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Manganese(I)-Catalyzed Transfer Hydrogenation and Acceptorless Dehydrogenative Condensation: Promotional Influence of the Uncoordinated N-Heterocycle

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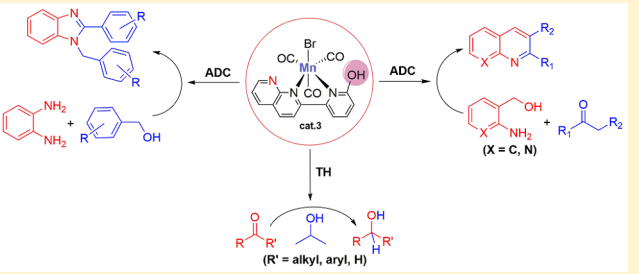
Supporting Information

ABSTRACT: The four bidentate manganese(I) complexes $[(C_5H_4N\text{-}C_5H_3N\text{-}OH)Mn(CO)_3Br]$ (**1**), $[(C_9H_6N\text{-}C_5H_3N\text{-}OH)Mn(CO)_3Br]$ (**2**), $[(C_8H_5N_2\text{-}C_5H_3N\text{-}OH)Mn(CO)_3Br]$ (**3**), and $[(C_8H_5N_2\text{-}C_5H_3N\text{-}OCH_3)Mn(CO)_3Br]$ (**4**) were synthesized. These complexes were tested as catalysts for the transfer hydrogenation of ketones, and **3** showed the highest activity. The reactions proceeded well with 0.5 mol % of catalyst loading and 20 mol % of *t*-BuOK at 85 °C for 24 h. Furthermore, **3** was also used as a catalyst for the synthesis of primary alcohols via transfer hydrogenation of aldehydes and the synthesis of 1,2-disubstituted benzimidazoles and quinolines via acceptorless dehydrogenative condensations.



INTRODUCTION

Complexes containing the 2-hydroxypyridyl fragment are significant metal−ligand synergistic catalysts, which have been widely used in many kinds of H_2-related reactions.[1,2] In the presence of a base, 2-hydroxypyridyl can be changed into 2-pyridonate, which directly affects the metal center.

Transfer hydrogenation (TH) using alcohol as the hydrogen sourse is an important and attractive method for reducing ketones and aldehydes to alcohols.[3] In comparison to catalytic hydrogenation, which has been extensively applied in organic synthesis and the pharmaceutical industry,[4] transfer hydrogenation can be carried out in conventional equipment: that is to say, there is no need to use autoclaves and other devices. However, although there have been some examples catalyzed by base-metal complexes,[5−7] the transfer hydrogenation of ketones and aldehydes still mainly relies on noble-metal catalysts, such as Rh,[8] Os,[9] Ir,[10] Pd,[11] and especially Ru,[12] which are expensive and raise toxicity concerns. In recent years, since the pioneer work of Beller et al.,[13] manganese(I)-catalyzed transfer hydrogenation has developed rapidly.[14] For example, in 2017, Sortais and co-workers reported a manganese(I) catalyst bearing 2-(aminomethyl)pyridine as the ligand, showing a TOF of up to 3600 h^{-1}.[14a] Later, The groups of Leitner, Kundu, and Pidko independently developed similar bidentate NN-Mn(I) complexes for such transformation.[14b−d] Perekalin et al. found that Shvo-type catalysts were also effective for transfer hydrogenation of ketones,[14e] and Kirchner's group developed an enantioselective Mn-based catalyst.[14f] In addition, very recently, Khusnutdinova's group reported a manganese(I) complex based on the 6,6′-dihydroxy-2,2′-bipyridine ligand for transfer hydrogenation of ketones, aldehydes, and imines, exhibiting activity superior to that of a similar complex with 2,2′-bipyridine as the ligand, indicating the important role of the hydroxypyridyl fragment.[14g]

In addition to transfer hydrogenation, Mn(I) catalysts have also been reported for acceptorless dehydrogenative condensations,[15] which are attributed to H_2-related reactions, as well. For instance, Srimani and co-workers developed a tridentate NNS-Mn(I) complex for the synthesis of benzimidazoles from aromatic diamines and alcohols.[16] Some other Mn(I) catalysts for the production of quinolones from 2-aminobenzyl alcohols with secondary alcohols (or ketones) have also been reported.[17]

In recent years, we developed a series of 2-hydroxypyridyl-based Ru and Ir complexes for transfer hydrogenation[18] and borrowing hydrogen reactions,[19] including acceptorless dehydrogenative coupling reactions.[19a] During the course of investigation, we found that a pendant N-heterocycle sometimes increased the catalytic efficiency dramatically.[19b,d] As an extension, herein we report the synthesis and catalytic activity of three Mn complexes containing 2-hydroxypyridyl and one containing 2-methoxypyridyl complexes, **1**−**4**. As expected, complex **3** with a 2-hydroxypyridyl moiety and an uncoordinated N-heterocycle is the best catalyst for transfer hydrogenation and acceptorless dehydrogenative condensations.

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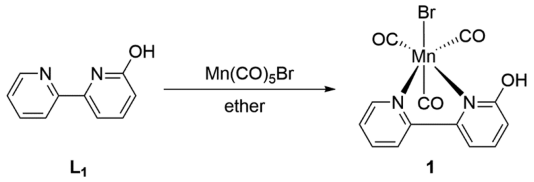
RESULTS AND DISCUSSION

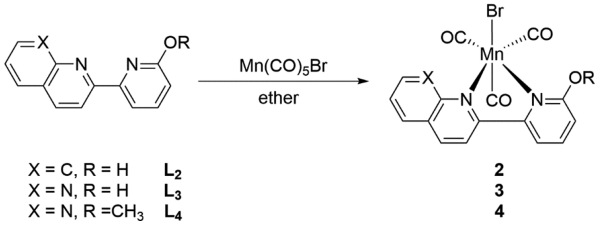
Synthesis and Characterization of Mn(I) Complexes. When C_5H_4N-C_5H_3N-OH ($\mathbf{L_1}$) was treated with $Mn(CO)_5Br$, the tricarbonyl bidentate complex [$(C_5H_4N$-C_5H_3N-OH$)Mn(CO)_3Br$] (**1**) was isolated in 88% yield (Scheme 1). The ^1H NMR spectrum of **1** in d_6-DMSO exhibits two groups of signals between 9.17 and 7.04 ppm for the pyridyl groups (7H) and one singlet at 13.04 ppm for the −OH group (1H). The IR spectrum displays three strong absorption peaks with nearly identical intensities at 2032, 1946, and 1924 cm^{-1} for the three terminal CO groups, suggesting their mutually cis configuration. The intense absorption band at 3094 cm^{-1} is consistent with the existence of an −OH group. The results indicate there are three CO groups, one bromide, and two pyridyl rings of ligand $\mathbf{L_1}$ coordinating with Mn.

Similarly, thermal treatment of C_9H_6N-C_5H_3N-OH ($\mathbf{L_2}$), $C_8H_5N_2$-C_5H_3N-OH ($\mathbf{L_3}$), and $C_8H_5N_2$-C_5H_3N-OCH_3 ($\mathbf{L_4}$) with $Mn(CO)_5Br$ generated the products [$(C_9H_6N$-C_5H_3N-OH$)Mn(CO)_3Br$] (**2**), [$(C_8H_5N_2$-C_5H_3N-OH$)Mn(CO)_3Br$] (**3**), and [$(C_8H_5N_2$-C_5H_3N-$OCH_3)Mn(CO)_3Br$] (**4**), respectively (Scheme 2). The −OH signals of **2** and **3** in their ^1H NMR spectra appear at 13.31 and 13.15 ppm, respectively, and the $-OCH_3$ signal is located at 4.22 ppm. Each of these three complexes shows three CO bands, suggesting the similarity of their structures with that of complex **1**. The CO bands of **2** are located at 2022, 1926, and 1912 cm^{-1}, red-shifted in comparison to those of **1**, indicating the more electron rich center.[12h] The CO bands of **3** (2020, 1949, and 1918 cm^{-1}) are comparable to those of **2**, suggesting the quinolyl group in complex **2** and the naphthyridyl group in complex **3** have a similar effect on their metal centers. The CO absorptions of **4** (2014, 1922, and 1896 cm^{-1}) demonstrate that $\mathbf{L_4}$ donates the most electron density to the metal center among the four ligands.

Scheme 1. Synthesis of Complex 1



Scheme 2. Synthesis of Complexes 2−4



Complex **3** were further identified by X-ray crystallography (Figure 1). The Mn ion is coordinated in an octahedral geometry. The ligand $\mathbf{L_3}$ coordinates with the Mn atom via its bipyridyl N atoms. As mentioned above, the three CO groups are facial, with one trans to the naphthalidine ring, the second trans to the pyridonate group, and the third trans to the Br atom. The C(1)−O(1) distance is 1.330(3) Å, in the range of a single bond.[12h,19]

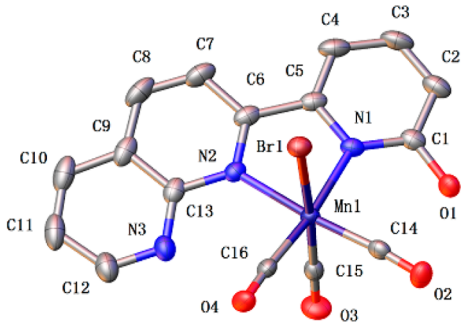
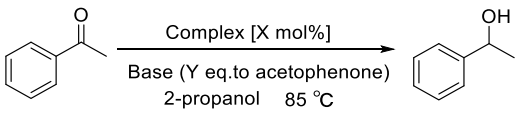


Figure 1. Molecular structure of complex **3**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): Mn(1)−N(1), 2.0642(18); Mn(1)−N(2), 2.0627(18); Mn(1)−Br(1), 2.5667(4); Mn(1)−C(14), 1.806(2); Mn(1)−C(15), 1.787(2); Mn(1)−C(16), 1.813(2); C(1)−O(1), 1.330(3); C(1)−C(2), 1.401(3); C(2)−C(3), 1.363(4); C(3)−C(4), 1.383(4); C(4)−C(5), 1.378(3); C(5)−N(1), 1.367(3), C(1)−N(1), 1.342(3).

Ketone Transfer Hydrogenation. Initially, we tested the catalytic activity of complexes **1**−**4** in a model reaction of transfer hydrogenation of acetophenone with 2-propanol (Table 1). The reactions were conducted at 85 °C in the presence of 0.5 mol % of catalyst for 24 h under a N_2 atmosphere, and the results are shown in Table 1. When complex **1** was selected as the catalyst and 10 mol % of *t*-BuOK was added as the base, the conversion was 74% (entry 1). Complex **2** was less active, giving a conversion of 48% (entry 2). As discussed above, the metal center of **2** is more electron rich than **1**; thus, in terms of electronic effects, **2** should have exhibited higher activity. Thus, the lower conversion is probably mainly due to steric hindrance. Interestingly, when the quinolyl in **2** was replaced by a naphthyridyl group, the resulting complex **3** gave a much better result (79%, entry 3), indicating that the uncoordinated N-heterocycle plays an

Table 1. Optimization of Conditions for the Transfer Hydrogenation of Acetophenone[a]



entry	complex (amt (mol %))	base (amt (equiv))	conversn (%)[b]
1	**1** (0.5)	*t*-BuOK (0.1)	74
2	**2** (0.5)	*t*-BuOK (0.1)	48
3	**3** (0.5)	*t*-BuOK (0.1)	79
4	**4** (0.5)	*t*-BuOK (0.1)	46
5	none	*t*-BuOK (0.1)	19
6[c]	**3** (0.5)	*t*-BuOK (0.1)	70
7	**3** (0.5)	*t*-BuOK (0.2)	90
8	**3** (0.3)	*t*-BuOK (0.2)	70
9[d]	**3** (0.5)	*t*-BuOK (0.2)	71
10[e]	**3** (0.5)	*t*-BuOK (0.2)	81
11	**3** (0.5)	KOH (0.2)	76
12	**3** (0.5)	K_2CO_3 (0.2)	15

[a]Reaction conditions unless noted otherwise: acetophenone (1.0 mmol), 2-propanol (2.5 mL), 24 h, N_2 atmosphere. [b]Determined by GC analysis based on acetophenone using dodecane as the internal standard. [c]T = 75 °C. [d]12 h. [e]18 h.

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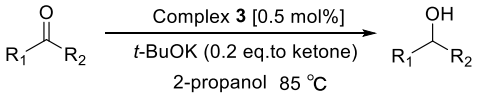
important role in the catalytic cycle, which is consistent with the results reported by other groups and our group previously.[19b,d,20] Although the metal center of **4** is more electron rich than **3** on the basis of the IR results, its efficiency was much lower (46%, entry 4), demonstrating the significance of the hydroxyl group. In the absence of any Mn complex, the reaction also proceeded with *t*-BuOK (10 mol %), while the conversion was only 19% (entry 5).[14e] **3** was then selected as the catalyst for further analysis. When the temperature was reduced to 75 °C, the conversion was also decreased to 70% (entry 6). When the amount of *t*-BuOK was increased to 20 mol %, the conversion reached 90% (entry 7). A catalyst loading of 0.3 mol % lowered the conversion to 70% (entry 8). Shorter reaction times also decreased the conversion (entries 9 and 10). Other bases such as KOH and K_2CO_3 did not perform as well as *t*-BuOK (entries 11 and 12).

With the optimal conditions in hand, a series of substrates were investigated, and the results are shown in Table 2. The electron-withdrawing and electron-donating groups, whether at the ortho, meta, or para position of acetophenone, did not obviously influence the isolated yields, which were in the range of 80−90% (entries 1−10). When aliphatic ketones were used, the yields were also satisfactory (77−81%, entries 11−15). Sterically hindered aromatic ketones, such as benzophenone and 1-(naphthalen-2-yl)ethan-1-one, gave isolated yields of diphenylmethanol and 1-(naphthalen-2-yl)ethan-1-ol of 81% and 83%, respectively (entries 16 and 17).

Aldehyde Transfer Hydrogenation. Complex **3** is also suitable for the transfer hydrogenation of aldehydes (Table 3). Six characteristic aromatic aldehydes, including benzaldehyde, 4-methoxybenzaldehyde, 3-methylbenzaldehyde, 4-fluorobenzaldehyde, 4-chlorobenzaldehyde, and 2-naphthaldehyde, were converted into the corresponding primary alcohols in yields between 70 and 85%, under conditions similar to those for ketone transfer hydrogenation (entries 1−6). 1-Heptanol could also be isolated in 60% yield under the conditions of 1.0 mol % catalyst with 10 mol % *t*-BuOK (entry 7). Although complex **3** is active for the transfer hydrogenation of both ketones and aldehydes, its efficiency still needs to be improved.[14] Especially, in comparison to the reported Ru catalysts, which showed TOF values higher than 10^6 h^{-1}, much progress is needed.[12i,m]

Synthesis of 1,2-Disubstituted Benzimidazoles. Acceptorless dehydrogenation condensation, which is mechanistically related to the borrowing hydrogen reaction, has now become an elegant pathway for the synthesis of N-heterocycles.[15−17] Recently, the synthesis of benzimidazoles catalyzed by an Mn(I) complex using 1,2-diaminobenzene and alcohol as starting materials was reported by Srimani's group for the first time (10 mol % of catalyst, 2 equiv of of *t*-BuOK, 140 °C and 20 h).[16] To our delight, complex **3** is also suitable for such transformations, and six different products were obtained in the presence of 2 mol % of catalyst and 1.5 equiv of *t*-BuOK at 130 °C for 20 h (Table 4). 1-Benzyl-2-phenyl-1*H*-benzo[*d*]-imidazole was generated in 82% yield from 1,2-diaminobenzene with benzyl alcohol (entry 1). No noteworthy change in the isolated yields was found when an electron-donating group (methoxy or methyl) was introduced at the ortho or para position of the benzyl alcohol (entries 2−4). However, an electron-withdrawing group, such as chloro, at the para position of benzyl alcohol decreased the activity dramatically (entry 5). 2-(Naphthalen-2-yl)-1-(naphthalen-2-ylmethyl)-1*H*-benzo[*d*]imidazole could also be isolated in a yield of 75%

Table 2. Transfer Hydrogenation of Ketones[a]



Entry	Ketone	Product	Yield [%][b]	TON
1			87	174
2			82	164
3			81	162
4			86	172
5			84	168
6			80	160
7			90	180
8			84	168
9			88	176
10			85	170
11			78	156
12			77	154
13			80	160
14			81	168
15			80	160
16			81	162
17			83	166

[a]Reaction condition: substrate (1.0 mmol), 2-propanol (2.5 mL), 24 h, N_2 atmosphere. [b]Isolated yield.

(entry 6). Although complex **3** is more effective than Srimani's Mn catalyst,[16] it is still not as competitive as Singh's Ir catalyst (0.1 mol % catalyst, 2 equiv of *t*-BuOK, 80 °C, and 6 h).[21]

Synthesis of Quinolines. The first report of Mn(I)-catalyzed quinoline synthesis from 2-aminobenzyl alcohol and 1-phenylethanol was presented by Kirchner and co-workers. The reactions were carried out in the presence of 5 mol % of

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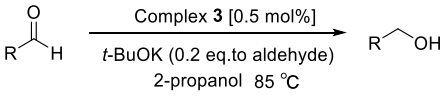
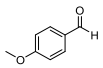
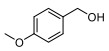
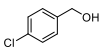
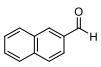
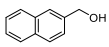
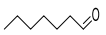
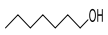
Table 3. Transfer Hydrogenation of Aldehydes[a]



Entry	Aldehyde	Product	Yield [%][b]	TON
1[c]			85	170
2			80	160
3			81	162
4			70	140
5			72	144
6			82	164
7[d]			60	120

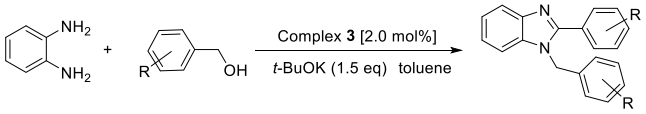
[a]Reaction conditions: aldehyde (1.0 mmol), 2-propanol (2.5 mL), 24 h, N_2 atmosphere. [b]Isolated yield. [c]When the catalyst loading was 0.3 mol %, the yield decreased to 70%. [d]Complex **3** (1.0 mol %), *t*-BuOK (10 mol %).

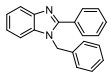
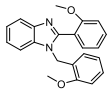
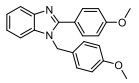
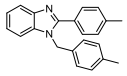
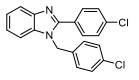
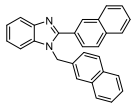
catalyst, 2.1 equiv of *t*-BuOK, and 1.0 equiv of KOH at 140 °C for 24 h.[17a] Later on, Srimani's group developed a tridentate NNS complex for the same reaction, and still 5 mol % catalyst was needed.[17b] Maji et al. recently used acetophenone to replace 1-phenylethanol and found the process proceeded well with $Mn(CO)_5Br$ (2 mol %) and a NNN-ligand (2 mol %) under basic conditions.[17c] We found that complex **3** could also catalyze the reaction of 2-aminobenzyl alcohol with acetophenone (Table 5). When **3** (2 mol %) and *t*-BuOK (1 equiv) were added, 2-phenylquinoline was obtained in 72% yield in toluene at 130 °C after 20 h (entry 1). When an electron-donating group was introduced to the ortho, meta, or para position of acetophenone, similar results were obtained (entries 2−4). However, electron-withdrawing groups decreased the yields slightly (entries 5−7). Propiophenone was also suitable for this reaction, giving 3-methyl-2-phenylquinoline in 72% yield (entry 8). Interestingly, 2-(6-methoxypyridin-2-yl)-1,8-naphthyridine (L_4), which was synthesized by the reaction of 2-aminonicotinaldehyde with 1-(6-methoxypyridin-2-yl)ethan-1-one, could also be obtained catalytically from (2-aminopyridin-3-yl)methanol and 1-(6-methoxypyridin-2-yl)-ethan-1-one (entry 9). Although complex **3** is comparable with Maji's Mn system,[17c] it is not as active as Verpoort's Ru system (1 mol % of catalyst, 1 equiv of base, 80 °C, and 1 h).[22]

CONCLUSIONS

In summary, four bidentate manganese complexes, including three with a 2-hydroxypyridyl group (**1**−**3**) and one with a 2-methoxypyridyl group (**4**), were synthesized. These complexes were tested as catalysts for ketone transfer hydrogenation, and complex **3** was the most active. With 0.5 mol % of catalyst loading and 20 mol % of *t*-BuOK at 85 °C for 24 h, a series of

Table 4. Scope of the Reaction To Synthesize 1,2-Disubstituted Benzimidazole[a]



Entry	Alcohol	Product	Yield.[%][b]	TON
1[c]			82	41
2			85	42.5
3			80	40
4			79	39.5
5			55	27.5
6			75	37.5

[a]Reaction conditions: 1,2-diaminobenzene (0.5 mmol), alcohol (1.5 mmol), toluene (3 mL), 130 °C, 20 h, N_2 atmosphere. [b]Isolated yield. [c]When the catalyst loading was 1.0 mol %, the yield decreased to 50%.

the corresponding secondary alcohols were obtained in satisfactory yields. The results indicate the importance of both the 2-hydroxy group and the uncoordinated N-heterocycle, which are important for the design of more effective catalysts. Furthermore, complex **3** was also suitable for aldehyde transfer hydrogenation, acceptorless dehydrogenation condensation of 1,2-diaminobenzene with alcohol, and acceptorless dehydrogenation condensation of 2-aminobenzyl alcohol with acetophenone, and a series of primary alcohols, 1,2-disubstituted benzimidazoles, and quinolines were isolated, respectively.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under an inert nitrogen atmosphere using a Schlenk line. Solvents were distilled from the appropriate drying agents under N_2 before use. All reagents were purchased from commercial sources. Liquid compounds were degassed by standard freeze−pump−thaw procedures prior to use. [2,2′-Bipyridin]-6-ol (L_1)[23] and 6-(quinolin-2-yl)pyridin-2-ol (L_2)[24] were prepared as previously described. The ^1H NMR spectra were recorded on a Bruker Avance 400 spectrometer. The ^1H NMR chemical shifts were referenced to residual solvent as determined relative to Me_4Si (δ 0 ppm). The $^{13}C\{^1H\}$ chemical shifts were reported in ppm relative to the carbon resonance of $CDCl_3$ (77.0 ppm). Elemental analyses were performed on a PerkinElmer 240C analyzer. High-resolution mass spectra (HR-MS) were recorded on a Varian 7.0 T FTICR-MS instrument by the ESI technique. IR spectra were recorded on a Nicolet iS5 FT-IR spectrometer. X-ray diffraction studies were carried out in a SuperNova X-ray single-

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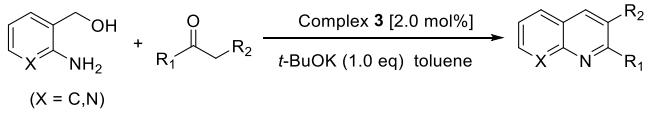
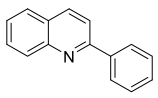
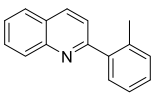
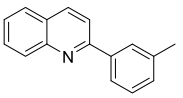
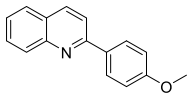
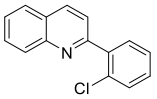
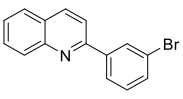
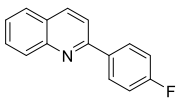
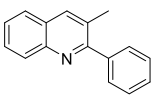
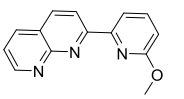
Table 5. Scope of the Reaction To Synthesize Quinoline[a]



		
72% (TON: 36) (Entry 1)[b]	72% (TON: 36) (Entry 2)	71% (TON: 35.5) (Entry 3)
		
75% (TON: 37.5) (Entry 4)	60% (TON: 30) (Entry 5)	62% (TON: 31) (Entry 6)
		
65% (TON: 32.5) (Entry 7)	72% (TON: 36) (Entry 8)	75% (TON: 37.5) (Entry 9)

[a]Reaction conditions: 2-aminoaryl alcohol (1.2 mmol), ketones (1.0 mmol), toluene (3 mL), 130 °C, 20 h, N_2 atmosphere, isolated yield. [b]When the catalyst loading was 1.0 mol %, the yield decreased to 42%.

crystal diffractometer or a Bruker D8 Quest X-ray diffractometer. Data collections were performed using four-circle kappa diffractometers equipped with CCD detectors. Data were reduced and then corrected for absorption. Solution, refinement, and geometrical calculations for all crystal structures were performed by SHELXTL. All of the GC measurements were performed on Agilent GC7890A equipment using an Agilent 19091B-102 (25 m, 220 μm) column.

Synthesis of 2-(6-Methoxypyridin-2-yl)-1,8-naphthyridine (L_4). A solution of 1-(6-methoxypyridin-2-yl)ethan-1-one (0.15 g, 0.98 mmol), 2-aminonicotinaldehyde (0.10 g, 0.82 mmol),and KOH (0.09 g, 1.64 mmol) was refluxed in ethanol (10 mL) with stirring for 4 h. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, v/v 1/1) to give the product as a pale yellow solid (0.19 g, 98%). Mp: 108 °C. Anal. Calcd for $C_{14}H_{11}N_3O$: C, 70.87; H, 4.67; N, 17.71. Found: C, 70.69; H, 4.61; N, 17.65. HRMS: calcd for $C_{14}H_{11}N_3O$ + H, 238.0980; found, 238.0988. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 9.15 (q, J = 2.0 Hz, 1H), 8.73 (d, J = 8.8 Hz, 1H), 8.49 (dd, J = 7.2, 0.4 Hz, 1H), 8.29 (d, J = 8.4 Hz, 1H), 8.23 (dd, J = 8.0, 1.6 Hz, 1H), 7.80−7.76 (m, 1H), 7.49 (q, J = 4.4 Hz, 1H), 6.86 (dd, J = 8.4, 0.8 Hz, 1H), 4.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 163.5, 159.4, 155.7, 153.7, 152.6, 139.6, 137.6, 137.0, 122.8, 122.0, 120.2, 115.6, 112.2, 53.4.

Synthesis of 6-(1,8-Naphthyridin-2-yl)pyridin-2-ol (L_3). A solution of 2-(6-methoxypyridin-2-yl)-1,8-naphthyridine (0.20 g, 0.84 mmol) in 5 mL of HBr (40% in water) was heated at reflux for 3 h. After it was cooled to room temperature, the solution was neutralized by slow addition of a saturated aqueous solution of NaOH. The aqueous solution was extracted with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated to afford the product as a yellow solid (0.18 g, 95%). Mp: 202 °C. Anal. Calcd for $C_{13}H_9N_3O$: C, 69.95; H, 4.06; N, 18.82. Found: C, 69.78; H, 4.01; N, 18.71. HRMS: calcd for $C_{13}H_9N_3O$ + H, 224.0824; found, 224.0834. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 10.85 (s, 1H), 9.19−9.17 (m, 1H), 8.34 (d, J = 8.8 Hz, 1H), 8.25 (dd, J = 8.4, 2.0 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.58−7.49 (m, 2H), 6.99 (d, J = 6.8 Hz, 1H), 6.71 (d, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 161.5, 154.0, 153.8, 149.8, 140.0, 139.0, 137.9, 135.9, 123.2, 122.0, 117.0, 104.1.

Synthesis of 1. A solution of L_1 (0.10 g, 0.58 mmol) and $Mn(CO)_5Br$ (0.18 g, 0.64 mmol) was heated in refluxing ether (10 mL) for 3 h. The yellow precipitate was collected, washed with ether, and dried under vacuum to provide **1** (0.20 g, 88%). Anal. Calcd for $C_{13}H_8N_2O_4BrMn$: C, 39.93; H, 2.06; N, 7.16. Found: C, 39.96; H, 2.09; N, 7.20. IR (ν_{CO}, KBr, cm^{-1}): 2032, 1946, 1924. IR (ν_{OH}, KBr, cm^{-1}): 3094. ^{1}H NMR (400 MHz, d_6-DMSO, ppm): 13.04 (s, 1H), 9.17 (d, J = 5.6 Hz, 1H), 8.52 (d, J = 8.0 Hz, 1H), 8.15 (t, J = 7.6 Hz, 1H), 8.10−8.08 (m, 1H), 8.02−7.98 (m, 1H), 7.65 (t, J = 6.4 Hz, 1H), 7.04 (d, J = 8.4 Hz, 1H).

Synthesis of 2. A solution of L_2 (0.10 g, 0.45 mmol) and $Mn(CO)_5Br$ (0.14 g, 0.50 mmol) was heated in refluxing ether (10 mL) for 3 h. The orange precipitate was collected, washed with ether, and dried under vacuum to provide **2** (0.35 g, 85%). Anal. Calcd for $C_{17}H_{10}N_2O_4BrMn$: C, 46.29; H, 2.29; N, 6.35. Found: C, 46.51; H, 2.35; N, 6.30. IR (ν_{CO}, KBr, cm^{-1}): 2022, 1926, 1912. IR (ν_{OH}, KBr, cm^{-1}): 3122. ^{1}H NMR (400 MHz, d_6-DMSO, ppm): 13.31 (s, 1H), 8.81−8.74 (m, 2H), 8.57 (d, J = 8.8 Hz, 1H), 8.24−8.18 (m, 2H), 8.06 (t, J = 7.2 Hz, 2H), 7.82 (t, J = 7.2 Hz, 1H), 7.09 (d, J = 8.8 Hz, 1H).

Synthesis of 3. A solution of L_3 (0.10 g, 0.45 mmol) and $Mn(CO)_5Br$ (0.14 g, 0.49 mmol) was heated in refluxing ether (10 mL) for 3 h. The red precipitate was collected, washed with ether, and dried under vacuum to provide **3** (0.38 g, 86%). Single crystals suitable for an X-ray crystallographic determination were grown with CH_3OH/ether at ambient temperature. Anal. Calcd for $C_{16}H_9N_3O_4BrMn$: C, 43.47; H, 2.05; N, 9.50. Found: C, 43.28; H, 2.07; N, 9.52. IR (ν_{CO}, KBr, cm^{-1}): 2020, 1949, 1918. IR (ν_{OH}, KBr, cm^{-1}): 3114. ^{1}H NMR (400 MHz, d_6-DMSO, ppm): 13.15 (s, 1H), 9.28 (d, J = 2.4 Hz, 1H), 8.84−8.82 (m, 1H), 8.73−8.68 (m, 2H), 8.35 (d, J = 7.2 Hz, 1H), 8.07 (t, J = 7.6 Hz, 1H), 7.91 (q, J = 4.0 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H).

Synthesis of 4. A solution of L_4 (0.10 g, 0.42 mmol) and $Mn(CO)_5Br$ (0.13 g, 0.46 mmol) was heated in refluxing ether (10 mL) for 3 h. The red precipitate was collected, washed with ether, and dried under vacuum to provide **4** (0.39 g, 85%). Anal. Calcd for $C_{17}H_{11}N_3O_4BrMn$: C, 44.76; H, 2.43; N, 9.21. Found: C, 44.88; H, 2.45; N, 9.15. IR (ν_{CO}, KBr, cm^{-1}): 2014, 1922, 1896. ^{1}H NMR (400 MHz, d_6-DMSO, ppm): 9.31−9.29 (m, 1H), 8.89−8.87 (m, 1H), 8.81−8.79 (m, 1H), 8.71 (dd, J = 8.0, 1.6 Hz, 1H), 8.53 (d, J = 7.6 Hz, 1H), 8.30 (t, J = 8.0 Hz, 1H), 7.93 (q, J = 4.0 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H), 4.22 (s, 3H).

General Procedure for Ketone and Aldehyde Transfer Hydrogenation. Under a nitrogen atmosphere, in a 15 mL Schlenk tube, a mixture of the ketone or aldehyde (1.0 mmol), 2-propanol (2.5 mL), complex **3** (0.5 mol %), and *t*-BuOK (20 mol %) was stirred at 85 °C for 24 h. The reaction mixture was cooled to room temperature, and 0.1 mL was sampled and immediately diluted with 5 mL of ethyl acetate precooled to 0 °C for GC analysis to calculate the conversion of the reaction. After the reaction was completed, the reaction mixture was condensed under reduced pressure and subjected to purification by flash silica gel column chromatography to afford the target product, which was identified by NMR analyses. All analytical data of the known compounds are consistent with those reported in the literature.

General Procedure for Synthesis of 1,2-Disubstituted Benzimidazoles. Under a nitrogen atmosphere, in a 15 mL Schlenk tube, a mixture of *o*-phenylenediamine (0.5 mmol), alcohol (1.5 mmol), complex **3** (2.0 mol %), and *t*-BuOK (0.75 mmol) was stirred at 130 °C in toluene for 20 h. After the reaction was completed, the reaction mixture was condensed under reduced pressure and subjected to purification by flash silica gel column chromatography to afford the target product, which was identified by NMR analyses. All analytical data of the known compounds are consistent with those reported in the literature.

General Procedure for Synthesis of Quinolines. Under a nitrogen atmosphere, in a 15 mL Schlenk tube, a mixture of 2-aminoaryl alcohol (1.2 mmol), ketone (1.0 mmol), complex **3** (2.0

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mol %), and *t*-BuOK (1.0 mmol) was stirred at 130 °C in toluene for 20 h. After the reaction was completed, the reaction mixture was condensed under reduced pressure and subjected to purification by flash silica gel column chromatography to afford the target product, which was identified by NMR analyses. All analytical data of the known compounds are consistent with those reported in the literature.

1-Phenylethan-1-ol.[14c] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.29−7.18 (m, 5H), 4.79−4.74 (m, 1H), 2.79 (s, 1H), 1.40 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 146.0, 128.5, 127.4, 125.5, 70.3, 25.2.

1-(2-Chlorophenyl)ethan-1-ol.[14c] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.59 (dd, J = 7.6, 1.6 Hz, 1H), 7.33−7.27 (m, 2H), 7.22−7.18 (m, 1H), 5.31−5.26 (m, 1H), 2.02 (s, 1H), 1.49 (d, J = 8.0, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.1, 131.7, 129.4, 128.4, 127.2, 126.4, 67.0, 23.5.

1-(3-Chlorophenyl)ethan-1-ol.[14g] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.36−7.35 (m, 1H), 7.28−7.20 (m, 3H), 4.87−4.82 (m, 1H), 2.16 (s, 1H), 1.46 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 147.9, 134.4, 129.8, 127.5, 125.7, 123.6, 69.8, 25.2.

1-(4-Chlorophenyl)ethan-1-ol.[14g] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.32−7.26 (m, 4H), 4.88−4.83 (m, 1H), 2.08 (s, 1H), 1.45 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 144.3, 133.1, 128.6, 126.8, 69.7, 25.3.

1-(2-Bromophenyl)ethan-1-ol.[18a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.59 (dd, J = 7.6, 1.6 Hz, 1H), 7.51 (dd, J = 7.6, 0.8 Hz, 1H), 7.36−7.32 (m, 1H), 7.15−7.10 (m, 1H), 5.26−5.21 (m, 1H), 2.00 (s, 1H), 1.48 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 144.3, 133.1, 128.6, 126.8, 69.7, 25.3.

1-(4-Fluorophenyl)ethan-1-ol.[14g] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.31−7.26 (m, 2H), 7.02−6.96 (m, 2H), 4.83−4.79 (m, 1H), 2.54 (s, 1H), 1.42 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 163.3, 160.9, 141.6, 127.1, 127.0, 115.3, 115.1, 69.7, 25.2.

1-(o-Tolyl)ethan-1-ol.[14g] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.50 (d, J = 7.6 Hz, 1H), 7.24−7.11 (m, 3H), 5.13−5.09 (m, 1H), 2.33 (s, 3H), 1.85 (s, 1H), 1.45 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.9, 134.3, 130.4, 127.2, 126.4, 124.5, 66.8, 24.0, 18.9.

1-(m-Tolyl)ethan-1-ol.[14g] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.23−7.20 (m, 1H), 7.16−7.12 (m, 2H), 7.07−7.06 (m, 1H), 4.83−4.78 (m, 1H), 2.34 (s, 3H), 2.22 (s, 1H), 1.45 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 145.9, 138.1, 128.4, 128.2, 126.2, 122.5, 70.4, 25.1, 21.5.

1-(3-Methoxyphenyl)ethan-1-ol.[18a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.26 (t, J = 8.0 Hz, 1H), 6.95−6.93 (m, 2H), 6.82−6.79 (m, 1H), 4.89−4.84 (m, 1H), 3.81 (s, 3H), 1.97 (s, 1H), 1.48 (d, J = 6.8, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 159.8, 147.6, 129.6, 117.7, 112.9, 110.9, 70.4, 55.2, 25.2.

1-(4-Methoxyphenyl)ethan-1-ol.[14g] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.29 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 4.86−4.81 (m, 1H), 3.79 (s, 3H), 1.96 (s, 1H), 1.46 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 159.0, 138.1, 126.7, 113.9, 70.0, 55.3, 25.0.

Heptan-2-ol.[14c] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.83−3.75 (m, 1H), 1.60 (s, 1H), 1.50−1.24 (m, 8H), 1.19 (d, J = 6.4 Hz, 3H), 0.89 (t, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 68.2, 39.3, 31.9, 25.5, 23.5, 22.6, 14.0.

Pentan-3-ol.[18b] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.49−3.43 (m, 1H), 1.58−1.37 (m, 5H), 0.95 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): 74.7, 29.6, 9.9.

Cyclopentanol.[14b] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 4.33−4.29 (m, 1H), 2.25 (s, 1H), 1.87−1.69 (m, 4H), 1.64−1.50 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): 73.8, 35.4, 23.3.

Cyclohexanol.[14b] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.62−3.56 (m, 1H), 2.37 (s, 1H), 1.98−1.84 (m, 2H), 1.80−1.65 (m, 2H), 1.62−1.48 (m, 1H), 1.33−1.11 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): 70.2, 35.5, 25.5, 24.2.

4-Phenylbutan-2-ol.[14g] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.29−7.25 (m, 2H), 7.21−7.15 (m, 3H), 3.84−3.76 (m, 1H), 2.78−2.61 (m, 2H), 2.09 (s, 1H), 1.82−1.68 (m, 2H), 1.21 (d, J = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 142.2, 128.5, 125.9, 67.5, 40.9, 32.2, 23.6.

Diphenylmethanol.[14e] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.38−7.30 (m, 8H), 7.27−7.23 (m, 2H), 5.81 (s, 1H), 2.92 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.8, 128.5, 127.6, 126.6, 76.3.

1-(Naphthalen-2-yl)ethan-1-ol.[14g] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.82−7.77 (m, 4H), 7.48−7.42 (m, 3H), 5.04−4.99 (m, 1H), 2.10 (s, 1H), 1.55 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 143.2, 133.4, 133.0, 128.3, 128.0, 127.7, 126.2, 125.8, 123.9, 123.8, 70.5, 25.2.

Phenylmethanol.[14g] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.33−7.20 (m, 5H), 4.55 (s, 2H), 2.85 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 140.9, 128.6, 127.6, 127.1, 65.1.

(4-Methoxyphenyl)methanol.[14g] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.23 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 4.52 (s, 2H), 3.77 (s, 3H), 2.55 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 159.1, 133.2, 128.7, 113.9, 64.7, 55.3.

m-Tolylmethanol.[25] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.23−7.19 (m, 1H), 7.12−7.06 (m, 3H), 4.55 (s, 2H), 2.62 (s, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 140.9, 138.2, 128.5, 128.3, 127.8, 124.1, 65.1, 21.4.

(4-Fluorophenyl)methanol.[14g] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.29−7.26 (m, 2H), 7.04−6.98 (m, 2H), 4.58 (s, 2H), 2.52 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 163.5, 161.1, 136.6, 128.8, 128.7, 115.4, 115.2, 64.4.

(4-Chlorophenyl)methanol.[14g] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.32−7.25 (m, 4H), 4.62 (s, 2H), 2.19 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 139.3, 133.3, 128.7, 128.3, 64.5.

Naphthalen-2-ylmethanol.[26] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.82−7.77 (m, 4H), 7.49−7.43 (m, 3H), 4.81 (s, 2H), 1.98 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 138.3, 133.4, 133.0, 128.4, 127.9, 127.8, 126.2, 125.9, 125.5, 125.2, 65.5.

Heptan-1-ol.[27] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 3.60 (t, J = 6.8 Hz, 2H), 2.00 (s, 1H), 1.57−1.50 (m, 2H), 1.36−1.18 (m, 8H), 0.88−0.84 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 62.9, 32.8, 31.8, 29.1, 25.7, 22.6, 14.1.

1-Benzyl-2-phenyl-1H-benzo[d]imidazole.[16] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.87 (d, J = 8.0 Hz, 1H), 7.71−7.67 (m, 2H), 7.48−7.42 (m, 3H), 7.36−7.29 (m, 4H), 7.25−7.21 (m, 2H), 7.11 (d, J = 6.4 Hz, 2H), 5.47 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 154.2, 143.1, 136.4, 136.0, 130.0, 129.9, 129.3, 129.1, 128.8, 127.8, 126.0, 123.1, 122.7, 120.0, 110.6, 48.4.

1-(2-Methoxybenzyl)-2-(2-methoxyphenyl)-1H-benzo[d]-imidazole.[28] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.85 (d, J = 8.0 Hz, 1H), 7.53 (dd, J = 7.6, 1.6 Hz, 1H), 7.46−7.42 (m, 1H), 7.28−7.17 (m, 4H), 7.04 (t, J = 7.6 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 6.82 (d, J = 8.4 Hz, 1H), 6.76 (t, J = 7.2 Hz, 1H), 6.70−6.68 (m, 1H), 5.23 (s, 2H), 3.77 (s, 3H), 3.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 157.6, 156.5, 152.5, 143.3, 135.5, 132.4, 131.4, 128.4, 127.8, 124.6, 122.5, 122.0, 120.8, 120.4, 119.8, 110.8, 110.8, 109.9, 55.2, 55.2, 43.6.

1-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-1H-benzo[d]-imidazole.[16] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.84 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 8.8 Hz, 2H), 7.32−7.27 (m, 1H), 7.24−7.20 (m, 2H), 7.04 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 5.39 (s, 2H), 3.85 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 160.9, 159.1, 154.1, 143.2, 136.1, 130.7, 128.5, 127.2, 122.8, 122.5, 122.5, 119.7, 114.4, 114.2, 110.4, 55.4, 55.3, 47.9.

1-(4-Methylbenzyl)-2-(p-tolyl)-1H-benzo[d]imidazole.[16] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.86 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.33−7.28 (m, 1H), 7.25−7.17 (m, 4H), 7.14 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 7.6 Hz, 2H), 5.41 (s, 2H), 2.41 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 154.4, 143.2, 140.0, 137.5, 136.1, 133.5, 129.7, 129.5, 129.2, 127.2, 125.9, 122.8, 122.6, 119.9, 110.5, 48.2, 21.5, 21.1.

1-(4-Chlorobenzyl)-2-(4-chlorophenyl)-1H-benzo[d]imidazole.[16] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.87 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.37−7.28 (m, 4H), 7.20 (d, J = 7.6 Hz, 1H), 7.02 (d, J = 8.0 Hz, 2H), 5.41 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 152.9, 143.1, 136.4, 135.9, 134.7, 133.9, 130.5, 129.4, 129.2, 128.4, 127.3, 123.5, 123.1, 120.2, 110.3, 47.8.

2-(Naphthalen-2-yl)-1-(naphthalen-2-ylmethyl)-1H-benzo[d]-imidazole.[16] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.13 (s, 1H), 7.88−

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7.76 (m, 6H), 7.67−7.64 (m, 2H), 7.50−7.39 (m, 5H), 7.30−7.20 (m, 4H), 5.61 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 154.3, 143.3, 136.4, 134.0, 133.8, 133.5, 132.9, 132.9, 129.3, 129.1, 128.6, 128.6, 127.9, 127.8, 127.3, 126.7, 126.7, 126.3, 126.1, 124.8, 123.9, 123.3, 122.9, 120.1, 110.6, 48.9.

2-Phenylquinoline.[2j] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.25 (d, J = 8.4 Hz, 2H), 8.18 (d, J = 7.2 Hz, 2H), 7.89 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.75 (t, J = 8.0 Hz, 1H), 7.56−7.52 (m, 3H), 7.49−7.46 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 157.4, 148.2, 139.6, 136.9, 129.7, 129.7, 129.4, 128.9, 127.6, 127.5, 127.2, 126.4, 119.0.

2-(o-Tolyl)quinoline.[2j] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.18 (t, J = 8.4 Hz, 2H), 7.84 (dd, J = 8.0, 0.8 Hz, 1H), 7.75−7.70 (m, 1H), 7.56−7.49 (m, 3H), 7.36−7.29 (m, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 160.4, 148.0, 140.8, 136.1, 136.1, 131.0, 129.8, 129.7, 129.7, 128.6, 127.6, 126.8, 126.5, 126.1, 122.4, 20.5.

2-(m-Tolyl)quinoline.[29] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.19 (t, J = 8.8 Hz, 2H), 8.01 (s, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.74−7.70 (m, 1H), 7.54−7.50 (m, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.28 (d, J = 7.6 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 157.6, 148.3, 139.7, 138.5, 136.7, 130.1, 129.7, 129.6, 128.8, 128.3, 127.5, 127.2, 126.2, 124.7, 119.2, 21.6.

2-(4-Methoxyphenyl)quinolone.[2j] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.19−8.17 (m, 4H), 7.86−7.81 (m, 2H), 7.76−7.72 (m, 1H), 7.54−7.50 (m, 1H), 7.08 (d, J = 8.8 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 160.9, 156.9, 148.3, 136.7, 132.2, 129.6, 129.5, 128.9, 127.5, 126.9, 125.9, 118.5, 114.3, 55.4.

2-(2-chlorophenyl)quinolone.[30] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.12 (t, J = 8.8 Hz, 2H), 7.79 (d, J = 8.0 Hz, 1H), 7.68−7.61 (m, 3H), 7.49 (t, J = 7.6 Hz, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.35−7.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 157.5, 148.1, 139.7, 135.7, 132.4, 131.7, 130.1, 129.9, 129.7, 127.6, 127.2, 127.2, 126.8, 122.8.

2-(3-Bromophenyl)quinolone.[30] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.25 (br s, 1H), 8.07−8.05 (m, 2H), 7.94 (d, J = 7.6 Hz, 1H), 7.70−7.66 (m, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.41 (t, J = 7.2 Hz, 1H), 7.25 (t, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 154.3, 147.0, 140.5, 135.8, 131.1, 129.5, 129.2, 128.7, 128.6, 127.7, 126.4, 125.5, 124.9, 122.0, 117.4.

2-(4-Fluorophenyl)quinolone.[30] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.15−8.07 (m, 4H), 7.75 (d, J = 8.8 Hz, 2H), 7.67−7.63 (m, 1H), 7.47−7.43 (m, 1H), 7.13 (t, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 164.0, 161.5, 155.2, 147.2, 135.8, 134.7, 128.7, 128.6, 128.4, 128.3, 126.4, 126.0, 125.3, 117.5, 114.8, 114.6.

3-Methyl-2-phenylquinoline.[2j] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.19 (d, J = 8.0 Hz, 1H), 8.06 (br s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.72−7.68 (m, 1H), 7.64−7.61 (m, 2H), 7.57−7.45 (m, 4H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 160.3, 137.1, 129.3, 129.0, 128.9, 128.4, 127.6, 126.7, 126.6, 20.6.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00475.

Crystallographic details for complex **3**, synthetic route of L_3, NMR spectra, and IR spectra of the new compounds (PDF)

Accession Codes

CCDC 1939902 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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