ACS Catalysis

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Iridium-Catalyzed Asymmetric Hydrogenation of Heteroaromatics Bearing a Hydroxyl Group, 3-Hydroxypyridinium Salts

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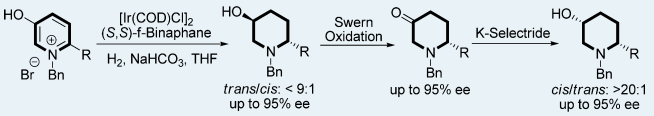
Supporting Information

ABSTRACT: A highly enantioselective hydrogenation of heteroaromatics bearing a hydroxyl group, 3-hydroxypyridinium salts, has been successfully developed using chiral iridium catalyst, providing a direct access to *trans* 6-substituted piperidin-3-ols with up to 95% ee. Swern oxidation of the hydrogenation products affords chiral 6-substituted piperidin-3-ones, which are easily reduced to *cis* 6-substituted piperidin-3-ols using K-selectride.



KEYWORDS: *iridium, asymmetric hydrogenation, 3-hydroxypyridinium salts, piperidin-3-ol, piperidin-3-one*

For its straightforwardness and high stereoselectivity, asymmetric hydrogenation of aromatic compounds is regarded as a promising method for the synthesis of chiral cyclic molecules.[1] Substrates such as pyridines,[2] quinolines,[3] isoquinolines,[4] quinoxalines,[5] indoles,[6] pyrroles,[7] furans,[8] thiophenes,[9] and aromatic carbocycles[10] have been reduced with high yields and selectivities. Despite these achievements, there is barely any report on asymmetric hydrogenation of aromatic compounds bearing a hydroxyl group to chiral ketones or alcohols. Taking pyridin-3-ol, for example, the high aromatic stability and strong coordination ability of the pyridine ring impede efficient hydrogenation. Three types of unsaturated bonds (C═C, C═N, and C═O) may exist during the hydrogenation process, making the chemoselectivity and stereoselectivity problematic. Once the aromaticity of pyridin-3-ol is destroyed, fast enol/ketone isomerization often takes place. Thus, racemic product often generates for the *ortho*-substituted pyridin-3-ol. These issues render asymmetric hydrogenation of pyridin-3-ol highly challenging.

Chiral piperidin-3-ol is a common motif widely embedded in natural products and pharmaceutical agents (Figure 1).[11] Its

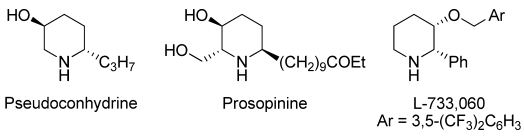


Figure 1. Natural products and pharmaceutical agents containing chiral piperidin-3-ol motif.

abundance and interesting biological activity have stimulated significant synthetic interests. Two common synthetic methodologies are intramolecular cyclization of acyclic amines with hydroxyl group at proper position,[11a] and ring expansion of chiral prolinols.[11b,c] Other useful methods include ring-closing metathesis of the unsaturated amines,[12a] oxidative kinetic resolution of racemic piperidin-3-ols[12b] and thermal reactions such as 1,3-dipolar cycloaddition or Diels−Alder.[12c,d] Being widely used, but the existing methods suffer drawbacks such as chiral starting materials, long synthetic steps, and low overall yields. Therefore, it is highly desirable to develop a direct and catalytic procedure to synthesize chiral piperidin-3-ols.

Asymmetric hydrogenation of pyridin-3-ols is one of the most straightforward approaches to chiral piperidin-3-ols. However, due to the difficulties described above, this method has hardly been used. Recently, our group reported a homogeneous iridium-catalyzed hydrogenation of 2-substituted 3-hydroxypyridinium salts. Due to the fast enol/ketone isomerization, racemic piperidin-3-ones were obtained with chiral iridium catalyst.[13] In connection with this endeavor, we envisaged that the hydrogenation of 6-substituted 3-hydroxypyridinium salts could avoid such a problem. Herein, we report an iridium-catalyzed asymmetric hydrogenation of 6-substituted 3-hydroxypyridinium salts to *trans* 6-substituted piperidin-3-ols with high enantioselectivities (Scheme 1, eq 1). In addition, the synthesis of chiral 6-substituted piperidin-3-ones and *cis* piperidin-3-ols is also realized (eq 2).

We began our exploration with 6-phenyl substituted **2a** as the model substrate (Table 1). Solvent screening showed that only THF gave a full conversion (entry 1). Diastereoisomers of **3a** and **5a** were obtained with 83:17 d.r., the ee of main isomer **3a** was 46%. No piperidin-3-one **4a** was detected. Subsequently, inorganic and organic bases were screened, but the initially used sodium bicarbonate was proved to be best (entries 5−8). The base was a necessary additive, and no reactivity was observed without it (entry 9). Different *N*-alkyl groups were also test, but the benzyl group was the most efficient (see the Supporting Information). Then, different chiral diphosphine ligands were

Received: November 20, 2015
Revised: February 26, 2016

DOI: 10.1021/acscatal.5b02625
ACS Catal. 2016, 6, 2368−2371

Scheme 1. Direct Synthesis of Piperidin-3-ols via Hydrogenation

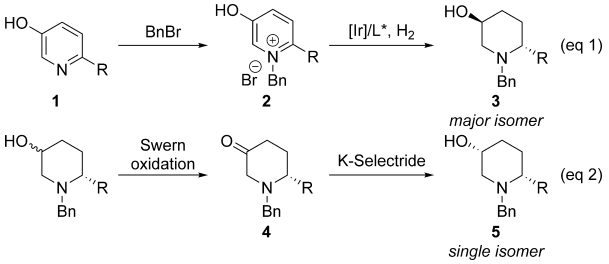
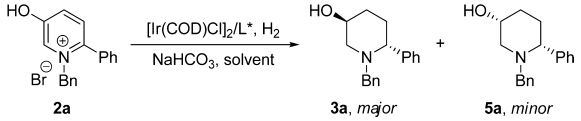
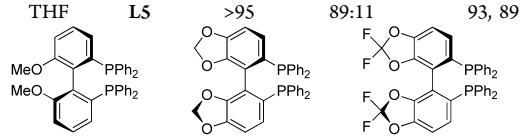


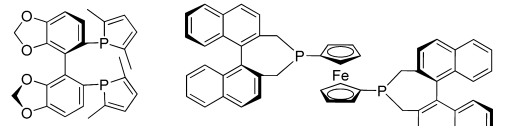
Table 1. Optimization of the Reaction Conditions[a]



entry	solvent	ligand	conv (%)[b]	*trans*/*cis*[b]	ee of **3a**, **5a** (%)[c]
1	THF	**L1**	>95	83:17	46, 48
2	DCM	**L1**	90	78:22	47, 17
3	EtOAc	**L1**	70	67:33	33, 54
4	^{i}PrOH	**L1**	15	61:39	37, 11
5[d]	THF	**L1**	>95	78:22	37, 40
6[e]	THF	**L1**	>95	76:24	38, 30
7[f]	THF	**L1**	>95	80:20	36, 37
8[g]	THF	**L1**	>95	81:19	38, 46
9[h]	THF	**L1**	<5	-	-
10	THF	**L2**	>95	82:18	48, 32
11	THF	**L3**	>95	78:22	59, 35
12	THF	**L4**	>95	75:25	75, 84
13	THF	**L5**	>95	89:11	93, 89



L1: (*R*)-MeO-BiPhep **L2:** (*R*)-SegPhos **L3:** (*R*)-DifluorPhos



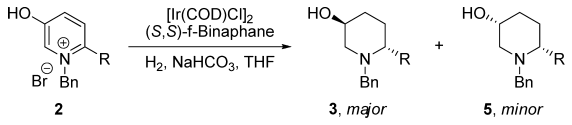
L4: (*R*)-MP^2-SegPhos **L5:** (*S*,*S*)-f-Binaphane

[a]Conditions: **2a** (0.20 mmol), $[Ir(COD)Cl]_2$ (1.5 mol %), **L*** (3.3 mol %); H_2 (600 psi), solvent (3.0 mL), if not noted, $NaHCO_3$ (0.20 mmol) was used, 40 °C, 24 h. [b]Determined by ^{1}H NMR. [c]Determined by chiral HPLC. [d]Na_2CO_3 (0.10 mmol). [e]K_3PO_4 (0.10 mmol). [f]DIPEA (0.20 mmol). [g]$KHCO_3$ (0.20 mmol). [h]$NaHCO_3$ was omitted.

screened, which were proved to be pivotal (entries 10−13). The ee of **3a** increased to 48% using SegPhos. A further increase was observed with MP^2−SegPhos (75% ee). Finally, to our delight, when f-Binaphane[14] was used, the d.r. increased to 89:11, and **3a** was obtained with 93% ee. The ee of *cis* **5a** was 89%. It should be noted that **3a** and **5a** could be easily separated by column chromatography. The absolute configuration of **3a** was determined to be (3*S*,6*R*) based on X-ray crystallographic analysis.

Having established the optimized conditions, we next examined the substrate scope (Table 2). For the electron-donating groups, excellent ee values were obtained regardless of the substituent positions (entries 2−5). Good activities and enantioselectivities maintained for the electron-withdrawing

Table 2. Substrate Scope of the 3-Hydroxypyridinium Salts[a]



entry	R	yield (%)[b]	*trans*/*cis*[c]	ee of **3** (%)[d]
1	Ph	98	89:11	93 (3*S*,6*R*)
2	3-MeC_6H_4	91	82:18	94 (+)
3	4-MeC_6H_4	93	90:10	94 (+)
4	3,5-$Me_2C_6H_3$	93	83:17	95 (+)
5	3-MeOC_6H_4	95	84:16	91 (+)
6	3,5-$F_2C_6H_3$	97	86:14	86 (+)
7	3-ClC_6H_4	95	88:12	90 (+)
8	4-ClC_6H_4	96	83:17	92 (+)
9	4-$CF_3C_6H_4$	97	83:17	93 (+)
10	4-$MeO_2CC_6H_4$	95	75:25	90 (+)
11[e]	2-naphthyl	90	49:51	81 (+)
12[f]	*n*-Pr	81	53:47	64 (+)
13	H	89	-	15 (−)

[a]Conditions: **2** (0.20 mmol), $[Ir(COD)Cl]_2$ (1.5 mol %), (*S*,*S*)-f-Binaphane (3.3 mol %), H_2 (600 psi), $NaHCO_3$ (0.20 mmol), THF (3.0 mL), 40 °C, 24 h. [b]Isolated yields of two isomers. [c]Determined by ^{1}H NMR. [d]Determined by chiral HPLC. [e]H_2 (1000 psi), 96% ee for the *cis* isomer. [f]H_2 (1000 psi), (*R*)-DTBM-SegPhos was used as ligand.

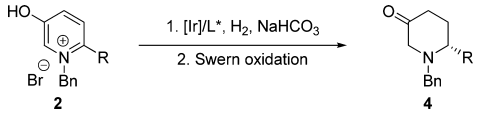
groups (entries 6−10). For the 2-naphthyl substituted 3-hydroxypyridinium salt, 81% ee was obtained for the *trans* isomer (entry 11), but the *cis* one was obtained with much higher ee (96%). The current system was highly compatible with alkyl substrate, and sterically bulky ligand DTBM-SegPhos was used to achieve moderate ee (entry 12). The *trans* propyl product was a direct precursor of (+)-pseudoconhydrine, removing the benzyl group could provide this natural alkaloid. Multiple steps were needed to obtain such intermediate in previous reports.[15] For the simple 3-hydroxypyridinium salt, only 15% ee was achieved (entry 13). 5-Phenyl substituted 3-hydroxypyridinium salt could also be hydrogenated, albeit with 10% ee (see the Supporting Information).

The chiral piperidin-3-one was a potentially useful intermediate for the diversified transformations of C═O. With the highly optical piperidin-3-ols in hand, we assumed that direct oxidation of the hydrogenation products without separation of the *trans* and *cis* isomers might afford piperidin-3-ones with high ee values. While PCC, Dess−Martin oxidation give poor yields, good results were obtained with Swern oxidation (Table 3, entry 1). Thus, the substrate scope was explored to test the generality. Either electron-donating (entries 2−5) or electron-withdrawing (entries 6−11) substituents on the aryl group were well-tolerated, affording the corresponding ketone products with high yields and enantioselectivities.

Since the iridium-catalyzed hydrogenation of 3-hydroxypyridinium salt **2** mainly affording the *trans* piperidin-3-ols, we paid our attention to the synthesis of *cis* piperidin-3-ols. To our delight, a single *cis* isomer **5a** was produced from the piperidin-3-one **4a** using K-selectride reduction. The *cis* **5a** obtained in this way had the same configuration with the minor isomer through the hydrogenation (Table 4, entry 1). The electronic properties of substituents on the phenyl ring did not exert noticeable effect on the selectivities (enties 2−11). All the 6-substituted piperidin-3-ols were provided with high diastereoselectivities (>20:1), and the ee values were in agreement

DOI: 10.1021/acscatal.5b02625
ACS Catal. 2016, 6, 2368−2371

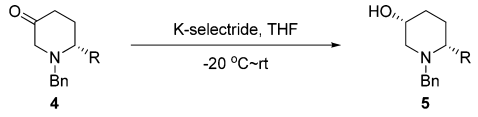
Table 3. Substrate Scope of the Piperidin-3-ones[a]



entry	R	yield (%)[b]	ee (%)[c]
1	Ph	93 (**4a**)	92 (*R*)
2	3-MeC_6H_4	89 (**4b**)	94 (+)
3	4-MeC_6H_4	91 (**4c**)	95 (+)
4	3,5-$Me_2C_6H_3$	81 (**4d**)	95 (+)
5	3-MeOC_6H_4	83 (**4e**)	90 (+)
6	3,5-$F_2C_6H_3$	85 (**4f**)	85 (+)
7	3-ClC_6H_4	83 (**4g**)	90 (+)
8	4-ClC_6H_4	78 (**4h**)	91 (+)
9	4-$CF_3C_6H_4$	81 (**4i**)	93 (+)
10	4-$MeO_2CC_6H_4$	82 (**4j**)	91 (+)
11	2-naphthyl	86 (**4k**)	87 (+)

[a]For details, see Supporting Information. [b]Isolated yields. [c]Determined by chiral HPLC.

Table 4. Substrate Scope of the *cis*-Piperidin-3-ols[a]



entry	R of **5**	yield (%)[b]	ee (%)[c]
1	Ph	91 (**5a**)	93 (+)
2	3-MeC_6H_4	81 (**5b**)	94 (+)
3	4-MeC_6H_4	84 (**5c**)	94 (+)
4	3,5-$Me_2C_6H_3$	86 (**5d**)	95 (+)
5	3-MeOC_6H_4	87 (**5e**)	91 (+)
6	3,5-$F_2C_6H_3$	91 (**5f**)	85 (+)
7	3-ClC_6H_4	91 (**5g**)	90 (+)
8	4-ClC_6H_4	85 (**5h**)	91 (+)
9	4-$CF_3C_6H_4$	90 (**5i**)	92 (+)
10[d]	4-$HOCH_2C_6H_4$	83 (**5j**)	91 (+)
11	2-naphthyl	92 (**5k**)	89 (+)

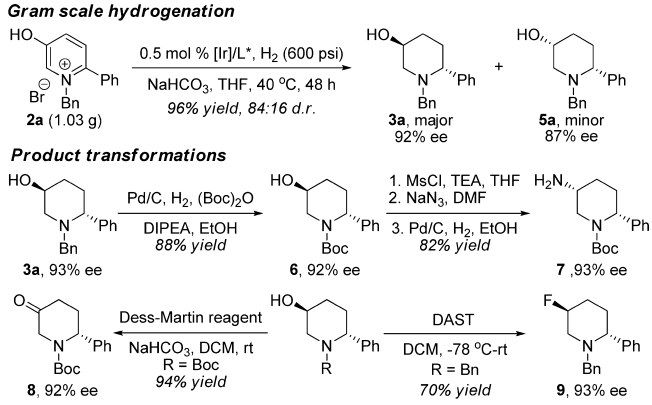
[a]For details, see Supporting Information. In all cases, the d.r. > 20:1. [b]Isolated yields. [c]Determined by chiral HPLC. [d]K-selectride (0.6 mmol), the ester group of **4j** was reduced to hydroxymethyl group.

with the ketones. Notably, the ester group of **4j** was reduced to hydroxymethyl during the reduction process.

To highlight the practical utility of our approach, a gram-scale asymmetric hydrogenation of **2a** was performed. Excellent yield and enantioselectivity maintained with 0.5 mol % catalyst loading (Scheme 2). With the chiral piperidin-3-ols in hand, several transformations were carried out. For instance, the benzyl group was easily removed though hydrogenolysis, and **6** was obtained after an *in situ* Boc-protection. Then, **6** was transformed into **7** bearing an amino group in three steps with total yield of 82%. The Boc-protected **6** could also be oxidized to **8** with Dess–Martin reagent at room temperature, which was complementary to Swern oxidation. When **3a** was treated with (*N*,*N*-diethylamino)sulfurtrifluoride (DAST), *trans*-3-fluoropiperidine **9** was obtained due to the involvement an aziridinium intermediate.[16] Notably, there was no significant loss in the enantiomeric purity during the above transformations.

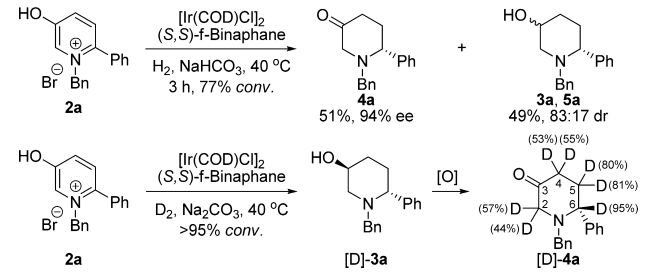
To probe the mechanism, the hydrogenation of **2a** was stopped at 3 h, and the reaction mixture was analyzed by ^{1}H

Scheme 2. Gram-Scale Experiment and Product Transformations



NMR (Scheme 3). With a 77% conversion of **2a**, 51% of the product was ketone **4a**. All the products had the same

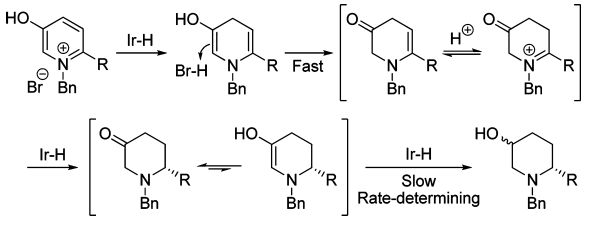
Scheme 3. Mechanistic Investigation



configuration on C6. Additionally, the hydrogenation of **2a** was conducted with D_2, and the deuteration pattern of product was determined after Swern oxidation. It was found that one deuterium atom was incorporated on C2 and C4, respectively. The deuterium incorporation was 95% on C6 and 80% on C5, which indicated an enamine–iminium tautomerization took place before the hydrogenation of the iminium salt. The extent of deuteration at the two diastereotopic positions of C2 was slightly different (57% vs 44%). A possible interpretation of this finding was that hydrogen/deuterium exchanged through keto–enol tautomerization on the chiral ketone **4a** during the hydrogenation.

On the basis of these results and general hydrogenation mechanism of pyridine,[2d,3c,17] a possible reaction pathway was proposed in Scheme 4. The salt **2** first undergoes 1,4-hydride addition to give a 1,4-dihydropyridine intermediate containing an enol structure, which is protonated to ketone by the *in situ*-formed HBr. Then, an enamine-iminium tautomerization takes place; subsequent hydrogenation of iminium salt delivers piperidin-3-one with high ee. The hydrogenation of piperidin-

Scheme 4. Proposed Reaction Pathway



DOI: 10.1021/acscatal.5b02625
ACS Catal. 2016, 6, 2368–2371

3-one proceeds through the substrate-controlled manner and leads to moderate d.r. of piperidin-3-ol, which has been confirmed by experimental studies (see the Supporting Information). It should be noted that an alternative mechanism that involves initial 1,2-reduction of salt is also operational.

In conclusion, the asymmtric hydrogenation of 6-substituted 3-hydroxypyridinium salts has been successfully realized, which represents a scarce example on the asymmetric hydrogenation of aromatics bearing a hydroxyl group. The *trans* 6-substituted piperidin-3-ols are obtained as the main products with excellent enantioselectivities. Direct Swern oxidation of hydrogenation products gives the chiral piperidin-3-ones, which are easily reduced to the *cis* 6-substituted piperidin-3-ols using K-selectride. Thus, the chiral 6-substituted piperidin-3-ones, *trans* and *cis* piperidin-3-ols can be easily accessed from the same starting materials, 3-hydroxypyridinium salts. Further efforts to realize the hydrogenation of other pyridinols and apply related methods to the synthesis of natural alkaloids are ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b02625.

Experimental materials and procedures, X-ray crystallographic analysis, NMR of substrates and products, and HPLC for racemic and chiral products (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the National Natural Science Foundation of China (21532006 and 21372220) is acknowledged.

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DOI: 10.1021/acscatal.5b02625
ACS Catal. 2016, 6, 2368−2371