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Highly Diastereo- and Enantioselective Ir-Catalyzed Hydrogenation of 2,3-Disubstituted Quinolines with Structurally Fine-Tuned Phosphine−Phosphoramidite Ligands

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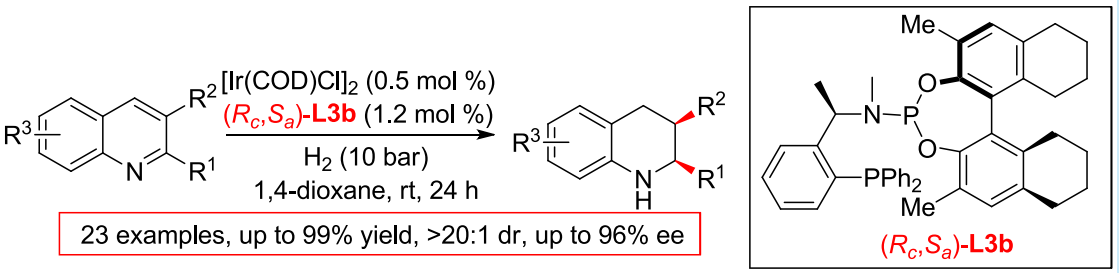
Supporting Information



ABSTRACT: A highly diastereo- and enantioselective Ir-catalyzed hydrogenation of unfunctionalized 2,3-disubstituted quinolines, especially 3-alkyl-2-arylquinolines, has been realized. The success of this hydrogenation is ascribed to the use of a structurally fine-tuned chiral phosphine−phosphoramidite ligand with a (S_a)-3,3′-dimethyl H_8-naphthyl moiety and (R_c)-1-phenylethylamine backbone. The hydrogenation displayed broad functional group tolerance, thus furnishing a wide range of optically active 2,3-disubstituted tetrahydroquinolines in up to 96% ee and with perfect *cis*-diastereoselectivity.

Optically active tetrahydroquinoline derivatives are important molecular scaffolds for many natural products, as well as useful building blocks for the synthesis of pharmaceuticals and bioactive compounds.[1] Due to its inherent efficiency and atom economy, catalytic asymmetric hydrogenation of quinolines should be one of the most direct and convenient approaches to chiral tetrahydroquinoline derivatives. Indeed, in the past decade, many successful examples have been reported based on various transition-metal catalytic systems and organocatalysts.[2−8] In comparison with much success in the hydrogenation of monosubstituted quinolines, asymmetric catalytic hydrogenation of 2,3-disubstituted quinolines represents a more difficult task due to the requisite diastereocontrol in the concurrent construction of two vicinal stereogenic centers. Zhou and some other groups have realized the catalytic asymmetric hydrogenation of various functionalized 2,3-disubstituted quinolines in high diastereo- and enantioselectivity, with a NO_2,[5a] phthaloyl,[5b,c] CF_3,[5d] NHTs,[5e] ester,[5f,g] or SCF_3[5h] functionality at the 3-position and an aryl or alkyl group at the 2-position of quinoline. However, the catalytic asymmetric hydrogenation of unfunctionalized 2,3-disubstituted quinolines remains a huge challenge. In 2009, Zhou et al. examined the $[Ir(COD)Cl]_2$/MeO-BIPHEP/I_2 system for the hydrogenation of 2,3-dialkylquinoline with up to 86% ee and high diastereoselectivity.[6] Fan and Yu reported a Ru-catalyzed asymmetric hydrogenation of 2,3-dialkylquinolines in up to 98% ee but with low diastereoselectivity.[7] However, both of the above catalytic systems were inefficient 3-alkyl-2-arylquinolines in terms of enantioselectivity. In 2015, Du reported a metal-free hydrogenation of 3-alkyl-2-arylquinolines using 5 mol % of chiral diene derived borane catalyst, providing the hydrogenation products in up to 80% ee.[8b] Therefore, the development of a new and efficient catalytic system for highly diastereo- and enantioselective hydrogenation of unfunctionalized 2,3-disubstituted quinolines, especially 3-alkyl-2-arylquinolines, remains a highly desirable and challenging task.

In the past decades, unsymmetrical hybrid chiral phosphine−phosphoramidite ligands have emerged as a novel and promising ligand class which exhibited unusual reactivities and stereoselectivities toward many challenging asymmetric catalytic reactions (Figure 1).[9] In particular, we have recently demonstrated the high efficiency of chiral 1-phenylethylamine-derived phosphine−phosphoramidite ligands in the Ir-catalyzed enantioselective hydrogenation of sterically hindered *N*-arylimines.[10] We therefore envisioned that this kind of ligand may be efficient for the Ir-catalyzed asymmetric hydrogenation of 3-alkyl-2-arylquinolines. As a result, herein we describe a highly diastereo- and enantioselective Ir-catalyzed hydrogenation of 3-alkyl-2-arylquinolines by employing a structurally fine-tuned chiral phosphine-phosphoramidite ligand with a 3,3′-dimethyl H_8-binaphthyl moiety derived from

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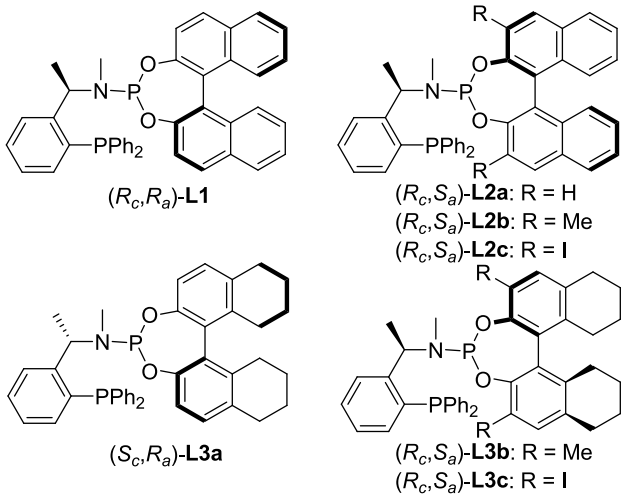
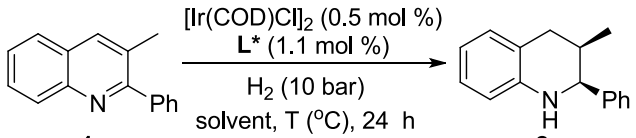


Figure 1. Unsymmetrical hybrid chiral phosphine−phosphoramidite ligands for catalytic asymmetric hydrogenation.

chiral 1-phenylethylamine, in which a wide range of optically active 2,3-disubstituted tetrahydroquinolines could be obtained in high yields and with up to 96% ee and perfect *cis*-diastereoselectivity. Interestingly, the matched configuration in this ligand was found to be *R*-central and *S*-axial chiralities, different with a (*R*,*R*)-configuration observed in the Ir-catalyzed asymmetric hydrogenation of *N*-arylimines.

We started our investigation with 3-methyl-2-phenylquinoline **1a** as a model substrate, and the hydrogenation was performed at 1 mol % of catalyst loading under a H_2 pressure of 10 bar (Table 1). Initially, we examined chiral phosphine−phosphoramidite ligand (R_c,R_a)-**L1** for this Ir-catalyzed asymmetric hydrogenation because of its demonstrated reactivity and enantioselectivity in various catalytic asymmetric hydrogenations.[10,11] Unfortunately, the hydrogenation led to very low enantioselectivity, although full conversion was achieved (entry 1). Interestingly, a substantial increase in the enantioselectivity to 52% ee was observed by replacing (R_c,R_a)-**L1** with its diastereomer (R_c,S_a)-**L2a** (entry 2), which proved to be unmatched in the Ir-catalyzed hydrogenation of *N*-arylimines.[10] It seems that the central chirality of ligand determined the absolute configuration of the product, as (R_c,R_a)-**L1** and (R_c,S_a)-**L2a** gave the product with same configuration (entries 1 and 2). I_2 additive was unnecessary to this hydrogenation, as also observed by Zhou et al. in the Ir-catalyzed hydrogenation of some *N*-heterocycles.[12] An attempt to improve the hydrogenation performance by screening the different solvents proved to be unsuccessful, and only moderate enantioselectivity was obtained in all cases (entries 2−7). Among various solvents, 1,4-dioxane was the best choice in terms of reactivity and enantioselectivity (entry 7). A further optimization of ligand structure with (R_c,S_a)- or (S_c,R_a)-absolute configuration was then performed in order to enhance the enantioselective induction of ligand. After extensive studies on the ligand modification, we disclosed that either the introduction of the substituent into 3,3′-positions of binaphthyl moiety or replacing it with the H_8-binaphthyl framework is favorable to improve the enantioselectivity (entries 8−10). In particular, a fine-tuned ligand (R_c,S_a)-**L3b** bearing a 3,3′-dimethyl H_8-binaphthyl backbone led to 3-methyl-2-phenyl-1,2,3,4-tetrahedroquinoline **2a** in full conversion, perfect *cis*-selectivity, and with 85% ee (entry 11). When the hydrogenation was performed at room temperature, the enantioselectivity could be significantly improved to 93% ee with full conversion maintained (entry 13). The efficiency of the present catalytic system was further demonstrated by performing the hydrogenation at the catalyst loading as low as 0.2 mol %, in which full conversion and 92% ee was achieved (entry 14). Furthermore, the hydrogenation performed at lower substrate concentration increased the enantioselectivity to 94% ee (entry 15).

Table 1. Optimization of Reaction Conditions[a]



entry	L*	solvent	*T* (°C)	conv[b] (%)	ee[c] (%)
1	**L1**	DCE	80	>95	6 (2*S*,3*R*)
2	**L2a**	DCE	80	>95	52 (2*S*,3*R*)
3[d]	**L2a**	DCE	80	>95	30 (2*S*,3*R*)
4	**L2a**	DCM	80	>95	49 (2*S*,3*R*)
5	**L2a**	toluene	80	90	50 (2*S*,3*R*)
6	**L2a**	benzene	80	87	52 (2*S*,3*R*)
7	**L2a**	THF	80	>95	35 (2*S*,3*R*)
8	**L2a**	1,4-dioxane	80	>95	58 (2*S*,3*R*)
9	**L2b**	1,4-dioxane	80	>95	78 (2*S*,3*R*)
10	**L2c**	1,4-dioxane	80	>95	79 (2*S*,3*R*)
11	**L3a**	1,4-dioxane	80	>95	63 (2*R*,3*S*)
12	**L3b**	1,4-dioxane	80	>95	85 (2*S*,3*R*)
13	**L3c**	1,4-dioxane	80	>95	77 (2*S*,3*R*)
14	**L3b**	1,4-dioxane	25	>95	93 (2*S*,3*R*)
15[e]	**L3b**	1,4-dioxane	25	>95	92 (2*S*,3*R*)
16[f]	**L3b**	1,4-dioxane	25	>95	94 (2*S*,3*R*)

[a]Reaction conditions: **1a** (0.4 mmol), $[Ir(COD)Cl]_2$ (0.5 mol %), **L*** (1.2 mol %), solvent (2 mL), 24 h, unless otherwise noted. [b]Conversion and dr were determined by ^1H NMR spectroscopy. In all cases, dr >20:1 was obtained. [c]Determined by HPLC analysis by using a chiral stationary phase. [d]I_2 (5 mol %) was added. [e]S/C = 500. [f]The use of 4 mL of 1,4-dioxane.

With the optimal $[Ir(COD)]Cl]_2$/(R_c,S_a)-**L3b** catalytic system, we then examined the scope of 2,3-disubstituted quinolines, and the results are summarized in Table 2. The hydrogenation proceeded in *cis*-diastereoselectivity and gave the hydrogenation products in >20:1 dr in all cases. Initially, various 2-aryl-3-methylquinolines were submitted to hydrogenation, and good to excellent performance was achieved in all cases. The results indicated that the substitution pattern on the phenyl ring showed some influence on the enantioselectivity.

Thus, *ortho*-substituted **1b** led to lower enantioselectivity in comparison with its *meta*- and *para*-analogues (**1c** and **1d**). The electronic property of the *para*-substituent on the phenyl ring hardly affected the hydrogenation outcome, and all substrates exhibited high yields and excellent enantioselectivities. 2-Naphthyl substrate **1i** also worked well, leading to the hydrogenation product **2i** in 95% yield and with 93% ee. Heteroaromatic substituents were not well tolerated. By increasing the catalyst loadings to 5 mol %, **1j** and **1k** could be completely hydrogenated in 89% ee and 95% ee, respectively. Different alkyl substituents at the 3-position of quinolines were next examined. Both ethyl and propyl groups were well tolerated, and good performance was achieved for

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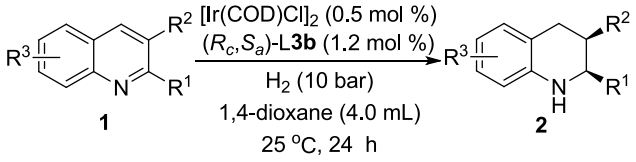
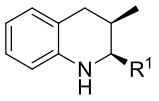
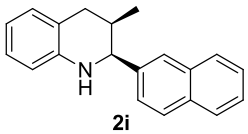
Table 2. Ir-Catalyzed Asymmetric Hydrogenation of 2-Alkyl-3-arylquinolines[a]

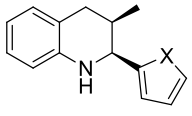




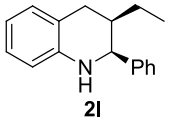
2a: R^1 = Ph, 96% yield, 94% ee
2b: R^1 = 2-FC_6H_4, 95% yield, 89% ee
2c: R^1 = 3-FC_6H_4, 96% yield, 93% ee
2d: R^1 = 4-FC_6H_4, 96% yield, 95% ee
2e: R^1 = 4-ClC_6H_4, 97% yield, 94% ee
2f: R^1 = 4-BrC_6H_4, 97% yield, 92% ee
2g: R^1 = 4-MeC_6H_4, 96% yield, 94% ee
2h: R^1 = 4-$MeOC_6H_4$, 99% yield, 92% ee



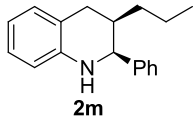
2i
95% yield, 93% ee



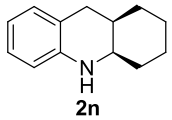
2j: X = O, 94% yield, 89% ee[b]
2k: X = S, 95% yield, 95% ee[b]



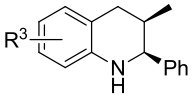
2l
96% yield, 91% ee



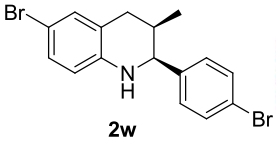
2m
97% yield, 90% ee



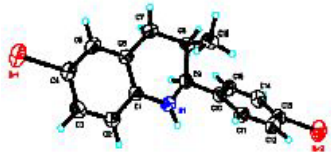
2n
97% yield, 83% ee

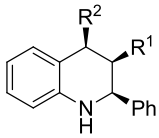


2o: R^3 = 5-Me, 68% yield, 95% ee[b]
2p: R^3 = 6-Me, 95% yield, 93% ee
2q: R^3 = 7-Me, 95% yield, 93% ee
2r: R^3 = 8-Me, 95% yield, 96% ee[c]
2s: R^3 = 6-OMe, 94% yield, 88% ee
2t: R^3 = 6-F, 95% yield, 96% ee
2u: R^3 = 6-Cl, 97% yield, 96% ee
2v: R^3 = 6-Br, 98% yield, 96% ee

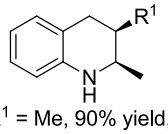


2w
97% yield, 92% ee

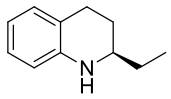




2x-1: R^1 = Ph, R^2 = H, 95% yield, 84% ee[d]
2x-2: R^1 = ^{i}Pr, R^2 = H, 85% yield, 57% ee[d]
2x-3: R^1 = Me, R^2 = Ph, no reaction[d]
2x-4: R^1 = H, R^2 = H, 96% yield, 93% ee[d]



2y-1: R^1 = Me, 90% yield, 18% ee[d]
2y-2: R^1 = Ph, 86% yield, 11% ee[d]



2z: 94% yield, 65% ee[d]

[a]Reaction conditions: **1** (0.4 mmol), $[Ir(COD)Cl]_2$ (0.5 mol %), **L3b** (1.2 mol %), 1,4-dioxane (4 mL), 10 bar of H_2, 25 °C, 24 h, unless otherwise noted. In all cases, dr >20:1. Isolated yield was provided, and ee was determined by HPLC analysis by using a chiral stationary phase. [b]$[Ir(COD)Cl]_2$ (2.5 mol %), **L3b** (6 mol %). [c]1,4-Dioxane/toluene (1 mL/3 mL), 0 °C. [d]I_2 (5 mol %) was added.

both substrates **1l** and **1m**. Cyclic substrate **1n** was also suitable for the hydrogenation, giving octahydroacridine **2n** in 97% yield and with 83% ee. The substituent on the phenyl moiety of quinolines displayed some effect on the reactivity and enantioselectivity. Thus, 5-Me-substituted substrate **1o** led to incomplete hydrogenation even at an elevated catalyst loading although excellent enantioselectivity was maintained. In comparison, the substrates **1p**–**r** bearing a methyl group at the 6-, 7-, or 8-position gave high yields and excellent enantioselectivities. The electronic property of the substituent at 6-position was somewhat sensitive to the hydrogenation. 6-Methoxy-substituted substrate **1s** led to 88% ee, obviously lower than its F, Cl, or Br analogues **1t**–**v**. The absolute configuration of the hydrogenation product is unambiguously confirmed by X-ray structure analysis of **2w**, to which a (2*S*,3*R*)-configuration was assigned. The aryl group at 2-position seems to be critical to this hydrogenation, as all 2-alkyl substrates led to low to moderate enantioselectivities (**2y**,**z**). Unfortunately, the present catalytic system did not tolerate 2,3,4-trisubstituted substrate (**2x**–**3**).

In conclusion, we have reported a highly diastereo- and enantioselective Ir-catalyzed hydrogenation of 3-alkyl-2-arylquinolines. The hydrogenation features broad substrate scope, no additive, and mild condition, thus generating a variety of optically active *cis*-3-alkyl-2-aryl-1,2,3,4-tetrahedronquinolines in high yield and enantioselectivity even at low catalyst loadings of 0.2 mol %. A structurally fine-tuned chiral phosphine–phosphoramidite ligand with an (S_a)-3,3′-dimethyl H_8-binaphthyl moiety and an (R_c)-1-phenylethylamine backbone should be critical to the success of this hydrogenation. The observation of the (R_c,S_a)-diastereomer of ligand as the matched configuration is opposed to that in the Ir-catalyzed asymmetric hydrogenation of *N*-arylimines with an (R_c,R_a)-matched configuration. Further development and application of this hydrogenation and further modification and application of chiral phosphine–phosphoramidite ligands are still underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.9b03925.

Experimental details and characterization data (PDF)

Accession Codes

CCDC 1954871 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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