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A dicationic nickel complex-catalyzed asymmetric synthesis of chiral benzylic amines: Evolution from reductive amination to borrowing hydrogen reaction

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ABSTRACT

Chiral benzylic amines are important motifs in medicines. A dicationic nickel complex of chiral diphosphine (*R*)-Ph-BPE promotes highly enantioselective reductive amination of aryl alkyl ketones with arylamines using isopropanol as hydrogen source. The reaction is easily scaled up in a gram-scale synthesis using 1 mol% nickel catalyst and it is applied to an asymmetric synthesis of (*S*)-rivastigmine. Building on this success, we achieved rare examples of asymmetric hydrogen borrowing reactions with *arylamines* using an Earth-abundant 3d metal, nickel.

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Chiral alkylamines are important motifs present in about 40 % of therapeutical agents (Fig. 1). Among common methods to prepare chiral amines [1–3], transition metal-catalyzed asymmetric (transfer) hydrogenation of ketimines and enamides using hydrogen gas is well developed [4–16]. In asymmetric transfer hydrogenation, formic acid, alcohols or other organic hydrogen donors are used instead. To date, most of these reactions rely on chiral complexes of noble transition metals rhodium [17–24], iridium [25–40], ruthenium [41–43] and palladium [44–47]. In the past decade, Earth-abundant, cheap 3d metal catalysts have emerged that catalyzed these processes [48,49], including the examples of iron [50–56], cobalt [57–66], manganese [67–71] and nickel [72–82].

Metal-catalyzed enantioselective reductive amination [83–90] offers several advantages over (transfer) hydrogenation (Fig. 1). It directly coverts ketones and amines to enantio-enriched amines [91–102], which bypasses the need of isolating and purifying ketimines, some of which are unstable during purification or storage.

Most of reported methods for asymmetric reductive amination used chiral complexes of noble metals, for example, ruthenium [103,104] and iridium [105]. The application of Earth-abundant 3d metal catalysts in this family of reactions still remains nascent, and examples of iron [106,107], cobalt [108], manganese [109], and nickel [110–112] only emerged recently. Since 2014, our group has contributed the development of nickel-catalyzed asymmetric transfer hydrogenation [113–115], reductive amination of ketones that used formic acid [111] and alcohols [116] as the hydrogen source (Fig. 2).

Metal-catalyzed asymmetric borrowing hydrogen reactions directly convert racemic alcohols to structurally diverse chiral amines without using any external hydrogen donor [117–121]. To date, most of catalytic enantioselective examples relied on highly active iridium and ruthenium catalysts, often working in concert with chiral phosphoric acids that play important roles of activating and conformationally controlling the *in situ* formed ketimines. For example, Yu *et al.* have successfully applied the cooperative catalysis in asymmetric synthesis of chiral benzylic amines, β-branched aliphatic amines and a series of azacycles, using a combination of (chiral) cyclopentadienyl complexes of iridium and chiral bulky phosphoric acids [122–134]. In other reports of Zhao [135] and Beller [136], ruthenium complexes of chiral diphosphines promoted enantioselective conversions of racemic 1,2-diols to special types of chiral amines, 1,2-aminoalcohols and oxazolidine-2-ones in good *ee* values.

In comparison, few asymmetric examples using chiral 3d metal complexes have been reported, however [137–139]. In 2017, we reported examples of nickel-catalyzed hydrogen borrowing reactions of racemic benzylic alcohols and a special type of *N*-acylhydrazines [112]. Catalytic dehydrogenation of alcohols occurred *in situ* and

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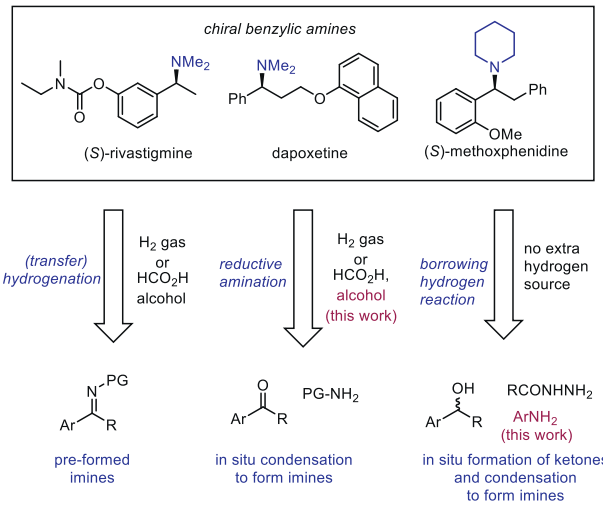


Fig. 1. Examples of chiral amine drugs and asymmetric methods of (transfer) hydrogenation, reductive amination and borrow hydrogen reactions. This reactions in this work using dicationic nickel catalyst are highlighted.

condensation of ketones and *N*-acylhydrazines readily formed stable *N*-acylhydrazones, the latter being substrates for asymmetric NiH insertion. However, an analogous reaction with *arylamines* resulted in 50 % yield and <30 % *ee* at 120 °C. The high temperature was detrimental to the effect to achieving high stereoselectivity (conditions: 1-phenylethanol, 4-anisylamine, 5 mol% $Ni(OTf)_2$ and (*R*)-Ph-BPE, and 3 Å MS or acetic acid in *t*-amyl alcohol 120 °C for 24 h).

In this work, we report two catalytic processes of asymmetric synthesis of chiral benzylic amines, using a dicationic nickel complex of chiral diphosphine (*R*)-Ph-BPE: (a) enantioselective reductive amination of aryl alkyl ketones and arylamines that uses isopropanol as hydrogen source; (b) nickel-catalyzed asymmetric borrowing hydrogen reaction with *arylamines* for the first time.

To address the inefficient condensation of ketones and arylamines, we elected to titanium alkoxides as strong dehydrating agents and they are also compatible with the chiral cationic nickel catalyst. This desiccant enabled us to perform the entire (de)hydrogenation cycle and achieve high levels of enantioselectivity at relatively moderate temperatures. Notably, the dicationic nickel complex itself was inefficient to promote the condensation *in situ*, as a metal-based Lewis acid.

In a study of a model reaction of acetophenone **1a** and anisidine **2a** we found that nickel triflate and nickel bistriflimide [$Ni(NTf_2)_2$] formed very active catalyst with (*R*)-Ph-BPE [140,141], giving benzylic amine **3a** in >90 % yield and 90 % *ee,* respectively (Table 1, entries 1 and 2). The nickel loading can be reduced and 2 and 1 mol% nickel triflate and (*R*)-Ph-BPE gave product **3a** in 84 % and 75 % yields, respectively (entries 3 and 4). However, the complexes of nickel bromide and acetate were catalytically inactive at all. Thus, we suggest that nickel complexes of triflate and triflimide produced a *cationic* nickel hydride complex *in situ* which is the active species for transfer hydrogenation. Other strongly donating diphosphines Duphos, QuinoxP* and BenzP* and Josiphos formed nickel complexes with $Ni(OTf)_2$ that gave products in 16 %–60 % *ee* values or no product at all.

$Ti(OiPr)_4$ proved to be critical to promoting *in situ* formation of imine **3a'** from the ketone and arylamine, without which product **3a** was generated only 16 % yield (Table 1, entry 5). Interesting the product was also firmed in an identical 90 % *ee*, suggesting that $Ti(OiPr)_4$ is not directly involved in a Lewis-acidic activation of imines in the stereo-determining step of hydride insertion. Isopropanol was the best solvent. In other solvents such as MeOH, EtOH, CF_3CH_2OH and toluene, the yield was only 44 %-66 % (entries 6–9). Under some conditions, some acetophenone was reduced to α-phenylethanol **1a'**, whiles *N*-isopropylaniline **2a'** was formed in significant amounts.

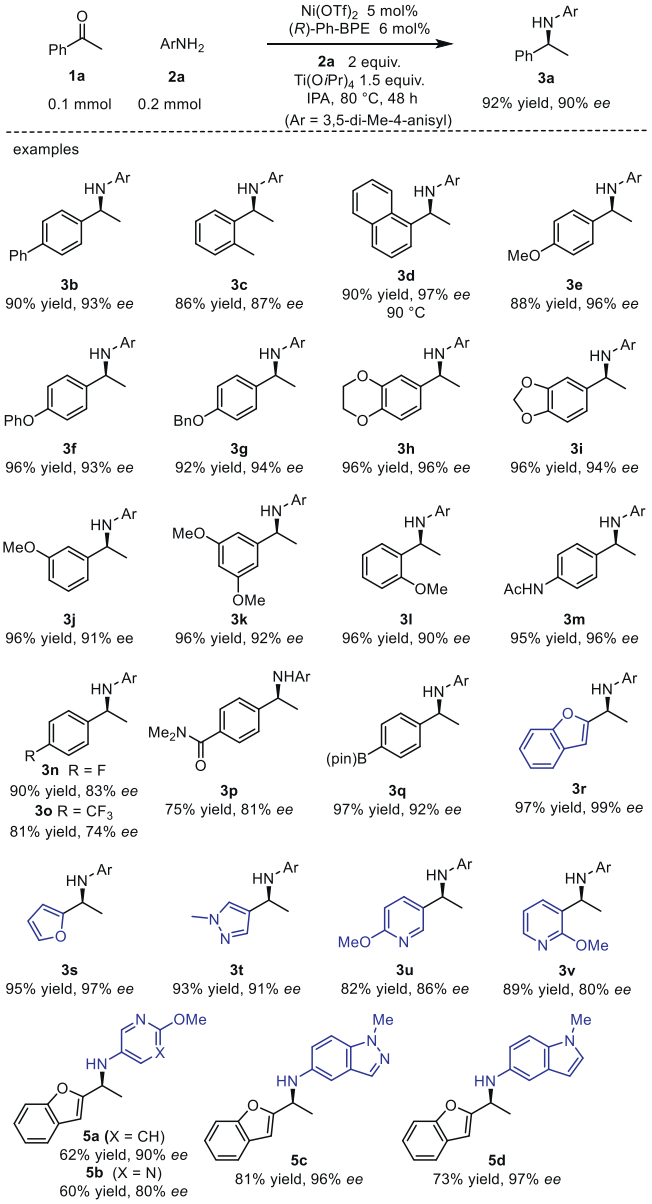
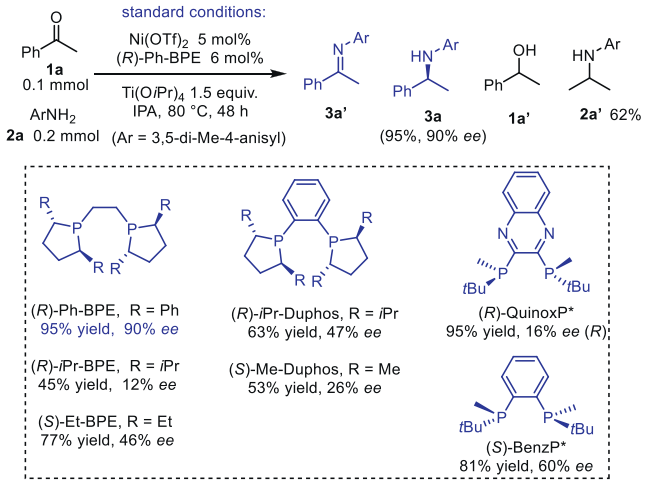


Fig. 2. One-pot asymmetric reductive amination of methyl (hetero)aryl ketones with anisidine **2a** (isolated yields on 0.1 mmol scale).

With one-pot procedure for reductive amination in hand, we studied the scope of aryl ketones with 3,5-dimethylanisidine **2a** (Fig. 2). An array of aryl methyl ketones reacted efficiently with 90 %-97 % *ee* in most examples. The ketones can have electron-donating and electron-withdrawing groups on aryl rings (**3e-3q**), *o*-tolyl, *o*-anisyl and a 1-naphthyl ring (**3c**, **3d** and **3l**), The reaction was tolerant of *N*-aryl acetamide and aryl pinacolborate (**3m**, **3q**). Notably, the ketones can also have heteroaryl rings such as (benzo)furan, pyrazole and 2-methoxypyridine. They reacted smoothly to give products in excellent yields and 80 %-99 % *ee* (**3r-3v**). However, 3-acetylpyridine cannot condense with anisidine **2a** even under forcing conditions that used dehydrating agents $Ti(OiPr)_4$, $Ti(OtBu)_4$ or molecular sieve in toluene at 140 °C.

Table 1
Screening of reaction conditions and chiral diphosphines in a model reductive amination of acetophenone **1a** (0.1 mmol) and 3,5-dimethyl-4-anisidine **2a** (0.2 mmol) in isopropanol (0.2 mL).



Entry	Conditions	Conv. **1a** (%)	**3a'** (%)	**3a** (%)	*ee* (%)	**1a'** (%)	**2a'** (%)
1	$Ni(OTf)_2$ 5%	97	0	95	90	0	62
2	$Ni(NTf_2)_2$ 5%	96	0	92	90	0	64
3	$Ni(OTf)_2$ 2%	88	9	84	90	0	37
4	$Ni(OTf)_2$ 1%	77	19	75	90	0	20
5	no $Ti(OiPr)_4$	91	0	16	90	48	105
6	MeOH	90	0	66	89	21	100
7	EtOH	100	0	44	88	36	46
8	CF_3CH_2OH	88	14	60	90	3	4
9	Toluene	75	4	43	81	6	73

Next, we explored the scope of (hetero)arylamines with 2-benzofuranyl ketone **4a** (Fig. 2). Both electron-rich aryl amines and electron-deficient anilines condensed well with the ketone and gave benzylic amines in high yields and >95% *ee* (Supporting information). Nitrogen-containing heteroaryl amines such as 2-methoxypyridine, 2-methoxypyrimidine, 1-methylind-2-azole, and indole (**5a-5d**), also provided products in excellent *ee*. We also tested benzylamine and α,α-dimethylbenzylamine as models of aliphatic amines in the reductive amination. They condensed well with acetophenone in the presence of $Ti(OiPr)_4$ to give keimines (as detected by GC and GCMS), but the latter failed to undergo reduction to produce benzylic amines.

Aryl ketones having ethyl, *n*-propyl, *n*-butyl and other alkyl chains also underwent reductive amination with anisidine **2a** (Fig. 3). To improve the efficiency of the condensation of ketimines, the reaction of ketones, anisidine **2a** and $Ti(OiPr)_4$ were heated in IPA at 80 °C for 10 h (incomplete condensation as checked by GC). Then, $Ni(OTf)_2$/(*R*)-Ph-BPE catalyst was added to initiate hydrogen transfer from isopropanol to benzyl/alkyl aryl ketones. The products were thus obtained in good yields and 82%-97% *ee* (**7a-i**).

We have scaled up a reductive amination using 5 mmol of 3-methoxyacetophenone and anisidine **2a** that gave 1.14 g of benzyl amine **3j** in 81% yield and 91% *ee* (Fig. 4a). We also applied the one-pot protocol to conduct reductive amination of aryl ketone **8a** to produce benzylic amine **8b** in 94% yield and 88% *ee* (Fig. 4b). The *N*-anisyl group of **8b** was readily removed by cerium ammonium nitrate (CAN) and subsequent *N,N*-dimethylation gave (*S*)-rivastigmine **8d**, a drug that is used for the treatment of dementia caused by Alzheimer disease.

Moreover, the procedure using $Ti(OiPr)_4$ was successfully applied to reductive amination of *N*-benzoylhydrazine, another type of common amines. The nickel catalyst of a Josiphos CyPF-Cy was used to improve the stereoselectivity of *N*-acyl hydrazine **9a** to 86% *ee* (Eq. 1). The N−N bond in the product can be reductively cleaved by Raney nickel or SmI_2 [142].

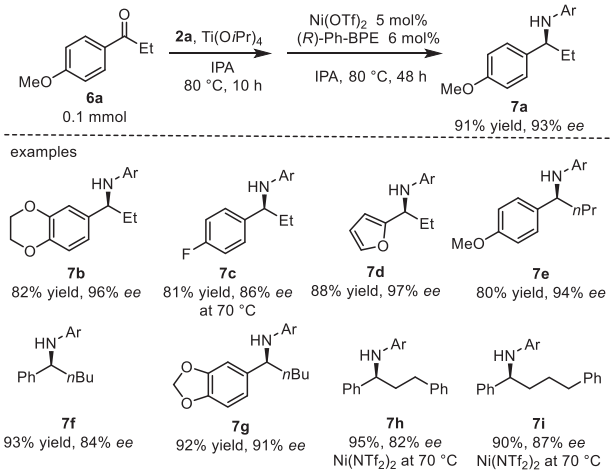


Fig. 3. Two-stage asymmetric reductive amination of benzyl/alkyl aryl ketones with anisidine **2a** (isolated yields on 0.1 mmol scale). Ar = 3,5-dimethylanisyl.

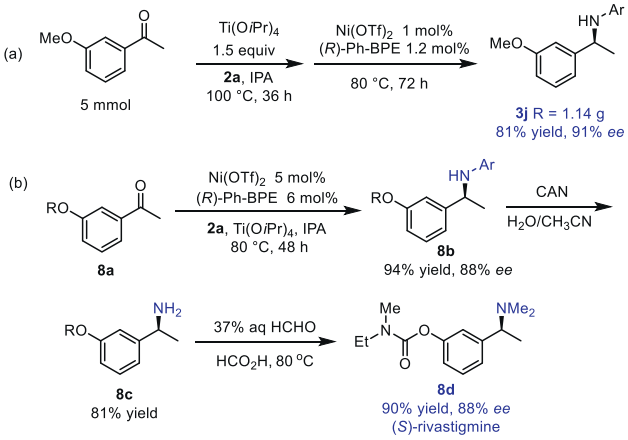
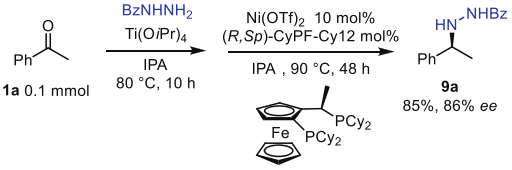


Fig. 4. (a) A scale-up reductive amination using 5 mmol of ketone. (b) Asymmetric synthesis of (*S*)-rivastigmine *via* nickel-catalyzed reductive amination. Ar = 3,5-dimethylanisyl and R = CONMeEt.

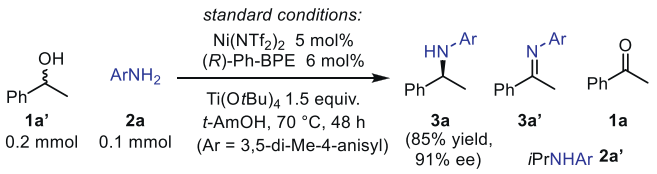


(1)

Next, we aimed to develop a nickel-catalyzed asymmetric borrowing hydrogen reaction, by using a model reaction of racemic 1-phenylethanol **1a'** and 3,5-dimethylanisidine **2a**. We added $Ti(OtBu)_4$ in dry *t*-amyl alcohol to promote the condensation of *in situ* formed acetophenone and arylamine **2a**. Under the optimized conditions, benzylic amine **3a** was isolated in 85% yield and 91% *ee*.

During condition optimization, we have identifieds and combined several key parameters to ensure good yields and excellent *ee* (Table 2): (a) addition of $Ti(OtBu)_4$ improved the yield of **3a** from <60% to 85% (entry 1). (b) Using $Ti(OiPr)_4$ (entry 2) or isopropanol solvent led to no formation of **3a** and a significant amount of *N*-isopropylaniline **2a'**. **2a'** was produced *via* the following reaction sequence: *In situ* dehydrogenation of isopropoxide to form acetone; acetone condensation with amine **2a** to form

Table 2
Optimization of reaction conditions in a model borrowing hydrogen reaction of racemic α-phenylethanol **1a'** (0.2 mmol), 3,5-dimethylanisidine **2a** (0.1 mmol) and $Ti(OtBu)_4$ (0.15 mmol) in *t*-amyl alcohol (0.1 mL).



Entry	Changes of conditions	Conv. **2a** (%)	**3a** (%)	*ee* (%)	**3a'** (%)	**1a** (%)	**2a'** (%)
1	no $Ti(OtBu)_4$	66	58	92	0	7	0
2	$Ti(OiPr)_4$	88	0	–	0	21	74
3	CF_3CH_2OH	100	71	85	0	16	0
4	*t*BuOH	90	64	92	2	6	0
5	*t*AmOH	89	85	91	1	4	0
6	Toluene	100	94	88	2	7	0
7	$Ni(OTf)_2$	46	31	90	3	6	0

the ketimine; finally, NiH reduction of the ketimine. Therefore, the formation of **2a'** was much faster than that of **3a** from 1-phenylethanol. (c) The model reaction was high-yielding in *t*-amyl alcohol or toluene (entries 3–6). (d) $Ni(NTf_2)_2$, having a higher solubility in IPA than $Ni(OTf)_2$, formed a more efficient catalyst of Ph-BPE than $Ni(OTf)_2$ (31 % yield in entry 7). We found that the stereoselectivity of the borrowing hydrogen reaction is quite sensitive to temperatures. For example, the reactions at 70 °C and 80 °C produced 91 % *ee* and 80 % *ee*, respectively.

With this optimized condition in hand, we have explored the scope of asymmetric borrowing hydrogen reaction using (hetero)aryl carbinols and anisidine **2a** shown in Fig. 5. Both electron-rich and electron-deficient aryl rings can be present on the alcohols. Notably, an array of heteroaryl rings including benzofuran, (benzo)thiophenes and in particular, substituted pyridine gave products **3r** and **3u-3w** in 83 %-99 % *ee*. Moreover, aryl carbinols having α-alkyl or α-benzyl groups reacted well to give products (**7h-7k**) in excellent yields and 81 %-87 % *ee*. In these examples, the condensation to form ketimines was more efficient in toluene than in *t*-amyl alcohol.

With regard to the scope of arylamines, we have tested some simple arylamines having electron-donating and electron-withdrawing substituents in reactions of racemic alcohol **4a**. The results are shown in Fig. 6. The stereoselectivity in most reactions was temperature-sensitive. For example, the reaction of 4-tolylamine gave product **5e** in 89 % *ee* at 70 °C and 81 % *ee* at 80 °C, respectively. Moreover, *para*-substituents on the arylamines also affect the *ee*s, for example, a methoxy group increases the *ee* (**5f**), whereas a fluorine substituent decreases it (**5g**). Di- or tri-substituents at 3,4-positions of arylamines are beneficial to the yields and selectivity (**5h-j**), but *ortho*-substituents are deleterious partly due to low efficiency of condensation to form imines. A benzofuran-derived heteroaryl amine reacted to give product **5k** in 95 % *ee* at 80 °C. Unfortunately, benzylamine or α,α-dimethylbenzylamine failed to produce the corresponding ketimines or benzylic imines under the hydrogen borrowing conditions.

We have attempted to probe nickel hydride species relevant to the catalytic reactions. Stirring a mixture of $Ni(OTf)_2$ and (*S*,*S*)-Ph-BPE (L) (in 1:1 or 1:2 molar ratios) in isopropanol at rt for 30 min produced cleanly a cationic complex $[(L)_2NiH]^+OTf^-$ (HRMS (*m*/*z*): 1071.4010 *versus* calculated 1071.4011 [72,143]. We believe that it reversibly dissociates one ligand *in situ* to produce monoligated complex $(L)NiH^+$ as the catalytic active species. The complex completely decomposed after heating at 80 °C for 1 h. Thus, we suggest

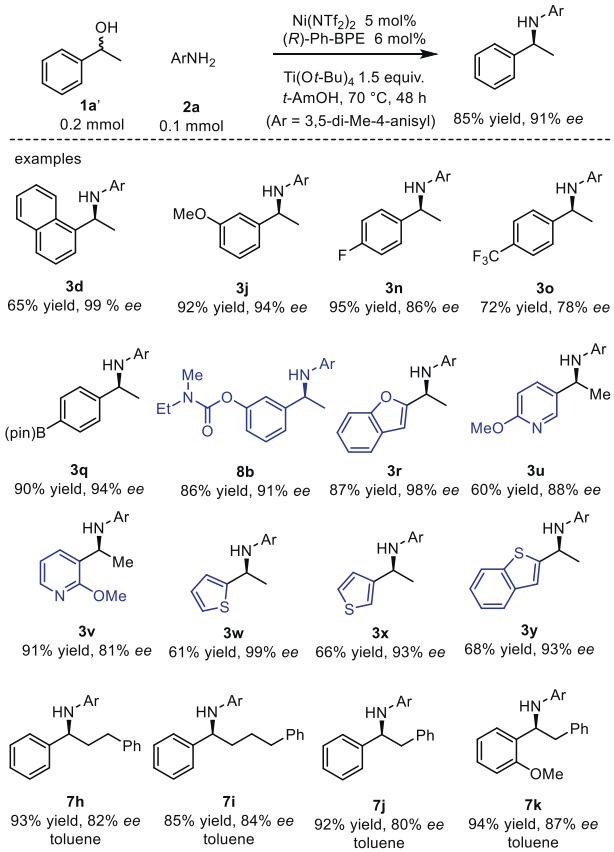


Fig. 5. Nickel-catalyzed asymmetric borrowing hydrogen reactions of benzylic alcohols and anisidine **2a** (isolated yields on 0.1 mmol scale).

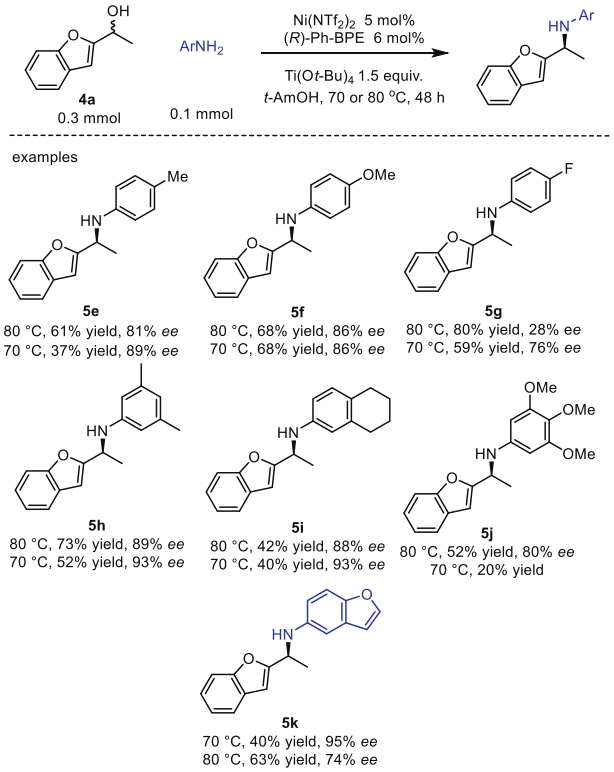


Fig. 6. Scope of arylamines in nickel-catalyzed borrowing hydrogen reactions (isolated yields on 0.1 mmol scale).

that the observed counteranion effect of nickel salts (entry 7 of Table 2) is associated with the rate of forming complex $[(L)_2NiH]^+$ or relative stability of active catalyst $(L)NiH^+$ at elevated reaction temperature.

In conclusion, we report a dicationic chiral nickel catalyst ligated with a strongly donating diphosphine, Ph-BPE for asymmetric synthesis of medicinally important benzylic amines in high levels of *ee*. The reductive amination of various alkyl aryl ketones with arylamines proceeded in high ees using isopropanol solvent as a green external hydrogen source [144–146]. The conditions are scalable and tolerant of sensitive polar groups and an array of heteroaryl rings. The key to the success is the use of titanium alkoxides as very efficient dehydrating agents that promoted fast aldimine condensation from ketones and arylamines, and at the same time, they are compatible with the dicationic nickel catalyst.

In 2017, we reported a nickel-catalyzed enantioselective hydrogen borrowing reaction of a special type of amines, *N*-acylhydrazines, proceeding *via* the intermediacy of *N*-acylhydrazones which are stable and readily formed [112]. Here, we report the first examples of highly enantioselective borrowing hydrogen reactions with arylamines which are promoted by an Earth-abundant metal, nickel.

CRediT authorship contribution statement

Xiuhua Wang: Methodology, Investigation, Formal analysis, Data curation. **Jianrong Steve Zhou:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition, Conceptualization.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2025.111148.

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