obtained in 81% yield with 92% *ee* in isopropanol (IPA; Table 1, entries 1–3; see also Table S1 in the Supporting Information). Further screening of catalysts (entries 3–6; see also Table S2) indicated that the Ir complex (*R*,*R*)-**C12** was optimal. Furthermore, the tandem reaction was found to be insensitive to temperature and hydrogen pressure (see Table S3). Remarkably, high chemoselectivity and enantioselectivity were observed at ambient temperature and H_2 pressure (Table 1, entries 7 and 8).

Under the optimized reaction conditions, the tandem reaction was examined with a variety of 2-quinoline aldehydes and aniline derivatives (Table 2). In most cases, the reactions proceeded smoothly to afford the desired vicinal diamines in high yield with excellent enantioselectivity. It was noticed that the aldehyde substrate **1c** bearing a methoxy group at the 6-position showed markedly low reactivity. A good yield and high enantioselectivity were observed only with 10 mol% of the catalyst at 50°C. Importantly, the reaction with sterically hindered aldehyde substrate **1g** bearing a methyl group at the 8-position proceeded smoothly even at ambient temperature and pressure to afford the chiral diamine in high yield with excellent enantioselectivity. In contrast, the yield and/or enantioselectivity decreased remarkably with an increase in steric hindrance in the aniline (products **3n** and **3o**).

To further improve the tandem reaction with sterically hindered substrates, a quick survey of catalysts with **1a** and mesitylamine revealed that good yield and excellent enantioselectivity could be achieved by using Ru complex (*R*,*R*)-**C8** (5 mol%) in the present of TfOH (10 mol%; see Table S4).[19] Under the modified reaction conditions, a range of sterically hindered chiral vicinal diamines were synthesized (Table 3). Thus, the tandem reaction of substrates with alkyl substituents at the 8-position of quinoline ring and/or 2,6-positions of the aniline ring proceeded smoothly to afford the desired

Table 1: Optimization of the reaction conditions.[a]

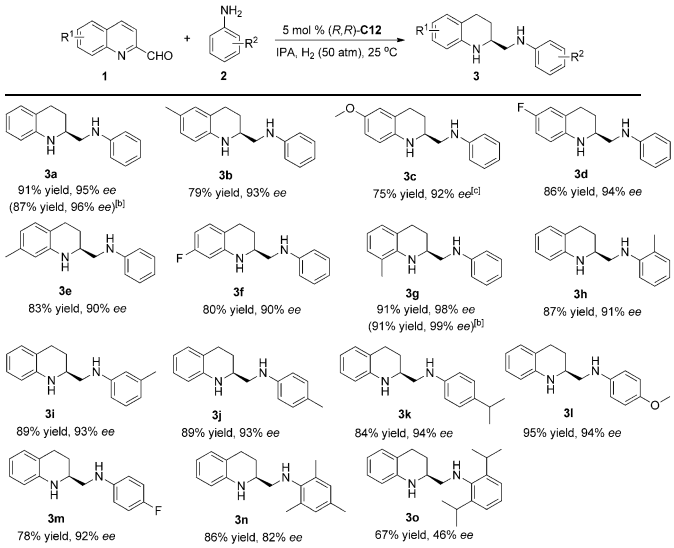


(*R*,*R*)-**C1**: R = 4-$CH_3C_6H_4$; R_n-arene = *p*-cymene
(*R*,*R*)-**C2**: R = CH_3; R_n-arene = *p*-cymene

Entry	Solvent	Catalyst	**3a**/**4a**/**5a**/**6a**/**7a**[b]	*ee* of **3a** [%][c]
1	MeOH	(*R*,*R*)-**C1**	36:–:51:7:6	83
2	EtOH	(*R*,*R*)-**C1**	59:–:24:–:17	87
3	IPA	(*R*,*R*)-**C1**	81:–:–:–:19	92
4	IPA	(*R*,*R*)-**C2**	74:–:–:–:26	92
5	IPA	(*R*,*R*)-**C8**	84:–:–:–:16	95
6	IPA	(*R*,*R*)-**C12**	91:–:–:–:9	94
7[d]	IPA	(*R*,*R*)-**C12**	92:–:–:–:8	95
8[d,e]	IPA	(*R*,*R*)-**C12**	87:–:–:–:13	96

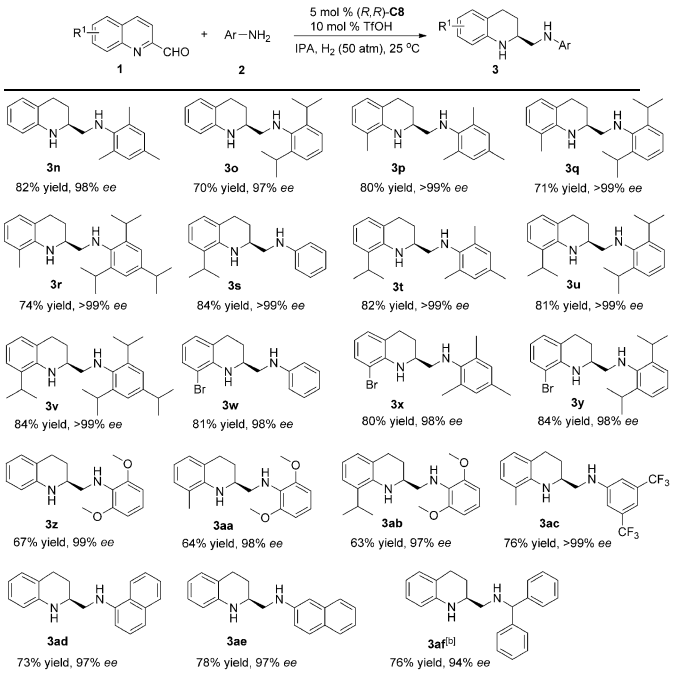
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), solvent (1.0 mL), catalyst (5 mol%), H_2 (50 atm), stirred at 50°C for 20 h. [b] Determined by ^{1}H NMR analysis of the crude product; full conversion was observed in all cases. [c] Determined by HPLC analysis with a chiral OD-H column. [d] The reaction was carried out at 25°C. [e] H_2 (1 atm).

Table 2: Scope of the synthesis of chiral vicinal diamines.[a]



[a] Reaction conditions: **1** (0.2 mmol), **2** (0.2 mmol), IPA (1.0 mL), (*R*,*R*)-**C12** (5 mol%), H_2 (50 atm), stirred at 25°C for 20 h. Yields correspond to isolated products. [b] H_2 (1 atm). [c] (*R*,*R*)-**C12** (10 mol%), 50°C.

Table 3: Scope of the synthesis of hindered chiral vicinal diamines.[a]

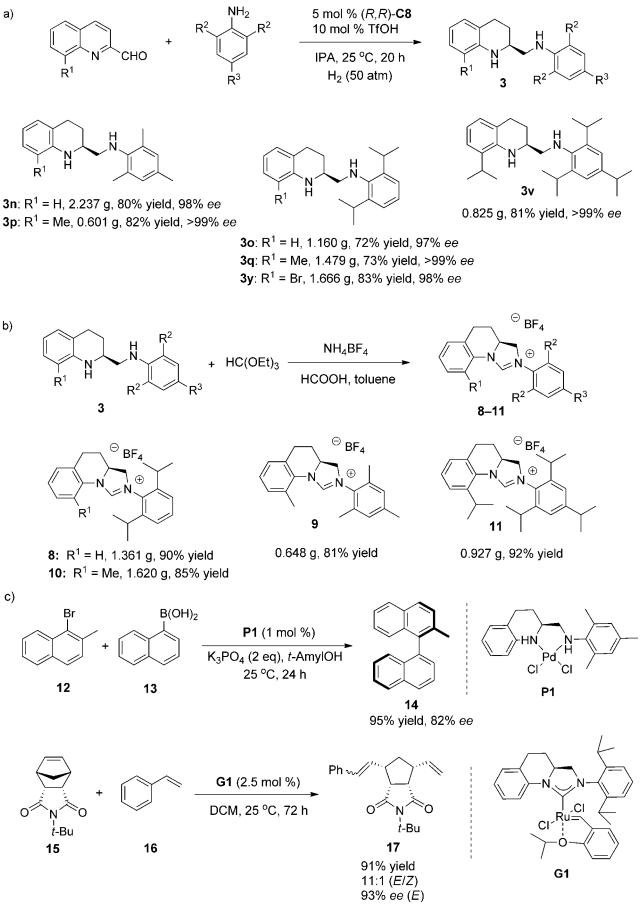


[a] Reaction conditions: **1** (0.2 mmol), **2** (0.2 mmol), IPA (1.0 mL), (*R*,*R*)-**C8** (5 mol%), TfOH (10 mol%), H_2 (50 atm), stirred at 25 °C for 20 h. Yields correspond to isolated products. [b] (*R*,*R*)-**C8** (10 mol%), 50 °C.

products **3n–v** in moderate to good yields with excellent enantioselectivity. Notably, a bromo group at the 8-position of the quinoline ring, which could be used for further functionalization, was well tolerated in this reaction. Additionally, reactions with anilines bearing electron-donating or electron-withdrawing groups gave the corresponding products **3z** and **3aa–c** in moderate yields but with excellent enantioselectivity. Furthermore, naphthylamines could also be applied to this tandem reaction with excellent enantioselectivity (products **3ad** and **3ae**). A reaction with benzhydrylamine as a substrate also proceeded smoothly with 10 mol% of (*R*,*R*)-**C8** at 50 °C (product **3af**). The absolute configuration of **3n** was determined to be *S* by comparison of the optical rotation with the reported value.[10d]

Finally, the usefulness and practicality of the current method was exemplified by scale-up syntheses and synthetic transformations of these *N*,*N*′-diaryl vicinal diamines (Scheme 2). Good yields and excellent enantioselectivity were observed in gram-scale reactions (Scheme 2a), and the obtained chiral diamines were readily converted into chiral benzimidazolium tetrafluoroborates, precursors of a new class of NHC ligands, in high yields (Scheme 2b). Furthermore, chiral Pd(**3n**)[20] and Ru(NHC)[10d] complexes were prepared and found to be efficient catalysts in the asymmetric Suzuki–Miyaura cross-coupling reaction[21] and asymmetric ring-opening cross-metathesis (AROCM)[22] (Scheme 2c), respectively. These results show the potential of these chiral diamines and NHCs in asymmetric catalysis.

In conclusion, we have developed an efficient and direct synthesis of chiral *N*,*N*′-diaryl vicinal diamines by iridium- or ruthenium-catalyzed tandem intermolecular reductive amination/asymmetric hydrogenation with 2-quinoline aldehydes and aromatic amines. Good yields and excellent enantioselectivity were observed for a wide range of chiral vicinal diamines. Several sterically hindered chiral NHC precursors were readily prepared from these enantiomerically pure diamines on a gram scale. Furthermore, both types of chiral ligand showed excellent stereoinduction in palladium-catalyzed asymmetric Suzuki–Miyaura cross-coupling and ruthenium-catalyzed asymmetric ring-opening cross-metathesis, respectively. Further studies on the application of these new chiral vicinal diamines and NHC ligands in asymmetric catalysis are ongoing in our laboratory.



Scheme 2. Scale-up syntheses and synthetic transformations. DCM = dichloromethane, Tf = trifluoromethanesulfonyl.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: asymmetric hydrogenation · N-heterocyclic carbenes · reductive amination · tandem reactions · vicinal diamines

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