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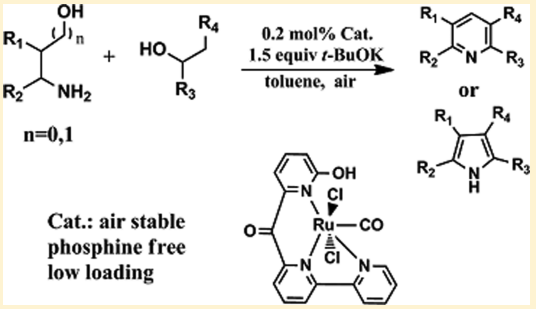
NNN-Ruthenium Catalysts for the Synthesis of Pyridines, Quinolines, and Pyrroles by Acceptorless Dehydrogenative Condensation

Danfeng Deng, Bowen Hu, Min Yang, and Dafa Chen*

MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemical Engineering & Technology, Harbin Institute of Technology, Harbin 150001, People's Republic of China

Supporting Information

ABSTRACT: The bidentate ruthenium complex $(HO\text{-}C_5H_3N\text{-}CO\text{-}C_5H_3N\text{-}C_5H_4N)Ru(CO)_2Cl_2$ (**2**) could transform to a tridentate product $(HO\text{-}C_5H_3N\text{-}CO\text{-}C_5H_3N\text{-}C_5H_4N)Ru(CO)Cl_2$ (**3**), which further reacted with CH_3ONa in the presence of PPh_3 to convert to two complexes $[(OC_5H_3N\text{-}CO\text{-}C_5H_3N\text{-}C_5H_4N)Ru(PPh_3)_2(CO)]Cl^-$ (**4**) and $[(OC_5H_3N\text{-}CO\text{-}C_5H_3N\text{-}C_5H_4N)Ru(PPh_3)(CO)Cl]$ (**5**), via −OH deprotonation. The catalytic coupling cyclizations of secondary alcohols with amino alcohols were investigated, and complex **3** exhibited the highest activity. The coupling reactions proceeded in air with only 0.2 mol % catalyst loading and had a broad scope for the synthesis of pyridines, quinolones, and pyrroles.



INTRODUCTION

The synthesis of N-heterocycles has drawn wide attention, as their motifs are applied in pharmaceuticals, dyes, and functional materials.[1] Nevertheless, classical approaches to these N-heterocycles still suffer from deficiencies like scarcity of the raw materials, complexity of the reaction steps and harsh reaction conditions. From a green chemistry perspective, atom economical, environment-friendly and effective methodologies for synthesizing N-heterocycles are in urgent demand.

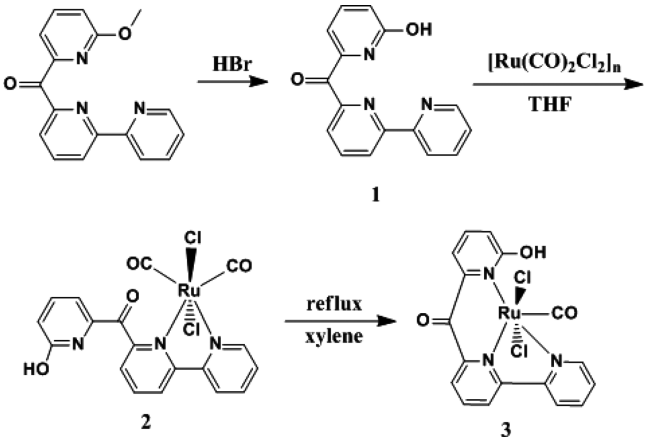
In recent years, the hydrogen autotransfer (HA) or borrowing hydrogen (BH) reaction has become an elegant protocol for the coupling of C−C and C−N bonds, which generates only water as a byproduct.[1d,2] Acceptorless dehydrogenation condensation (ADC), which is mechanistically related to the HA/BH reaction, enables the synthesis of aromatic N-heterocycles from secondary alcohols with amino alcohols.[3−15] For instance, the groups of Kempe,[4] Milstein,[5] Saito,[6] Beller,[7] Sun,[8] Yu,[9] and others[10] reported efficient Ru- and Ir-catalyzed coupling cyclization, and a series of pyridines, pyrroles, and quinolones were synthesized. However, most of their catalysts were synthesized on the basis of air-sensitive phosphine ligands. In recent years, a few noble-metal-free catalysts, such as Fe,[11] Mn,[12] Cu,[13] Co,[14] and Ni[15] complexes, were also developed for the synthesis of N-heterocycles, while high catalyst loading (2−10 mol %) and long reaction time (16−24 h) were almost inevitable. Therefore, it is still significative to explore the relatively low cost ruthenium complexes with nonphosphine ligands as the catalysts for such transformations.

Recently, Kundu and co-workers reported several NNN-Ru complexes with a 2-hydroxypyridyl moiety for the synthesis of N-alkylated amines and quinolones under an N_2 atomsphere.[16] In addition, over the past few years, our group has also designed a range of ruthenium complexes bearing NNN tridentate ligands with such a moiety, which were mainly applied to the transfer hydrogenation of ketones.[17] As an extension, we herein report new types of NNN-ruthenium complexes with a 2-hydroxypyridyl fragment showing high catalytic efficiency for the synthesis of pyridines, quinolones, and pyrroles; notably, the catalytic reactions could be carried out in air.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Ligand and Complexes. As shown in Scheme 1, ligand **1** was obtained by the reaction of HBr (40% in water) with (6-methoxypyridin-2-yl)(6-(pyridin-2-yl)pyridin-2-yl)methanone at reflux for 3 h in

Scheme 1. Synthesis of 1−3



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81% yield. When **1** was treated with $[Ru(CO)_2Cl_2]_n$ in refluxing THF for 24 h, the yellow bidentate NN-Ru complex **2** was isolated in 72% yield. The ^{1}H NMR spectrum of **2** in d_6-DMSO shows nine signals between 9.24 and 6.86 ppm for its aromatic protons. The IR spectrum of **2** exhibits two strong CO absorptions at 2060 and 1998 cm^{-1} with equal intensity.

In refluxing xylene, **2** further transformed into the red complex **3**, accompanied by the release of one molecule of CO (Scheme 1). **3** could be obtained by the reaction of **1** with $[Ru(CO)_2Cl_2]_n$ in refluxing xylene as well. The IR spectrum of **3** reveals a CO peak at 1965 cm^{-1}.

The molecular structures of **2** (Figure 1) and **3** (Figure 2) were further confirmed by X-ray crystallography. The central Ru

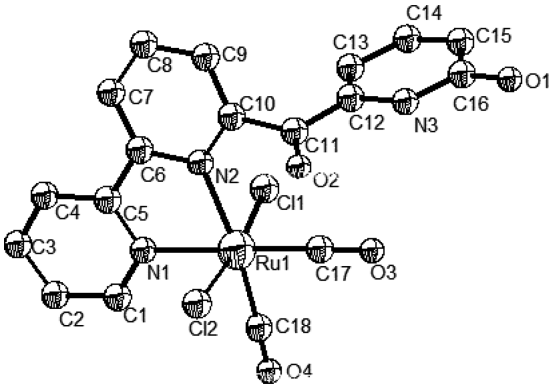

Figure 1. Molecular structure of complex **2**. Hydrogen atoms and solvents have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ru(1)−N(1), 2.112(2); Ru(1)−N(2), 2.149(2); Ru(1)−Cl(1), 2.3786(10); Ru(1)−Cl(2), 2.3811(9); Ru(1)−C(17), 1.876(3); Ru(1)−C(18), 1.895(4); N(1)−Ru(1)−C(17), 179.56(14); N(2)−Ru(1)−C(18), 171.41(11); Cl(1)−Ru(1)−Cl(2), 172.79(3).

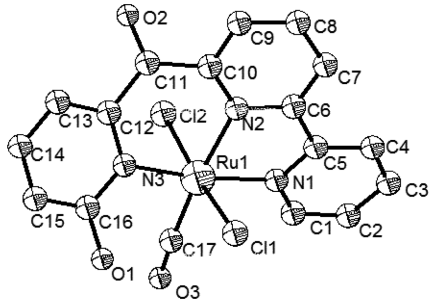

Figure 2. Molecular structure of complex **3**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ru(1)−N(1), 2.053(3); Ru(1)−N(2), 2.078(3); Ru(1)−N(3), 2.120(3); Ru(1)−Cl(1), 2.4190(11); Ru(1)−Cl(2), 2.4076(10); Ru(1)−C(17), 1.873(5); C(16)−O(1), 1.327(5); N(2)−Ru(1)−C(17), 172.67(16); N(1)−Ru(1)−N(3), 169.63(13); Cl(1)−Ru(1)−Cl(2), 173.27(4).

atoms of both complexes are in octahedral coordination environments. In complex **2**, Ru(1) is coordinated with two pyridyl groups, two CO groups, and two Cl atoms. The two Cl atoms are *trans* to each other, while the two CO groups are in *cis* geometry, consistent with its IR data. The N(1)−Ru(1)−C(17), N(2)−Ru(1)−C(18) and Cl(1)−Ru(1)−Cl(2) angles are 179.56, 171.41, and 172.79°, respectively, implying their almost linear arrangement. Different from complex **2**, **3** is a pincer type ruthenium complex, with three pyridyl rings, two trans Cl atoms, and one CO group coordinating with Ru(1). The Ru(1)−N(1), Ru(1)−N(2), and Ru(1)−N(3) distances are 2.053(3), 2.078(3), and 2.120(3) Å, respectively, comparable to those in complex **2**.

Treatment of **3** with CH_3ONa in the presence of PPh_3 in methanol generated complex **4** (Scheme 2). The ^{1}H NMR spectrum of **4** exhibits 40 protons at 9.62−6.85 ppm, suggesting the existence of two PPh_3 groups. A singlet at 28.9 ppm is appeared in its ^{31}P NMR, indicating the trans configuration of the PPh_3 groups. The IR spectroscopy analysis shows one CO band at 1967 cm^{-1}. From these data, the structure of **4** was regarded as an ionic pincer complex with one Cl$^-$ anion.

One of the PPh_3 groups could be replaced by a Cl$^-$ anion when complex **4** was heated in refluxing toluene, generating product **5** (Scheme 2). From the ^{1}H NMR spectrum, there are only 25 protons in **5**, demonstrating one less PPh_3 group in comparison to **4**. Together with the IR absorption (1958 cm^{-1} for one CO), **5** was concluded to be a neutral complex with a Ru−Cl bond.

The molecular structures of **4** (Figure 3) and **5** (Figure 4) were also confirmed by X-ray crystallography. Complex **4** shows a trans configuration of the PPh_3 groups, and the P(1)−Ru(1)−P(2) angle is 176.40°, consistent with its NMR data. The C−O distances in the pyridonate groups (1.248(7) Å for **4** and 1.252(2) Å for **5**) are consistent with C═O double bonds, indicating that the −OH group in **3** was deprotonated in the presence of CH_3ONa.

Catalysis. To find the optimal conditions for the synthesis of N-heterocycles, the reaction of 3-aminobutan-1-ol with 1-phenylethanol was selected as the model reaction (Table 1, top). *t*-BuOK and complex **3** were chosen as the base and precatalyst, respectively. The base amount and the ratio of amino alcohol to secondary alcohol were explored first. Solvent and catalyst amounts were also tested in the same way (for details see the Supporting Information). The conditions for entry 2 in Table 1 were selected as the optimal conditions (2 mmol of 3-aminobutan-1-ol, 4 mmol of 1-phenylethanol, 3 mmol of *t*-BuOK, 3 mL of toluene, and 0.2 mol % of complex **3** for 6 h in the air). It is worth noting that, when the amount of catalyst **3** was increased from 0.2% to 0.4%, an unstable unknown byproduct which has not been identified appeared, decreasing the yield from 84% to 70% (Table S4, entry 4).[4b,8] Next, complexes **2**−**5** were tested as catalysts and complex **3** showed the best efficiency (Table 1, entries 1−4). Parts of the excess 1-phenylethanol were dehydrogenated to the acetophenone (Table 1, entry 2). Different bases were also explored, and *t*-BuOK was the most suitable one, indicating that a stronger base should be beneficial for the desired product (Table 1, entries 5−8). The N_2 atmosphere had almost no influence on the reaction (Table 1, entry 9).

On the basis of the results above, various γ-amino alcohols with secondary alcohols were tested for their reactivity (Table 2). When 1-phenylethanol was chosen as the secondary alcohol, the corresponding pyridine and quinolone derivatives were isolated in high yields, such as 80% for 2-methyl-6-phenylpyridine (Table 2, entry 1), 87% for 2,6-diphenylpyridine (Table 2, entry 6), and 89% for 2-phenylquinoline (Table 2, entry 11). An electron-donating group at the para position of 1-phenylethanol increased the activity slightly (Table 2, entries 3, 8, and 13), while an electron-withdrawing group decreased the yields notably (Table 2, entries 2, 7, and 12).[4e] 1-Phenylpropanol was also tested for the reaction, and the yields decreased slightly owing to steric hindrance (Table 2, entries 5,

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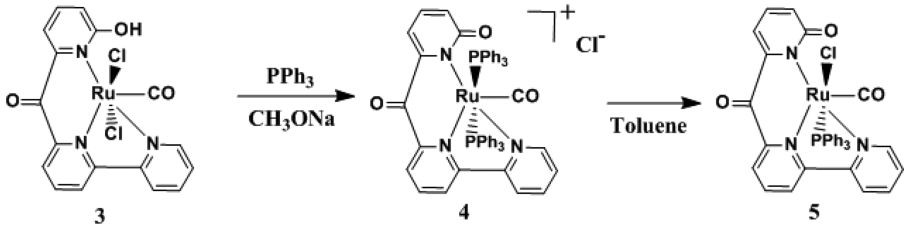
Scheme 2. Synthesis of 4 and 5



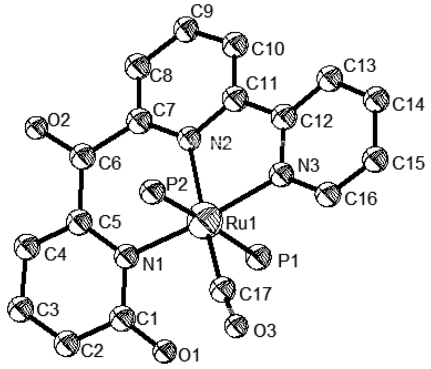


Figure 3. Molecular structure of complex **4**. Hydrogen atoms, phenyl rings on PPh_3 ligands, and solvents have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ru(1)−N(1), 2.081(4); Ru(1)−N(2), 2.092(4); Ru(1)−N(3), 2.107(4); Ru(1)−P(1), 2.4572(13); Ru(1)−P(2), 2.4043(13); Ru(1)−C(17), 1.869(5); C(1)−O(1), 1.248(7); N(2)−Ru(1)−C(17), 172.60(2); N(1)−Ru(1)−N(3), 169.21(17); P(1)−Ru(1)−P(2), 176.40(5).

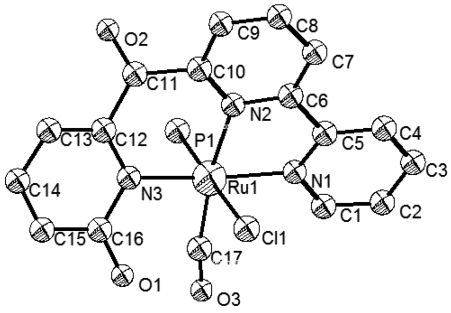
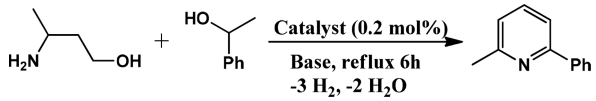


Figure 4. Molecular structure of complex **5**. Hydrogen atoms and phenyl rings on the PPh_3 ligand have been omitted for clarity. Selected bond distances (Å) and angles (deg): Ru(1)−N(1), 2.0666(14); Ru(1)−N(2), 2.0892(14); Ru(1)−N(3), 2.1036(14); Ru(1)−P(1), 2.2959(5); Ru(1)−Cl(1), 2.4464(5); Ru(1)−C(17), 1.8672(18); C(16)−O(1), 1.252(2); N(2)−Ru(1)−C(17), 171.33(7); N(1)−Ru(1)−N(3), 167.55(6); P(1)−Ru(1)−Cl(1), 178.165(17).

10, and 14). In addition, secondary alcohols with only alkyl substituents were also suitable for this reaction, and the products were obtained in good yields (Table 2, entries 4 and 9).

In addition, the reactions of *β*-amino alcohols with secondary alcohols were conducted, and a series of pyrrole derivatives were obtained (Table 3). Similarly, 1-phenylethanol and 1-(4-methoxyphenyl)ethanol reacted well with 2-amino-1-butanol and 2-amino-3-methyl-1-pentanol, respectively (Table 3, entries 1, 3, 5, and 7), while 1-(4-chlorophenyl)ethanol gave moderate yields (Table 3, entries 2 and 6). 1-Phenylpropanol and 2-heptanol were also not as good as 1-phenylethanol (Table 3, entries 4, 8, and 9). However, when 2-amino-2-phenylethanol was selected as the *β*-amino alcohol, the major product was the

Table 1. Optimization of Reaction Conditions for the Synthesis of 2-Methyl-6-phenylpyridine[a]



entry	Cat.	base	yield[b](%)
1	**2**	*t*-BuOK	64
2	**3**	*t*-BuOK	84[c]
3	**4**	*t*-BuOK	59
4	**5**	*t*-BuOK	67
5	**3**	NaOH	72
6	**3**	K_2CO_3	0
7	**3**	NaOMe	57
8	**3**	KOH	75
9	**3**	*t*-BuOK	85[d]

[a]Conditions unless specified otherwise: amino alcohol (2 mmol), secondary alcohol (4 mmol), base (3 mmol), toluene (3 mL), air, catalyst (0.2 mol %), 110 °C, 6 h. [b]Yields determined by GC analysis by using dodecane as the internal standard. [c]The ratio of 1-phenylethanol, acetophenone, and 2-methyl-6-phenylpridine is about 7:3:10 in the resulting mixture. [d]The reaction was carried out under an N_2 atmosphere.

corresponding ketone transformed from the secondary alcohol, and no pyrrole derivative was detected (Table 3, entries 10−12).

The reaction mechanism of our work might be consistent with relevant literature reports (Scheme 3).[4a,5a,b,8,10] First, the secondary alcohol is functionalized by the catalyst to form the corresponding ketone with loss of a molecule of hydrogen. Then the amine group of the amino alcohol attacks the ketone to generate an imine intermediate, after which a second hydrogen is lost. Due to the promotion of base, C−C coupling occurs, and the resulting cyclized intermediate dissociates water and hydrogen to give the final product.

■ CONCLUSIONS

In summary, four ruthenium complexes bearing NNN ligands with a 2-hydroxypyridyl or 2-pyridonate fragment have been synthesized and were applied to the synthesis of pyridines, quinolones, and pyrroles via an ADC mechanism. These bifunctional NNN-Ru complexes, especially complex **3**, are efficient for such transformations. It is also worth noting that these one-step, environmentally benign, and atom-economical ADC reactions were carried out in air. Our current work provides alternative methods for the synthesis of N-heterocycles, and other experimental studies are ongoing to explore more active transition-metal catalysts.

■ EXPERIMENTAL SECTION

All of the manipulations were carried out under an atmosphere of dry nitrogen using vacuum-line and oven-dried standard Schlenk techniques if not mentioned otherwise. All solvents were dried from

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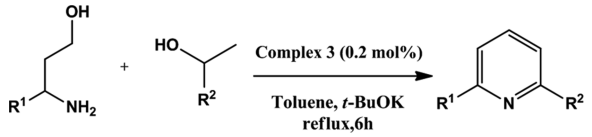
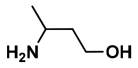
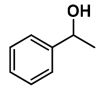
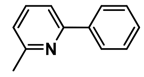
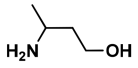
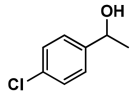
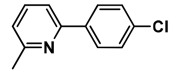
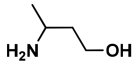
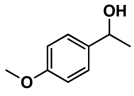
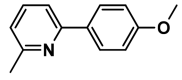
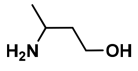
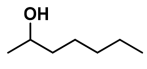
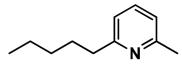
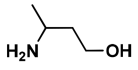
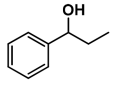
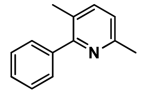
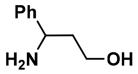
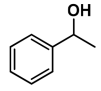
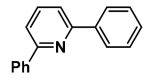
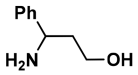
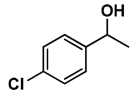
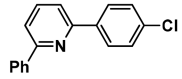
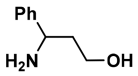
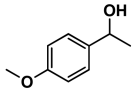
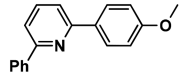
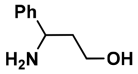
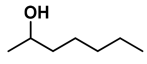
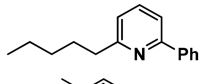
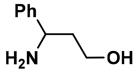
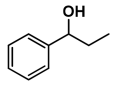
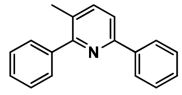
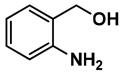
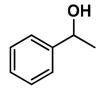
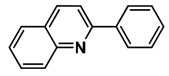
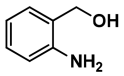
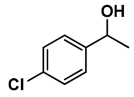
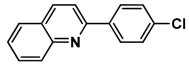
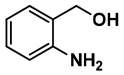
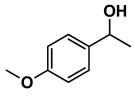
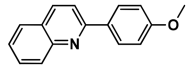
Table 2. Synthesis of Pyridines and Quinolones Using Various γ-Amino Alcohols and Secondary Alcohols[a]



Entry	γ-Amino alcohols	Secondary alcohol	Product	Isolated yield[b](%)
1				80
2				42
3				90
4				75
5				72
6				87
7				55
8				90
9				78
10				77
11				89
12				60
13				91
14				83

[a]Conditions: amino alcohol (2 mmol), secondary alcohol (4 mmol), *t*-BuOK (3 mmol), toluene (3 mL), air, catalyst (0.2 mol %), 110 °C, 6 h. [b]Yields of isolated product.

the appropriate drying agents under N_2 before use. All reagents were obtained from commercial suppliers and used without further purification, with the exception of $[Ru(CO)_2Cl_2]_n$[18] and (6-methoxypyridin-2-yl)(6-(pyridin-2-yl)pyridin-2-yl)methanone,[17b]

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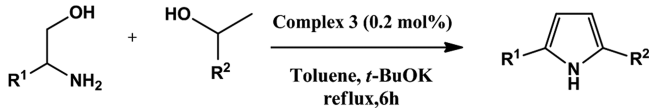
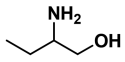
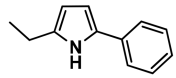
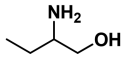
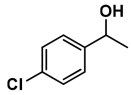
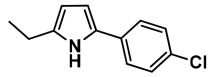
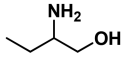
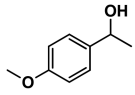
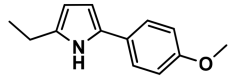
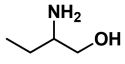
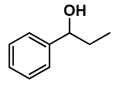
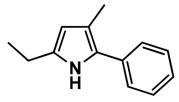
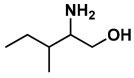
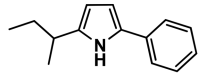
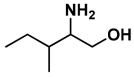
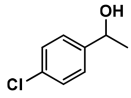
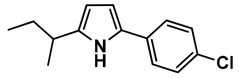
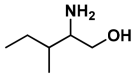
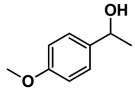
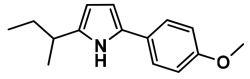
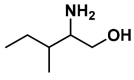
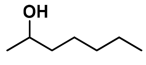
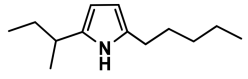
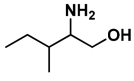
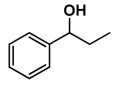
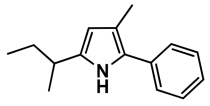
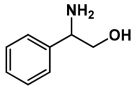
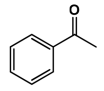
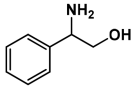
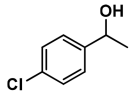
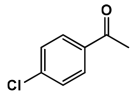
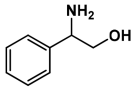
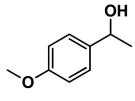
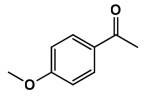
Table 3. Synthesis of Pyrroles Using Various β-Amino Alcohols and Secondary Alcohols[a]



Entry	β-Amino alcohols	Secondary alcohol	Product	Isolated yield[b]
1				87
2				47[c]
3				90
4				73
5				85
6				57
7				91
8				79
9				53
10				45[c]
11				39[c]
12				78

[a]Conditions: amino alcohol (2 mmol), secondary alcohol (4 mmol), *t*-BuOK (3 mmol), toluene (3 mL), air, catalyst (0.2 mol %), 110 °C, 12 h. [b]Yields of isolated product. [c]Yields determined by GC analysis by using dodecane as the internal standard.

which were synthesized by the methods reported in the literature. The ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer. The ^{1}H NMR chemical shifts were referenced to the residual solvent as determined relative to Me_4Si (δ 0 ppm). The $^{31}P\{^{1}H\}$ chemical shifts were reported in ppm relative to external 85% H_3PO_4. The $^{13}C\{^{1}H\}$ chemical shifts were reported in ppm relative to the carbon resonance of $CDCl_3$ (77.0 ppm) or d_6-DMSO (39.5 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. For single-crystal X-ray diffraction, suitable crystals were placed in a cooled N_2 stream at 173(2) K on an SuperNova X-ray single-crystal diffractometer (complexes **2**–**4**) or a Bruker D8 Quest X-ray diffractometer (complex **5**). Data collections were performed using four-circle κ diffractometers equipped with CCD detectors. Data were reduced and then corrected for

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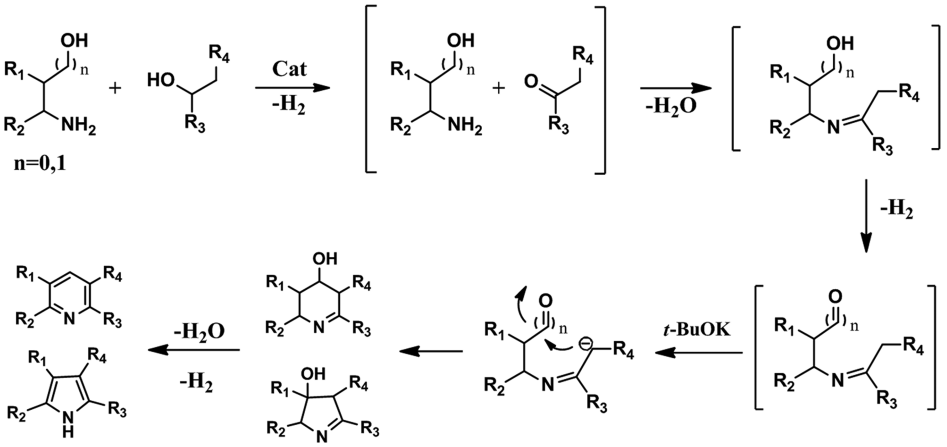
Scheme 3. Plausible Mechanism of Formation of Aromatic N-Heterocycles



absorption.[19] Solution, refinement, and geometrical calculations for all crystal structures were performed with SHELXTL.[20] All of the GC measurements were performed on Agilent GC7890A equipment using an Agilent 19091B-102 (25 m, 220 μm) column.

Synthesis of 1. A solution of (6-methoxypyridin-2-yl)(6-(pyridin-2-yl)pyridin-2-yl)methanone (2.70 g, 9.28 mmol) in 15 mL of HBr (40% in water) was heated at reflux for 3 h. After it was cooled to room temperature, the yellow solution was neutralized by slow addition of a saturated aqueous solution of NaOH. The aqueous solution was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated to afford **1** as a yellow solid (2.20 g, 81%). Mp: 193 °C. HR-MS (ESI): calcd for $C_{16}H_{11}N_3O_2$ + H, 278.0929; found, 278.0931. ^{1}H NMR (400 MHz, d_6-DMSO, ppm): 11.82 (s, 1H), 8.76 (d, J = 4.4 Hz, 1H), 8.67 (d, J = 7.6 Hz, 1H), 8.30 (d, J = 8.0 Hz, 1H), 8.24 (t, J = 8 Hz, 1H), 8.10 (d, J = 7.6 Hz, 1H), 8.01 (t, J = 7.6 Hz, 1H), 7.71−7.67 (m,, 1H), 7.55−7.51 (m, 1H), 7.27 (d, J = 6.8 Hz, 1H), 6.77 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, d_6-DMSO, ppm): 181.5, 162.0, 155.5, 154.3, 152.8, 149.5, 139.8, 139.7, 138.9, 137.6, 127.7, 125.3, 125.1, 124.7, 121.3, 113.2.

Synthesis of 2. A solution of **1** (1.00 g, 3.61 mmol) and $[Ru(CO)_2Cl_2]_n$ (0.823 g, 3.61 mmol) in dried THF (150 mL) was refluxed with stirring for 24 h. The mixture was cooled to room temperature, and the yellow precipitate was collected, washed with ether, and dried under vacuum to provide **2** (1.31 g, 72%). Single crystals suitable for X-ray crystallographic determination were grown with CH_2Cl_2/CH_3OH/*n*-hexane at ambient temperature. Mp: 224 °C. Anal. Calcd for $C_{18}H_{11}Cl_2N_3O_4Ru$: C, 42.79; H, 2.19; N, 8.32. Found: C, 42.63; H, 2.34; N, 8.24. IR (ν_{CO}, KBr, cm^{-1}): 2060 (s), 1998 (s). ^{1}H NMR (400 MHz, d_6-DMSO, ppm): 11.95 (s, 1H), 9.24 (d, J = 5.2 Hz, 1H), 8.98 (d, J = 8 Hz, 1H), 8.90 (d, J = 8.4 Hz, 1H), 8.54 (t, J = 8 Hz, 1H), 8.42 (t, J = 7.2 Hz, 1H), 8.14 (d, J = 8 Hz, 1H), 7.90 (t, J = 6 Hz, 1H), 7.65 (t, J = 5.6 Hz, 1H), 6.86 (d, J = 9.2 Hz, 2H).

Synthesis of 3. *Method a.* A solution of **2** (0.507 g, 1.00 mmol) in xylene (30 mL) was refluxed with stirring for 24 h. The mixture was cooled to room temperature, and the brick red precipitate was collected, washed with ether, and dried under vacuum to provide **3** (0.455 g, 90%). Single crystals suitable for X-ray crystallographic determination were grown with CH_2Cl_2/CH_3OH/*n*-hexane at ambient temperature. Mp: 228 °C. Anal. Calcd for $C_{17}H_{11}Cl_2N_3O_3Ru$: C, 42.78; H, 2.32; N, 8.80. Found: C, 42.74; H, 2.50; N, 8.74. IR (ν_{CO}, KBr, cm^{-1}): 1965 (s). ^{1}H NMR (400 MHz, d_6-DMSO, ppm): 11.42 (s, 1H), 9.32 (d, J = 5.6 Hz, 1H), 8.91 (d, J = 7.6 Hz, 1H), 8.77 (d, J = 8.0 Hz, 1H), 8.44 (t, J = 8.0 Hz, 1H), 8.32 (t, J = 7.6 Hz, 1H), 8.14 (m, 2H), 7.85 (t, J = 6.8 Hz, 1H), 7.73 (d, J = 7.2 Hz, 1H), 7.30 (d, J = 8.4 Hz, 1H),.

Method b. A solution of **1** (1.00 g, 3.61 mmol) and $[Ru(CO)_2Cl_2]_n$ (0.823 g, 3.61 mmol) in xylene (100 mL) was refluxed with stirring for 24 h. The mixture was cooled to room temperature, and the brick red precipitate was collected, washed with ether, and dried under vacuum to provide **3** (1.38 g, 80%).

Synthesis of 4. CH_3ONa (0.045 g, 0.84 mmol) was added to a solution of **3** (0.200 g, 0.42 mmol) and PPh_3 (0.219 g, 0.84 mmol) in dried methanol (10 mL) with stirring, and this mixture was then refluxed for 3 h. After the mixture was cooled to room temperature, the precipitate was collected, washed with ether, and dried under vacuum to provide **4** as a red powder (0.350 g, 86%). Single crystals suitable for X-ray crystallographic determination were grown with CH_2Cl_2/*n*-hexane at ambient temperature. Mp: 232 °C. Anal. Calcd for $C_{53}H_{40}ClN_3O_3P_2Ru$: C, 65.94; H, 4.18; N, 4.35. Found: C, 65.82; H, 4.31; N, 4.34. IR (ν_{CO}, KBr, cm^{-1}): 1967 (s). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 9.62 (d, J = 8.4 Hz, 1H), 9.46 (d, J = 7.6 Hz, 1H), 8.35−8.28 (m, 2H), 8.11 (d, J = 7.6 Hz, 1H), 7.96 (t, J = 7.2 Hz, 1H), 7.35 (t, J = 7.2 Hz, 6H), 7.13−6.99 (m, 15H), 6.91−6.85 (m, 13H). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): 28.95.

Synthesis of 5. *Method a.* A solution of **4** (0.200 g, 0.21 mmol) was refluxed for 3 h in toluene. After the mixture was cooled to room temperature, the precipitate was collected, washed with ether, and dried under vacuum to provide **5** as a red powder (0.120 g, 82%). Single crystals suitable for X-ray crystallographic determination were grown with CH_3OH/diethyl ether at ambient temperature. Mp: 229 °C. Anal. Calcd for $C_{35}H_{25}ClN_3O_3PRu$: C, 59.79; H, 3.58; N, 5.98. Found: C, 59.77; H, 3.74; N, 5.97. IR (ν_{CO}, KBr, cm^{-1}): 1958 (s). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.58 (br s, 1H), 8.48 (d, J = 4.8 Hz, 1H), 8.33 (br s, 1H), 8.15 (t, J = 8.0 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.76 (t, J = 7.6 Hz, 1H), 7.73−7.00 (m, 19H). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): 48.71.

Method b. CH_3ONa (0.023 g, 0.42 mmol) was added to a solution of **3** (0.200 g, 0.42 mmol) and PPh_3 (0.109 g, 0.42 mmol) in dried toluene (20 mL) with stirring, and this mixture was then refluxed for 12 h. The mixture was cooled to room temperature, and the organic phase was evaporated under vacuum. The crude product was purified by column chromatography on silica gel to provide **5** as a red powder (0.150 g, 51%).

General Procedure for the Synthesis of Substituted Pyridines, Quinolones, and Pyrroles. In air, the secondary alcohol (4.0 mmol), amino alcohol (2.0 mmol), complex **3** (2 mg, 0.004 mmol), *t*-BuOK (0.336g, 3 mmol), and 3 mL of toluene were mixed and stirred at 110 °C. After 6 or 12 h, the reaction mixture was cooled to room temperature and 0.1 mL was sampled and immediately diluted with 5 mL of CH_2Cl_2 precooled to 0 °C for GC analysis to calculate the conversation and product selectivity 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.

2-Methyl-6-phenylpyridine.[8] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.02 (d, J = 7.6 Hz, 2H), 7.65 (t, J = 7.6 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.50 (t, J = 7.2 Hz, 2H), 7.43 (t, J = 7.6 Hz, 1H), 7.12 (d, J = 7.6

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Hz, 1H), 2.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 158.4, 157.0, 139.8, 136.9, 128.7, 127.0, 121.6, 117.6, 24.7.

2-Methyl-6-(4-chlorophenyl)pyridine.[21] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.96 (d, J = 8.8 Hz, 2H), 7.65 (t, J = 7.6 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 7.6 Hz, 1H), 2.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 158.5, 155.6, 138.1, 137.1, 134.9, 128.8, 128.3, 121.9, 117.4, 24.7.

2-Methyl-6-(4-methoxyphenyl)pyridine.[22] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.98 (d, J = 8.8 Hz, 2H), 7.62 (t, J = 7.6 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.06 (d, J = 7.6 Hz, 2H), 7.01 (d, J = 9.2 Hz, 2H), 3.88 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 160.4, 158.1, 156.6, 136.9, 132.3, 128.3, 120.9, 116.9, 114.1, 55.4, 24.7.

2-Methyl-6-pentylpyridine.[23] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.49 (t, J = 7.6 Hz, 1H), 6.98 (d, J = 2.8 Hz, 1H), 6.96 (d, J = 2.8 Hz, 1H), 2.77 (t, J = 8.0 Hz, 2H), 2.55 (s, 3H), 1.74 (m, 2H), 1.35 (m, 4H), 0.93 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 161.9, 157.6, 136.5, 120.4, 119.5, 38.5, 31.7, 29.9, 24.5, 22.6, 14.0.

3,6-Dimethyl-2-phenylpyridine.[24] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.54−7.37 (m, 6H), 7.07 (d, J = 7.6 Hz, 1H), 2.66 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 157.9, 155.3, 140.7, 138.9, 128.9, 127.9, 127.5, 121.8, 24.1, 19.5.

2,6-Diphenylpyridine.[9] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.25 (d, J = 6.8 Hz, 4H), 7.86−7.82 (m, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.60−7.49 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 156.9, 139.6, 137.5, 129.1, 128.8, 127.1, 118.7.

2-(4-Chlorophenyl)-6-phenylpyridine.[25] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.18−8.12 (m, 4H), 7.84 (t, J = 7.6 Hz, 1H), 7.74−7.67 (m, 2H), 7.56−7.46 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 157.0, 155.6, 139.2, 137.8, 137.7, 135.1, 129.2, 128.9, 128.8, 128.3, 127.0, 119.0, 118.4.

2-(4-Methoxyphenyl)-6-phenylpyridine.[13] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.16 (t, J = 8.8 Hz, 4H), 7.81 (t, J = 8.0 Hz, 1H), 7.67 (d, J = 7.2 Hz, 2H), 7.53 (t, J = 7.2 Hz, 2H), 7.46 (t, J = 7.2 Hz, 1H), 7.05 (d, J = 8.8 Hz, 2H), 3.908 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 160.6, 156.7, 156.5, 139.4, 137.5, 132.0, 129.0, 128.7, 128.4, 127.1, 118.1, 114.1, 55.4.

2-Pentyl-6-phenylpyridine.[5a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.03 (d, J = 7.2 Hz, 2H), 7.67 (t, J = 7.9 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.2 Hz, 2H), 7.42 (t, J = 7.2 Hz, 1H), 7.11 (d, J = 7.6 Hz, 1H), 2.89 (t, J = 7.6 Hz, 2H), 1.88−1.80 (m, 2H), 1.44−1.29 (m, 4H), 0.97−0.90 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 162.4, 156.7, 136.9, 128.7, 128.6, 127.1, 121.0, 117.8, 38.4, 31.7, 29.5, 22.6, 14.1.

2,6-Diphenyl-3-methylpyridine.[26] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.11 (d, J = 7.6 Hz, 2H), 8.01 (d, J = 7.2 Hz, 1H), 7.68 (d, J = 5.2 Hz, 2H), 7.53−7.43 (m, 7H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 158.2, 154.6, 141.0, 139.4, 139.3, 132.9, 129.3, 129.2, 128.6, 128.6, 128.5, 128.0, 126.9, 118.7, 19.9.

2-Phenylquinoline.[8] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.26−8.19 (m, 4H), 7.91 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.76 (t, J = 8.4 Hz, 1H), 7.59−7.48 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 157.4, 148.2, 139.6, 136.9, 129.7, 129.6, 129.4, 128.9, 127.6, 127.5, 127.2, 126.3, 119.0.

2-(4-Chlorophenyl)quinolone.[13] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.25 (d, J = 8.8 Hz, 1H), 8.20−8.14 (m, 3H), 7.87−7.84 (m, 2H), 7.76 (t, J = 6.8 Hz, 1H), 7.58−7.51 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 156.0, 148.1, 137.9, 137.1, 135.6, 129.9, 129.6, 128.9, 127.5, 127.2, 126.6, 118.6.

2-(4-Methoxyphenyl)quinolone.[13] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.18 (d, J = 8.8 Hz, 1H), 7.86−7.81 (m, 2H), 7.74 (t, J = 8.4 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.08 (d, J = 8.8 Hz, 2H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 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.

3-Methyl-2-phenylquinolone.[27] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.19 (d, J = 8.0 Hz, 1H), 8.06 (s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 2H), 7.57−7.45 (m, 4H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 160.3, 137.2, 129.3, 129.0, 128.9, 128.4, 128.3, 127.6, 126.7, 126.6, 20.6.

2-Ethyl-5-phenyl-1H-pyrrole.[9] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.18 (s, 1H), 7.49 (d, J = 7.2 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 6.48 (t, J = 2.8 Hz, 1H), 6.04 (t, J = 2.8 Hz, 1H), 2.74 (q, J = 7.6 Hz, 2H), 1.34 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 135.7, 133.1, 130.6, 128.8, 125.7, 123.4, 106.3, 106.0, 21.0, 13.6.

2-Ethyl-5-(4-methoxyphenyl)-1H-pyrrole.[12b] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.07 (s, 1H), 7.40 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 12.8 Hz, 2H), 6.33 (t, J = 3.2 Hz, 1H), 6.00 (t, J = 2.8 Hz, 1H), 3.85 (s, 3H), 2.71 (q, J = 7.6 Hz, 2H), 1.32 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 157.9, 134.9, 130.6, 126.2, 124.9, 114.3, 105.9, 104.8, 55.3, 21.0, 13.7.

5-Ethyl-3-methyl-2-phenyl-1H-pyrrole.[9] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.87 (s, 1H), 7.45−7.42 (m, 4H), 7.28−7.25 (m, 1H), 5.93 (s, 1H), 2.71 (q, J = 7.6 Hz, 2H), 2.323 (s, 3H), 1.342 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 134.0, 133.9, 128.7, 126.6, 126.0, 125.5, 116.3, 108.6, 20.9, 13.6, 12.6.

2-(1-Methylpropyl)-5-phenyl-1H-pyrrole.[14a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.22 (s, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.27 (t, J = 7.0 Hz, 1H), 6.56 (t, J = 3.2 Hz, 1H), 6.11 (t, J = 3.2 Hz, 1H), 2.87−2.78 (m, 1H), 1.85−1.65 (m, 2H), 1.40 (d, J = 7.2 Hz, 3H), 1.05 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 139.4, 133.2, 130.4, 128.9, 125.7, 123.5, 106.0, 105.8, 34.6, 30.4, 20.2, 12.0.

2-(1-Methylpropyl)-5-(4-chlorophenyl)-1H-pyrrole. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.09 (s, 1H), 7.41−7.32 (m, 4H), 6.45 (t, J = 3.2 Hz, 1H), 6.02 (t, J = 3.2 Hz, 1H), 2.80−2.71 (m, 1H), 1.78−1.58 (m, 2H), 1.33 (d, J = 7.2 Hz, 3H), 0.97 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 139.7, 131.6, 131.0, 129.2, 128.9, 124.5, 106.5, 106.0, 34.5, 30.3, 20.1, 11.9. HR-MS (ESI): calcd for $C_{14}H_{16}ClN$ + H, 234.7445; found, 234.7441.

2-(1-Methylpropyl)-5-(4-methoxyphenyl)-1H-pyrrole. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.05 (s, 1H), 7.41 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 6.35 (t, J = 3.2 Hz, 1H), 6.00 (t, J = 2.8 Hz, 1H), 3.86 (s, 3H), 2.80−2.71 (m, 1H), 1.74−1.61 (m, 2H), 1.33 (d, J = 7.2 Hz, 3H), 0.98 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 157.9, 138.5, 130.3, 126.3, 124.9, 114.3, 105.4, 104.7, 55.3, 34.4, 30.3, 20.1, 11.9. HR-MS (ESI): calcd for $C_{15}H_{19}NO$ + H, 230.3254; found, 230.3256.

2-(1-Methylpropyl)-3-methyl-5-phenyl-1H-pyrrole. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.82 (s, 1H), 7.44−7.38 (m, 4H), 7.24−7.20 (m, 1H), 5.88 (d, J = 3.2 Hz, 1H), 2.74−2.66 (m, 1H), 2.28 (s, 3H), 1.75−1.54 (m, 2H), 1.30 (d, J = 7.2 Hz, 3H), 0.96 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 137.6, 134.0, 128.6, 126.3, 125.9, 125.4, 116.1, 108.0, 34.3, 30.2, 20.0, 12.6, 11.9. HR-MS (ESI): calcd for $C_{15}H_{19}N$ + H, 214.3260; found, 214.3255.

2-(1-Methylpropyl)-5-pentyl-1H-pyrrole. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.66 (s, 1H), 5.85 (d, J = 2.8 Hz, 2H), 2.74−2.65 (m, 1H), 2.61 (d, J = 7.6 Hz, 2H), 1.73−1.55 (m, 4H), 1.43−1.39 (m, 4H), 1.30 (d, J = 6.8 Hz, 3H), 0.99−0.95 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 136.2, 131.1, 104.3, 103.3, 34.3, 31.7, 30.3, 29.4, 27.9, 22.5, 20.0, 14.1, 11.9. HR-MS (ESI): calcd for $C_{13}H_{23}N$ + H, 194.3364; found, 194.3361.

4-Methoxyacetophenone.[28] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.93 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 9.2 Hz, 2H), 3.85 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 196.8, 163.5, 130.6, 113.7, 55.4, 26.3.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00359.

Crystallographic details for complexes **2**−**5**, screening reactions, and IR and NMR spectra of the new compounds (PDF)

Accession Codes

CCDC 1845517−1845520 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 Cam-

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bridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail for D. C.: dafachen@hit.edu.cn.

ORCID

Dafa Chen: 0000-0002-7650-4024

Notes

The authors declare no competing financial interest.

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