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Ruthenium-catalyzed acceptorless dehydrogenative coupling of *o*-aminobenzyl alcohols with ketones to quinolines in the presence of carbonate salt

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ABSTRACT

A ruthenium complex bearing a functional 2,2′-bibenzimidazole ligand [(*p*-cymene)Ru($BiBzImH_2$)Cl][Cl] was designed, synthesized and found to be a general and highly efficient catalyst for the synthesis of quinolines via acceptorless dehydrogenative coupling of *o*-aminobenzyl alcohols with ketones in the presence of carbonate salt. It was confirmed that NH units in the ligand are crucial for catalytic activity. The application of this catalytic system for the scale-gram synthesis of biologically active molecular was also undertaken. Notably, this research exhibits new potential of metal–ligand bifuctional catalysts for acceptorless dehydrogenative reactions.

1. Introduction

Quinolines represent an important class of nitrogen-containing heterocycles which were frequently found in the alkaloid family [1]. They exhibited also a wide range of biological properties and were utilized as ligands of transition metal catalysts and organocatalysts [2,3], and building blocks of functional materials [4]. For this reason, a series of classical synthetic methods, such as Skraup, Doebner-von Miller, Conrad-Limpach, Pfitzinger and Friedlaeder synthesises, have been developed in past decades [5]. Among them, Friedlaeder synthesises, e.g. acid or base-mediated coupling of *o*-aminobenzaldehydes with ketones, are considered to be one of the most straightforward methods to access quinolines although *o*-aminobenzaldehydes are very unstable materials and prone to self-condensation [6]. In recent years, transition metal-catalyzed oxidative cyclization of *o*-aminobenzyl alcohols with ketones as a modified Friedlaeder synthesises have been reported [7]. However, these procedures required extra addition of large excess of ketones, unsaturated olefines or molecular oxygen as sacrificial hydrogen acceptors to generate in situ *o*-aminobenzaldehydes from *o*-aminobenzyl alcohols. More recently, much attention has been paid to the development of transition metal-catalyzed acceptorless dehydrogenative reactions with the liberation of hydrogen gas [8]. Such methodologies provide the clearest and most atom-economical processes as alternatives to traditional oxidation reactions. Several groups have reported acceptorless dehydrogenative coupling of *o*-aminobenzyl alcohols with ketones to quinolines catalyzed by iridium [9], ruthenium [10], nickel [11], manganese [12] and rhenium complexes [13]. However, all these procedures required the presence of large amount of inorganic strong base (KOH, *t*BuOK), and thus the potential of practical application is still highly restricted.

Fujita and co-workers have developed a series of Cp*Ir complexes bearing a bipyridine or a bipyridonate ligand, which exhibited high activities for acceptorless dehydrogenation of alcohols and N-heterocycles [14], and hydrogen production from an alcohol-water solution under basic conditions based on the concept of ligand-promoted dehydrogenation [15]. We have also demonstrated that such Cp*Ir complexes are highly effective metal–ligand bifunctional catalysts for hydrogen auto-transfer process [16], acceptorless dehydrogenative cyclization [17], and transfer hydrogenation of aldehydes and ketones [18]. As part of a continuing interest in the field, we turned our attention from iridium complexes to ruthenium ones because ruthenium is much cheaper than iridium [19]. Herein, we with to describe the design and synthesis, of a ruthenium complex bearing a 2,2′-bibenzimidazole ligand that contains a tautomerism structure and protic hydrogens like α-hydroxypyridine (Scheme 1). Furthermore, this complex was found to be a general and highly efficient

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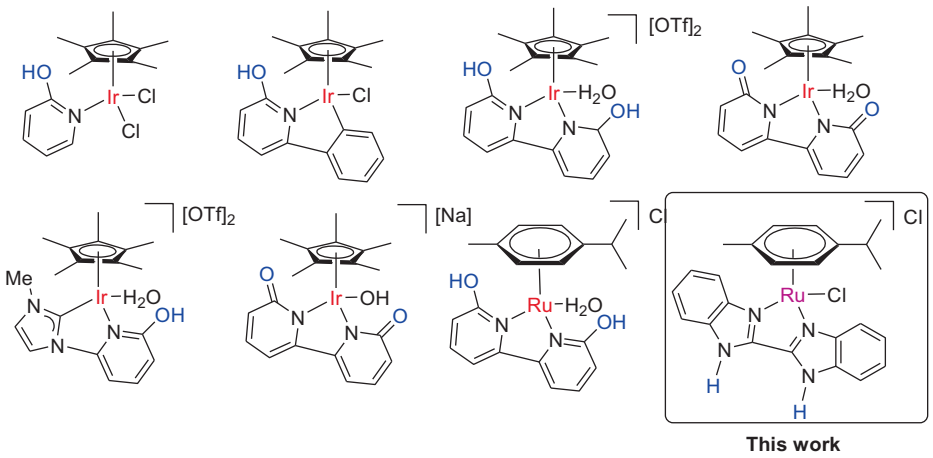


Scheme 1. Metal-Ligand Bifunctional Catalysts for Acceptorless Dehydrogenation.

catalyst for the acceptorless dehydrogenative coupling of *o*-aminobenzyl alcohols with ketones to quinolines in the presence of carbonate.

2. Result and discussion

The synthetic procedure to prepare the designed ruthenium complex [(*p*-cymene)Ru(BiBzImH$_2$)Cl][Cl] was outlined in Scheme 2. The reaction of [(*p*-cymene)RuCl$_2$]$_2$ with 2,2′- bibenzimidazole (2.2 equiv) was performed in THF at 60 °C for 12 h. The formed yellow solid was collected by filtration and then washed with THF. The complex is stable to air and moisture both in the solid state and in solution. The crystal for X-ray crystallography was obtained and its molecular structure was shown in Fig. 1 with pertinent bond lengths and angles. 2,2′-Bibenzimidazole ligand is bonded to ruthenium center with two nitrogen atoms with a bond angle of 76.60 (19) in a chelating fashion. Bond lengths of N1-Ru and N3-Ru are 2.118 (5) Å and 2.135 (5) Å, respectively.

With the synthesized [(*p*-cymene)Ru(BiBzImH$_2$)Cl][Cl] (cat. **1**) in hand, we investigated its catalytic activity for the acceptorless dehydrogenative coupling of *o*-aminobenzyl alcohol (**1a**) with acetophenone (**2a**). In the presence of cat. **1** (1 mol %) and Cs_2CO_3 (0.5 equiv), the reaction was carried out at 125 °C for 12 h to afford the product **3aa** in 92% yield (Table 1, entry 1). Using its analog [(*p*-cymene)Ru(BiBzImMe$_2$)Cl][Cl] (cat. **2**) as an alternative catalyst, the product **3aa** was obtained in only 16% yield (Table 1, entry 2). In the case of ruthenium complexes bearing a functional α-hydroxypyridine ligand [(*p*-cymene)Ru (6,6′-(OH)$_2$bpy)(H$_2$O)] [OTf]$_2$ (cat. **3**) and its analog [(*p*-cymene) (6,6′-(OMe)$_2$bpy)(H$_2$O)] [OTf]$_2$ (cat. **4**), product **3aa** was obtained in 89% and 19% yields, respectively (Table 1, entries 3–4). Obviously, NH or OH units in the ligand are crucially important for the catalytic activity of ruthenium complexes. When other ruthenium complexes (cat. **5**–**11**) were examined, reactions afforded the product **3aa** in 14–41% yields (Table 1, entries 5–11). Then, cat. **1** was chosen as a catalyst for further investigation. Tries to use of K_2CO_3 or Na_2CO_3 as an alternative base, to reduce the amount of Cs_2CO_3, and to decrease reaction temperature resulted in relatively low yields (Table 1, entries 12–15).

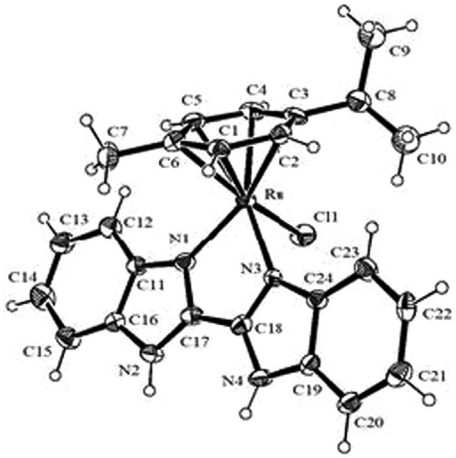
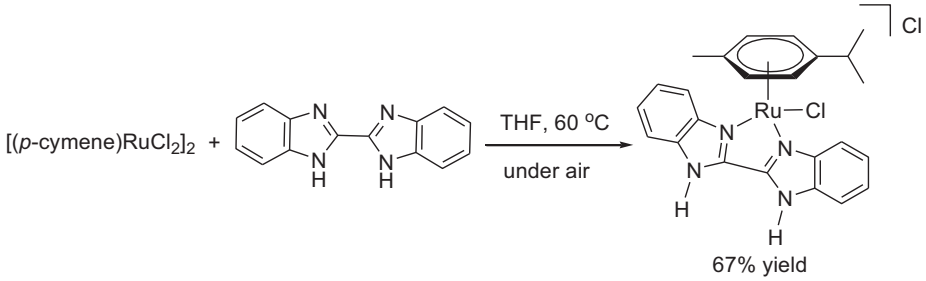
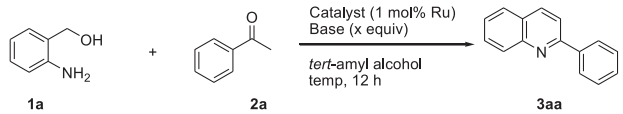


Fig. 1. X-ray structure of [(*p*-cymene)Ru(BiBzImH$_2$)Cl][Cl] (thermal ellipsoids set at 50% probability). Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [deg]: Ru-N1, 2.118 (5); Ru-N3, 2.135 (5); Ru-C1, 2.175 (6); Ru-C4, 2.178(6); Ru-C5, 2.191 (6); Ru-C2, 2.194 (6); Ru-C6, 2.202 (7); Ru-C3, 2.214 (6); Ru-Cl, 2.3982 (18); N1-Ru-N3, 76.60 (19); N1-Ru-Cl1, 85.24 (15); N3-Ru-Cl1, 84.90 (15).



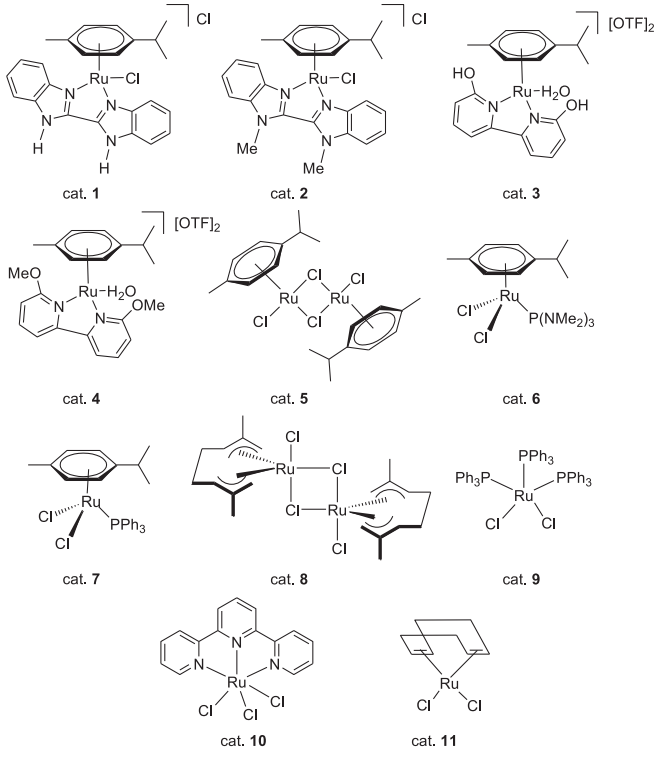
Scheme 2. The Synthesis of [(*p*-cymene)Ru(BiBzImH$_2$)Cl][Cl].

Table 1
Coupling of *o*-Aminobenzyl Alcohol (**1a**) with Acetophenone (**2a**) under Various Conditions.[a]



1a 2a 3aa

Entry	Catalyst	Base	Temp.	x	Yield (%)[b]
1	cat. **1**	**Cs_2CO_3**	**125**	**0.5**	**92 (86)[c]**
2	cat. **2**	Cs_2CO_3	125	0.5	16
8	cat. **3**	Cs_2CO_3	125	0.5	89
4	cat. **4**	Cs_2CO_3	125	0.5	19
5	cat. **5**	Cs_2CO_3	125	0.5	23
6	cat. **6**	Cs_2CO_3	125	0.5	25
7	cat. **7**	Cs_2CO_3	125	0.5	31
8	cat. **8**	Cs_2CO_3	125	0.5	28
9	cat. **9**	Cs_2CO_3	125	0.5	34
10	cat. **10**	Cs_2CO_3	125	0.5	41
11	cat. **11**	Cs_2CO_3	125	0.5	14
12	cat. **1**	K_2CO_3	125	0.5	90
13	cat. **1**	Na_2CO_3	125	0.5	85
14	cat. **1**	Cs_2CO_3	125	0.2	78
15	cat. **1**	Cs_2CO_3	115	0.5	81



[a]Reaction conditions: **1a** (1 mmol), **2a** (1.2 mmol), catalyst (1 mol % Ru), base (x equiv), *tert*-amyl alcohol (1 mL), 12 h.
[b]Yield was determined based on the ^{1}H NMR spectrum of the crude reaction mixture with 1,3,5-trimethoxybenzene as the internal standard.
[c]Isolated yield.

Having established the optimal conditions (Table 1, entry 1), the scope of reaction with respect to ketones was conducted and these results are outlined in Table 2. Transformations of acetophenones bearing an electron-rich substituent gave the corresponding products **3ab**-**3ah** in 76–84% yields. Acetophenones bearing one or two halogen atoms were also readily cyclized to desired products **3ai**-**3ao** in 77–85% yields.

Furthermore, this system was applied to substrates bearing more serious electron-deficient substituents, such as trifluoromethyl and trifluoromethoxy groups, affording corresponding products **3ap** and **3aq** in 80% and 84% yields, respectively. Readily reducible or labile substituents, such as nitro and cyano groups, were well tolerated, reactions afforded desired products **3ar** and **3as** in 82% and 85% yields, respectively. When 1-(4-phenylphenyl)ethanone and 1-(pyrazin-2-yl)ethanone were used, corresponding products **3at** and **3au** were made in 80% and 76% yields, respectively. Non-methyl ketones, such as propiophenone, *n*-butyrophenone and 1-tetralone could be converted to corresponding quinolines **3av-3ax** in 77–82% yields. For aliphatic ketones, such as 1-cyclopropylethanone and 3,3-dimethylbutan-2-one, desired products **3ay** and **3az** were successfully isolated in 86% and 83% yields, respectively.

To expand further generality of reaction, the couplings with respect to *o*-aminobenzyl alcohols were investigated (Table 3). Transformations of *o*-aminobenzyl alcohols bearing an electron-rich substituent gave corresponding products **3ba** and **3ca** in 84% and 87% yields, respectively. Similarly, desired products **3da-3ga** were obtained in 81–85% yields when *o*-aminobenzyl alcohols bearing an electron-efficient substituent were utilized as substrates.

Based experimental results, two possible simultaneous mechanisms for the present synthesis of quinolines *via* acceptorless dehydrogenative coupling of *o*-aminobenzyl alcohols with ketones were presented (Scheme 3). The initial step of reaction involved the formation of species **A** via the reaction of cat. **1** with Cs_2CO_3. With the process of the activation of alcohols, the ligand accepted a proton to give alkoxy ruthenium species **B**, which further underwent *ß*-hydrogen elimination to give aldehydes and ruthenium hydride species **C**. In mechanism I, the ligand-promoted simultaneous hydrogen transfer from the hydride on the ruthenium and the proton on the ligand resulted in the regeneration of catalytic species **A** and the liberation of a molecular hydrogen. Furthermore, a base-promoted cross-aldol condensation between ketones and resulting *o*-aminobenzaldehydes afforded *α,ß*-unsaturated ketones, followed by an intramolecular cyclodehydration occurred to give quinolines. In mechanism II, after a base-promoted cross-adol condensation between ketones and resulting aldehydes, the hydride on the ruthenium and proton on the ligand of species **C** were simultaneously transferred to the C=C bond of *α,ß*-unsaturated ketones, resulted in the regeneration of catalytic species **A** and the liberation of *α*-alkylated ketones, which underwent sequential intramolecular cyclodehydration/dehydrogenation to afford corresponding quinolines.

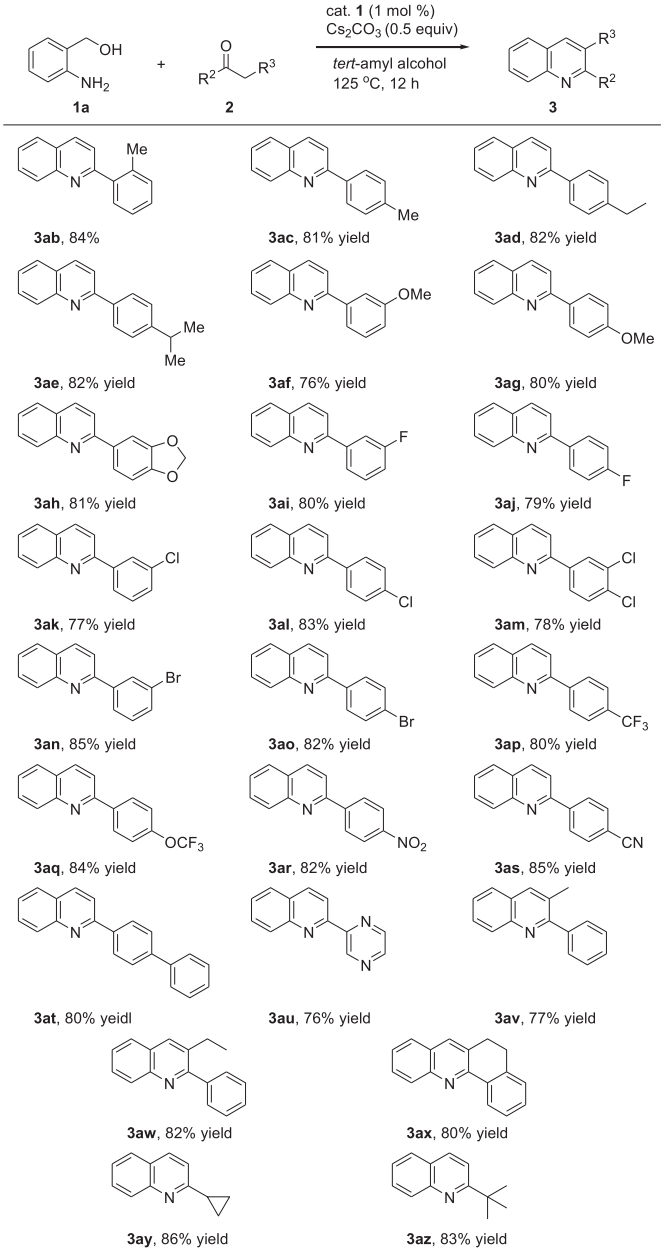
To support the proposed mechanism for acceptorless dehydrogenation, the liberation of gas in the process of model reaction was collected through a water displacement (Table 1, entry 1). This gas was determined to molecular hydrogen by GC analysis and was calculated to be 87% yield (299.15 K, 100,300 Pa, 21.6 mL).

As outlined in Scheme 4, the gram-scale synthesis of a biologically active molecule (Na^+ channel antagonists) was represented in order to demonstrate the application of this catalytic system. Under standard conditions, the coupling of 1a (25 mmol) and **2a** (30 mmol, 1.2 equiv) gave the product **3aa** in 85% yield. Subsequently, the reduction of **3aa** was carried out in the presence of $NaBH_3CN$ (2 equiv) to afford the product **4** in 71% yield, which are further reacted with NH_2CN (7 equiv) to give the desired product **5** in 30% yield according to the previous report [20].

3. Conclusions

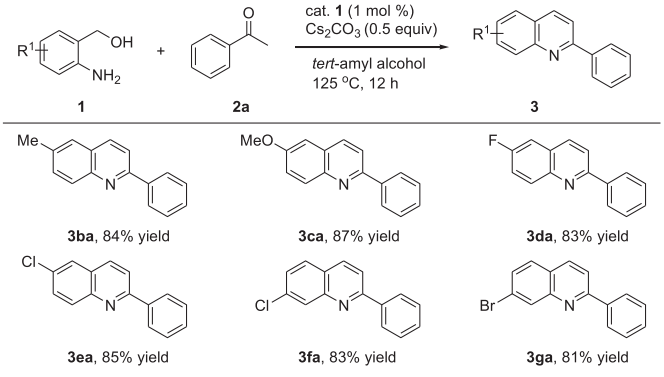
In summary, we demonstrated the design and synthesis of a ruthenium complex bearing a functional 2,2′-bibenzimidazole ligand and developed it as the first catalyst for acceptorless dehydrogeantive coupling of *o*-aminobenzyl alcohols with ketones to quinolines in the presence of carbonate salt. Under environmen-

Table 2
Scope of Reaction with Respect to Ketone.[a,b]



[a] Reaction conditions: **1a** (1 mmol), **2** (1.2 mmol), cat. **1** (1 mol %), Cs_2CO_3 (0.5 equiv), *tert*-amyl alcohol (1 mL), 125 °C, 12 h.
[b] Isolated yield.

Table 3
Scope of Reaction with Respect to *o*-Aminobenzyl Alcohols.[a,b]



[a] Reaction conditions: **1** (1 mmol), **2a** (1.2 mmol), cat. **1** (1 mol %), Cs_2CO_3 (0.5 equiv), *tert*-amyl alcohol (1 mL), 125 °C, 12 h.
[b] Isolated yield.

tally benign conditions, a series of desirable products were obtained in high yields. It was confirmed that NH units in the ligand are crucial for catalytic activity. The application of this catalytic system for the scale-gram synthesis of biologically active molecular was also undertaken. Notably, this research exhibits new potential of metal–ligand bifuctional catalysts for acceptorless dehydrogenative reactions.

4. Experimental section

4.1. General experimental details

High-resolution mass spectra (HRMS) were obtained on a HPLC-Q-TOF-MS (Micro) spectrometer and are reported as *m/z* (relative intensity). Accurate masses are reported for the molecular ion $[M]^+$, $[M + H]^+$ or $[M - Cl]^+$. Melting points were measured on a X-6 micro-melting apparatus. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded at 500 MHz. Chemical shifts are reported in delta (δ) units, parts per million (ppm) downfield from tetramethylsilane or ppm relative to the center of the singlet at 7.26 ppm for $CDCl_3$ and 3.31 ppm for CD_3OD. Coupling constants *J* values are reported in Hertz (Hz), and the splitting patterns were designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. $^{13}C\{^1H\}$ NMR spectra were recorded on a 125 MHz spectrophotometer with broadband ^1H decoupling. Chemical shifts for $^{13}C\{^1H\}$ NMR spectra are reported in delta (δ) units, ppm relative to the center of the triplet at 77.0 ppm for $CDCl_3$ and 49.0 ppm for CD_3OD. ^{13}C NMR spectra were routinely run with broadband decoupling. Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates.

[(*p*-cymene)Ru(6,6′-$(OH)_2$bpy)(H_2O)][OTf]$_2$ (cat. **3**) [19c], [(*p*-cymene)Ru(6,6′-$(OMe)_2$bpy)(H_2O)][OTf]$_2$ (cat. 4) [19c], [(*p*-cymene)$RuCl_2]_2$ (cat. **5**) [21], {(*p*-cymene)$RuCl_2[P(NMe_2)_3]$} (cat. **6**) [22], [(*p*-cymene)$RuCl_2(PPh_3)$] (cat. **7**) [23], [{$RuCl(\mu\text{-}Cl)(\eta^3\text{:}\eta^3\text{-}C_{10}H_{16})$}$_2$] (cat. **8**) [24], [$RuCl_2(PPh_3)_3$] (cat. **9**) [25], [$(terpy)_3RuCl_3$] (cat. **10**) [26] and [Ru(cod)Cl_2] (cat. **11**) [27] were synthesized according the previous reports.

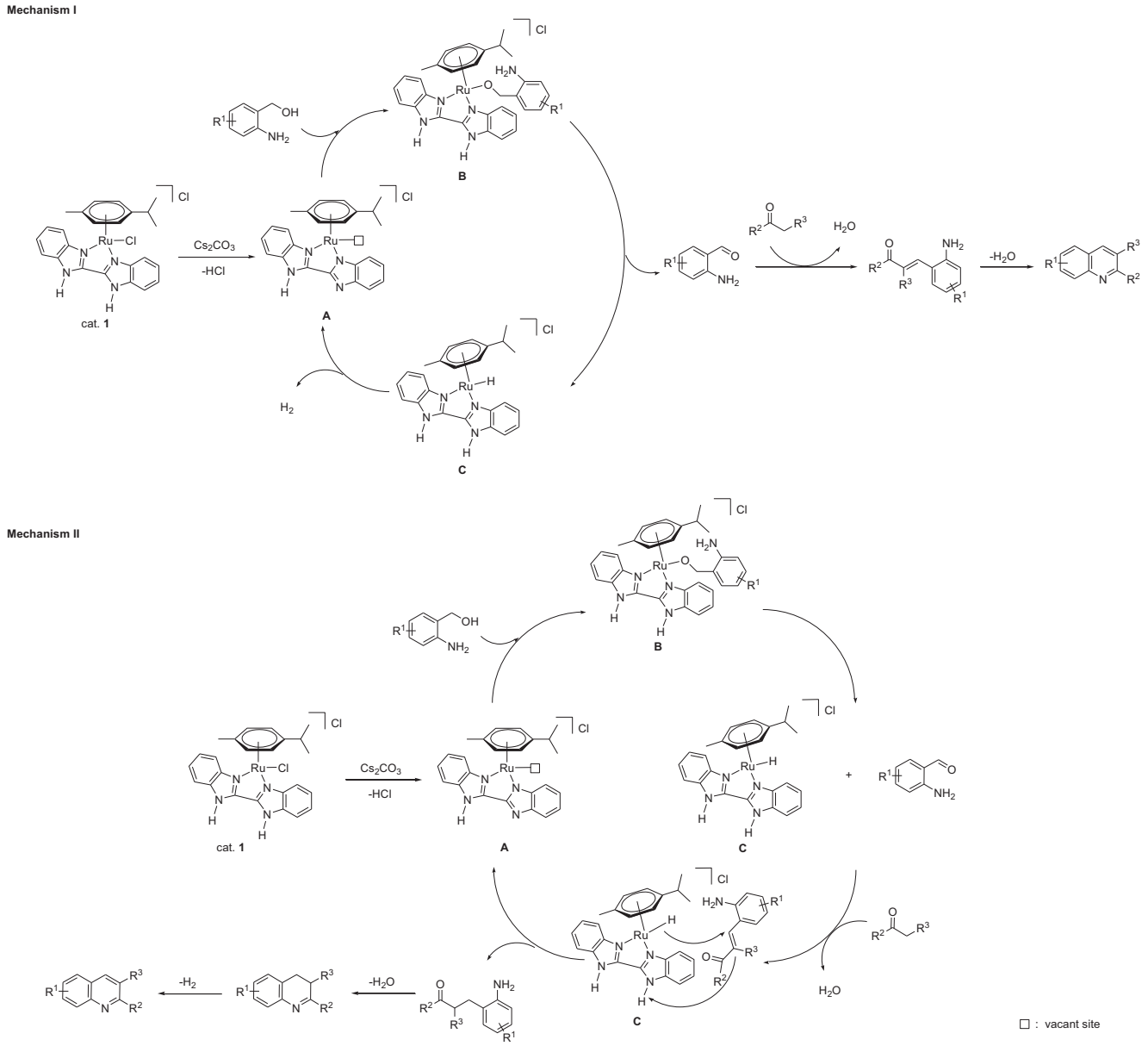
4.2. Procedure for the synthesis of [(p-cymene)Ru(BiBzImH$_2$)Cl][Cl]

To an oven-dried Schlenk tube were added [(*p*-cymene)$RuCl_2]_2$ (100 mg, 0.163 mmol), 2-(1H-benzo[d]imidazol-2-yl)-1H-benzo[d]imidazole (84 mg, 0.359 mmol, 2.2 equiv) and THF (6 mL), and the mixture was heated at 60 °C for 12 h. The reaction mixture was allowed to cool to ambient temperature. Then, the precipitate was filtered and washed with THF, affording the resulting product.

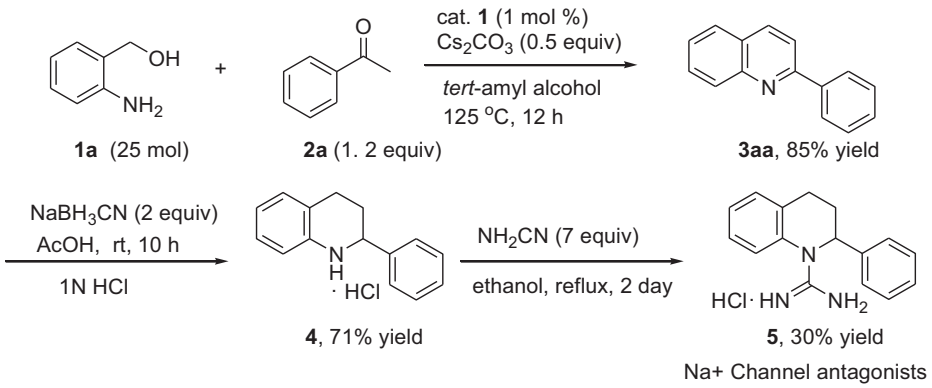
[(*p*-cymene)Ru(BiBzImH$_2$)Cl][Cl]. Yellow solid; 67% yield (110 mg); mp > 300 °C; ^1H NMR (500 MHz, CD_3OD) 8.13 (d, *J* = 8.1 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.68–7.61 (m, 4H), 6.45 (d, *J* = 6.1 Hz, 2H), 6.25 (d, *J* = 6.1 Hz, 2H), 2.45–2.43 (m, 1H), 2.31 (s, 3H), 0.93 (d, *J* = 6.9 Hz, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, CD_3OD) δ 143.5, 143.0, 136.2, 127.7, 126.7, 118.8, 115.3, 84.6, 80.6, 32.5, 22.3, 19.4. HRMS (ESI) *m/z* calcd for $C_{24}H_{24}ClN_4Ru^+$ $(M)^+$ 505.07275, found 505.07269.

4.3. Procedure for the synthesis of [(p-cymene)Ru(BiBzImMe$_2$)Cl][Cl]

To an oven-dried Schlenk tube were added [(*p*-cymene)$RuCl_2]_2$ (100 mg, 0.163 mmol), 1-methyl-2-(1-methyl-1H-benzo[d]imida



Scheme 3. Proposed Reaction Mechanisms.



Scheme 4. The Gram-Scale Synthesis of Biologically Active Molecule (Na^+ Channel Antagonists).

zol-2-yl)-1H-benzo[d]imidazole (94 mg, 0.359 mmol, 2.2 equiv) and THF (6 mL), and the mixture was heated at 60 °C for 12 h. The reaction mixture was allowed to cool to ambient temperature. Then, the precipitate was filtered and washed with THF, affording the resulting product.

[(*p*-cymene)Ru(BiBzImMe$_2$)Cl][Cl]. Yellow solid; 62% yield (108 mg); mp > 300 °C; ^{1}H NMR (500 MHz, CD_3OD) 8.15–8.13 (m, 2H), 7.92–7.90 (m, 2H), 7.73–7.69 (m, 4H), 6.42 (d, *J* = 6.0 Hz, 2H), 6.26 (d, *J* = 6.1 Hz, 2H), 4.46 (s, 6H), 2.42–2.39 (m, 1H), 2.26 (s, 3H), 0.92 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (125 MHz, CD_3OD) δ 144.8, 142.7, 138.3, 128.1, 127.2, 119.4, 113.7, 84.9, 81.1, 36.0, 32.4, 22.3, 19.4. HRMS (ESI) *m*/*z* calcd for $C_{26}H_{28}ClN_4Ru^+$ $(M + H)^+$ 533.10405, found 533.10425.

4.4. Procedure for acceptorless dehydrogenative coupling of ketones with o-aminobenzyl alcohols to quinolines catalyzed by [(p-cymene)Ru(BiBzImH$_2$)Cl][Cl]

In a round-bottomed flask with a condenser tube were added *o*-aminobenzyl alcohols **1** (1 mmol) and ketones **2** (1.2 mmol, 1.2 equiv), cat. **1** (6 mg, 0.01 mmol, 1 mol %), Cs_2CO_3 (163 mg, 0.5 mmol, 0.5 equiv) and *tert*-amyl alcohol (1 mL). The reaction mixture was heated at 125 °C in an oil bath for 12 h and then cooled to ambient temperature, concentrated in *vacuo* and purified by flash column chromatography with hexane/ethyl acetate (10:1, v/v) to afford corresponding products.

2-Phenylquinoline (3aa) [28]. White solid; 86% yield (177 mg); mp 84–85 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22–8.16 (m, 4H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.54–7.50 (m, 3H), 7.46 (t, *J* = 7.3 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.3, 148.3, 139.6, 136.7, 129.7, 129.6, 129.3, 128.8, 127.5, 127.4, 127.1, 126.2, 118.9.

2-(*o*-Tolyl)quinoline (3ab) [29]. White solid; 84% yield (184 mg); mp 75–76 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20–8.15 (m, 2H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.57–7,49 (m, 3H), 7.34–7.39 (m, 3H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 160.3, 147.9, 140.7, 136.0, 136.0, 130.8, 129.7, 129.6, 128.5, 127.5, 126.7, 126.4, 126.0, 122.3, 20.3.

2-(*p*-Tolyl)quinoline (3ac) [28]. White solid; 81% yield (177 mg); mp 74–75 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (t, *J* = 9.8 Hz, 2H), 8.08 (d, *J* = 8.1 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.2, 148.2, 139.3, 136.8, 136.6, 129.6, 129.5, 127.4, 127.0, 126.0, 118.8, 21.3.

2-(4-Ethylphenyl)quinoline (3ad) [30]. White solid; 82% yield (192 mg); mp 48–49 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (t, *J* = 8.4 Hz, 2H), 8.09 (d, *J* = 8.2 Hz, 2H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.0 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 2H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.4, 148.3, 145.7, 137.1, 136.6, 129.6, 129.5, 128.4, 127.5, 127.4, 127.1, 126.1, 118.9, 28.7, 15.5.

2-(4-Isopropylphenyl)quinoline (3ae) [31]. Light yellow solid; 82% yield (202 mg); mp 86–87 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20–8.15 (m, 2H), 8.10 (d, *J* = 8.2 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 3.02–2.96 (m, 1H), 1.31 (d, *J* = 7.0 Hz, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 157.4, 150.3, 148.3, 137.3, 136.6, 129.7, 129.5, 127.5, 127.4, 127.0, 126.9, 126.0, 118.9,34.0, 23.9.

2-(3-Methoxyphenyl)quinoline (3af) [30]. Light yellow solid; 76% yield (179 mg); mp 107–108 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (t, *J* = 9.5 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.77–7.76 (m, 1H), 7.73–7.69 (m, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 7.02–7.00 (m, 1H), 3.92 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 161.1, 157.1, 148.2, 141.1, 136.7, 129.8, 129.7, 129.6, 127.4, 127.2, 126.3, 120.0, 119.1, 115.3, 112.7, 53.4.

2-(4-Methoxyphenyl)quinoline (3ag) [28]. White solid; 80% yield (188 mg); mp 122–123 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19–8.13 (m, 4H), 7.85–7.79 (m, 2H), 7.71 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 160.8, 156.9, 148.3, 136.6, 132.3, 129.5, 128.9, 127.4, 126.9, 125.9, 118.5, 114.2, 55.4.

2-(Benzo[d][1,3]dioxol-5-yl)quinoline (3ah) [29]. Light yellow solid; 81% yield (202 mg); mp 87–88 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16–8.11 (m, 2H), 7.79–7.74 (m, 3H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.50–7.47 (m, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.03 (s, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.6, 148.8, 148.4, 148.2, 136.6, 134.1, 129.6, 129.5, 127.4, 127.0, 126.0, 121.7, 118.6, 108.4, 107.9, 101.3.

2-(3-Fluorophenyl)quinoline (3ai) [32]. Pale-yellow solid; 80% yield (179 mg); mp 47–48 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.6 Hz, 1H), 8.18 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.7 Hz, 2H), 7.85–7.82 (m, 2H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.50–7.46 (m, 1H), 7.17–7.14 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 164.3 (d, $J_{C\text{-}F}$ = 244.2 Hz), 155.8, 148.2, 142.0 (d, $J_{C\text{-}F}$ = 7.8 Hz), 136.9, 130.3 (d, $J_{C\text{-}F}$ = 8.1 Hz), 129.8, 129.8, 127.5, 127.4, 126.6, 123.1, 118.7, 116.2 (d, $J_{C\text{-}F}$ = 20.9 Hz), 114.6 (d, $J_{C\text{-}F}$ = 22.6 Hz).

2-(4-Fluorophenyl)quinoline (3aj) [33]. White solid; 79% yield (176 mg); mp 90–91 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22–8.14 (m, 4H), 7.83 (d, *J* = 8.7 Hz, 2H), 7.73 (t, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 8.7 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 164.8 (d, $J_{C\text{-}F}$ = 247.5 Hz), 156.2, 148.2, 136.9, 135.8, 129.8, 129.7, 129.4 (d, $J_{C\text{-}F}$ = 8.3 Hz), 127.5, 127.1, 126.3, 118.6, 115.8 (d, $J_{C\text{-}F}$ = 21.5 Hz).

2-(3-Chlorophenyl)quinoline (3ak) [31]. Light yellow solid; 77% yield (184 mg); mp 91–92 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17–8.13 (m, 3H), 7.99–7.97 (m, 1H), 7.77–7.74 (m, 2H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 5.3 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.6, 148.1, 141.3, 136.9, 134.8, 129.9, 129.8, 129.7, 129.2, 127.6, 127.4, 127.2, 126.5, 125.5, 118.5.

2-(4-Chlorophenyl)quinoline (3al) [32]. White solid; 83% yield (198 mg); mp 110–111 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.6 Hz, 1H), 8.16–8.12 (m, 3H), 7.86–7.83 (m, 2H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 8.6 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 156.0, 148.2, 138.0, 136.9, 135.5, 129.8, 129.7, 129.0, 128.8, 127.5, 127.2, 126.5, 118.5.

2-(3,4-Dichlorophenyl)quinoline (3am) [29]. Light yellow solid; 78% yield (214 mg); mp 105–106 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 2.1 Hz, 1H), 8.22 (d, *J* = 8.6 Hz, 1H), 8.15 (d, *J* = 8.5 Hz, 1H), 7.99 (dd, *J* = 8.4 and 2.1 Hz, 1H), 7.83–7.79 (m, 2H), 7.74 (t, *J* = 7.7 Hz, 1H), 7.57–7.53 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 154.4, 148.1, 139.4, 137.0, 133.5, 133.1, 130.6, 129.9, 129.7, 129.3, 127.4, 127.3, 126.7, 126.4, 118.1.

2-(3-Bromophenyl)quinoline (3an) [29]. White solid; 85% yield (242 mg); mp 73–74 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.19–8.15 (m, 2H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.81–7.78 (m, 2H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.5, 148.1, 141.6, 136.9, 132.1, 130.5, 130.2, 129.8, 129.7, 127.4, 127.3, 126.6, 126.0, 123.1, 118.6.

2-(4-Bromophenyl)quinoline (3ao) [29]. White solid; 82% yield (233 mg); mp 114–115 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.6 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 2H), 7.85–7.82 (m, 2H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 155.9, 148.2, 138.5, 136.9, 131.9, 129.8, 129.7, 129.1, 127.5, 127.2, 126.5, 123.9, 118.4.

2-(4-(Trifluoromethyl)phenyl)quinoline (3ap) [32]. White solid; 80% yield (219 mg); mp 122–123 °C; ^{1}H NMR (500 MHz,

$CDCl_3$) δ 8.27–8.22 (m, 3H), 8.19 (d, J = 8.5 Hz, 1H), 7.86–7.82 (m, 2H), 7.77–7.73 (m, 3H), 7.55 (t, J = 7.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 155.6, 148.2, 142.9, 137.1, 131.2 (q, J_{C-F} = 32.2 Hz), 129.9, 129.8, 127.8, 127.5, 127.4, 126.8, 125.7, 125.7, 125.3 (q, J_{C-F} = 270.4 Hz), 118.7.

2-(4-(Trifluoromethoxy)phenyl)quinoline (3aq). Light yellow oil; 84% yield (243 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 8.25–8.15 (m, 4H), 7.85–7.83 (m, 2H), 7.76–7.73 (t, J = 7.7 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.38 (d, J = 8.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 115.8, 150.2, 148.2, 138.3, 137.0, 129.9, 129.7, 129.1, 127.5, 127.2, 126.6, 121.6 (q, J_{C-F} = 256.5 Hz), 121.1, 118.6. HRMS (ESI) m/z calcd for $C_{16}H_{11}F_3NO^+$ $(M + H)^+$ 290.07873, found 290.07880.

2-(4-Nitrophenyl)quinoline (3ar) [34]. Yellow solid; 82% yield (205 mg); mp 134–135 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.38–8.34 (m, 4H), 8.31 (d, J = 8.6 Hz, 1H), 8.20 (d, J = 8.4 Hz, 1H), 7,93 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.78 (t, J = 7.7 Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 154.5, 148.3, 148.2, 145.4, 137.3, 130.2, 129.9, 128.2, 127.5, 127.3, 124.0, 118.7.

4-(Quinolin-2-yl)benzonitrile (3as) [35]. Yellow solid; 85% yield (196 mg); mp 92–93 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.30–8.27 (m, 3H), 8.18 (d, J = 8.4 Hz, 1H), 7.89 (t, J = 9.7 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 7.79–7.76 (m, 1H), 7.60–7.57 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 154.9, 148.2, 143.7, 137.3, 132.6, 130.1, 129.9, 128.0, 127.6, 127.5, 127.1, 118.8, 118.6, 112.7.

2-([1,1′-Biphenyl]-4-yl)quinoline (3at) [29]. White solid; 80% yield (226 mg); mp 178–179 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.27–8.18 (m, 4H), 7.94 (d, J = 8.6 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.78–7.74 (m, 3H), 7.69 (d, J = 7.2 Hz, 2H), 7.54 (t, J = 7.1 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 156.9, 148.3, 142.1, 140.6, 138.5, 136.8, 129.7, 129.7, 128.8, 127.9, 127.5, 127.5, 127.2, 127.1, 126.3, 118.8.

2-(Pyrazin-2-yl)quinoline (3au) [36]. Light yellow solid; 76% yield (158 mg); mp 156–157 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.66–8.64 (m, 2H), 8.50 (d, J = 8.6 Hz, 1H), 8.32 (d, J = 8.6 Hz, 1H), 8.22 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.77 (t, J = 7.7 Hz, 1H), 7.61–7.58 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 154.1, 151.3, 147.9, 144.6, 144.1, 143.5, 137.1, 130.0, 129.9, 128.4, 127.6, 127.3, 118.7.

3-Methyl-2-phenylquinoline (3av) [29]. Light yellow oil; 77% yield (169 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.5 Hz, 1H), 8.01 (s, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.66 (t, J = 7.7 Hz, 1H), 7.60–7.58 (m, 2H), 7.53–7.47 (m, 3H), 7.45–7.42 (m, 1H), 2.46 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 160.5, 146.6, 140.9, 136.7, 129.3, 129.2, 128.8, 128.7, 128.3, 128.1, 127.6, 126.7, 126.4, 20.6.

3-Ethyl-2-phenylquinoline (3aw) [29]. Light yellow oil; 82% yield (192 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.5 Hz, 1H), 8.04 (s, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.66 (t, J = 7.7 Hz, 1H), 7.55–7.41 (m, 6H), 2.78 (q, J = 7.5 Hz, 2H), 1.19 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 160.6, 146.3, 140.9, 135.2, 134.9, 129.2, 128.7, 128.7, 128.2, 128.0, 127.7, 126.7, 126.3, 26.0, 14.7.

5,6-Dihydrobenzo[c]acridine (3ax) [33]. White solid; 80% yield (185 mg); mp 62–63 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, J = 7.6 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 7.92 (s, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.64 (t, J = 7.7 Hz, 1H), 7.48–7.41 (m, 2H), 7.37 (t, J = 7.4 Hz, 1H), 7.28 (d, J = 7.4 Hz, 1H), 3.13 (t, J = 7.0 Hz, 2H), 3.01 (t, J = 6.9 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 153.4, 147.6, 139.4, 134.7, 133.6, 130.5, 129.6, 129.4, 128.6, 127.9, 127.8, 127.3, 126.9, 126.0, 28.8, 28.4.

2-Cyclopropylquinoline (3ay) [37]. Light yellow oil; 86% yield (146 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.98–7.96 (m, 2H), 7.72 (d, J = 8.2 Hz, 1H), 7.62 (t, J = 7.7 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.13 (d, J = 8.5 Hz, 1H), 2.27–2.22 (m, 1H), 1.15–1.07 (m, 4H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 163.4, 147.8, 135.9, 129.3, 128.4, 127.4, 126.7, 125.2, 119.1, 18.0, 10.2.

2-(Tert-butyl)quinoline (3az) [38]. Light yellow oil; 83% yield (154 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 8.2 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.52 (d, J = 8.7 Hz, 1H), 7.46 (t, J = 7.4 Hz, 1H), 1.47 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 169.2, 147.4, 135.8, 129.4, 128.9, 127.2, 126.4, 125.6, 118.2, 38.1, 30.1.

6-methyl-2-phenylquinoline (3ba) [39]. White solid; 84% yield (184 mg); mp 60–61 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.15–8.10 (m, 3H), 8.07 (d, J = 8.5 Hz, 1H), 7.83 (d, J = 8.6 Hz, 1H), 7.57–7.50 (m, 4H), 7.46–7.43 (m, 1H), 2.54 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 156.4, 146.8, 139.7, 136.0, 131.9, 129.3, 129.0, 128.7, 127.4, 127.1, 126.3, 118.9, 21.5.

6-methoxy-2-phenylquinoline (3ca) [40]. White solid; 87% yield (204 mg); mp 128–129 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.14–8.06 (m, 4H), 7.84 (d, J = 8.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.44 (t, J = 7.3 Hz, 1H), 7.40 (dd, J = 9.2 and 2.7 Hz, 1H), 7.10 (d, J = 2.5 Hz, 1H), 3.95 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 157.7, 155.1, 144.4, 139.8, 135.5, 131.2, 128.9, 128.8, 128.1, 127.3, 122.3, 119.3, 105.0, 55.5.

6-fluoro-2-phenylquinoline (3da) [41]. White solid; 83% yield (186 mg); mp 90–91 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.17–8.14 (m, 4H), 7.90 (d, J = 8.7 Hz, 1H), 7.55–7.43 (m, 5H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 161.3 (d, J = 246.5 Hz), 156.7, 145.3, 139.3, 136.1 (d, J = 4.9 Hz), 132.2 (d, J = 9.0 Hz), 129.4, 128.8, 127.4, 119.9, 119.7, 119.6, 110.5 (d, J = 21.5 Hz).

6-chloro-2-phenylquinoline (3ea) [41]. White solid; 85% yield (204 mg); mp 109–110 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.16–8.09 (m, 4H), 7.90 (d, J = 8.6 Hz, 1H), 7.80 (s, 1H), 7.66 (dd, J = 9.0 and 2.4 Hz, 1H), 7.53 (d, J = 7.4 Hz, 2H), 7.49–7.46 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 157.5, 146.6, 139.2, 135.8, 131.9, 131.3, 130.5, 129.5, 128.9, 127.7, 127.5, 126.1, 119.7.

7-chloro-2-phenylquinoline (3fa) [42]. White solid; 83% yield (200 mg); mp 110–111 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.20–8.15 (m, 4H), 7.89 (d, J = 8.6 Hz, 1H), 7.77 (d, J = 8.7 Hz, 1H), 7.55–7.52 (m, 2H), 7.49–7.47 (m, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 158.2, 148.6, 139.1, 136.5, 135.4, 129.6, 128.8, 128.6, 128.6, 127.5,127.2, 125.4, 119.0.

7-bromo-2-phenylquinoline (3ga) [43]. White solid; 81% yield (229 mg); mp 113–114 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.18–8.14 (m, 3H), 7.89 (d, J = 8.6 Hz, 1H), 7.68 (d, J = 8.7 Hz, 1H), 7.60 (dd, J = 8.6 and 1.8 Hz, 1H), 7.54–7.46 (m, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 158.1, 148.9, 139.1, 136.6, 132.0, 129.7, 129.7, 128.9, 128.7, 127.6, 125.7, 123.7, 119.2.

2-Phenyl-1,2,3,4-tetrahydroquinoline Hydrochloride (4) [20]. Colorless oil, 71% yield (3.48 g); ^1H NMR (500 MHz, $CDCl_3$) δ 7.40–7.33 (m, 4H), 7.30–7.27 (m, 1H), 7.01 (t, 2H, J = 7.7 Hz), 6.65 (t, J = 7.3 Hz, 1H), 6.55 (d, J = 7.9 Hz, 1H), 4.45 (dd, J = 9.3 and 3.0 Hz, 1H), 2.96–2.89 (m, 1H), 2.76–2.71 (m, 1H), 2.14–2.10 (m, 1H), 2.03–1.95 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 144.8, 144.7, 129.3, 128.5, 127.4, 126.9, 126.5, 120.8, 117.1, 113.9, 56.2, 31.0, 26.4.

1-Carboximidamido-2-phenyl-1,2,3,4-tetrahydroquinoline Hydrochloride (5) [20]. White solid, 30% yield (1.04 g); mp 206–207 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, J = 7.4 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.28 (t, J = 7.2 Hz, 1H), 7.00 (t, 2H, J = 7.5 Hz), 6.65 (t, J = 7.4 Hz, 1H), 6.54 (d, J = 7.4 Hz, 1H), 4.45 (dd, J = 9.4 and 3.2 Hz, 1H), 2.95–2.89 (m, 1H), 2.76–2.71 (m, 1H), 2.13–2.09 (m, 1H), 2.03–1.95 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 144.8, 144.7, 129.3, 128.5, 127.4, 126.9, 126.5, 120.9, 117.6, 117.1, 113.9, 56.2, 30.9, 26.3.

4.5. Procedure for the hydrogen evolution experiment [44]

1a (1 mmol, 123 mg), **2a** (145 mg, 1.2 mmol, 1.2 equiv), cat. **1** (6 mg, 0.01 mmol, 1 mol %), Cs_2CO_3 (165 mg, 0.5 mmol, 0.5 equiv)

and *tert*-amyl alcohol (1 mL) were added to a 5 mL thick walled glass vessel with a condenser tube, which was previously degassed three times and placed under a N_2 atmosphere. The vessel was connected to the gas collection apparatus (standard water displacement apparatus, using a graduated cylinder to determine volume), and the entire system was flushed with N_2 for 5 min and allowed to equilibrate for 5 min. The reaction was stirred vigorously at 125 °C for 12 h. The presence of hydrogen in the collected gas was confirmed by GC analysis.

The GC analysis was performed on a gas chromatograph with TCD detector. Injector temperature = 150 °C, column temprature = 80 °C, detector temperature (TCD) = 80 °C, carrier gas = N_2, t = 0.558 min.

The volume of 1 mol of H_2 at 299.15 K, 100,300 Pa was calculated according to the van der Waals equation as shown below

$(p + \frac{n^2a}{V^2})(V\text{-}nb) = nRT$where R = 8.3145 $m^3 \cdot Pa \cdot mol^{-1} \cdot K^{-1}$; T = 299.15 K; p = 100 300 Pa; a = 0.02476 $Pa \cdot m^6 \cdot mol^{-2}$; b = 0.026 61 × 10^{-3} $m^3 \cdot mol^{-1}$; thus, V (H_2, 299.15 K, 100 300 Pa) = 24.8 $L \cdot mol^{-1}$.

The collected volume of gas in this experiment above was 21.6 mL, which corresponds to 0.87 mmol of H_2.

*4.6. Procedure for the gram-scale synthesis of 2-phenylquinoline **(3aa)***

In a round-bottomed flask with a condenser tube were added **1a** (3.08 g, 25 mmol) and **2a** (3.61 g, 30 mmol, 1.2 equiv), cat. **1** (127 mg, 0.25 mmol, 1 mol %), Cs_2CO_3 (4.08 g, 12.5 mmol, 0.5 equiv) and *tert*-amyl alcohol (25 mL). The reaction mixture was heated at 125 °C in an oil bath for 12 h and then cooled to ambient temperature, concentrated in *vacuo*, and purified by flash column chromatography with hexane/ethyl acetate (10:1, v/v) to afford the corresponding product **3aa** in 85% yield (4.37 g).

*4.7. Procedure for the synthesis of 2-phenyl-1,2,3,4-tetrahydroquinoline hydrochloride **(4)***

To a round bottom flask was added quinoline **3aa** (3.08 g, 15 mmol) and glacial acetic acid (10 mL). To the resulting solution was added $NaBH_3CN$ (1.89 g, 30 mmol, 2 equiv) in one portion while stirring. The reaction mixture was stirred for 10 h at room temperature. Then, the mixture was cooled to room temperature, concentrated in vacuo and was added to a saturated aqueous solution of sodium carbonate, The aqueous solution was extracted with ethyl acetate for three times. 5 mL of 1 N HCl in ethyl ether was added to the organic layer which were then concentrated in vacuo, and purified by flash column chromatography with hexane/ethyl acetate (10:1, v/v) to afford the corresponding product.

*4.8. Procedure for the synthesis of 1-carboximidamido-2-phenyl-1,2,3,4-tetrahydroquinoline hydrochloride **(5)***

To a solution of **4** (2.96 g, 12 mmol) in 30 mL of ethanol was added cyanamide (3.53 g, 84 mmol, 7 equiv), and the mixture was heated to reflux for 2 days. The solvent was evaporated, water was added, and the product was extracted with ethyl acetate. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated. Purification of the crude mixture was achieved on silica gel with chloroform/methanol (9:1, v/v) as an eluent. The solid obtained was washed successively with water and ethyl ether and dried in vacuo to give pure product.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2020.12.016.

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