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Half-Sandwich Ruthenium Complexes for One-Pot Synthesis of Quinolines and Tetrahydroquinolines: Diverse Catalytic Activity in the Coupled Cyclization and Hydrogenation Process

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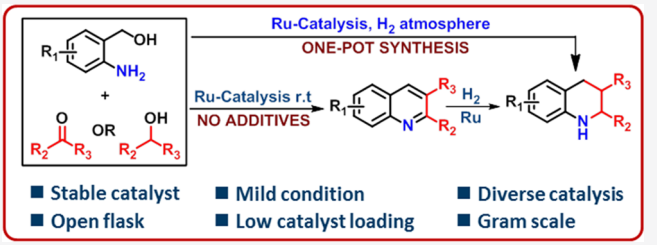
ABSTRACT: Four types of half-sandwich ruthenium complexes with an N,O-coordinate mode based on hydroxyindanone-imine ligands have been prepared in good yields. These stable ruthenium complexes exhibited high activity in the catalytic synthesis of quinolines from the reactions of amino alcohols with different types of ketones or secondary alcohols under very mild conditions. Moreover, the methodology for the direct one-pot synthesis of tetrahydroquinoline derivatives from amino alcohols and ketones has been also developed on the basis of the continuous catalytic activity of this ruthenium catalyst in the selective hydrogenation of the obtained quinoline derivatives with a low catalyst loading. The corresponding products, quinolines and tetrahydroquinoline derivatives, were afforded in good to excellent yields. The efficient and diverse catalytic activity of these ruthenium complexes suggested their potential large-scale application. All of the ruthenium complexes were characterized by various spectroscopies to confirm their structures.



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INTRODUCTION

Group 8 and 9 metal complexes with half-sandwich motifs $[[Cp^{\#}MCl_2]_2$ (M = Ru, Ir, or Rh), where $Cp^{\#}$ = Cp*, *p*-cymene] have been widely studied because of their diverse catalytic activity, good stability, and easy functionalization.[1−4] Among these compounds, half-sandwich ruthenium(II) arene motifs were often used as building blocks in the synthesis of different complexes that exhibited potential for application in catalysis, supramolecular chemistry, and biochemistry.[5−10] Recent research showed that the half-sandwich ruthenium(II) complexes bearing Schiff base ligands can serve as efficient catalysts in various types of organic reactions.[11−16] Nitrogen-donor Schiff base ligands were often employed in the preparation of coordination compounds because their steric and electronic effects can be altered conveniently. One type of nitrogen-donor ligand is the N,O-chelate mode Schiff base ligand, which was frequently studied because different types of metal complexes in various oxidation states can be formed by using the ligands.[17,18] Therefore, the interaction between Schiff base ligands and the half-sandwich ruthenium motif in N,O-chelate mode should be examined.[19,20]

The preparation of quinoline derivatives has attracted considerable attention in organic synthesis because they are important intermediates in fine chemicals and pharmaceuticals, so a number of synthetic methods have been developed to build this N-heterocyclic structure because of its wide utilization in antibacterial, anti-inflammatory, and other areas.[21] The application of these traditional reactions is limited due to the low stereoselectivity and yields, multiple reaction steps, and harsh conditions. The preparation of quinoline under the catalysis of transition metal complexes has attracted considerable attention in recent years,[22−34] and several Ru catalysis methods also have been developed (see Figure 1 for a sampling of previous work): (i) reactions between anilines and trialkylamines catalyzed by $RuCl_3$, $SnCl_2$, and dppm with the hex-1-enein as the additive,[28] (ii) $RuCl_2(DMSO)_4$-catalyzed condensation of 2-aminophenyl ketone derivatives with alcohols with benzophenone as the additive,[29] (iii) reaction of 2-aminobenzyl alcohol with ketones catalyzed by Grubbs catalyst or the Ru(arene) complex,[30] and (iv) reaction of amino alcohol with secondary alcohol catalyzed by the ruthenium hydrido complex.[31,32] However, the drawbacks of these methods such as the high reaction temperature and long reaction time, the high catalyst loading, the instability of the ruthenium catalysts, and the need for additives limited their application.

Because of the high catalytic efficiency of the half-sandwich ruthenium catalysts, the preparation and application of the half-sandwich ruthenium complexes with new structures should be explored. We report herein four types of N,O-coordinate half-sandwich ruthenium complexes bearing the hydroxyindanone-imine motif. Preliminary results suggested good catalytic activity

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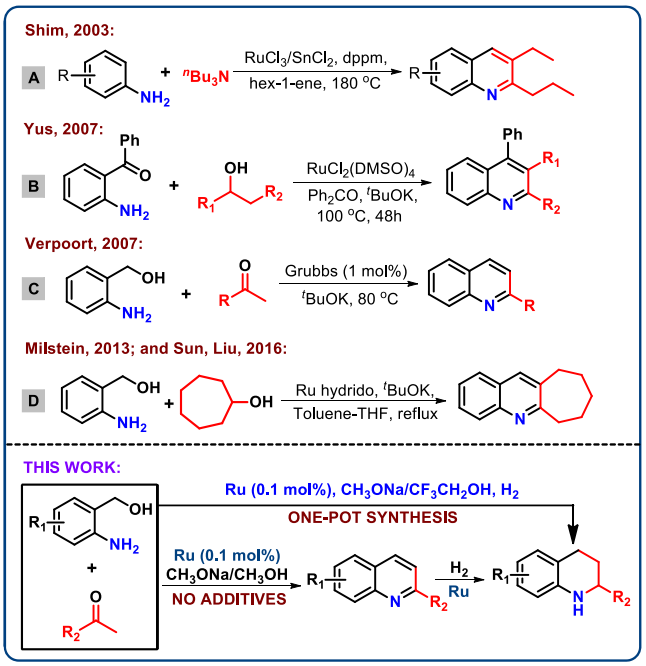


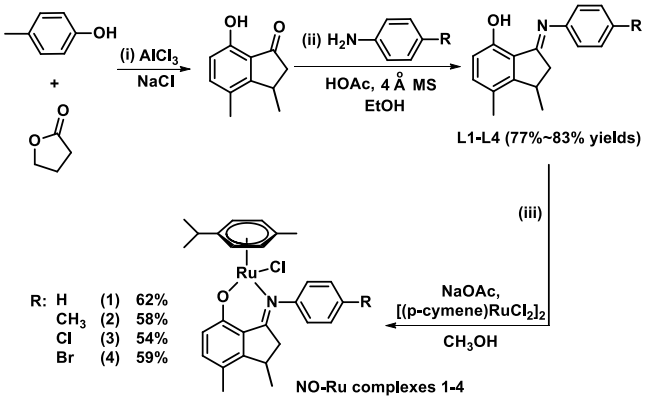
Figure 1. Sampling of Ru catalysis methods for quinoline synthesis.

of the ruthenium catalysts in the synthesis of quinoline through a one-pot process under mild conditions. Additionally, the ruthenium complex can continuously catalyze the selective hydrogenation of the obtained quinolines under a H_2 atmosphere. Therefore, the methodology for the one-pot synthesis of tetrahydroquinoline derivatives has been also developed, which combined cyclization and hydrogenation based on the continuous catalytic activity of the ruthenium catalyst in the selective catalytic hydrogenation of quinolines. All of the prepared compounds were fully characterized, and the structures of the ruthenium complexes were precisely confirmed using single-crystal X-ray diffraction. In addition, the effects that influenced the catalytic activity of the ruthenium complexes were also discussed.

RESULTS AND DISCUSSION

Synthesis of the Ligands and Half-Sandwich Ruthenium Complexes. As shown in Scheme 1, the starting material 7-hydroxy-3,4-methylindan-1-one was prepared through the $AlCl_3$-catalyzed Friedel–Crafts reaction between 4-methylphenol and γ-butyrolactone. NaCl was added to the reaction mixture to decrease the fusing temperature of $AlCl_3$. Hydroxyindanone-imine ligands **L1**–**L4** were obtained in good yields through the reaction of indanone with arylamines in an equimolar ratio in refluxing ethanol. It is noteworthy that molecular sieves are essential for the preparation of the ligands. New N,O-coordinate half-sandwich ruthenium(II) complexes **1**–**4** were formed in moderate yields by the interaction of the ligands and $[(p\text{-cymene})RuCl_2]_2$ in the presence of NaOAc in refluxing CH_3OH for 6 h (Scheme 1). All of the pure products were isolated as brown powder that is air and moisture stable for several weeks. Ru(II) complexes **1**–**4** exhibited only slight solubility in chloroform, tetrahydrofuran, toluene, dichloromethane, and DMSO, affording brown-colored solutions that were insoluble in nonpolar solvents. The characterization data for all of the half-sandwich Ru(II) complexes match well with the expected general molecular formula.

Scheme 1. Synthesis of N,O-Chelate Half-Sandwich Ru(II) Complexes 1–4[a]



[a]Reaction conditions: (i) 4-methylphenol (1.1 equiv), γ-butyrolactone (1.0 equiv), $AlCl_3$ (1.5 equiv), NaCl (7.5 equiv), 200 °C, 2 min; (ii) amines (1.2 equiv), HOAc (3 drops), 4 Å molecular sieves (0.1 g), EtOH, reflux, 24 h; (iii) $[(p\text{-cymene})RuCl_2]_2$ (0.5 equiv), NaOAc (2.0 equiv), CH_3OH, reflux, 6 h.

The ultraviolet–visible spectra of the target ruthenium complexes **1**–**4** in a CH_3CN solution exhibited strong ligand-centered (LC) π–π^* and n–π^* transitions located around 240–270 nm and ligand-to-metal charge transfer (LMCT) absorptions in the range of 310–360 nm (see the Supporting Information).[17] The broad stretching absorption in the range of 3300–3500 cm^{-1} in the infrared (IR) spectra of the ligands was assigned to the hydroxyl group. The disappearance of the signals in this region in the IR spectra of complexes **1**–**4** indicated Ru–O bond formation through deprotonation of the –OH group. The imine group vibration bands of the ligands (1630–1650 cm^{-1}) are shifted to high fields (1610–1620 cm^{-1}) because of the formation of the N,O-chelate mode between the metal center and the imine group. The singlet at δ 8.19 in the ^1H NMR spectra of the ligands was attributed to the –OH group. The coordination of the Ru–O bond was further confirmed by the disappearance of this signal. Groups of multiplets around δ 6.70–7.80 were observed in the ^1H NMR spectra of the ruthenium complexes, which can be assigned to the aromatic protons of the ligands in **1**–**4**.

Crystal Structures of Ruthenium Complexes. X-ray diffraction was performed to precisely elaborate the structure of the obtained half-sandwich ruthenium complexes. Qualified single crystals of the ruthenium complexes for X-ray determination were obtained by liquid diffusion of *n*-hexane into a saturated solution of the target products in CH_2Cl_2. Complexes **1** and **4** crystallized in monoclinic space groups $P2(1)/n$ and $P2(1)/c$, respectively (Figure 2). Crystallographic data are summarized in Table 1. The crystal structure showed the N,O-chelate mode of the ruthenium center obviously in which hydroxyindanone-imine served as a bidentate ligand. The geometry of the metal center in the two complexes both showed distorted octahedral conformations, supposing that half-sandwich motif afforded three coordination points. The half-sandwich metal corner was coordinated by N, O, and Cl atoms. For complex **1**, the Ru–Cl bond distance of 2.4353(5) Å is inconsistent with other structurally similar (*p*-cymene)Ru(II) complexes.[35] The longer Ru–N bond distance of 2.0957(16) Å in comparison with the Ru–O bond distance of 2.0649(15) Å indicates the weaker interaction between the nitrogen atom and metal center. The small dihedral angle between the N(1)–

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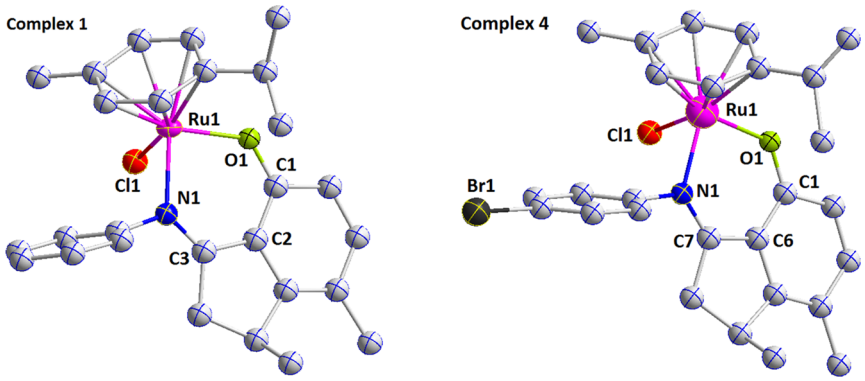

Figure 2. Molecular structures of **1** and **4** with thermal ellipsoids drawn at the 30% level. All hydrogen atoms have been omitted for the sake of clarity. Selected bond lengths (angstroms) and angles (degrees). Complex **1**: Ru(1)−N(1), 2.0957(16); Ru(1)−O(1), 2.0649(15); Ru(1)−Cl(1), 2.4353(5); C(3)−N(1), 1.300(3); C(1)−O(1), 1.305(3); O(1)−Ru(1)−N(1), 90.16(6); O(1)−Ru(1)−Cl(1), 85.49(5); Cl(1)−Ru(1)−N(1), 83.18(5); Ru(1)−O(1)−C(1), 126.82(13); Ru(1)−N(1)−C(3), 124.79(14). Complex **4**: Ru(1)−N(1), 2.099(2); Ru(1)−O(1), 2.074(2); Ru(1)−Cl(1), 2.4376(8); C(7)−N(1), 1.301(4); C(1)−O(1), 1.303(4); O(1)−Ru(1)−N(1), 90.01(9); O(1)−Ru(1)−Cl(1), 85.19(7); Cl(1)−Ru(1)−N(1), 84.73(7); Ru(1)−O(1)−C(1), 126.87(19); Ru(1)−N(1)−C(7), 125.0(2).

Table 1. Crystallographic Data and Structure Refinement Parameters for 1 and 4

	1	4
chemical formula	$C_{27}H_{30}ClNORu$	$C_{27}H_{29}BrClNORu$
formula weight	521.04	599.94
T (K)	173(2)	173(2)
λ (Å)	0.71073	0.71073
crystal system	monoclinic	monoclinic
space group	$P2(1)/n$	$P2(1)/c$
a (Å)	10.0915(5)	10.6081(7)
b (Å)	14.0422(7)	13.5729(9)
c (Å)	17.4255(10)	17.8991(12)
α (deg)	90	90
β (deg)	106.140(2)	102.774(2)
γ (deg)	90	90
V (Å^3)	2372.0(2)	2513.4(3)
Z	8	4
ρ (Mg m^{-3})	1.459	1.585
μ (mm^{-1})	4.400	5.400
$F(000)$	1072	1208
θ range (deg)	4.596−58.221	4.407−58.000
no. of reflections collected	35639	36419
data/restraints/parameters	5044/0/301	5319/75/324
goodness of fit on F^2	1.118	1.163
final R indices [$I > 2\sigma(I)$[a]]	R_1 = 0.0257, wR_2 = 0.0647	R_1 = 0.0351, wR_2 = 0.0830
largest difference peak and hole (e Å^{-3})	0.497 and −0.369	1.359 and −1.033

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ (based on reflections with $F_o^2 > 2\sigma F^2$). $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (also with $F_o^2 > 2\sigma F^2$).

Ru(1)−O(1) and N(1)−C(3)−C(2)−C(1)−O(1) planes suggests the planarity of the Ru(1)−O(1)−C(1)−C(2)−C(3)−N(1) six-membered ring of complex **1**. The structure of complex **4** is similar to that of complex **1**.

Quinoline Synthesis under [NO]Ru Catalysis. Transition metal-catalyzed oxidative cyclization of ketones and amino alcohol for the preparation of quinoline derivatives represented a green and sustainable chemical process because no toxic byproducts were generated in this reaction. Moreover, various quinoline derivatives could be prepared by using different cheap and readily available ketones as starting materials. Thus, the oxidative cyclization reaction under catalysis of N,O-chelate half-sandwich ruthenium complexes **1**−**4** was explored. The reaction of acetophenone with 2-aminobenzyl alcohol under open flask conditions catalyzed by complex **1** is considered as a model reaction for screening various reaction factors such as reaction temperature, time, catalyst loading, solvents, and bases (Table 2). The initial reaction was performed in methanol with 1.0 equiv of KOH as the base at room temperature for 6 h (1 mol % catalyst loading), and the expected product **5a** was generated in a moderate yield of 62% (Table 2, entry 1). Different bases were employed in the reaction to increase the yield of the product. The highest yield of 93% was obtained when CH_3ONa was used in the reaction (Table 2, entries 2−8). No products were observed in the absence of a base (Table 2, entry 9). As expected, the performance of inorganic bases was better than that of organic bases probably because catalytic activity was lost through the coordinate interaction between the N donor of the organic bases and the Ru center of the catalyst.[15] Low yields may also be caused by the low basicity of the organic bases. **5a** was furnished in excellent yields in CH_3OH after screening several solvents (Table 2, entries 10−15). We next investigated the catalyst loading to pursue the highest TON value because the mole ratio of the catalyst and substrate (C/S) is important in industrial application. No obvious change in yield was observed when the catalyst loading was decreased from 1.0 to 0.1 mol %. However, a serious decrease in the product yield was found with a further decrease in the catalyst loading to 0.05 mol % (Table 2, entries 16−18). Therefore, the optimal condition of the reaction, in an open flask at room temperature, was obtained after screening different reaction parameters. Target product **5a** was isolated in 93% yield under mild conditions (CH_3OH/CH_3ONa, 0.1 mol % catalyst loading, room temperature, 6 h). The catalytic activity of complexes **2**−**4** was also investigated under the optimal conditions, which exhibited a similar efficiency (Table 2, entries 19−21). A poor result was found when $[(p\text{-cym})RuCl_2]_2$ was employed as the catalyst (Table 2, entry 22).

We next explored the universality of this reaction under optimized conditions. The oxidative cyclization of 2-aminobenzyl alcohol with various types of ketones catalyzed by complex **1** readily occurred, and the corresponding quinoline derivatives were afforded in desirable yields. Ketones with electron-donating and electron-withdrawing groups both gave

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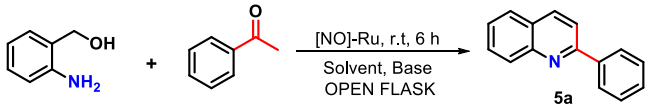
Table 2. Quinoline Synthesis under Catalysis of N,O-Chelate Ruthenium Complexes[a]



entry	catalyst (mol %)	base	solvent	yield[b] (%)	TON	TOF (h^{-1})
1	**1** (1)	KOH	CH_3OH	62	62	10.3
2	**1** (1)	K_2CO_3	CH_3OH	46	46	7.7
3	**1** (1)	NaOH	CH_3OH	55	55	9.2
4	**1** (1)	CH_3ONa	CH_3OH	93	93	15.5
5	**1** (1)	^tBuONa	CH_3OH	84	84	14.0
6	**1** (1)	K_3PO_4	CH_3OH	33	33	5.5
7	**1** (1)	Et_3N	CH_3OH	trace	–	–
8	**1** (1)	pyridine	CH_3OH	trace	–	–
		DBU	CH_3OH	trace	–	–
9	**1** (1)	–	CH_3OH	–	–	–
10	**1** (1)	CH_3ONa	1,4-dioxane	77	77	12.8
11	**1** (1)	CH_3ONa	toluene	65	65	10.8
12	**1** (1)	CH_3ONa	THF	81	81	13.5
13	**1** (1)	CH_3ONa	DMF	83	83	13.8
14	**1** (1)	CH_3ONa	DMSO	72	72	12.0
15	**1** (1)	CH_3ONa	CH_2Cl_2	58	58	9.7
16	**1** (0.5)	CH_3ONa	CH_3OH	92	184	30.7
17	**1** (0.1)	CH_3ONa	CH_3OH	93	930	155
18	**1** (0.05)	CH_3ONa	CH_3OH	79	1580	263
19	**2** (0.1)	CH_3ONa	CH_3OH	92	920	153
20	**3** (0.1)	CH_3ONa	CH_3OH	93	930	155
21	**4** (0.1)	CH_3ONa	CH_3OH	93	930	155
22	[(*p*-cym)$RuCl_2$]$_2$ (0.1)	CH_3ONa	CH_3OH	8	120	20

[a]Reaction conditions: 2-aminobenzyl alcohol (1.0 mmol), acetophenone (1.0 mmol), base (1.1 mmol), solvent (2 mL), room temperature, open flask. [b]The yield was determined by GC analysis, and *n*-tridecane was used as the internal standard.

positive results [**5a**–**e** (Table 3, entries 1–5, respectively)]. The substituent position indicated little influence on the yields of the products by using *o*-, *m*-, and *p*-methylacetophenone as starting materials in the oxidative cyclization reaction [**5f** and **5g** (Table 3, entries 2, 6, and 7, respectively)]. Heteroaryl ketones were also employed in the reaction under standard conditions. The cyclization coupling of 2-aminobenzyl alcohol with 2-acetylfuran, 2-acetylthiophene, and 2-acetylpyridine afforded the desired products in 88%, 91%, and 90% yields, respectively [**5h**–**j**, respectively (Table 3, entries 8–10, respectively)]. This process worked well with cyclic aliphatic ketones, and the products were afforded in excellent yields. A slightly lower yield was observed when the smaller cyclic aliphatic ketones were used [**5k** and **5l** (Table 3, entries 11 and 12, respectively)]. Linear aliphatic ketones gave the corresponding quinoline derivatives in lower yields (78–84%) [**5m** and **5n** (Table 3, entries 13 and 14, respectively)]. To our delight, this catalytic system showed good stereoselectivity, and only one product (**5n**) was observed in good yield when an asymmetric ketone was used in the reaction in comparison with the results in which a mixture of two quinolines was formed, as reported by Verpoort.[30] Aminobenzyl alcohols with both electron-donating and electron-withdrawing groups also afforded positive results [**5o** and **5p** (Table 3, entries 15 and 16, respectively)].

On the basis of the results mentioned above, we were encouraged to investigate quinoline derivatives from the catalytic oxidative cyclization of 2-aminobenzyl alcohol and alcohols that were used as an alternative to ketones, because the preparation of quinoline derivatives from cheap alcohols is a useful methodology in organic synthesis. In particular, the employment of secondary alcohols in this protocol remains a challenge. Fortunately, our catalytic system also showed good efficiency for the synthesis of quinoline derivatives by a one-pot procedure using amino alcohol and secondary alcohols as starting materials under refluxing conditions. The reactions of amino alcohol with various secondary alcohols were carried out, and the products were furnished in moderate to good yields [**5a**–**n** (Table 4)]. Linear aliphatic secondary alcohols also gave the corresponding quinoline derivatives in lower yields (Table 4, entries 6–9). The current catalyst showed an efficiency higher than that of the Milstein catalyst.[31]

A gram-scale production of the oxidative cyclization of 2-aminobenzyl alcohol with acetophenone was carried out with 0.1 mol % catalyst **1** under optimal conditions. Analytically pure **5a** and **5k** were obtained in 92% and 90% isolated yields, respectively (Figure 3). The two examples suggest that our methodology with stable ruthenium catalysts can be utilized in industrial production.

Catalytic hydrogenation of N-heterocycles has attracted a great deal of interest because of their wide use in the synthesis of pharmaceuticals and agrochemicals. On the other hand, the transition metal-catalyzed hydrogenation methodology using clean H_2 as the reductive reagent is a green and sustainable way, which avoided the production of the large amount of waste.[36] We have reported several half-sandwich ruthenium and iridium complexes that were used for the catalytic hydrogenation process.[35,37] Therefore, we wonder if the N,O-chelate ruthenium complexes reported here could also be catalytically active in the hydrogenation of quinolones obtained in the reactions described above. Different solvents were investigated in the quinoline reduction by utilizing complex **1** (0.1 mol %) as the catalyst at 60 °C under a H_2 atmosphere (6 atm) (Table 5, entries 1–6). To our delight, the catalytic hydrogenation process occurred smoothly in CF_3CH_2OH. The high polarity and low nucleophilicity of CF_3CH_2OH can facilitate the dissociation of the chloride ligand of the catalyst, which is the necessary step during the catalytic hydrogenation cycle.[38] Increases in the catalyst loading showed little influence on the yield of the product (Table 5, entry 7). No reaction was detected when the reaction was conducted at room temperature (Table 5, entry 8). The hydrogenation reaction hardly occurred with a [(*p*-cymene)$RuCl_2$]$_2$ catalyst and without any catalyst (Table 5, entries 9 and 10, respectively).

A variety of quinoline derivatives were employed in the catalytic hydrogenation under the optimal conditions. Hydrogenation was found to be tolerant of different functional groups, and the tetrahydroquinoline derivatives were afforded in good yields (Table 6, **6a**–**i**). The phenyl rings in the substrates were intact, suggesting the selectivity of the catalyst for the hydrogenation of N-heterocycles. Additionally, the dehalogenation of C_{Ar}–X bonds was not observed, hence making the product valuable for further reactions (such as cross-coupling reactions) (Table 6, **6c**). 2-Heterocycle-substituted quinolines were also efficiently and selectively hydrogenated in good yields (Table 6, **6d**–**f**).

Experimental results indicated that the N,O-chelate Ru complexes can catalyze both cyclization coupling of amino-

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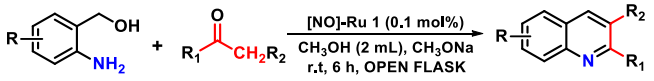
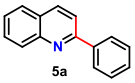
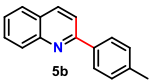
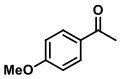
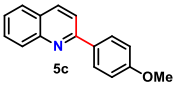
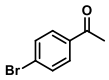
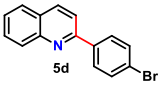
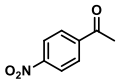
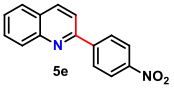
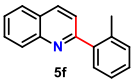
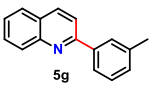
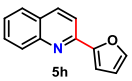
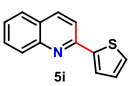
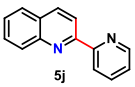
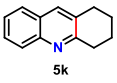
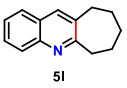
Table 3. Substrate Scope of Cyclization of Aminobenzyl Alcohols with Ketones[a]



Entry	Amino Alcohol	Ketones	Products	Yields/%[b]	TON	TOF/h^{-1}
1			 5a	93 (90)	930	155
2			 5b	96 (92)	960	160
3			 5c	95 (92)	950	158
4			 5d	95 (91)	950	158
5			 5e	91 (88)	910	152
6			 5f	94 (90)	940	157
7			 5g	96 (93)	960	160
8			 5h	88 (85)	880	147
9			 5i	91 (87)	910	152
10			 5j	90 (85)	900	150
11			 5k	91 (87)	910	152
12			 5l	96 (93)	960	160
13			 5m	83 (78)	830	138
14			5n	84 (80)	840	140
15			5o	86 (82)	860	143
16			5p	85 (82)	850	142

[a]Reaction conditions: complex **1** (0.1 mol %), aminobenzyl alcohols (1.0 mmol), ketones (1.1 mmol), CH_3ONa (1.2 mmol), CH_3OH (2 mL), room temperature, 6 h, open flask. [b]The yield was determined by GC analysis, and *n*-tridecane was used as the internal standard. Isolated yields (%) are provided in parentheses.

benzyl alcohol with ketones and selective hydrogenation of quinoline derivatives. Inspired by the diverse catalytic activity of the half-sandwich Ru complexes, we investigated one-pot synthesis of tetrahydroquinoline derivatives by using amino-

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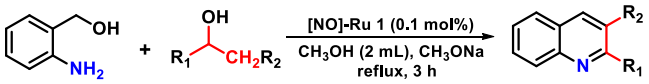
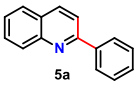
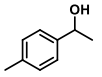
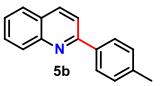
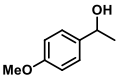
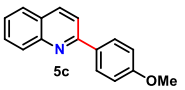
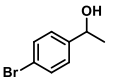
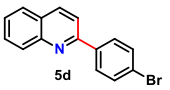
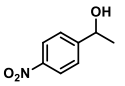
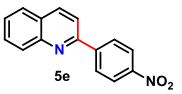
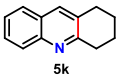
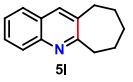
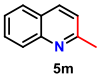
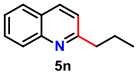
Table 4. Scope of the Reaction between 2-Aminobenzyl Alcohol and Secondary Alcohols[a]



Entry	Ketones	Products	Yields/%[b]	TON	TOF/h^{-1}
1		 5a	91 (88)	910	303
2		 5b	94 (90)	940	313
3		 5c	94 (91)	940	313
4		 5d	89 (86)	890	297
5		 5e	90 (88)	900	300
6		 5k	92 (88)	920	307
7		 5l	94 (91)	940	313
8		 5m	78 (75)	780	260
9		 5n	76 (72)	760	253

[a]Reaction conditions: complex **1** (0.1 mol %), 2-aminobenzyl alcohol (1.0 mmol), secondary alcohols (1.2 mmol), CH_3ONa (1.2 mmol), CH_3OH (2 mL), reflux, 3 h. [b]The yield was determined by GC analysis, and *n*-tridecane was used as the internal standard. Isolated yields (%) are provided in parentheses.

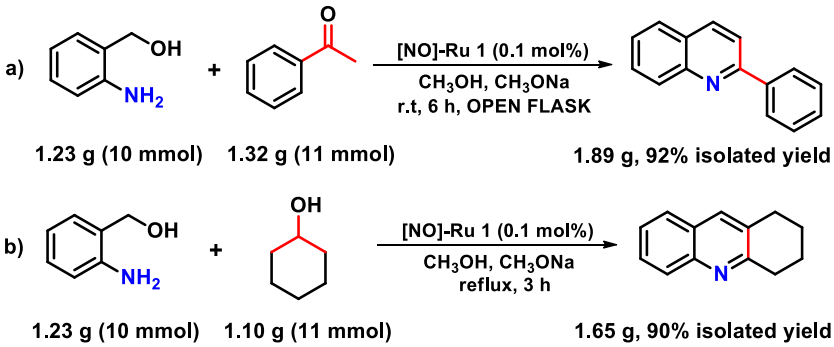


Figure 3. Gram-scale reaction study.

benzyl alcohol and ketones as starting materials that combined two reactions together. Fortunately, the reaction of aminobenzyl alcohol and ketones afforded the desired products smoothly under the sequential catalysis of complex **1** in a H_2 atmosphere by using CF_3CH_2OH as the solvent. Both electron-donating and electron-withdrawing substituents on the phenyl ring of ketones were well tolerated in the reaction (Table 7, entries 1−11). This homogeneous catalysis for the direct synthesis of tetrahydroquinoline derivatives complements quite well the heterogeneuous catalysis reported very recently.[39]

CONCLUSIONS

In summary, we have prepared a series of half-sandwich N,O-chelate ruthenium complexes that exhibited excellent catalytic activity in the synthesis of both quinoline and tetrahydroquinoline derivatives. The synthesis of quinoline derivatives starting from amino alcohols and ketones as well as secondary alcohols has been accomplished under very mild conditions. On the other hand, the ruthenium catalyst also exhibited good efficiency in the hydrogenation of quinoline derivatives under a H_2

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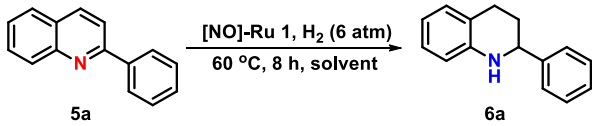
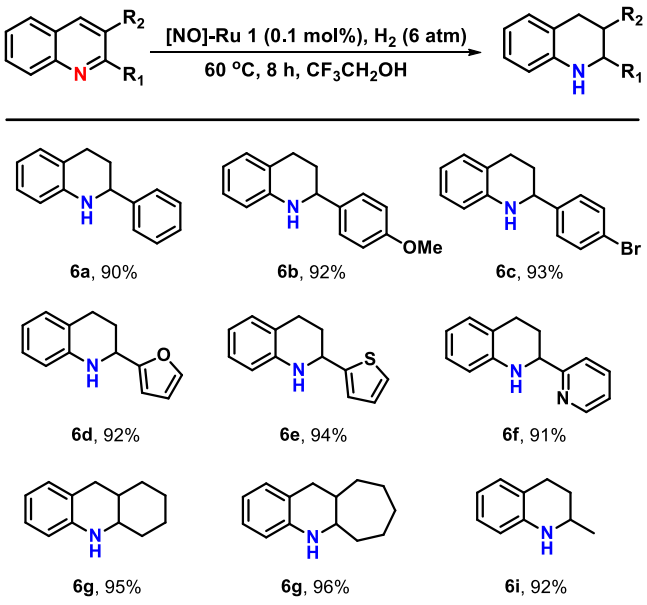
Table 5. Optimization for the Catalytic Hydrogenation of Quinoline[a]



entry	catalyst (mol %)	solvent	yield (%)[b]	TON	TOF (h^{-1})
1	0.1	MeOH	11	110	13.8
2	0.1	THF	trace	–	–
3	0.1	toluene	–	–	–
4	0.1	DMF	trace	–	–
5	0.1	CH_2Cl_2	–	–	–
6	0.1	CF_3CH_2OH	89	890	111
7	0.5	CF_3CH_2OH	90	900	112
8[c]	0.1	CF_3CH_2OH	–	–	–
9[d]	0.1	CF_3CH_2OH	trace	–	–
10[e]	–	CF_3CH_2OH	–	–	–

[a]Reaction conditions: **5a** (1.0 mmol), complex **1** (0.1 mol %), solvent (2.0 mL), H_2 (6 atm), 8 h, 60 °C. [b]The yield was determined by GC analysis, and *n*-tridecane was used as the internal standard. [c]Reaction at room temperature. [d]$[(p\text{-cym})RuCl_2]_2$ used as the catalyst. [e]Without a catalyst.

Table 6. Scope of the Catalytic Hydrogenation of Quinoline Derivatives[a,b]



[a]Reaction conditions: quinolines (1.0 mmol), complex **1** (0.1 mol %), CF_3CH_2OH (2.0 mL), H_2 (6 atm), 8 h, 60 °C. [b]The yield was determined by GC analysis, and *n*-tridecane was used as the internal standard.

atmosphere with a low catalyst loading, so the methodology for the one-pot synthesis of tetrahydroquinoline derivatives has been also developed, which combined the two reactions of cyclization and hydrogenation together on the basis of the continuous catalytic activity of the ruthenium catalyst in the selective hydrogenation of quinolines. The stability, diverse catalytic activity, and good efficiency made them attractive in industrial applications.

EXPERIMENTAL SECTION

General Data. Half-sandwich ruthenium complexes **1**–**4** were synthesized under an atmosphere of argon using standard Schlenk techniques. Chemicals were used as commercial products without further purification. ^1H NMR (500 MHz) spectra were recorded with a Bruker DMX-500 spectrometer. Elemental analysis was performed on an Elementar vario EL III analyzer. IR (KBr) spectra were recorded with the Nicolet FT-IR spectrophotometer.

Synthesis of 7-Hydroxy-3,4-methylindan-1-one. 4-Methylphenol (11 mmol, 1.1 equiv), γ-butyrolactone (10 mmol, 1.1 equiv), $AlCl_3$ (15 mmol, 1.5 equiv), and NaCl (75 mmol, 7.5 equiv) were mixed together, and the mixture was stirred at 200 °C for 2 min. After the reaction mixture had cooled to room temperature, the mixture was poured into the HCl (10 wt %) solution. Then the solution was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layer was dried and concentrated. The crude product was recrystallized in an *n*-hexane/Et_2O mixed solvent to give a white solid (yield of 41%): ^1H NMR (500 MHz, $CDCl_3$) δ 9.00 (s, 1H, OH), 7.16 (d, *J* = 8.2 Hz, 1H, ArH), 6.58 (d, *J* = 8.2 Hz, 1H, ArH), 3.39–3.33 (s, 1H, ArCH), 2.88 (dd, *J* = 7.5, 7.5 Hz, 1H, CH_2), 2.25–2.21 (m, 1H, CH_2, overlapped with $ArCH_3$), 2.22 (s, 3H, $ArCH_3$), 1.25 (d, *J* = 7.0 Hz, 3H, $CHCH_3$). Elemental analysis calcd (%) for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.03; H, 6.80.

Synthesis of Hydroxyindanone-imine Ligands L1–L4. The mixture of 7-hydroxy-3,4-methylindan-1-one (1.0 mmol, 1.0 equiv), corresponding aromatic amines (1.2 mmol, 1.1 equiv), and 4 Å molecular sieves (0.1 g) in EtOH (10 mL) in a 25 mL Schlenk tube was refluxed for 24 h. The reaction mixture was filtered, and the solvent was removed under reduced pressure. Column chromatography of the crude products (6:1 PE:EA) gave **L1**–**L4** in good yields.

L1. Yellow solid; 81% isolated yield; ^1H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H, −OH), 7.38 (t, *J* = 7.7 Hz, 2H, ArH), 7.16–7.12 (m, 2H, ArH), 7.03 (d, *J* = 7.5 Hz, 2H, ArH), 6.75 (d, *J* = 8.0 Hz, 1H, ArH), 3.47–3.44 (m, 1H, CH), 3.06 (dd, *J* = 7.5, 7.5 Hz, 1H, CH_2), 2.40–2.37 (m, 1H, CH_2), 2.29 (s, 3H, $ArCH_3$), 1.27 (d, *J* = 7.0 Hz, 3H, $CHCH_3$); IR (KBr, disk) ν 3359 (ν_{O-H}), 2915 (ν_{C-H}), 1659 ($\nu_{C=N}$), 1023 (ν_{C-O}), 768 (ν_{Ar-H}) cm^{-1}. Elemental analysis calcd (%) for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.32; H, 6.75; N, 5.66.

L2. Light yellow solid; 78% isolated yield; ^1H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H, −OH), 7.19 (d, *J* = 8.0 Hz, 2H, ArH), 7.13 (d, *J* = 8.0 Hz, 1H, ArH), 6.95 (d, *J* = 8.0 Hz, 2H, ArH), 6.74 (d, *J* = 8.0 Hz, 1H, ArH), 3.48–3.42 (m, 1H, CH), 3.10 (dd, *J* = 8.0, 8.0 Hz, 1H, CH_2), 2.43–2.39 (m, 1H, CH_2), 2.36 (s, 3H, $ArCH_3$), 2.28 (s, 3H, $ArCH_3$), 1.27 (d, *J* = 7.0 Hz, 3H, $CHCH_3$); IR (KBr, disk) ν 3367 (ν_{O-H}), 2920 (ν_{C-H}), 1652 ($\nu_{C=N}$), 1018 (ν_{C-O}), 766 (ν_{Ar-H}) cm^{-1}. Elemental analysis calcd (%) for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.41; H, 7.20; N, 5.37.

L3. Yellow solid; 72% isolated yield; ^1H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H, −OH), 7.34 (d, *J* = 8.5 Hz, 2H, ArH), 7.15 (d, *J* = 8.0 Hz, 1H, ArH), 6.97 (d, *J* = 9.0 Hz, 2H, ArH), 6.75 (d, *J* = 8.0 Hz, 1H, ArH), 3.49–3.43 (m, 1H, CH), 3.05 (dd, *J* = 8.0, 8.0 Hz, 1H, CH_2), 2.38–2.34 (m, 1H, CH_2), 2.29 (s, 3H, $ArCH_3$), 1.28 (d, *J* = 7.0 Hz, 3H, $CHCH_3$); IR (KBr, disk) ν 3447 (ν_{O-H}), 2963 (ν_{C-H}), 1640 ($\nu_{C=N}$), 1080 (ν_{C-O}), 769 (ν_{Ar-H}) cm^{-1}. Elemental analysis calcd (%) for $C_{17}H_{16}ClNO$: C, 71.45; H, 5.64; N, 4.90. Found: C, 71.52; H, 5.62; N, 4.97.

L4. Yellow solid; 76% isolated yield; ^1H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H, −OH), 7.49 (d, *J* = 8.5 Hz, 2H, ArH), 7.15 (d, *J* = 8.0 Hz, 1H, ArH), 6.91 (d, *J* = 8.5 Hz, 2H, ArH), 6.75 (d, *J* = 8.0 Hz, 1H, ArH), 3.49–3.43 (m, 1H, CH), 3.05 (dd, *J* = 7.5, 7.5 Hz, 1H, CH_2), 2.37–2.37 (m, 1H, CH_2), 2.29 (s, 3H, $ArCH_3$), 1.21 (d, *J* = 7.0 Hz, 3H, $CHCH_3$); IR (KBr, disk) ν 3403 (ν_{O-H}), 2960 (ν_{C-H}), 1643 ($\nu_{C=N}$), 1010 (ν_{C-O}), 761 (ν_{Ar-H}) cm^{-1}. Elemental analysis calcd (%) for $C_{17}H_{16}BrNO$: C, 61.83; H, 4.88; N, 4.24. Found: C, 61.89; H, 4.93; N, 4.15.

Synthesis of N,O-Chelate Half-Sandwich Ruthenium Complexes 1–4. A mixture of $[(p\text{-cymene})RuCl_2]_2$ (0.1 mmol, 0.5 equiv), NaOAc (0.4 mmol, 2.0 equiv), and ligands **L1**–**L4** (0.2 mmol, 1.0 equiv) was stirred at 60 °C in methanol (5 mL) for 6 h. The mixture was

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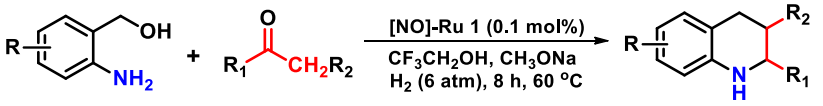
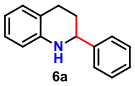
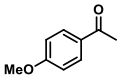
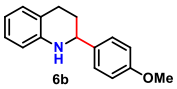
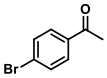
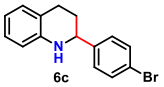
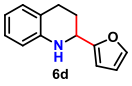
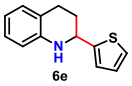
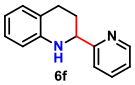
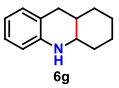
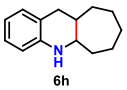
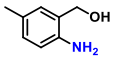
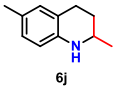
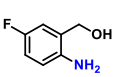
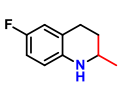
Table 7. One-Pot Synthesis of Tetrahydroquinoline Derivatives[a]



Entry	Amino Alcohol	Ketones	Products	Yields/%[b]	TON	TOF/h^{-1}
1			 6a	89	890	111
2			 6b	91	910	114
3			 6c	91	910	114
4			 6d	88	880	110
5			 6e	89	890	111
6			 6f	86	860	108
7			 6g	90	900	112
8			 6h	84	840	105
9			 6i	80	800	100
10			 6j	78	780	97.5
11			 6k	77	770	96.2

[a]Reaction conditions: aminobenzyl alcohols (1.0 mmol), ketones (1.1 mmol), CH_3ONa (1.1 mmol), complex **1** (0.1 mol %), CF_3CH_2OH (2.0 mL), H_2 (6 atm), 8 h, 60 °C. [b]The yield was determined by GC analysis, and *n*-tridecane was used as the internal standard.

filtered and concentrated to give the crude products that were further purified by silica gel column chromatography (6:1 CH_2Cl_2:EA) to afford pure N,O-chelate half-sandwich ruthenium complexes.

1. Brown solid; 62% isolated yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0 Hz, ArH, 1H), 7.51−7.45 (m, ArH, 2H), 7.32 (t, J = 7.5 Hz, ArH, 1H), 7.07−7.00 (m, ArH, 2H), 6.78 (d, J = 10.0 Hz, ArH, 1H), 5.32 (d, J = 6.0 Hz, *p*-cymene-H, 1H), 5.14−5.11 (m, *p*-cymene-H, 2H), 5.04 (d, J = 6.0 Hz, *p*-cymene-H, 1H), 3.18−3.08 (m, C*H*CH$_3$, 1H), 2.91−2.86 [m, C*H*(CH$_3$)$_2$, 1H], 2.71−2.61 (m, CHC*H*$_2$, 2H), 2.09 (s, ArCH$_3$, 3H), 1.68 (s, *p*-cymene-CH$_3$, 3H), 1.45 (d, J = 7.5 Hz, 3H, CHC*H*$_3$), 1.11 [d, J = 7.0 Hz, CH(C*H*$_3$)$_2$, 6H]; IR (KBr, disk) υ 2963 (υ_{C-H}), 1615 ($\upsilon_{C=N}$), 1015 (υ_{C-O}), 760 (υ_{Ar-H}) cm^{-1}. Elemental analysis calcd (%) for $C_{27}H_{30}ClNORu$: C, 62.24; H, 5.80; N, 2.69. Found: C, 62.18; H, 5.75; N, 2.79. MS (ESI, m/z): 486 [M − Cl]$^+$.

2. Yellow brown solid; 58% isolated yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66−7.62 (m, ArH, 2H), 7.00 (d, J = 7.5 Hz, ArH, 2H), 6.75 (d, J = 7.5 Hz, ArH, 2H), 5.31 (d, J = 6.0 Hz, *p*-cymene-H, 1H), 5.18 (d, J = 6.0 Hz, *p*-cymene-H, 1H), 5.10 (d, J = 6.0 Hz, *p*-cymene-H, 1H), 5.02 (d, J = 6.0 Hz, *p*-cymene-H, 1H), 3.17−3.09 (m, C*H*CH$_3$, 1H), 2.90−2.85 [m, C*H*(CH$_3$)$_2$, 1H], 2.72−2.61 (m, CHC*H*$_2$, 2H), 2.43 (s, ArCH$_3$, 3H), 2.09 (s, ArCH$_3$, 3H), 1.69 (s, *p*-cymene-CH$_3$, 3H), 1.40 (d, J = 7.5 Hz, 3H, CHC*H*$_3$), 1.08 [d, J = 7.5 Hz, CH(C*H*$_3$)$_2$, 6H]; IR (KBr, disk) υ 2965 (υ_{C-H}), 1612 ($\upsilon_{C=N}$), 1010 (υ_{C-O}), 768 (υ_{Ar-H}) cm^{-1}. Elemental analysis calcd (%) for $C_{28}H_{32}ClNORu$: C, 62.85; H, 6.03; N, 2.62. Found: C, 62.89; H, 6.10; N, 2.57. MS (ESI, m/z): 500 [M − Cl]$^+$.

3. Brown solid; 54% isolated yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 7.5 Hz, ArH, 2H), 7.01 (d, J = 7.5 Hz, ArH, 2H), 6.75−6.73 (m, ArH, 2H), 5.33 (d, J = 6.0 Hz, *p*-cymene-H, 1H), 5.19 (d, J = 6.0

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Hz, *p*-cymene-H, 1H), 5.10 (d, *J* = 6.0 Hz, *p*-cymene-H, 1H), 5.03 (d, *J* = 6.0 Hz, *p*-cymene-H, 1H), 2.89−2.84 (m, C*H*CH$_3$, 1H), 2.72−2.60 [m, C*H*(CH$_3$)$_2$ and C*H*CH$_2$, 3H], 2.09 (s, ArCH$_3$, 3H), 1.69 (s, *p*-cymene-CH$_3$, 3H), 1.21 (d, *J* = 7.5 Hz, 3H, CHC*H*$_3$), 1.09 [d, *J* = 7.5 Hz, CH(C*H*$_3$)$_2$, 6H]; IR (KBr, disk) υ 2960 (υ_{C-H}), 1618 ($\upsilon_{C=N}$), 1019 (υ_{C-O}), 763 (υ_{Ar-H}) cm^{-1}. Elemental analysis calcd (%) for $C_{27}H_{29}Cl_2NORu$: C, 58.38; H, 5.26; N, 2.52. Found: C, 58.42; H, 5.25; N, 2.60. MS (ESI, *m*/*z*): 520 [M − Cl]$^+$.

4. Brown solid; 59% isolated yield; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.60 (d, *J* = 7.5 Hz, ArH, 2H), 7.01 (d, *J* = 7.5 Hz, ArH, 2H), 6.77−6.73 (m, ArH, 2H), 5.33 (d, *J* = 6.0 Hz, *p*-cymene-H, 1H), 5.19 (d, *J* = 6.0 Hz, *p*-cymene-H, 1H), 5.10 (d, *J* = 6.0 Hz, *p*-cymene-H, 1H), 5.02 (d, *J* = 6.0 Hz, *p*-cymene-H, 1H), 2.89−2.84 (m, C*H*CH$_3$, 1H), 2.72−2.60 [m, C*H*(CH$_3$)$_2$ and C*H*CH$_2$, 3H], 2.26 (s, ArCH$_3$, 3H), 1.75 (s, *p*-cymene-CH$_3$, 3H), 1.51 (d, *J* = 7.5 Hz, 3H, CHC*H*$_3$), 1.09 [d, *J* = 7.5 Hz, CH(C*H*$_3$)$_2$, 6H]; IR (KBr, disk) υ 2955 (υ_{C-H}), 1615 ($\upsilon_{C=N}$), 1021 (υ_{C-O}), 765 (υ_{Ar-H}) cm^{-1}. Elemental analysis calcd (%) for $C_{27}H_{29}ClBrNORu$: C, 54.05; H, 4.87; N, 2.33. Found: C, 54.11; H, 4.82; N, 2.31. MS (ESI, *m*/*z*): 564 [M − Cl]$^+$.

General Procedure for the Synthesis of Quinolines from Amino Alcohols with Ketones. 2-Aminobenzyl alcohol (1.0 mmol), ketone (1.1 mmol), CH$_3$ONa (1.1 mmol), and complex **1** (0.001 mmol) were mixed in CH$_3$OH (2 mL), and the mixture was stirred at room temperature for 6 h. After the reaction, the mixture was diluted with CH$_2$Cl$_2$ and washed with brine. Organic layers were combined, dried over Na$_2$SO$_4$, filtered, and evaporated to give the crude products that were further purified by silica gel column chromatography (5:1 PE:EA) to furnish pure products.

General Procedure for the Synthesis of Quinolines from Amino Alcohols with Secondary Alcohols. 2-Aminobenzyl alcohol (1.0 mmol), secondary alcohol (1.1 mmol), CH$_3$ONa (1.1 mmol), and complex **1** (0.001 mmol) were mixed in CH$_3$OH (3 mL), and the mixture was refluxed for 3 h. After the reaction, the mixture was diluted with CH$_2$Cl$_2$ and washed with brine. Organic layers were combined, dried over Na$_2$SO$_4$, filtered, and evaporated to give the crude products that were further purified by silica gel column chromatography (5:1 PE:EA) to furnish pure products.

General Procedure for the Hydrogenation of Quinolines. In a typical run, quinoline (1.0 mmol), complex **1** (0.001 mol), and CF$_3$CH$_2$OH (3 mL) were charged in a 5 mL vial. The vial was then transferred to an autoclave. The autoclave was pressurized with H$_2$ (6 atm) and disconnected from the H$_2$ source. The autoclave was heated to 60 °C. After the reaction, the resultant mixture was extracted with diethyl ether (2 × 5 mL) and dried over anhydrous Na$_2$SO$_4$. The organic solution was concentrated, and the residue was dissolved in hexane and assessed by GC-MS.

General Procedure for the One-Pot Synthesis of Tetrahydroquinolines. In a typical run, 2-aminobenzyl alcohol (1.0 mmol), ketone (1.1 mmol), CH$_3$ONa (1.1 mmol), complex **1** (0.001 mmol), and CF$_3$CH$_2$OH (3 mL) were charged in a 5 mL vial. The vial was then transferred into an autoclave. The autoclave was pressurized with H$_2$ (6 atm) and disconnected from the H$_2$ source. The autoclave was heated to 60 °C. After the reaction, the mixture was extracted with diethyl ether (2 × 5 mL) and dried over anhydrous Na$_2$SO$_4$. The organic solution was concentrated, and the residue was dissolved in hexane and assessed by GC-MS.

X-ray Crystallography. Diffraction data of the complex were collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). All of the data were collected at room temperature, and the structure was determined by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL).[40] SADABS[41] absorption corrections were applied to the data; all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions. All calculations were performed using the Bruker program Smart.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00955.

^{1}H NMR spectra of **L1**−**L4** and ruthenium complexes **1**−**4** and FT-IR spectra of the complex (PDF)

Accession Codes

CCDC 1966541−1966542 contain 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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