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Iridium-Catalyzed Transfer Hydrogenation of 1,10-Phenanthrolines using Formic Acid as the Hydrogen Source

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Abstract: The iridium-catalyzed highly regioselective transfer hydrogenation of a variety of 2-substituted and 2,9-disubstituted 1,10-phenanthrolines under mild conditions with formic acid as the hydrogen source is described. In the presence of a catalytic amount of the iridium complex $[Cp^*IrCl_2]_2$, the transfer hydrogenation proceeded smoothly in 1,4-dioxane under ligand-free conditions, exclusively leading to a range of 1,2,3,4-tetrahydro-1,10-phenanthroline products in high yields. The catalyst generated *in situ* from $[Cp^*IrCl_2]_2$ and (*R*,*R*)-$(CF_3)_2C_6H_3SO_2$-dpen [*N*-(2-amino-1,2-diphenylethyl)-3,5-bis(trifluoromethyl)benzenesulfonamide] could efficiently catalyze the asymmetric transfer hydrogenation of these 1,10-phenanthrolines in isopropyl alcohol (*i*-PrOH) to afford chiral 1,2,3,4-tetrahydro-1,10-phenanthrolines in high yields with up to >99% *ee*. The key to the success of the reduction is the choice of solvent and hydrogen source.

Keywords: iridium; 1,10-phenanthrolines; reduction; 1,2,3,4-tetrahydro-1,10-phenanthrolines; transfer hydrogenation

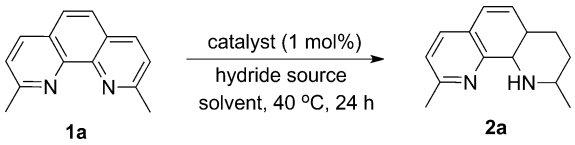
Transition metal-catalyzed transfer hydrogenation reactions employing a hydrogen donor other than molecular hydrogen have become a powerful rival to the hydrogenation reaction because of their versatility, operational simplicity and safety.[1] The past two decades have witnessed considerable progress in the transfer hydrogenation of carbonyl compounds and imines, and the catalytic systems based on ruthenium, rhodium and iridium complexes are notable for their remarkable catalytic performance.[1c–m,2] Meanwhile, the transition metal-catalyzed transfer hydrogenation of N-heteroarenes has drawn the attention of synthetic chemists, and a variety of N-heteroaryl compounds, such as quinolines, quinoxalines, isoquinolines, indoles, pyridines and pyrazines have been successfully reduced with high selectivities by using isopropyl alcohol or formate as the hydrogen source in the presence of an Ru, Rh or Ir catalyst.[3] It is noteworthy that Xiao and his co-workers found that the transfer hydrogenation of N-heteroarenes including asymmetric reduction of quinolines could be smoothly performed in water without calling for organic solvents and ligand modification.[3i,k–m] However, despite these exciting advances, there is still much room for improvement, particularly in terms of N-heteroaryl substrate scope and catalytic efficiency.

Unlike 1,10-phenanthroline and its derivatives, which have been extensively studied as one of the most versatile bidentate ligands in organometallic chemistry and catalysis,[4] the partially reduced 1,2,3,4-tetrahydro- and 1,2,3,4,7,8,9,10-octahydro-1,10-phenanthrolines have attracted much less interest despite the fact that they can serve as important ligands for olefin polymerization,[5] as valuable synthetic intermediates to prepare chiral materials,[6] as antagonists with potent activity against HIV-1[7] and as vicinal diamine and N-heterocyclic carbene ligands.[8] As a direct consequence, the construction of these compounds is largely underexplored. Traditional methods for the preparation of 1,2,3,4-tetrahydro- and 1,2,3,4,7,8,9,10-octahydro-1,10-phenanthrolines primarily rely on reduction with stoichiometric or excess amounts of reducing agent[8b,9] and transition metal-catalyzed heterogeneous hydrogenation.[10] The substituted phenanthrolines could also be reduced using a Hantzsch dihydropyridine under the catalysis of BINOL-derived phosphoric acid (BINOL: 1,1′-binaphthol).[11] Based on a cyclometallated Ir(III) catalyst, Xiao and co-workers reported the partial hydrogenation of 2,9-dimethyl-1,10-phenanthroline to give the 1,2,3,4-tetrahydro-1,10-phenanthroline product under mild conditions.[12] Notably, Fan and co-workers found that 2-substituted and 2,9-disubstituted 1,10-

phenanthroline derivatives could undergo efficient asymmetric hydrogenation catalyzed by a cationic ruthenium complex, providing 1,2,3,4-tetrahydro- and 1,2,3,4,7,8,9,10-octahydro-1,10-phenanthroline products in high yields and selectivities.[13] In consideration of the limitations of these known protocols and the appeal of transition metal-catalyzed transfer hydrogenation, it appears very attractive to develop efficient catalytic systems for the transfer hydrogenation of 1,10-phenanthrolines.[14] Following our continuing interest in reducing N-heteroarenes,[15] herein we report that $[Cp^*IrCl_2]_2$ could efficiently catalyze the transfer hydrogenation of 2- and 2,9-substituted 1,10-phenanthroline derivatives with HCO_2H as the hydrogen source in 1,4-dioxane under ligand-free conditions to give 1,2,3,4-tetrahydro-1,10-phenanthroline products in high yields, and the combination of $[Cp^*IrCl_2]_2$ with chiral $(CF_3)_2C_6H_3SO_2$-dpen constitutes an efficient catalytic system for the asymmetric transfer reduction of 1,10-phenanthroline derivatives to give chiral 1,2,3,4-tetrahydro-1,10-phenanthroline products in up to >99% *ee*.

We initiated our investigation with the screening of the reaction conditions for transfer hydrogenation of 2,9-dimethyl-1,10-phenanthroline (**1a**) in the presence of a transition metal catalyst derived from a half-sandwich complex (Rh, Ir or Ru). Considering the substantial advantage of using water as the reaction medium,[16] we first tried the reduction of **1a** in water with HCO_2H as the hydrogen source under the catalysis of $[Cp^*IrCl_2]_2$. After 24 h, the reaction afforded the partial hydrogenation product, 2,9-dimethyl-1,2,3,4-tetrahydro-1,10-phenanthroline (**2a**) in 87% isolated yield, and no double reduced product was detected (Table 1, entry 1). Encouraged by this result, we then screened other solvents, such as MeOH, EtOH, *i*-PrOH, TFE (trifluoroethyl alcohol), THF (tetrahydrofuran), CH_2Cl_2, toluene, DMSO (dimethyl sulfoxide), CH_3CN, DMF (*N*,*N*-dimethylformamide) and 1,4-dioxane. Among these solvents, 1,4-dioxane afforded the best result, and **2a** was isolated in 96% yield (Table 1, entries 2–12). Realizing that the choice of hydrogen source may affect the transformation efficiency, we then examined the performance other hydrogen sources. Indeed, no reduction was observed using HCO_2Na or HCO_2Li as the hydrogen source (Table 1, entries 13 and 14). With the frequently employed azeotropic HCO_2H/NEt_3 (5/2) mixture as the hydrogen source, the reaction occurred, but a significantly diminished yield was obtained (Table 1, entry 15). Obviously, the reduction favors the strong acidic conditions, and **1a** is probably reduced through an ionic mechanism in its protonated form. A similar substrate activation strategy is well known among transition metal-catalyzed reduction reactions.[17] Further optimization indicated that carrying out the reduction at room temperature decreased the yield of isolated **2a** to 82% (Table 1, entry 16). We also investigated the catalytic performance of other half-sandwich complexes, but they were inferior to $[Cp^*IrCl_2]_2$ (Table 1, entries 17–19). In the absence of the catalyst precursor, no reaction took place (Table 1, entry 20).

Table 1. Screening conditions for catalytic transfer hydrogenation of **1a**.[a]



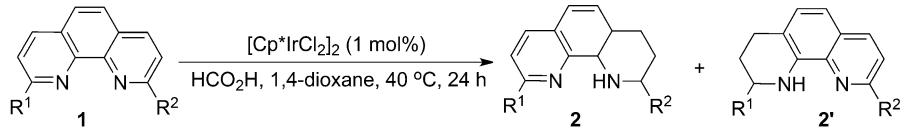
1a **2a**

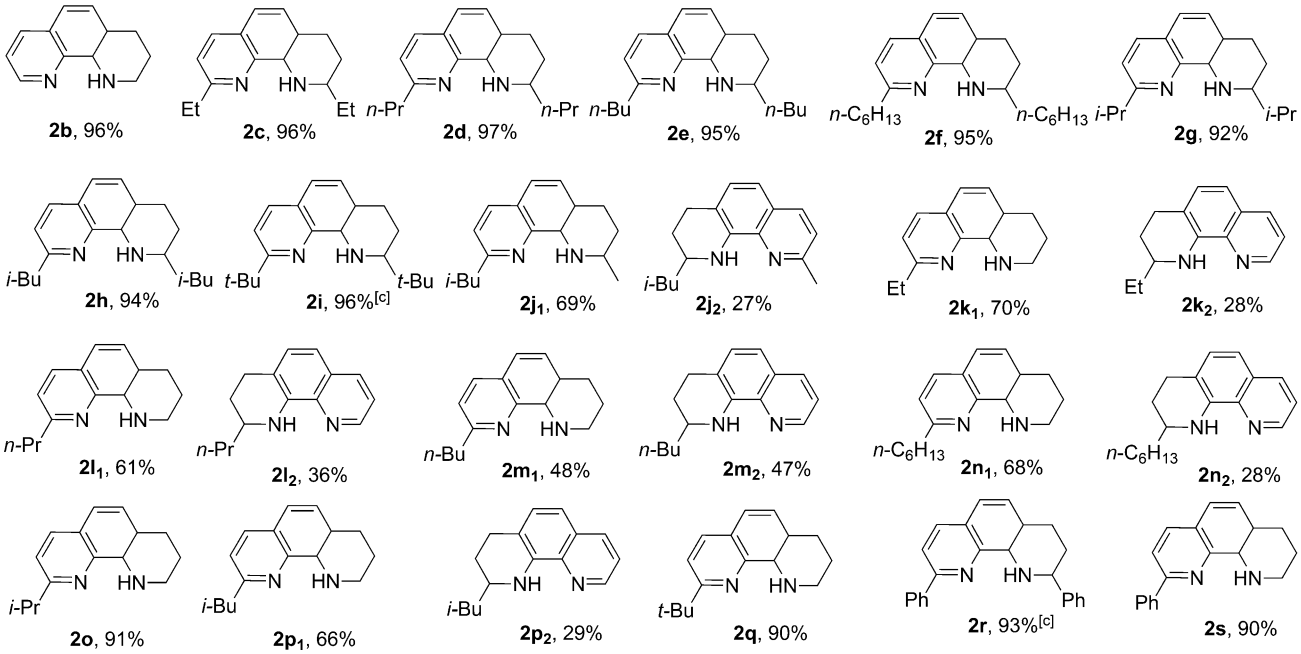
Entry	Catalyst precursor	Hydrogen source	Solvent	Yield [%][b]
1	$[Cp^*IrCl_2]_2$	HCO_2H	H_2O	87
2	$[Cp^*IrCl_2]_2$	HCO_2H	MeOH	25
3	$[Cp^*IrCl_2]_2$	HCO_2H	EtOH	33
4	$[Cp^*IrCl_2]_2$	HCO_2H	*i*-PrOH	50
5	$[Cp^*IrCl_2]_2$	HCO_2H	TFE	NR
6	$[Cp^*IrCl_2]_2$	HCO_2H	THF	68
7	$[Cp^*IrCl_2]_2$	HCO_2H	CH_2Cl_2	trace
8	$[Cp^*IrCl_2]_2$	HCO_2H	toluene	12
9	$[Cp^*IrCl_2]_2$	HCO_2H	DMSO	trace
10	$[Cp^*IrCl_2]_2$	HCO_2H	CH_3CN	39
11	$[Cp^*IrCl_2]_2$	HCO_2H	DMF	57
12	**$[Cp^*IrCl_2]_2$**	**HCO_2H**	**1,4-dioxane**	**96**
13	$[Cp^*IrCl_2]_2$	HCO_2Na	1,4-dioxane	NR
14	$[Cp^*IrCl_2]_2$	HCO_2Li	1,4-dioxane	NR
15	$[Cp^*IrCl_2]_2$	HCO_2H/NEt_3 (5/2)	1,4-dioxane	34
16[c]	$[Cp^*IrCl_2]_2$	HCO_2H	1,4-dioxane	82
17	$[Cp^*RhCl_2]_2$	HCO_2H	1,4-dioxane	NR
18[d]	[Ru]	HCO_2H	1,4-dioxane	NR
19[e]	[Ru]	HCO_2H	1,4-dioxane	NR
20	none	HCO_2H	1,4-dioxane	NR

[a] *Reaction conditions:* **1a** (0.2 mmol), catalyst precursor (1 mol%), hydrogen source (1.6 mmol), solvent (2.0 mL), 40 °C, 24 h. NR = no reaction.
[b] Isolated yield.
[c] Room temperature.
[d] $[Ru(p\text{-cymene})_2Cl_2]_2$ was employed.
[e] $[Ru(benzene)_2Cl_2]_2$ was employed.

With the optimized reaction conditions in hand, we then investigated the generality of this reduction reaction. As shown in Table 2, the simple 1,10-phenanthroline (**1b**) and symmetrical 2,9-dialkylated 1,10-phenanthrolines (**1c–f**) proceeded smoothly to generate the partially hydrogenated products (**2b–f**) in excellent yields, suggesting that the reaction was insensitive to the length of the side chain. It was observed that the symmetrical 1,10-phenanthrolines with bulky substituents at the 2- and 9-positions (**1g** and **1h**) participated well in this reaction, and the corresponding products (**2g** and **2h**) were isolated in 92% and 94% yields, respectively. The more bulky 2,9-di-*tert*-butyl-1,10-phenanthroline (**1i**) was also reduced, although a higher catalyst loading (2 mol%) was required. The

Table 2. Ir-catalyzed transfer hydrogenation of 1,10-phenanthrolines.[a,b]





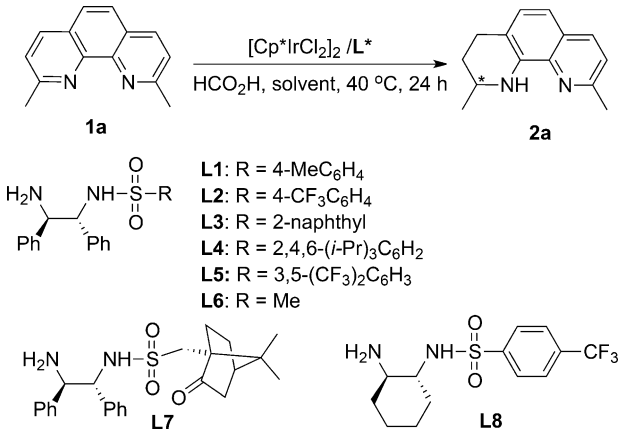
[a] *Reaction conditions:* **1** (0.2 mmol), $[Cp^*IrCl_2]_2$ (1 mol%), HCO_2H (1.6 mmol), 1,4-dioxane (2.0 mL), 40 °C, 24 h.
[b] Isolated yield.
[c] $[Cp^*IrCl_2]_2$ (2 mol%) was employed.

unsymmetrical 2,9-dialkylated 1,10-phenanthroline **1j** underwent selective reduction, delivering a mixture of regioisomeric products $\mathbf{2j_1}$ and $\mathbf{2j_2}$ with the former as the major product due to steric hinderance. Likewise, the 2-alkylated 1,10-phenanthrolines (**1k**–**1n**, **1p**) gave regioisomeric products ($\mathbf{2k_1}$, $\mathbf{2k_2}$, $\mathbf{2m_1}$, $\mathbf{2m_2}$, $\mathbf{2n_1}$, $\mathbf{2n_2}$, $\mathbf{2p_1}$, $\mathbf{2p_2}$) with low regioselectivities. Interestingly, 2-isopropyl-1,10-phenanthroline (**1o**) and 2-(*tert*-butyl)-1,10-phenanthroline (**1q**) could readily engage in the reduction, exclusively affording **2o** and **2q** in 91% and 90% yields, respectively, as a result of the strong steric hinderance. However, 2,9-diphenyl-1,2,3,4-tetrahydro-1,10-phenanthroline (**1r**) was less reactive, requiring a higher catalyst loading (2 mol%) to reach a high isolated yield of the reduction product **2r**. In contrast, 2-phenyl-1,10-phenanthroline (**1s**) showed good reactivity to provide the reduction product **2s** in 90% yield, and the reduction took place exclusively at the unsubstituted pyridyl ring. It should be noted that only one pyridyl ring was reduced in all cases studied, and full reduction of the two pyridyl rings was not observed.

We also examined the transfer hydrogenation of quinoline (**1t**), quinaldine (**1u**), isoquinoline (**1v**) and 4,7-phenanthroline (**1w**) under the current catalytic conditions. Transfer reduction of **1u** and **1w** led to the formation of 2-methyl-1,2,3,4-tetrahydroquinoline (**2u**) and 1,2,3,4-tetrahydro-4,7-phenanthroline (**2w**) in 80% and 35% yields, respectively, but no reaction was observed in the case of **1t** or **1v**.

Encouraged by these results, we next turned our attention to the asymmetric transfer hydrogenation of these 1,10-phenanthroline derivatives. We first examined the asymmetric reduction of **1a** with HCO_2H in different solvents in the presence of a chiral iridium catalyst generated *in situ* from $[Cp^*IrCl_2]_2$ and the Noyori ligand Ts-dpen (**L1**)[18] (Table 3, entries 1–11). A dramatic solvent effect was observed, and the use of *i*-PrOH as the solvent was the most beneficial in terms of enantioselectivity (Table 3, entry 4). Although 1,4-dioxane delivered the best yield, a very low enantioselectivity was obtained (Table 3, entry 11). With *i*-PrOH as the solvent, a survey of various chiral diamine ligands was then carried out. It was found that both steric and electronic effects of these ligands have a profound influence on the reaction efficiency and enantioselectivity (Table 3, entries 12–18), and (*R*, *R*)-$(CF_3)_2C_6H_3SO_2$-dpen (**L5**)

Table 3. Screening conditions for the asymmetric transfer hydrogenation of **1a**.[a,b]



Entry	Solvent	Ligand	Yield [%][b]	*ee* [%][c]
1	H_2O	**L1**	90	4
2	MeOH	**L1**	42	87
3	EtOH	**L1**	47	90
4	*i*-PrOH	**L1**	65	92
5	THF	**L1**	77	71
6	CH_2Cl_2	**L1**	trace	ND
7	DMSO	**L1**	trace	ND
8	DMF	**L1**	70	81
9	CH_3CN	**L1**	58	52
10	toluene	**L1**	16	37
11	1,4-dioxane	**L1**	95	17
12	*i*-PrOH	**L2**	81	97
13	*i*-PrOH	**L3**	69	84
14	*i*-PrOH	**L4**	30	22
15	***i*-PrOH**	**L5**	**94**	**98**
16	*i*-PrOH	**L6**	82	94
17	*i*-PrOH	**L7**	86	97
18	*i*-PrOH	**L8**	19	48
19[d]	*i*-PrOH	**L5**	NR	ND

[a] *Reaction conditions:* **1a** (0.2 mmol), $[Cp^*IrCl_2]_2$ (1 mol%), ligand (2.4 mol%), HCO_2H (1.6 mmol), solvent (2.0 mL), 40 °C, 24 h. ND = not detected.
[b] Isolated yield.
[c] Determined by HPLC analysis.
[d] No HCO_2H was added.

proved to be the best choice, and the desired product was furnished with 94% yield and 98% *ee* (Table 3, entry 15). We finally examined the asymmetric reduction of **1a** in *i*-PrOH in the absence of HCO_2H, but no reaction occurred (Table 3, entry 19). Obviously *i*-PrOH did not serve as a hydrogen source in this case.

A variety of 2,9-disubstituted and 2-substituted 1,10-phenanthroline derivatives were then subjected to asymmetric transfer hydrogenation under the optimized reaction conditions (Table 4). As expected, various symmetrical 2,9-dialkylated 1,10-phenanthroline derivatives were readily reduced, affording the corresponding chiral products in excellent yields and enantioselectivities in almost all the cases.[19] It is notable that more than 99% *ee* values were achieved in the reduction of compounds **1d** and **1e**. The size of the alkyl substituent did not influence the enantioselectivity of reaction as evidenced by the fact that excellent *ee* values were observed in the reduction of bulky substrates **1g** and **1h**. However, in the case of the more sterically demanding substrate **1i**, only the racemic product was isolated. The unsymmetrical 2,9-dialkyl-substituted 1,10-phenanthroline substrate (**1j**) could give the two chiral products [(*R*)-$\mathbf{2j_1}$ and (*R*)-$\mathbf{2j_2}$] with high enantioselectivities, albeit with low regioselectivities. The current catalytic system did not work well for the asymmetric reduction of 2-substituted 1,10-phenanthrolines (**1k**–**1n**), and very low enantioselectivities were obtained [(*R*)-$\mathbf{2k_1}$–(*R*)-$\mathbf{2n_2}$]. In these monosubstituted substrates, the absence of a second substituent makes the facial discrimination less effective, thereby leading to lower *ee* values. The reduction of 2,9-diphenyl 1,10-phenanthroline (**1r**) only resulted in the formation of racemic product. We also carried out the asymmetric transfer hydrogenation of quinaldine (**1u**) using HCO_2H and HCO_2H/Et_3N (5/2) azeotrope as the hydrogen source, respectively. The reaction with HCO_2H gave the desired product (*R*)-2-methyl-1,2,3,4-tetrahydroquinoline [(*R*)-**2u**] in 86% yield and 68% *ee*, whilst using the azeotrope resulted in a lower yield of 57% and a similar *ee* value of 67%. Obviously, the addition of NEt_3 is detrimental to the reaction.

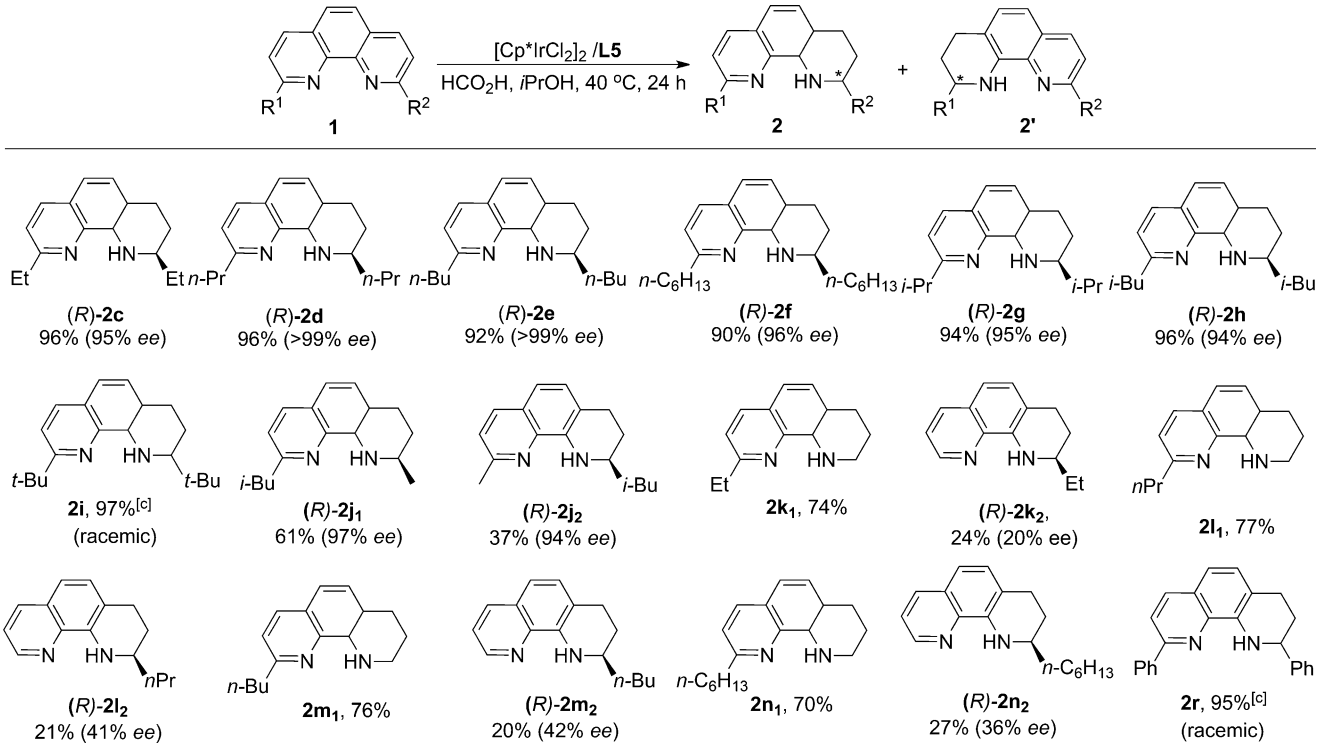
In conclusion, we have developed mild and efficient transfer hydrogenation reaction conditions that allow selective reduction of a wide range of 2-substituted and 2,9-disubstituted 1,10-phenanthrolines to exclusively give 1,2,3,4-tetrahydro-1,10-phenanthroline products in high yields and enantioselectivities (up to >99% *ee*) using HCO_2H as the hydrogen source. It is noteworthy that the choice of solvent and hydrogen source is critical to catalysis. The present catalysis is operationally simple, and provides a valuable alternative to the known methods for 1,10-phenanthroline reduction. Further studies toward the full reduction of the two pyridyl rings of 1,10-phenanthrolines are currently underway in our laboratory.

Experimental Section

General Procedure for Transfer Hydrogenation of 1,10-Phenanthrolines

A mixture of 1,10-phenanthroline **1** (0.2 mmol), HCO_2H (75.0 mg, 1.6 mmol), $[Cp^*IrCl_2]_2$ (1.6 mg, 1 mol%), 1,4-dioxane (2.0 mL) was stirred at 40 °C for 24 h under an N_2 atmosphere. After cooling down to room temperature, water (10.0 mL) was added to the reaction mixture. The reaction mixture was extracted with CH_2Cl_2 (3×10.0 mL). The combined organic layer was dried with anhydrous Na_2SO_4 for a while and filtered. The filtrate was concentrated by

Table 4. Ir-catalyzed asymmetric transfer hydrogenation of 1,10-phenanthrolines.[a,b]



[a] *Reaction conditions:* **1** (0.2 mmol), $[Cp^*IrCl_2]_2$ (1 mol%), **L5** (2.4 mol%), HCO_2H (1.6 mmol), *i*-PrOH (2.0 mL), 40 °C, 24 h.
[b] Isolated yield. Enantiomeric excess was determined by HPLC.
[c] $[Cp^*IrCl_2]_2$ (2 mol%) and **L5** (4.8 mol%) were employed.

vacuum evaporation and the residue was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane to give the pure 1,2,3,4-tetrahydro-1,10-phenanthroline product.

General Procedure for Asymmetric Transfer Hydrogenation of 1,10-Phenanthrolines

A mixture of 1,10-phenanthroline **1** (0.2 mmol), HCO_2H (75.0 mg, 1.6 mmol), $[Cp^*IrCl_2]_2$ (1.6 mg, 1 mol%), (*R*,*R*)-$(CF_3)_2C_6H_3SO_2$-dpen (2.3 mg, 2.4 mol%), *i*-PrOH (2.0 mL) was stirred at 40 °C for 24 h under an N_2 atmosphere. After cooling down to room temperature, water (10.0 mL) was added to the reaction mixture. The aqueous solution was extracted with CH_2Cl_2 (3×10.0 mL). The combined organic layer was dried with anhydrous Na_2SO_4 for a while and filtered. The filtrate was concentrated by vacuum evaporation and the residue was purified by column chromatography on silica gel using a mixture of ethyl acetate and hexane to give the pure chiral 1,2,3,4-tetrahydro-1,10-phenanthroline product.

Acknowledgements

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