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Synthetic Methods

Synthesis of Chiral Exocyclic Amines by Asymmetric Hydrogenation of Aromatic Quinolin-3-amines

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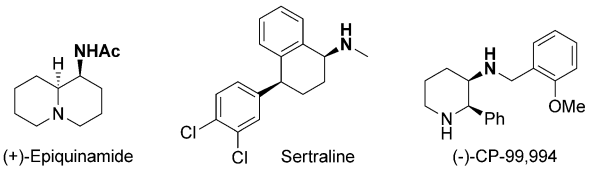
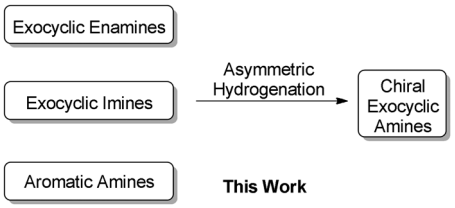
Abstract: Asymmetric hydrogenation of aromatic quinolin-3-amines was successfully developed with up to 94% enantiomeric excess (*ee*). Introduction of the phthaloyl moiety to the amino group is crucial to eliminate the inhibition effect caused by the substrate and product, to activate the aromatic ring, and to improve the diastereoselectivity. This new methodology provides direct and facile access to chiral exocyclic amines. Notably, this report is the first on the highly enantioselective hydrogenation of aromatic amines.

Optically active exocyclic amines are useful intermediates for organic synthesis and serve as chiral catalysts in various asymmetric transformations.[1] Meanwhile, they are also present in a wide variety of biologically active molecules, including natural and unnatural products (Scheme 1), such as quinolizidine alkaloid (+)-epiquinamide,[2] the selective serotonine reuptake inhibitor antidepressant Sertraline (Zoloft®),[3] and the substance P antagonists (−)-CP-99,994.[4]



Scheme 1. Selected biologically active molecules containing the chiral exocyclic amine motif.

Owing to simplicity and excellent atom economy, asymmetric hydrogenation of exocyclic enamines, imines, and aromatic amines provides an attractive approach to the corresponding enantiopure exocyclic amines (Scheme 2).[5] To date, various



Scheme 2. The synthesis of chiral exocyclic amines by means of direct asymmetric hydrogenation.

simple exocyclic enamines and imines have been successfully hydrogenated by transition-metal catalysts with high enantiomeric excess (*ee*).[1,6] However, as far as we know, for aromatic amines, there is little information available in the literature, despite the good availability and easy preparation of such compounds. The intrinsic problems are apparent: Firstly, the inherent stability resulting from aromaticity might impede the hydrogenation. Secondly, the strong coordination and poisoning ability of the substrate and the reduced product might deactivate the catalysts. Thirdly, the stereoselectivity is difficult to control. In view of the great achievements made in the area of asymmetric hydrogenation of aromatic compounds,[6d,7–17] and also as a part of our sustained efforts in this area,[7a,b,d,f] we wish to report our initial findings on the development of the first asymmetric hydrogenation of aromatic amines, quinolin-3-amines, providing the corresponding exocyclic amines with excellent yields, diastereoselectivities, and enantioselectivities.

Initially, 2-toluidine was selected as a model substrate. The original experiment was conducted in THF with a $[Ir(cod)Cl]_2$/(*S*)-SegPhos/I_2 (cod = 1,5-cyclooctadiene) catalytic system. Unfortunately, no reaction was observed (Scheme 3, [Eq. (1)]). Considering the strong coordination and poisoning ability of 2-toluidine, and the corresponding hydrogenation product,[5,7] an electron-withdrawing *p*-toluenesulfonyl group (Ts) was introduced to decrease this substrate and product inhibition effect. In addition, the electron-withdrawing property of the Ts group could also activate the substrates by decreasing the electron density at the aromatic ring. Therefore, *N*-Ts-protected 2-toluidine was then tested. Disappointedly, no desired product was observed. In consideration of the strong aromaticity of the benzene ring, bicyclic 2-butylquinolin-3-amine, with relatively lower aromatic stabilization, was tested,[7b] however, no reactivity was observed. To our delight, *N*-Ts-protected 2-butylquinolin-3-amine could be smoothly hydrogenated with full conversion. Unfortunately, the diastereoselectivity was relatively poor (5:1; Scheme 3, [Eq. (2)]). Several other protecting

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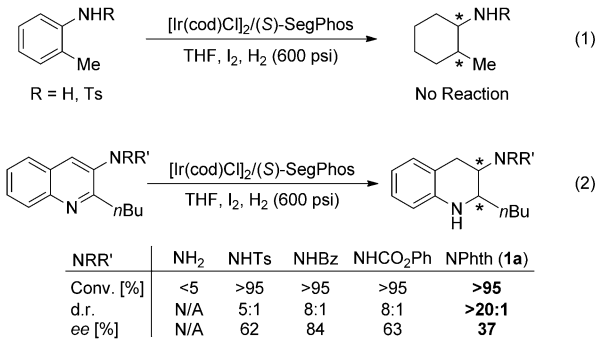
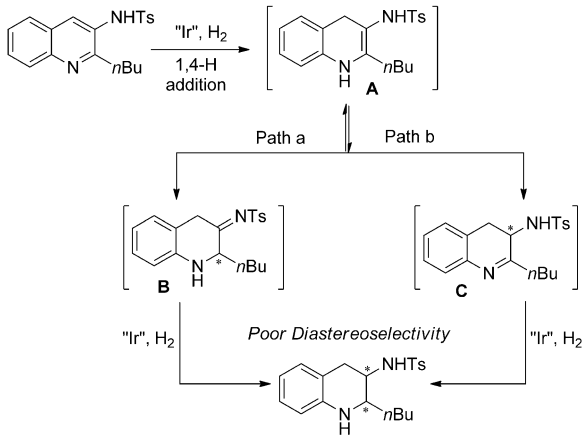


NRR'	NH_2	NHTs	NHBz	$NHCO_2Ph$	NPhth (**1a**)
Conv. [%]	<5	>95	>95	>95	**>95**
d.r.	N/A	5:1	8:1	8:1	**>20:1**
ee [%]	N/A	62	84	63	**37**

Scheme 3. Asymmetric hydrogenation of typical aromatic amines.

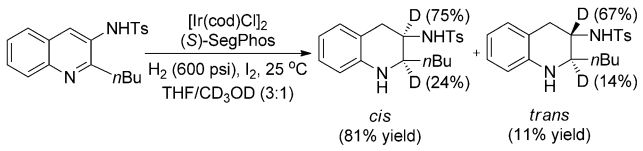
groups, such as benzoyl (Bz) and phenyloxycarbonyl (COOPh), were also surveyed, however, they all failed to give the satisfactory diastereoselectivities.

Considering the mechanism proposed for the hydrogenation of quinolines,[8b,e,g,k,18] we suspected that the poor diastereoselectivity may be attributed to the reasons outlined in Scheme 4. Once partially reduced intermediate **A** is formed there are two possible pathways for further hydrogenation: 1) Isomerization to exocyclic imine **B** (path a); 2) isomerization to



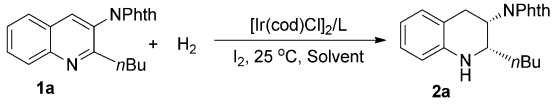
Scheme 4. Possible reasons for the poor diastereoselectivity.

endocyclic imine **C** (path b). In agreement with this assumption, an isotopic labeling experiment using CD_3OD as the deuterium source showed that the deuterium atoms were incorporated at the C2 position with 24% and the C3 position with 75% for the *cis* product. For the *trans* product the deuterium atoms were incorporated at the C2 position with 14% and the C3 position with 67% (Scheme 5). We envisioned that the isomerization to the exocyclic imine (path a) might be impeded if the amino group was doubly protected. Therefore, the phthaloyl group (phth), which is easily introduced, and removed under mild conditions, was employed for further testing. Gratifyingly, *N*-phth-protected 2-(2-butylquinolin-3-yl)isoindoline-1,3-dione (**1a**) could be successfully hydrogenated with full conversion and excellent diastereoselectivity (>20:1; Scheme 3, [Eq. (2)]), a promising 37% *ee* was also obtained.



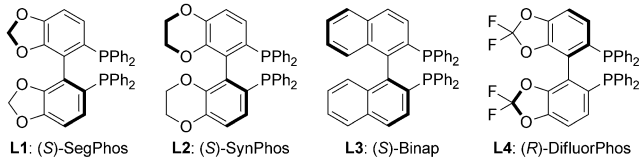
Scheme 5. Isotopic labeling experiment.

Table 1. Evaluation of the reaction parameters.[a]



Entry	Solvent	Ligand	H_2 [psi]	Conversion [%]	*ee* [%][b]
1	THF	**L1**	600	>95	37
2	toluene (T)	**L1**	600	40	67
3	1,4-dioxane	**L1**	600	92	7
4	CH_2Cl_2	**L1**	600	36	22
5	Et_2O	**L1**	600	45	34
6	toluene/THF (1:1)	**L1**	600	>95	77
7	toluene/THF (2:1)	**L1**	600	>95	80
8	toluene/THF (3:1)	**L1**	600	>95	83
9	toluene/THF (3:1)	**L1**	400	>95	85
10	toluene/THF (3:1)	**L1**	200	76	87
11	toluene/THF (3:1)	**L2**	400	45	73
12	toluene/THF (3:1)	**L3**	400	74	35
13	toluene/THF (3:1)	**L4**	400	>95	87[e]
14	toluene/THF (3:1)	**L4**	200	>95	89[e]
15[c]	toluene/THF (3:1)	**L4**	200	>95	93[e]
16[d]	toluene/THF (3:1)	**L4**	200	<5	N/A

[a] Reaction conditions: **1a** (0.1 mmol), $[Ir(cod)Cl]_2$ (2.0 mol%), ligand (4.4 mol%), I_2 (10.0 mol%), solvent (3.0 mL), 25 °C, 18 h. Reaction conversion and d.r. were determined by ^1H NMR spectroscopy. In all cases d.r. > 20:1. [b] Determined by HPLC analysis by using a chiral stationary phase. [c] 5.0 mol% of I_2. [d] Without I_2. [e] The opposite enantiomer was obtained. N/A = not applicable.

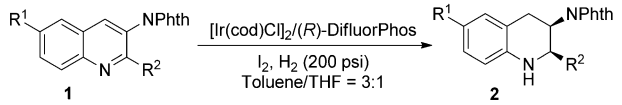


Thus, our further studies moved to explore the asymmetric hydrogenation of **1a** (Table 1). A survey of different reaction mediums indicated that a mixed solvent of toluene and THF with a ratio of 3:1 gave the best result, in terms of both conversion and enantioselectivity (>95% conversion, 83% *ee*; Table 1, entry 8). It is worth noting that excellent diastereoselectivity was achieved regardless of which solvent was used (Table 1, entries 1–8). The pressure effect on the reaction was also investigated. The results showed that a slight improvement of enantioselectivity was achieved at lower hydrogen pressure, but the conversion decreased (Table 1, entries 8–10). Next, various commercially available chiral bisphosphine ligands were evaluated (Table 1, entries 11–13). The electron-deficient (*R*)-DifluorPhos, which was originally developed by Genêt and co-workers in 2004,[19] gave the best enantioselectivity (87% *ee*; Table 1, entry 13). Notably, when the hydrogen

pressure decreased to 200 psi, the *ee* value was improved to 89% without any deterioration of the conversion (Table 1, entry 14), indicating that Ir/(*R*)-DifluorPhos is a more reactive catalyst system than Ir/(*R*)-SegPhos. When half the amount of I_2 was employed (5.0 mol%), a much better enantioselectivity was achieved (93% *ee*; Table 1, entry 15). The effect of iodine as an additive is very important; no reaction was observed in the absence of iodine (Table 1, entry 16). Therefore, the optimal conditions were established as: [{Ir(cod)Cl}$_2$]/(*R*)-Difluorphos, I_2 (5.0 mol%), H_2 (200 psi), toluene/THF (3:1), 25 °C.

With the optimized conditions in hand, we tested the scope of substrates to probe the versatility of our catalytic system, the results are summarized in Table 2. Good enantioselectivities

Table 2. Catalytic asymmetric hydrogenation of aromatic amines **1**.[a]



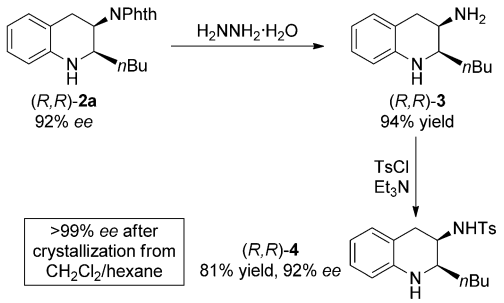
Entry	1	R^1/R^2	*T* [°C]	Yield [%][b]	*ee* [%][c]
1	**1a**	H/*n*Bu	25	99 (**2a**)	93 (*R*,*R*)
2[d]	**1b**	H/Me	70	97 (**2b**)	81 (+)
3	**1c**	H/Et	45	97 (**2c**)	90 (+)
4	**1d**	H/*n*Pr	45	94 (**2d**)	92 (+)
5	**1e**	H/*i*Bu	45	99 (**2e**)	94 (+)
6	**1f**	H/*i*Pentyl	45	97 (**2f**)	88 (+)
7	**1g**	H/*n*Hexyl	25	97 (**2g**)	92 (+)
8	**1h**	H/Phenethyl	25	99 (**2h**)	93 (+)
9	**1i**	H/(*E*)-Styryl[e]	25	97 (**2h**)	90 (+)
10[d]	**1j**	H/Ph	70	97 (**2j**)	40 (+)
11	**1k**	MeO/*n*Bu	45	97 (**2k**)	87 (+)

[a] Reaction conditions: **1** (0.1 mmol), [Ir(cod)Cl]$_2$ (2.0 mol%), (*R*)-DifluorPhos (4.4 mol%), I_2 (5.0 mol%), toluene/THF (3:1, 3.0 mL), 18 h. The d.r. of the products wad determined by ^{1}H NMR spectroscopy. In all cases the d.r. > 20:1. [b] Isolated yield. [c] Determined by HPLC analysis by using a chiral stationary phase. [d] H_2 (40 psi). [e] The conjugated double bond was also hydrogenated.

(81–94%) and excellent yields (94–99%) were obtained for all the substrates bearing an alkyl group at the 2-position of the quinoline motif (Table 2, entries 1–8). For the interesting 2-styryl-substituted derivative **1i**, the conjugated double bond was also hydrogenated and 90% enantioselectivity was observed (Table 2, entry 9). The phenyl-substituted substrate **1j** could also be completely transformed with moderate enantioselectivity (97% yield, 40% *ee*; Table 2, entry 10). The hydrogenation of 6-methoxy-substituted substrate **1k** gave the corresponding product **2k** with 97% yield and 87% *ee* (Table 2, entry 11).

The phthaloyl group could be easily removed by using hydrazine hydrate, without loss of optical purity. The absolute configuration of hydrogenation product **2a** was determined to be *cis*-(*R*,*R*) based on single-crystal X-ray diffraction analysis of its *N*-tosyl derivative **4**, after the protection of **3** with *p*-toluenesulfonyl chloride (Scheme 6).[20]

The key factor in the successful asymmetric hydrogenation of aromatic amines is the introduction of the phthaloyl group,



Scheme 6. Removal of the phthaloyl group and determination of the absolute configuration of **2a**.

which has several advantages: 1) Suppression of the strong coordination and poisoning ability of the substrate, and the corresponding reduced product, towards the catalyst. 2) Activation of the substrate by decreasing the electron density at the aromatic rings. 3) Improving the diastereoselectivity by inhibition of side-reaction pathways. 4) This group can be easily introduced and removed.

In conclusion, we have developed an iridium-catalyzed asymmetric hydrogenation of aromatic quinolin-3-amines, with up to 94% *ee*. This new methodology provides a direct and facile access to a series of valuable chiral exocyclic amines, which are otherwise difficult to attain. Though the substrate scope is limited, the method described herein is the first report on enantioselective hydrogenation of aromatic amines with high enantioselectivity. Further mechanistic studies of the reaction and investigations on the application of the developed strategy are currently ongoing in our laboratory.

Experimental Section

General procedure

In a nitrogen-filled glovebox, a mixture of [Ir(cod)Cl]$_2$ (1.3 mg, 0.002 mmol) and (*R*)-DifluorPhos (3.0 mg, 0.0044 mmol) in toluene/THF (3:1, 1.0 mL) was stirred at room temperature for 10 min, then substrate **1** (0.10 mmol) and I_2 (1.3 mg, 0.005 mmol), together with the solvent (2.0 mL) were added to the reaction mixture. The hydrogenation was performed under H_2 (200 psi) in a stainless-steel autoclave at the specified temperature for 18 h. After carefully releasing the hydrogen, purification was performed by silica gel column chromatography, eluted with hexane/EtOAc, to give the desired product. The enantiomeric excesses were determined by chiral HPLC analysis.

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Keywords: aromatic amines · asymmetric hydrogenation · chirality · exocyclic amines

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[20] CCDC-962689 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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