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Iridium-Catalyzed Asymmetric Hydrogenation of Pyrrolo[1,2-*a*]pyrazinium Salts

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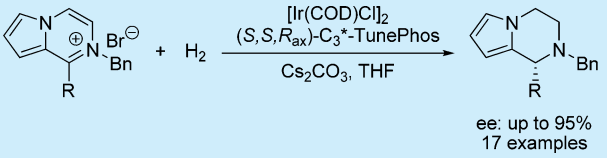
Supporting Information

ABSTRACT: Highly enantioselective iridium-catalyzed hydrogenation of pyrrolo[1,2-*a*]pyrazinium salts has been achieved, providing a direct access to chiral 1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrazine derivatives with up to 95% ee. The key feature of the reaction is the addition of cesium carbonate, which increases the conversion and prohibits the racemization pathway of products.



1,2,3,4-Tetrahydropyrrolo[1,2-*a*]pyrazines are considered to be an important class of heterocycles for their potential antihypersensitive, antiarrhythmic, antiamnesic, antihypoxic, psychotropic, and aldose reductase inhibition activities.[1] Especially, chiral 1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrazines have been found in several natural products such as Hanishin and Longamide B (Figure 1).[2] The chiral skeleton is also

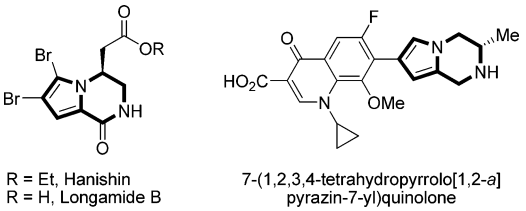


Figure 1. Some natural products and bioactive molecules containing the 1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrazine skeleton.

present in bioactive compounds such as 7-(1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrazin-7-yl)quinolone, which has exhibited potent in vivo efficacy in a murine lethal systemic infection model.[3] The position of the methyl group on the tetrahydropyrazine ring as well as the *S*-configuration is important for this efficacy.

Although many efforts have been devoted to the synthesis of chiral 1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrazines, most of these materials are synthesized *via* chiral starting materials or auxiliaries,[4] and there are quite a few methods for the catalytic asymmetric preparation of these intriguing heterocycles.[5] Thus, the development of a simple and flexible asymmetric synthetic method is highly desirable. According to retrosynthesis, the asymmetric hydrogenation of easily available pyrrolo[1,2-*a*]pyrazines is one of the most straightforward to access optically active 1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrazines. However, to the best of our knowledge, this method has hardly been used. Only a few reports have been published, starting from partially saturated 3,4-dihydropyrrolo[1,2-*a*]pyrazines.[6]

During the past decades, asymmetric hydrogenation of aromatic and heteroaromatic compounds has emerged as a powerful strategy for the synthesis of saturated or partially saturated cyclic molecules.[7] Many aromatic substrates such as quinolines,[8] isoquinolines,[9] quinoxalines,[10] pyridines,[11] indoles,[12] pyrroles,[13] furans,[14] imidazoles,[15] thiophenes,[16] and carbocyclic aromatic rings[17] have been successfully hydrogenated with excellent enantioselectivities. The finding of a robust catalyst and proper activation of inactive aromatic compounds are key points for the successful implementation of the reaction. Substrate activation is a quite efficient and generally used strategy. With proper activators, such as Brønsted acids,[18] chloroformates,[9a] or benzyl bromides,[9c,11f] the aromaticity of substrates can be partially destroyed, which facilitates hydrogenation.

Pyrrolo[1,2-*a*]pyrazines are bicyclic aromatics with one nitrogen atom in the bridgehead position of the fused pyrazine and pyrrole rings. Similar to pyridine and isoquinoline, both the substrate and the hydrogenated product possess a strong coordination ability. Once partially hydrogenated, the reserved pyrrole ring is relatively sensitive to acid, which further increases the difficulty in selective reduction of these substrates.

We envisaged that the activation of pyrrolo[1,2-*a*]pyrazine with benzyl bromide would efficiently reduce the coordination ability of the substrate and improve the reactivity for hydrogenation (Scheme 1). Herein, we disclose an iridium-catalyzed asymmetric hydrogenation of pyrrolo[1,2-*a*]pyrazinium salts, providing the chiral 1,2,3,4-tetrahydropyrrolo-[1,2-*a*]pyrazines with up to 95% ee.

We began our studies with 2-benzyl-1-phenylpyrrolo[1,2-*a*]pyrazin-2-ium bromide **2a** as the model substrate using

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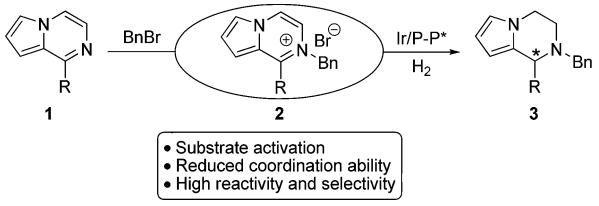
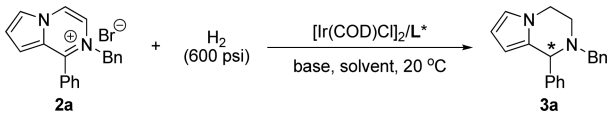
Scheme 1. Synthesis of Chiral 1,2,3,4-Tetrahydropyrrolo[1,2-*a*]pyrazine *via* Asymmetric Hydrogenation



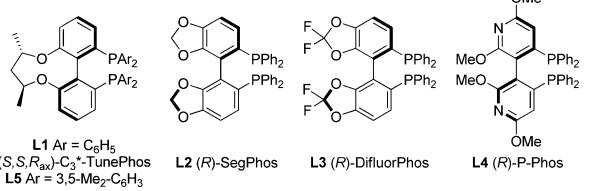
$[Ir(COD)Cl]_2$/(S,S,R_{ax})-C_3*-TunePhos as the catalyst (Table 1). Initial exploration of reaction conditions revealed the

Table 1. Optimization of the Reaction Conditions[a]



entry	solvent	ligand	base (equiv)	conv (%)[b]	ee (%)[c]
1	CH_2Cl_2	**L1**	–	28	8
2	toluene	**L1**	–	14	58
3	THF	**L1**	–	40	64
4	EtOAc	**L1**	–	26	55
5	THF	**L1**	TEA (0.8)	>95	3
6	THF	**L1**	NaOH (0.8)	>95	52
7	THF	**L1**	$NaHCO_3$ (0.8)	>95	76
8	THF	**L1**	Na_2CO_3 (0.4)	>95	76
9	THF	**L1**	K_2CO_3 (0.4)	>95	85
10	THF	**L1**	Cs_2CO_3 (0.4)	>95	87
11	THF	**L1**	Cs_2CO_3 (0.5)	>95	88
12	THF	**L1**	Cs_2CO_3 (0.6)	>95	90
13	THF	**L2**	Cs_2CO_3 (0.6)	>95	87
14	THF	**L3**	Cs_2CO_3 (0.6)	>95	86
15	THF	**L4**	Cs_2CO_3 (0.6)	>95	79
16[d]	THF	**L1**	Cs_2CO_3 (0.6)	>95	92

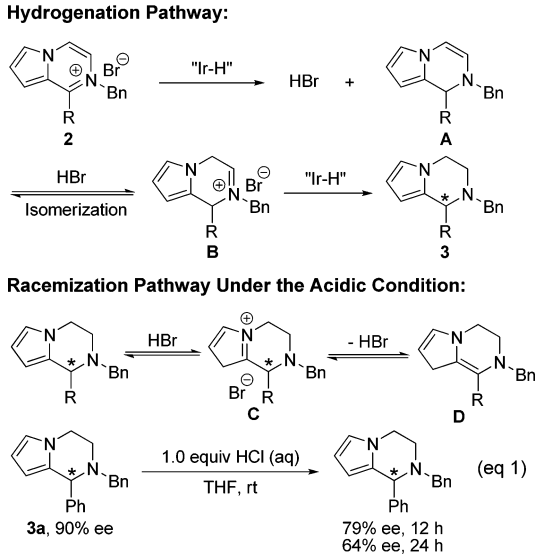
[a]Conditions: **2a** (0.20 mmol), $[Ir(COD)Cl]_2$ (1.5 mol %), (S,S,R_{ax})-C_3*-TunePhos (3.3 mol %), H_2 (600 psi), solvent (3.0 mL), 20 °C, 24 h; TEA = triethylamine. [b]Determined by ^{1}H NMR. [c]Determined by HPLC with chiral column. [d]H_2 (400 psi).



importance of the solvent. THF gave a much higher yield than other solvents, but only moderate enantioselectivity was obtained (entries 1−4).

Considering the structural similarity of pyrrolo[1,2-*a*]pyrazine with isoquinoline, we proposed the following reaction pathway based on our previous work.[9c] As shown in Scheme 2, the substrates first undergo a 1,2-hydride addition to give a 1,2-dihydropyrrolo[1,2-*a*]pyrazine intermediate **A**, which would isomerize to an iminium salt **B** in the presence of *in situ* generated HBr. Subsequent hydrogenation of the iminium salt gives the product. The *in situ* generated HBr is important for the reaction to proceed forward.

Scheme 2. A Proposed Hydrogenation Mechanism and the Racemization Pathway of 3a under the Acidic Condition



According to literature reports, molecules with a similar structure to **3a** are easy to racemize on silica gel.[4a] We speculated that the low ee value was caused by the partial racemization of **3a** under the acidic conditions through enamine/iminium isomerization (Scheme 2). To verify this assumption, the product **3a** was mixed with 1.0 equiv of HCl (aq) and stirred at room temperature (eq 1 in Scheme 2). The ee of **3a** dropped from 90% to 79% in 12 h. Upon further stirring, the ee dropped to 64%. Based on these results, we decided to neutralize part of the HBr to prevent the substantial racemization of the product. To our surprise, upon adding 0.8 equiv of triethylamine (TEA), full conversion was realized, but the ee value was quite low (entry 5).[19] This was possibly due to the coordination of the organic base to the catalyst. When the inorganic base was added, the reaction proceeded well with increased enantioselectivity. A screen of several kinds of inorganic bases showed that Cs_2CO_3 was the best choice, giving full conversion with 87% ee (entries 6−10).

To our delight, when excess Cs_2CO_3 was added to the reaction system, better enantioselectivities were obtained with no detection of the 1,2-dihydropyrrolo[1,2-*a*]pyrazine intermediate (entries 11−12). Because of the relatively poor solubility of Cs_2CO_3 in THF, the neutralization rate may be slower than the rate of HBr generated. So the reaction proceeded well in the presence of excess Cs_2CO_3. Other commercially available chiral diphosphine ligands were also tested under the same conditions, but no ligand gave a better result than the initially used (S,S,R_{ax})-C_3*-TunePhos (entries 13−15). A decrease of the hydrogen pressure had a positive effect on enantioselectivity (92% ee, entry 16). Thus, the optimized conditions were established as $[Ir(COD)Cl]_2$/(S,S,R_{ax})-C_3*-TunePhos/Cs_2CO_3/THF.

With the optimized reaction conditions in hand, the scope of iridium-catalyzed asymmetric hydrogenation of pyrrolo[1,2-*a*]pyrazinium salts was explored (Table 2). In general, the transformations performed well with moderate to excellent yields under the standard conditions. The position and electronic effect of substituents on the phenyl ring had a great influence on the enantioselectivity. Substrates bearing eletron-donating groups on the 3-position gave much higher ee

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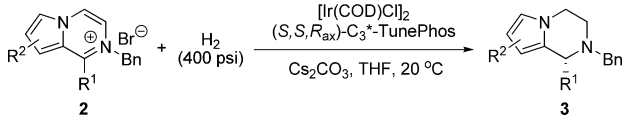
Table 2. Scope of the Asymmetric Hydrogenation of Pyrrolo[1,2-*a*]pyrazinium Salts[a]



entry	R^1, R^2	yield (%)[b]	ee (%)[c]
1	Ph, H	97 (**3a**)	92 (*R*)
2	3-MeC_6H_4, H	91 (**3b**)	89 (−)
3	3-MeOC_6H_4, H	90 (**3c**)	93 (−)
4	4-MeC_6H_4, H	93 (**3d**)	80 (−)
5[d]	4-^{t}BuC_6H_4, H	91 (**3e**)	82 (−)
6	4-FC_6H_4, H	93 (**3f**)	87 (−)
7	3-ClC_6H_4, H	96 (**3g**)	94 (−)
8	4-ClC_6H_4, H	94 (**3h**)	87 (−)
9	3,5-$F_2C_6H_3$, H	97 (**3i**)	92 (−)
10	4-$CF_3C_6H_4$, H	97 (**3j**)	95 (−)
11	4-NCC_6H_4, H	94 (**3k**)	94 (−)
12	4-$EtO_2CC_6H_4$, H	82 (**3l**)	80 (−)
13[d]	4-PhC_6H_4, H	95 (**3m**)	88 (−)
14	2-naphthyl, H	74 (**3n**)	92 (−)
15[e]	Me, H	97 (**3o**)	60 (−)
16	Ph, 6-Me	93 (**3p**)	73 (−)
17	Ph, 6-Ph	85 (**3q**)	75 (−)

[a]Conditions: **2** (0.20 mmol), $[Ir(COD)Cl]_2$ (1.5 mol %), (S,S,R_{ax})-C_3*-TunePhos (3.3 mol %), Cs_2CO_3 (0.12 mmol), H_2 (400 psi), THF (3.0 mL), 20 °C, 24 h. [b]Isolated yield. [c]Determined by HPLC. [d]Cs_2CO_3 (0.10 mmol) was used, 36 h. [e]**L5** was used as the ligand.

values than those on the 4-position (entries 2−5). However, for electron-withdrawing groups, generally high ee values were obtained (entries 6−10). Notably, a substrate with a 4-CF_3 group gave the best enantioselectivity (95% ee, entry 10). The reaction system was also compatible with a cyano group and gave excellent ee (94% ee; entry 11), but for the ester group, a lower 80% ee was obtained (entry 12). For the biphenyl and naphthyl substituted substrates, good enantioselectivities were maintained (entries 13−14). 1-Methyl-pyrrolo[1,2-*a*]pyrazine was a suitable reaction partner, but only moderate enantioselectivity was obtained (60% ee, entry 15). Substrates with substituents on the pyrrole ring were also tested, providing the corresponding products with good yields and moderate ee values (entries 16−17).

After a single recrystallization from dichloromethane and *n*-hexane, the product **3a** could be obtained in 81% yield with up to >99% ee. The absolute configuration of product **3a** was determined to be *R* based on single-crystal X-ray diffraction analysis (Figure 2).[20]

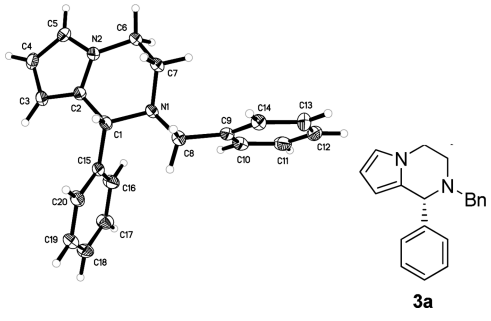
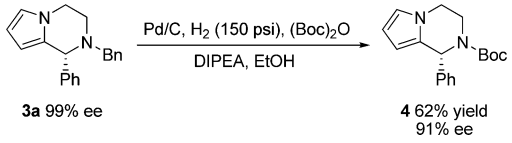


Figure 2. X-ray crystal structure of compound **3a**.

Finally, to demonstrate the practicality of our approach, we directed our efforts to the removal of the benzyl group (Scheme 3). When **3a** was subjected to 150 psi of H_2 in the presence of 5% Pd/C, $(Boc)_2O$, and DIPEA in ethanol for 2 days, the desired product **4** was obtained in 62% yield with a slight drop of the ee value. The main side product arose from the opening of the piperazine ring (see the Supporting Information).

Scheme 3. Removal of the Benzyl Group



In conclusion, we have successfully realized the asymmetric hydrogenation of pyrrolo[1,2-*a*]pyrazinium salts with an iridium catalyst. This method provides a direct access to chiral 1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrazine derivatives with high to excellent ee values. The key feature of the reaction is the addition of cesium carbonate, which increases the conversion and prohibits the racemization pathway of products. Further efforts to illuminate the mechanism and apply this strategy to other challenging heteroaromatic compounds are ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, X-ray structures, data for the determination of enantiomeric excess, and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Peresada, V. P.; Medvedev, O. S.; Likhosherstov, A. M.; Skoldinov, A. P. *Khim.-Farm. Zh.* **1987**, *21*, 1054. (b) Likhosherstov, A. M.; Filippova, O. V.; Peresada, V. P.; Kryzhanovskii, S. A.; Vititnova, M. B.; Kaverina, N. V.; Reznikov, K. M. *Pharm. Chem. J.* **2003**, *37*, 6. (c) Seredenin, S. B.; Voronina, T. A.; Beshimov, A.; Peresada, V. P.; Likhosherstov, A. M. RU 2099055, 1997. (d) Seredenin, S. B.; Voronina, T. A.; Likhosherstov, A. M.; Peresada, V. P.; Molodavkin, G. M.; Halikas, J. A. US 5378846, 1995, 10 pp. (e) Negoro, T.; Murata, M.; Ueda, S.; Fujitani, B.; Ono, Y.; Kuromiya, A.; Komiya, M.; Suzuki, K.; Matsumoto, J.-i. *J. Med. Chem.* **1998**, *41*, 4118.

(2) (a) Papeo, G.; Gómez-ZuritaFrau, M. A.; Borghi, D.; Varasi, M. *Tetrahedron Lett.* **2005**, *46*, 8635. (b) Al-Mourabit, A.; Zancanella, M. A.; Tilvic, S.; Romo, D. *Nat. Prod. Rep.* **2011**, *28*, 1229.

(3) Zhu, B.; Marinelli, B. A.; Goldschmidt, R.; Foleno, B. D.; Hilliard, J. J.; Bush, K.; Macielag, M. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 4933.

(4) (a) Gualandi, A.; Cerisoli, L.; Monari, M.; Savoia, D. *Synthesis* **2011**, 909. (b) Bhowmik, S.; Kumar, A. K. S.; Batra, S. *Tetrahedron*

Lett. **2013**, *54*, 2251. (c) Li, G.; Rowland, G. B.; Rowland, E. B.; Antilla, J. C. *Org. Lett.* **2007**, *9*, 4065.
(5) He, Y.; Lin, M.; Li, Z.; Liang, X.; Li, G.; Antilla, J. C. *Org. Lett.* **2011**, *13*, 4490.
(6) For the hydrogenation of 3,4-dihydropyrrolo[1,2-*a*]pyrazines, see: (a) Skoldinov, A. P.; Likhosherstov, A. M.; Peresada, V. P. DE 2832488, 1980. (b) Skoldinov, A. P.; Likhosherstov, A. M.; Peresada, V. P. GB 2025936, 1980. (c) Skoldinov, A. P.; Likhosherstov, A. M.; Peresada, V. P. SU 798104, 1981. (d) Markus, H.; Tanja, W.; Sibylle, M.; Jens, N.; Andreas, G.; Valerjans, K.; Ronalds, Z.; Elina, E.; WO 2009095254, 2009.
(7) For reviews on hydrogenation of aromatics, see: (a) Wang, D.-S.; Chen, Q.-A.; Lu, S.-M.; Zhou, Y.-G. *Chem. Rev.* **2012**, *112*, 2557. (b) Fleury-Brégeot, N.; de La Fuente, V.; Castillón, S.; Claver, C. *ChemCatChem* **2010**, *2*, 1346. (c) Zhou, Y.-G. *Acc. Chem. Res.* **2007**, *40*, 1357. (d) Glorius, F. *Org. Biomol. Chem.* **2005**, *3*, 4171. (e) Lu, S.-M.; Han, X.-W.; Zhou, Y.-G. *Chin. J. Org. Chem.* **2005**, *25*, 634. (f) Xie, J.-H.; Zhou, Q.-L. *Acta Chim. Sinica* **2012**, *70*, 1427.
(8) For selected works on asymmetric hydrogenation of quinolines, see: (a) Wang, W.-B.; Lu, S.-M.; Yang, P.-Y.; Han, X.-W.; Zhou, Y.-G. *J. Am. Chem. Soc.* **2003**, *125*, 10536. (b) Zhao, Y.-J.; Wang, Y.-Q.; Zhou, Y.-G. *Chin. J. Catal.* **2005**, *26*, 737. (c) Rueping, M.; Antonchick, A. P.; Theissmann, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 3683. (d) Guo, Q.-S.; Du, D.-M.; Xu, J. *Angew. Chem., Int. Ed.* **2008**, *47*, 759. (e) Zhou, H.; Li, Z.; Wang, Z.; Wang, T.; Xu, L.; He, Y.; Fan, Q.-H.; Pan, J.; Gu, L.; Chan, A. S. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 8464. (f) Wang, C.; Li, C.; Wu, X.; Pettman, A.; Xiao, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 6524. (g) Wang, D.-W.; Wang, D.-S.; Chen, Q.-A.; Zhou, Y.-G. *Chem.—Eur. J.* **2010**, *16*, 1133. (h) Wang, T.; Zhuo, L.-G.; Li, Z.; Chen, F.; Ding, Z.; He, Y.; Fan, Q.-H.; Xiang, J.; Yu, Z.-X.; Chan, A. S. C. *J. Am. Chem. Soc.* **2011**, *133*, 9878. (i) Chen, Q.-A.; Gao, K.; Duan, Y.; Ye, Z.-S.; Shi, L.; Yang, Y.; Zhou, Y.-G. *J. Am. Chem. Soc.* **2012**, *134*, 2442. (j) Tu, X.-F.; Gong, L.-Z. *Angew. Chem., Int. Ed.* **2012**, *51*, 11346. (k) Cai, X.-F.; Chen, M.-W.; Ye, Z.-S.; Guo, R.-N.; Shi, L.; Li, Y.-Q.; Zhou, Y.-G. *Chem.—Asian J.* **2013**, *8*, 1381.
(9) For selected works on asymmetric hydrogenation of isoquinolines, see: (a) Lu, S.-M.; Wang, Y.-Q.; Han, X.-W.; Zhou, Y.-G. *Angew. Chem., Int. Ed.* **2006**, *45*, 2260. (b) Shi, L.; Ye, Z.-S.; Cao, L.-L.; Guo, R.-N.; Hu, Y.; Zhou, Y.-G. *Angew, Chem., Int. Ed.* **2012**, *51*, 8286. (c) Ye, Z.-S.; Guo, R.-N.; Cai, X.-F.; Chen, M.-W.; Shi, L.; Zhou, Y.-G. *Angew. Chem., Int. Ed.* **2013**, *52*, 3685. (d) Iimuro, A.; Yamaji, K.; Kandula, S.; Nagano, T.; Kita, Y.; Mashima, K. *Angew. Chem., Int. Ed.* **2013**, *52*, 2046. (e) Guo, R.-N.; Cai, X.-F.; Shi, L.; Ye, Z.-S.; Chen, M.-W.; Zhou, Y.-G. *Chem. Commun.* **2013**, *49*, 8537.
(10) For selected works on asymmetric hydrogenation of quinoxalines, see: (a) Bianchini, C.; Barbaro, P.; Scapacci, G.; Farnetti, E.; Graziani, M. *Organometallics* **1998**, *17*, 3308. (b) Tang, W.; Xu, L.; Fan, Q.-H.; Wang, J.; Fan, B.; Zhou, Z.; Lam, K.-H.; Chan, A. S. C. *Angew. Chem., Int. Ed.* **2009**, *48*, 9135. (c) Rueping, M.; Tato, F.; Schoepke, F. R. *Chem.—Eur. J.* **2010**, *16*, 2688. (d) Chen, Q.-A.; Wang, D.-S.; Zhou, Y.-G.; Duan, Y.; Fan, H.-J.; Yang, Y.; Zhang, Z. *J. Am. Chem. Soc.* **2011**, *133*, 6126. (e) Gartigny, D.; Berhal, F.; Nagano, T.; Phansavath, P.; Ayad, T.; Gênet, J.-P.; Ohshima, T.; Mashima, K.; Ratovelomanena-Vidal, V. *J. Org. Chem.* **2012**, *77*, 4544.
(11) For selected works on asymmetric hydrogenation of pyridines, see: (a) Glorius, F.; Spielkamp, N.; Holle, S.; Goddard, R.; Lehmann, C. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 2850. (b) legault, C. Y.; Charette, A. B. *J. Am. Chem. Soc.* **2005**, *127*, 8966. (c) Rueping, M.; Antonchick, A. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 4562. (d) Wang, X.-B.; Zeng, W.; Zhou, Y.-G. *Tetrahedron Lett.* **2008**, *49*, 4922. (e) Tang, W.-J.; Tan, J.; Xu, L.-J.; Lam, K.-H.; Fan, Q.-H.; Chan, A. S. C. *Adv. Synth. Catal.* **2010**, *352*, 1055. (f) Ye, Z.-S.; Chen, M.-W.; Chen, Q.-A.; Shi, L.; Duan, Y.; Zhou, Y.-G. *Angew. Chem., Int. Ed.* **2012**, *51*, 10181.
(12) For selected works on asymmetric hydrogenation of indoles, see: (a) Kuwano, R.; Sato, K.; Kurokawa, T.; Karube, D.; Ito, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7614. (b) Kuwano, R.; Kashiwabara, M. *Org. Lett.* **2006**, *8*, 2653. (c) Wang, D.-S.; Chen, Q.-A.; Li, W.; Yu, C.-B.; Zhou, Y.-G.; Zhang, X. *J. Am. Chem. Soc.* **2010**, *132*, 8909. (d) Duan, Y.; Chen, M.-W.; Ye, Z.-S.; Wang, D.-S.; Chen, Q.-A.; Zhou, Y.-G. *Chem.—Eur. J.* **2011**, *17*, 7193. (e) Wang, D.-S.; Tang, J.; Zhou, Y.-G.; Chen, M.-W.; Yu, C.-B.; Duan, Y.; Jiang, G.-F. *Chem. Sci.* **2011**, *2*, 803. (f) Duan, Y.; Chen, M.-W.; Chen, Q.-A.; Yu, C.-B.; Zhou, Y.-G. *Org. Biomol. Chem.* **2012**, *10*, 1235.
(13) For works on asymmetric hydrogenation of pyrroles, see: (a) Kuwano, R.; Kashiwabara, M.; Ohsumi, M.; Kusano, H. *J. Am. Chem. Soc.* **2008**, *130*, 808. (b) Wang, D.-S.; Ye, Z.-S.; Chen, Q.-A.; Zhou, Y.-G.; Yu, C.-B.; Fan, H.-J.; Duan, Y. *J. Am. Chem. Soc.* **2011**, *133*, 8866.
(14) For selected works on asymmetric hydrogenation of furans, see: (a) Kaiser, S.; Smidt, S. P.; Pfaltz, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 5194. (b) Ortega, N.; Urban, S.; Beiring, B.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 1710. (c) Wysocki, J.; Ortega, N.; Glorius, F. *Angew. Chem., Int. Ed.* **2014**, *53*, DOI: 10.1002/anie.201310985.
(15) For selected work on asymmetric hydrogenation of imidazoles, see: Kuwano, R.; Kameyama, N.; Ikeda, R. *J. Am. Chem. Soc.* **2011**, *133*, 7312.
(16) For selected work on asymmetric hydrogenation of thiophenes, see: Urban, S.; Beiring, B.; Ortega, N.; Paul, D.; Glorius, F. *J. Am. Chem. Soc.* **2012**, *134*, 15241.
(17) For selected works on asymmetric hydrogenation of carbocyclic aromatic rings, see: (a) Urban, S.; Ortega, N.; Glorius, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 3803. (b) Kuwano, R.; Morioka, R.; Kashiwabara, M.; Kameyama, N. *Angew. Chem., Int. Ed.* **2012**, *51*, 4136. (c) Ye, Z.-S.; Shi, L.; Zhou, Y.-G. *Synlett* **2014**, *25*, 928.
(18) For a review, see: Yu, Z.; Jin, W.; Jiang, Q. *Angew. Chem., Int. Ed.* **2012**, *51*, 6060.
(19) For a base to increase conversion in the hydrogenation of quinolinium salts, see: Dragan, V.; McWilliams, J. C.; Miller, R.; Sutherland, K.; Dillon, J. L.; O'Brien, M. K. *Org. Lett.* **2013**, *15*, 2942.
(20) CCDC 962691 contains the supplementary crystallographic data for this paper. These can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.