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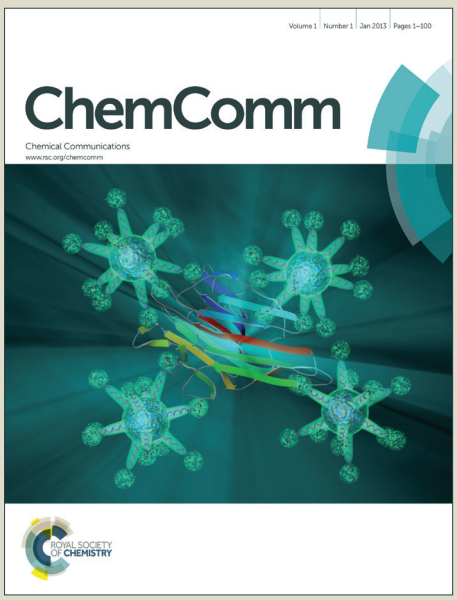

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Catalytic Asymmetric Hydrogenation of Quinoline Carbocycles: Unusual Chemoselectivity in the Hydrogenation of Quinolines

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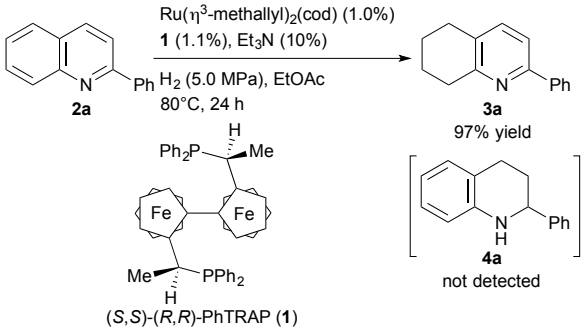
Ryoichi Kuwano,*[a,b] Ryuhei Ikeda[a] and Kazuki Hirasada[a]

The reduction of quinolines selectively took place on their carbocyclic rings to give 5,6,7,8-tetrahydroquinolines, when the hydrogenation was conducted in the presence of Ru(η^3-methallyl)$_2$(cod)–PhTRAP catalyst. The chiral ruthenium catalyst converted 8-substituted quinolines into chiral 5,6,7,8-tetrahydroquinolines with up to 91:9 er.

Catalytic asymmetric hydrogenation of heteroarene or arene is an attractive approach for creating a chiral center on 5- or 6-membered ring.[1] The potential usefulness has stimulated many chemists to develop chiral catalyst for the asymmetric reduction of heteroarenes during the last decade. Nowadays, asymmetric catalysis allows various heteroarenes to be converted to the fully or partly saturated chiral heterocycles with high enantiomeric excesses. As compared to heteroarenes, carbocyclic arenes have been unexplored as the substrates of the catalytic asymmetric hydrogenation, because they are highly stabilized with their aromaticity.[2,3] Overcoming the difficulty in breaking the aromaticity, Glorius successfully developed the asymmetric hydrogenation of the carbocycles in 6-alkyl-2,3-diphenylquinoxalines, which were converted to the corresponding 5,6,7,8-tetrahydroquinoxalines with up to 94:6 er.[4] Subsequently, we reported that substituted naphthalenes were hydrogenated with high enantioselectivities through the chiral catalyst, which is composed of ruthenium and trans-chelating chiral bisphosphine ligand, PhTRAP (**1**).[5,6]

Quinoline is the most studied substrate for the catalytic asymmetric hydrogenation of arenes.[7–9] Commonly, its pyridine ring was exclusively reduced to give optically active 1,2,3,4-tetrahydroquinoline, even when a chiral ruthenium complex was used as the catalyst.[10] Anomalistically, the carbocycle of quinoline is known to be selectively reduced with hydrogen in the presence of achiral PtO_2[11] or Chaudret's catalyst.[12] The stereoselective hydrogenation of quinoline carbocycles has been developed by using the platinum catalyst, but the reaction requires a stoichiometric chiral auxiliary to modify the substrate.[13] Here, we report a catalytic asymmetric hydrogenation of quinoline carbocycles to yield optically active 5,6,7,8-tetrahydroquinolines. PhTRAP–ruthenium catalyst allows the hydrogenation of various 8-substituted quinolines to give the corresponding tetrahydroquinolines with good enantioselectivities.

We have developed highly enantioselective hydrogenations of various heteroarenes with a chiral catalyst, **1**–ruthenium complex.[14] In the course of our study on the asymmetric hydrogenation, the hydrogenation of 2-phenylquinoline (**2a**) was attempted by using Ru(η^3-methallyl)$_2$(cod)–**1**–Et_3N catalyst (Scheme 1). To our surprise, the dearomatization of **2a** exclusively took place on its carbocycle to afford 5,6,7,8-tetrahydroquinoline **3a** in 97% yield. No formation of **4a** was detected in the reaction. The unusual chemoselectivity stimulated us to develop the catalytic asymmetric hydrogenation of quinoline carbocycles.

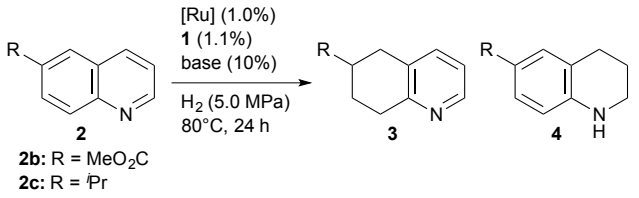


Scheme 1 Ruthenium-catalyzed hydrogenation of **2a**

The hydrogenation of quinoline-6-carboxylate **2b** was carried out under the reaction condition indicated in Scheme 1 (Table 1, entry 1). The substrate **2b** was completely consumed within 24 h, but its pyridine moiety was selectively reduced to

give 1,2,3,4-tetrahydroquinoline **4b** as the major product. A small amount of 5,6,7,8-tetrahydroquinoline **3b** was obtained from the reaction. The enantiomeric ratio of **3b** was only 66:34. The molar ratio of **3b** to **4b** and the enantiopurity of **3b** scarcely varied in the absence of Et_3N (entry 2). These results suggest that the trialkylamine might be insufficient in basicity for the desired chemoselective hydrogenation. Various bases were evaluated for the reaction of **2b** (entries 3–6). The use of a guanidine or amidine base, which is more basic than Et_3N,[15] facilitated the hydrogenation of the carbocycle (entries 3 and 4). The chemoselectivity was reversed when DBU was used in place of Et_3N. Furthermore, alkali metal carbonates were favorable for the desired hydrogenation (entries 5 and 6). The percentage of **3b** rose with the increasing polarity of solvent (entries 7–11). The trans-chelating property of **1**[6a] may be crucial for the selective reduction of the carbocyclic arenes. The pyridine ring of **2b** was selectively reduced when the hydrogenation was conducted with common bidentate bisphosphines, which chelate to a transition-metal in a cis manner.[16] In contrast to the chemoselectivity, the stereoselectivity was scarcely affected by the base additive and the solvent. Enantiomeric ratio of the hydrogenation product remarkably increased when 6-alkylquinoline **2c** was used as the substrate, but the molar ratio of **3c** to **4c** was *ca.* 1:1 (entry 12). The isopropyl group of **2c** may sterically obstruct the interaction between the catalyst and the carbocycle.

Table 1 Hydrogenation of 6-substituted quinolines[a]



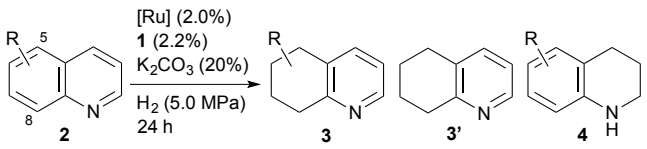
2b: R = MeO_2C
2c: R = ^{i}Pr

Entry	2	Base	Solvent	3:4[b]	Er (3)[c]
1	**2b**	Et_3N	EtOAc	7:93	66:34
2	**2b**	–	EtOAc	7:93	66:34
3	**2b**	TMG[d]	EtOAc	30:70	67:33
4	**2b**	DBU	EtOAc	72:28	67:33
5	**2b**	K_2CO_3	EtOAc	88:12	67:33
6	**2b**	Cs_2CO_3	EtOAc	93:7[e]	65:35
7	**2b**	K_2CO_3	toluene	8:92	66:34
8	**2b**	K_2CO_3	THF	64:36	70:30
9	**2b**	K_2CO_3	*i*-PrOH	93:7[f]	67:33
10	**2b**	DBU	*i*-PrOH	85:15	67:33
11	**2b**	K_2CO_3	MeOH	86:14	60:40
12[g]	**2c**	DBU	*i*-PrOH	47:53[h]	81:19

[a] [Ru] = Ru(η^3-methallyl)$_2$(cod). [b] Determined by the ^{1}H NMR analysis of reaction mixture. The ^{1}H NMR analysis indicated full conversion of **2** in all entries. [c] Determined by HPLC analysis. [d] TMG = 1,1,3,3-Tetramethylguanidine. [e] **3b** was isolated in 86% yield. [f] A small amount of isopropyl ester was formed. [g] For 48 h. [h] **3c** and **4c** were isolated in 33% and 46% yield, respectively.

To investigate the effect of the position of substituent on quinoline core, we conducted the hydrogenations of a series of methoxyquinolines in 2-propanol with the **1**–ruthenium catalyst (Table 2). Quinolines **2d** and **2e**, which have a methoxy group on the pyridine ring, were exclusively converted to achiral **3d** and **3e**, respectively (entries 1 and 2). Also 5,6,7,8-tetrahydroquinolines **3f**–**3h** are preferentially formed in the hydrogenations of **2f**–**2h**, which have a methoxy group on the carbocyclic ring (entries 3–5). The reactions, however, were accompanied by formation of 1,2,3,4-tetrahydroquinoline **4**. The substituent on 5-, 6-, or 7-position might somewhat hinder the formation of **3**. The enantiomeric ratios of **3f**–**3h** were moderate. Meanwhile, the hydrogenation of 8-methoxyquinoline (**2i**) took place on its carbocycle without the reduction of its heterocycle (entry 6). The position of the methoxy group affected the enantioselectivity as well as the chemoselectivity. The hydrogenation product **3i** was obtained with higher enantiomeric ratio than **3f**–**3h**. The ruthenium catalyst cleaved the benzylic C–O bond to form **3'** in 2-propanol. The undesired hydrogenolysis was completely suppressed by conducting the reaction in an aprotic solvent, such as ethyl acetate (entry 7). Furthermore, the enantioselectivity was scarcely affected by the reaction temperature (entry 8). The catalyst loading can be reduced to 0.5% without loss of enantioselectivity (entry 9). The chemoselectivity completely inverted in the hydrogenation of 7,8-disubstituted quinoline **2j**, which exclusively gave the achiral 1,2,3,4-tetrahydroquinoline **4j** in low yield (entry 10).

Table 2 Hydrogenation of methoxyquinolines[a]



2d: R = 3-MeO
2e: R = 4-MeO
2f: R = 5-MeO
2g: R = 6-MeO
2h: R = 7-MeO
2i: R = 8-MeO
2j: R = 8-MeO-7-Ph

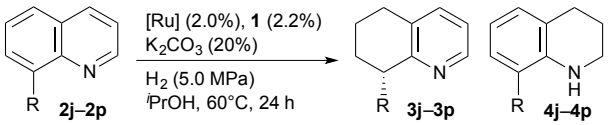
Entry	2	Solvent	Temp/°C	3:3':4[b]	Yield/%[c]	Er (3)[d]
1	**2d**	^{i}PrOH	80	100:0:0	91	–
2	**2e**	^{i}PrOH	80	100:0:0	99	–
3	**2f**	^{i}PrOH	80	52:40:8	40	71:29
4	**2g**	^{i}PrOH	80	75:0:25	79	79:21
5	**2h**	^{i}PrOH	80	86:0:14	84	68:32
6	**2i**	^{i}PrOH	80	86:14:0	79	90:10
7	**2i**	EtOAc	80	100:0:0	90	91:9
8	**2i**	EtOAc	60	100:0:0	80	91:9
9[e]	**2i**	EtOAc	60	100:0:0	94	91:9
10[f]	**2j**	EtOAc	60	0:0:24	–	–

[a] [Ru] = Ru(η^3-methallyl)$_2$(cod). [b] Determined by the ^{1}H NMR analysis of reaction mixture. The ^{1}H NMR analysis indicated full conversion of **2** unless otherwise noted. [c] Isolated yields. [d] Determined by HPLC analysis. [e] With 0.5% catalyst loading. [f] 24% conversion.

As shown in Table 3, the **1**–ruthenium catalyst converted various 8-substituted quinolines to the corresponding chiral 5,6,7,8-tetrahydroquinolines with good enantiomeric ratios. As with methoxyquinoline **2i**, protected 8-hydroxyquinoline **2j** was hydrogenated to **3j** with 90:10 er in high yield (entry 1). The reduction of the aryl-substituted quinolines **2k**–**2m** also selectively took place on their carbocycles to give the desired chiral products **3k**–**3m** with 86:14 er (entries 2–4). The enantiomeric ratio was scarcely affected by the electronic property of the para-substituent in **2l** or **2m**. The ortho-substituent of **2n** disturbed the stereoselectivity as well as the chemoselectivity (entry 5). For the hydrogenation of 8-alkylquinolines, [RuCl(*p*-cymene)(**1**)]Cl exhibited higher enantioselectivity than *in-situ*-generated Ru(η^3-methallyl)$_2$(cod)–**1** catalyst (entries 6 and 7). The preformed

catalyst transformed **2o** and **2p** into **3o** and **3p** with 89:11 and 91:9 er, respectively (entries 7 and 8).

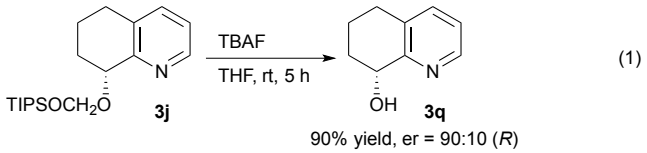
Table 3 Hydrogenation of 8-substituted quinolines[a]



Entry	R (**2**)	**3**:**4**[b]	Yield/%[c]	Er (**3**)[d]
1[e]	$TIPSOCH_2O$ (**2j**)	100:0	97	90:10
2[f]	Ph (**2k**)	96:4	87	86:14
3	4-$MeOC_6H_4$ (**2l**)	100:0	94	86:14
4	4-$CF_3C_6H_4$ (**2m**)	100:0	88	86:14
5	2-MeC_6H_4 (**2n**)	71:29	56	70:30
6	Me (**2o**)	96:4[g]	75	88:12
7[h]	Me (**2o**)	94:6[g]	71	89:11
8[h]	cHex (**2p**)	94:6	86	91:9

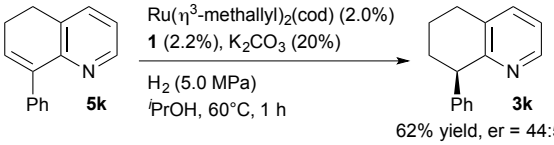
[a] [Ru] = Ru(η^3-methallyl)$_2$(cod). [b]Determined by the ^{1}H NMR analysis of reaction mixture. The ^{1}H NMR analysis indicated full conversion of **2** in all entries. [c] Isolated yields. [d] Determined by HPLC analysis. [e] In EtOAc. [f] At 40 °C for 48 h. [g] Determined by the GC analysis of reaction mixture. [h] [Ru(*p*-cymene)(**1**)]Cl and DBU were used in place of Ru(η^3-methallyl)$_2$(cod)–**1** and K_2CO_3, respectively.

The hydrogenation product **3j** was treated with TBAF to give 8-hydroxy-5,6,7,8-tetrahydroquinoline **3q** with little loss of the enantiopurity (eqn 1).[17] The optically active alcohol **3q** is useful as a chiral building block for preparing chiral catalysts[18] or various 8-substituted tetrahydroquinolines.[19] The absolute configuration of **3q** was assigned to be *R* with the sign of its optical rotation.

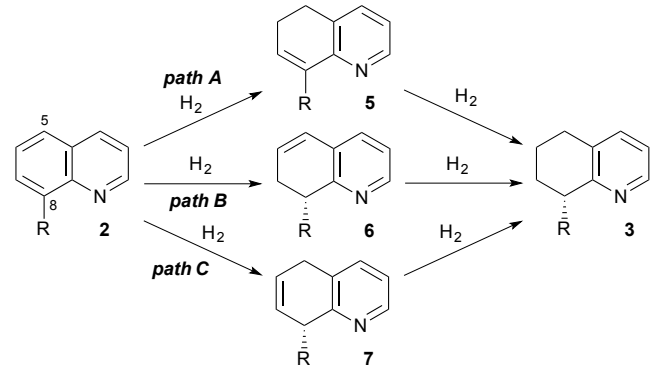


(1)

As shown in Scheme 2, three pathways can be speculated for the present ruthenium-catalyzed hydrogenation of quinoline carbocycles. In path A, the C5–C6 double bond is first saturated with H_2 to dearomatize the carbocycle, and then the remaining C–C double bond in the resulting intermediate **5** is enantioselectively hydrogenated with the chiral ruthenium catalyst to give the optically active product **3**. Path B or C starts from the hydrogenation of the C7–C8 double bond or the 1,4-addition of H_2 to the C5–C8 1,3-diene moiety, respectively. In these pathways, the dearomatization of the carbocycle is accompanied by the chiral induction. To confirm the possibility of path A, the hydrogenation of 5,6-dihydroquinoline **5k** was carried out under the optimized condition for the asymmetric hydrogenation of **2** (eqn 2). The hydrogenation product **3k** was obtained with low enantiomeric ratio. The observed stereoselectivity rules out path A.

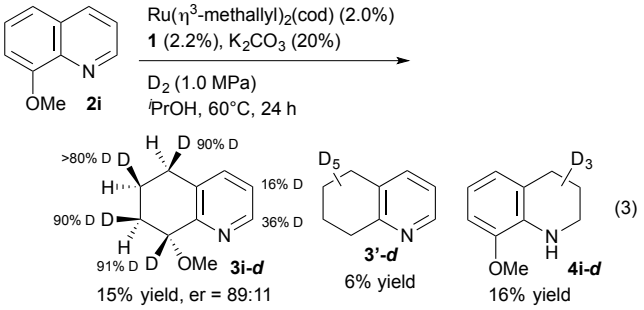


(2)



Scheme 2 Three possible pathways for the hydrogenation of quinoline carbocycles.

To further investigate the pathway of the hydrogenation, the deuterations of **2i** and **2k** were carried out with the **1**–ruthenium catalyst. The use of D_2 induced the reduction of the pyridine ring as well as significantly decreased the reaction rate.[16] Although D_2 scarcely reacted with **2k**, substrate **2i** was deuterated to give **3i-*d*** in 15% yield (by ^{1}H NMR) (eqn 3). The deuteration of **2i** was accompanied with the formations of **3'-*d*** and **4i-*d***. In **3i-*d***, four deuterium atoms were incorporated at each of the 5-, 6-, 7-, and 8-positions with all cis stereochemistry. The stereochemistry may also rule out path A if the initial step does not proceed with a high degree of enantioface discrimination. Furthermore, the observed deuterium distribution suggests that the present hydrogenation of quinoline carbocycles involves no migration of the C–C double bond in dihydroquinoline intermediate **6** or **7**.



(3)

In conclusion, the PhTRAP–ruthenium complex allows the hydrogenation of quinolines **2** to selectively produce 5,6,7,8-tetrahydroqunolines **3**. The unusual chemoselectivity may be caused by the trans-chelating property of the chiral ligand. Various 8-substituted quinolines were converted to the corresponding products **3** with good enantiomeric ratio (up to 91:9). Additionally, some experimental results suggested that the aromaticity-breaking step is accompanied by the chiral induction in the present asymmetric hydrogenation of quinoline carbocycles, while the chiral induction took place in the reduction of alkenyl ether intermediate in the asymmetric hydrogenation of naphthalenes reported by us.[5] Further mechanistic studies are in progress.

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Notes and references

[a] Department of Chemistry, Graduate School of Sciences, and International Research Center for Molecular Systems (IRCMS), Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan.
[b] JST ACT-C, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan.

† Electronic Supplementary Information (ESI) available: Experimental details and analytical data. See DOI: 10.1039/c000000x/

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