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A Versatile Ru(II)-NNP Complex Catalyst for the Synthesis of Multisubstituted Pyrroles and Pyridines

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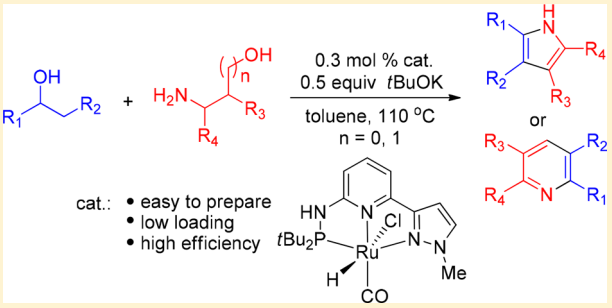
Supporting Information

ABSTRACT: A pincer-type Ru(II)-NNP complex bearing a pyrazolyl-(NH-P*t*Bu$_2$)-pyridine ligand was synthesized and structurally characterized by NMR, IR, elemental analysis, and X-ray single-crystal crystallographic determinations, which efficiently catalyzed the synthesis of multisubstituted pyrroles and pyridines by means of the reactions of secondary alcohols and *β*- or *γ*-amino alcohols through deoxygenation and selective C−N and C−C bond formation. The coupling reactions took place with 0.3 mol % catalyst loading and tolerated diverse functional groups. The present work provides an alternative method to construct highly active transition-metal complex catalysts from readily available ligands.



INTRODUCTION

Nitrogen-containing heterocyclic compounds pyrroles and pyridines ubiquitously exist in natural products, pharmaceuticals, and functional materials.[1] The pyrrole scaffold is a prominent structural motif of porphinoid cofactors, heme b, chlorophyll a, vitamin B_{12}, and factor 430[2a] and many natural products.[2b] Pyrrole-based drugs usually exhibit significant pharmacological properties such as antibacterial,[3] antifungal,[4] anti-inflammatory,[5] antioxidative,[6] and antitumor.[7] Pyridine frameworks are found in many fungicides, herbicides, and drugs.[8] Pyridine-based compounds can act as effective ligands in coordination chemistry and have also been used to construct highly active transition-metal complex catalysts for homogeneous catalysis.[9] Diverse protocols have been developed for the synthesis of N-heterocyclic compounds.[10] Knorr, Hantzsch, and Paal−Knorr reactions have been well established for the synthesis of pyrroles, and Hantzsch, Chichibabin, Bohlmann−Rahtz, and Kröhnke reactions have been used to access pyridine derivatives. However, these methods often suffer from drawbacks such as difficult availability of the starting materials, time-consuming procedures, and harsh reaction conditions. Syntheses of functionalized N-heterocyclic compounds through the reactions of secondary alcohols with amino alcohols have recently attracted much attention[11] due to the high atom economy of the methods and ready availability of the reactants.[12] The catalytic synthesis of aromatic N-heterocycles from such alcohols is usually based on acceptorless dehydrogenation (AD) reactions,[13] involving formation of imine intermediates by dehydrogenative condensation of the secondary alcohol and amino alcohol substrates[14] and subsequent cyclization to give the N-heterocyclic compounds.[15] In this area, Kempe's group reported catalytic pyrrole and pyridine synthesis by means of Ir complex catalysts.[12,15d] Milstein et al. applied a pincer ruthenium(II) bipyridylphosphine complex with 0.5 mol % loading to promote the synthesis of pyrrole, pyridine, and quinoline derivatives, respectively.[16] Saito's group employed a Ru(II)-NP complex as the catalyst to synthesize pyrroles from ketones and amino alcohols.[17] Sun et al. developed a ruthenium(II)-NNP complex catalyst system for the preparation of pyridines and quinolines.[18] Recently, manganese complexes have been reported for the synthesis of quinolines and pyrroles from secondary alcohols and amino alcohols by Kirchner et al.[19a] and Kempe[19b] et al., respectively. The typical Kempe- and Milstein-type transition-metal complexes feature an NH moiety in the PNP[12] and NNP[20] ligands, which usually bestows the resultant transition-metal complexes with enhanced catalytic activity.[21] Such an NH effect has been well-known in Noyori-type Ru(II) complex catalysts for hydrogenation and transfer hydrogenation of ketones[22] and also in other systems.[23]

During our ongoing investigation of Ru(II) complex catalysts, we developed a series of highly active pincer-type Ru(II) pyrazolyl-(NH-imidazol-2-yl)-pyridine complex catalysts which can be applied at very low loadings for transfer hydrogenation of ketones.[24] Intrigued by the high catalytic

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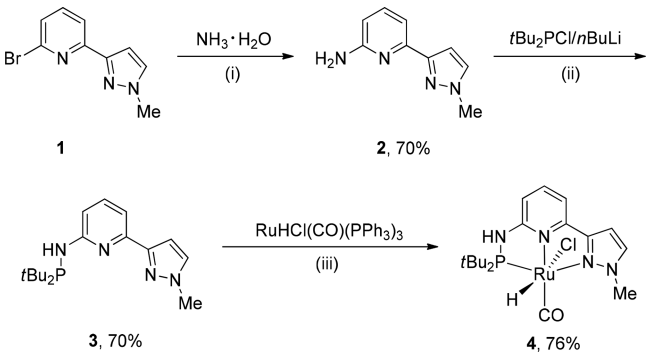
activity of Kempe- and Milstein-type transition-metal complex catalysts, we reasonably envisioned that a pyrazolyl-(NH-PR_2)-pyridine ligand might be suitable for the construction of an active Ru(II) complex catalyst. Herein, we disclose the construction of a versatile Ru(II) pyrazolyl-(NH-P*t*Bu_2)-pyridine complex and its catalytic behaviors in the synthesis of multisubstituted pyrroles and pyridines.

RESULTS AND DISCUSSION

Synthesis and Characterization of Ligands and Complexes. The target ligand, that is, pyrazolyl-(NH-P*t*Bu_2)-pyridine (**3**), and its ruthenium hydride complex **4** were prepared as depicted in Scheme 1. Treatment of 2-bromo-6-(1-methyl-1*H*-pyrazol- 3-yl)pyridine (**1**)[24e] with aqueous ammonia in the presence of Cu_2O gave 6-(1-methyl-1*H*-pyrazol-3-yl)pyridin-2-amine (**2**) in 70% yield. Compound **2** was then reacted with *t*Bu_2PCl in the presence of *n*BuLi to afford ligand **3** (70%). Reacting equimolar amounts of **3** and $RuHCl(CO)(PPh_3)_3$ in refluxing 1,4-dioxane led to Ru(II)-NNP complex **4** (76%). The NMR analyses of the free ligand and its complex are consistent with their compositions. The ^{1}H NMR spectrum of complex **4** exhibited a doublet at −19.40 ppm (J_{PH} = 27.7 Hz) for the Ru-H hydride, and a doublet appeared at 205.3 ppm (J_{PC} = 7.1 Hz) for the CO ligand in its ^{13}C NMR spectrum. The ^{31}P resonance signals of the *t*Bu_2P moieties in the free ligand and complex **4** appeared at 59.4 and 156.9 ppm, respectively, suggesting coordination between the metal center and the phosphorus atom of the ligand in the complex. The IR spectral analysis revealed the absorption peaks of Ru-H and CO functionalities at 2024 and 1929 cm^{-1}, respectively. The molecular structure of complex **4** was further confirmed by an X-ray single-crystal crystallographic determination (Figure 1; see the Supporting Information for details). In the solid state, the central ruthenium atom of complex **4** is situated in a distorted-octahedral geometry, with the CO ligand positioned trans to the pyridyl nitrogen atom and the hydride trans to the chloride. The Cl−Ru−H and C(1)−Ru−N(2) angles are 166.1 and 174.6°, respectively, implying that the hydride and chloride functionalities are almost linearly arranged at the two sides of the ligand plane. The Ru−H bond is 1.60 Å, which is similar to those (1.53−1.55 Å) in the reported RuH complexes.[24c,f]

Scheme 1. Synthesis of Complex 4[a]



[a]Conditions: (i) **1** (490 mg, 2.0 mmol), $NH_3·H_2O$ (4 mL), Cu_2O (42 mg, 0.3 mmol), DMEDA (*N*,*N*′-dimethyl-1,2-ethanediamine) (54 mg, 0.6 mmol), K_2CO_3 (84 mg, 0.6 mmol), ethylene glycol (4 mL), 110 °C, 12 h, 70%; (ii) **2** (174 mg, 1.0 mmol), Et_3N (0.17 mL, 1.2 mmol), *n*BuLi (0.5 mL, 1.2 mmol), *t*Bu_2PCl (0.23 mL, 1.2 mmol), toluene (5 mL), −78 to 80 °C, 12 h, 70%; (iii) **3** (105 mg, 0.3 mmol), $RuHCl(CO)(PPh_3)_3$ (314 mg, 0.3 mmol), 1,4-dioxane (5 mL), 0.1 M Pa N_2, reflux, 2 h, 76%.

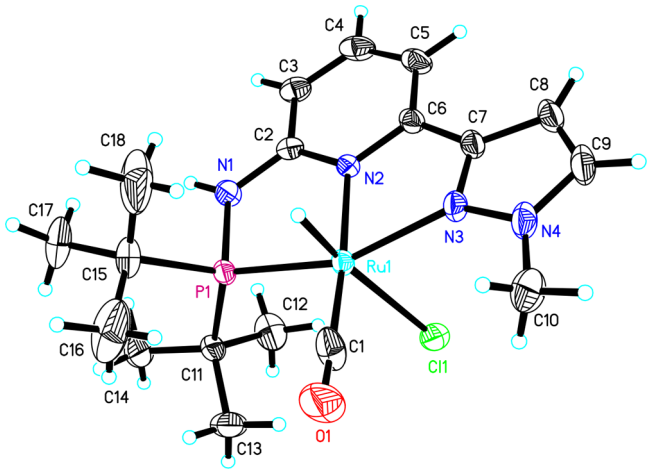
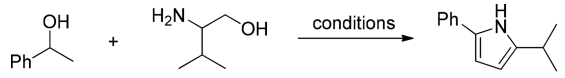


Figure 1. Molecular structure of complex **4**.

Synthesis of Pyrroles. Initially, the reaction of 1-phenylethanol (**5a**) with 2-amino-3-methylbutan-1-ol (**6a**) was performed to optimize the conditions for the dehydrogenative cross-coupling reactions to form the target pyrrole products. With 0.2 mol % loading of complex **4** as the catalyst and 0.5 equiv of *t*BuOK as the base, the reaction of **5a** and **6a** in a 1:1 molar ratio was carried out in refluxing toluene for 12 h, forming the target product 2-isopropyl-5-phenyl-1*H*-pyrrole (**7a**) in 83% yield (Table 1, entry 1). Increasing the catalyst loading to 0.3 mol % remarkably enhanced the yield to 94% (Table 1, entry 2), but further increase in the catalyst loading could not improve the product efficiency (Table 1, entry 3). Lowering the base loading to 0.4−0.1 equiv led to lower yields for the target product (83−69%), exhibiting a remarkable base effect (Table 1, entries 4−6). Different bases and solvents were also screened for the reaction (see the Supporting Information for details). The optimal conditions were thus obtained as those for entry 2 in Table 1.

Table 1. Screening of Reaction Conditions[a]



5a 6a 7a

entry	amt of catalyst **4** (mol %)	amt of *t*BuOK (equiv)	yield[b] (%)
1	0.2	0.5	83
2	0.3	0.5	94
3	0.4	0.5	93
4	0.3	0.4	83
5	0.3	0.3	79
6	0.3	0.1	69

[a]Conditions: **5a** (2 mmol), **6a** (2 mmol), toluene (2 mL), 110 °C, 0.1 MPa N_2, 12 h. [b]Yields determined by GC-MS analysis by using *m*-xylene as the internal standard.

Next, the scope of secondary alcohols **5** was explored under the optimized reaction conditions (Table 2). Both aryl and alkyl secondary alcohols reacted well with 2-amino-3-methylbutan-1-ol (**6a**) to form the target pyrrole products of type **7** in good to excellent yields. The analogues of **5a**, that is,

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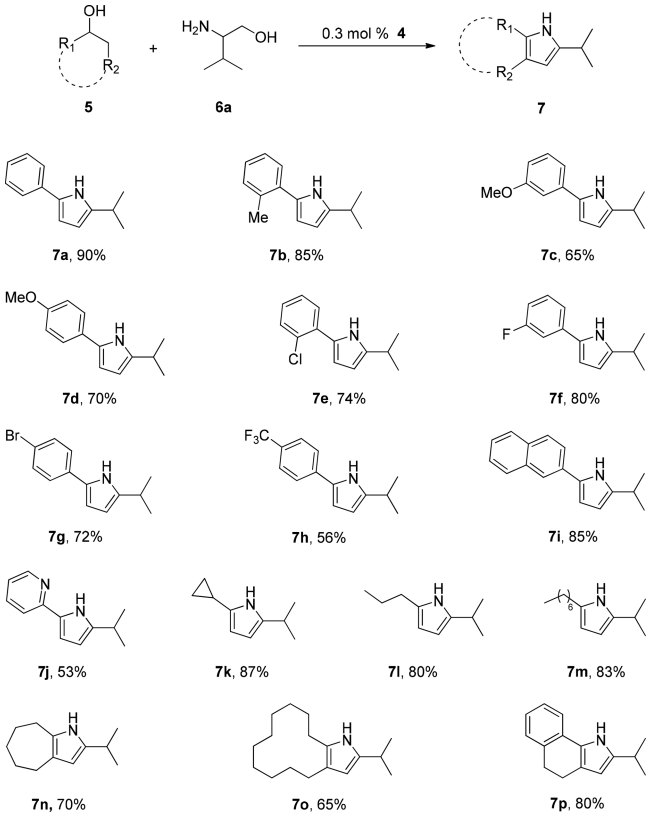
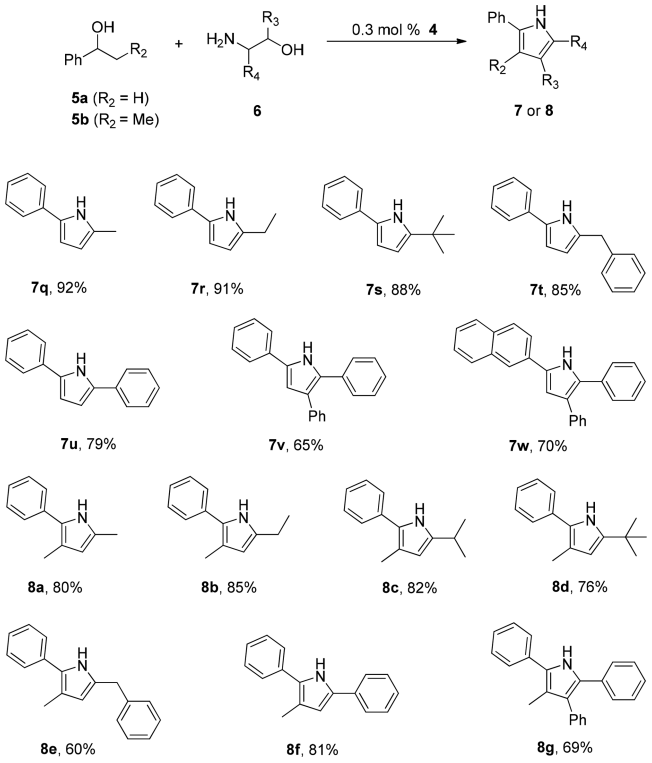
Table 2. Scope of Secondary Alcohols (5)[a]



[a]Conditions: **5** (2 mmol), **6a** (2 mmol), complex **4** (0.006 mmol), *t*BuOK (1 mmol), toluene (2 mL), 110 °C, 0.1 MPa N_2, 12 h. Yields refer to the isolated products.

Table 3. Scope of *β*-Amino Alcohols (6)[a]



[a]Conditions: **5a** or **5b** (2 mmol), **6** (2 mmol), complex **4** (0.006 mmol), *t*BuOK (1 mmol), toluene (2 mL), 110 °C, 0.1 MPa N_2, 12 h. Yields refer to the isolated products.

substituted 1-arylethanols, exhibited various reactivities. *o*-Methyl-substituted 1-phenylethanol reacted efficiently with **6a** to give the corresponding product **7b** in 85% yield, while *m*-OMe- and *p*-OMe-bearing substrates only achieved 65−70% yields to form products **7c,d**. Halo-substituted 1-phenylethanols also reacted well with **6a** to afford **7e−g** (72−80%). A 4-trifluoromethyl substituent demonstrated an obvious negative electronic effect on the yield of **7h** (56%). Unexpectedly, bulky 1-(2-naphthyl)ethanol exhibited good reactivity to form **7i** (85%). The lower yield of **7j** (53%) in the case of using a heteroaromatic substrate, that is, 1-(2-pyridyl)ethanol, is presumably due to the strong binding of the pyridyl nitrogen atom to the catalytically active metal center. Acyclic aliphatic secondary alcohols were efficiently transformed to the correspon ding pyrroles **7k−m** in 80−87% yields, and cyclic secondary alcohols, that is, cycloheptanol, cyclododecanol, and 1,2,3,4-tetrahydronaphthalen-1-ol, also reacted with **6a** to yield the target 2,3,5-trisubstituted bicyclic and tricyclic pyrroles **7n** (70%), **7o** (65%), and **7p** (80%), respectively. Except for **7a** and **7n**, all of the other pyrroles, that is, **7b−m,o,p**, are unknown compounds.

Then, the protocol generality was investigated by performing the reactions of 1-phenylethanol (**5a**) and 1-phenylpropanol (**5b**) with a variety of *β*-amino alcohols (Table 3). All of the reactions afforded 2-phenyl-substituted pyrroles. Under the standard conditions, the reactions of **5a** with 2-aminopropan-1-ol (**6b**), 2-aminobutan-1-ol (**6c**), and 2-amino-3,3-dimethylbutan-1-ol (**6d**) gave the target pyrrole products **7q−s** in excellent yields (88−92%). These amino alcohols exhibited reactivities similar to that of 2-amino-3-methylbutan-1-ol (**6a**) in comparison to the formation of **7a** (90%). Variation of the alkyl moiety (R_4) in the amino alcohols from methyl to ethyl and isopropyl had no obvious effect on the reaction efficiency. The use of benzyl-functionalized *β*-amino alcohol slightly deteriorated the yield of **7t** (85%). However, when aryl-functionalized *β*-amino alcohols were used as the substrates, the product yields dropped from 79% for **7u** to 65% for **7v** as the steric hindrance of the amino alcohols was increased. 1-(2-Naphthyl)ethanol reacted with 2-amino-1,2-diphenylethanol (**6g**) to form triaryl-substituted pyrrole **7w** (70%). Alcohol **5b** also efficiently reacted with *β*-amino alcohols, but its reactions gave the products in yields usually lower than those of the corresponding reactions using alcohol **5a**. Thus, trisubstituted pyrroles of type **8**, that is, pyrroles **8a−f**, were obtained in 60−85% yields, while their disubstituted analogues **7q−u** were accessed in 79−92% yields. Tetrasubstituted pyrrole **8g** was also prepared from the reaction of **5b** with the sterically hindered *β*-amino alcohol **6g**.

In order to further probe into the catalyst activity, both sterically hindered substrates were applied in the reactions (eq 1). Reacting 1,2-diphenylethanol (**5c**) or 1-phenyl-3-*p*-tolylpropan-1-ol (**5d**) with 2-amino-1,2-diphenylethanol (**6g**) under the standard conditions only led to the corresponding dehydrogenation products, that is, ketones **9a** (76%) and **9b** (88%), respectively, and no target pyrrole products were formed, revealing that these sterically hindered ketones could not further react with the *β*-amino alcohol to generate the imine intermediates for further cyclization to the pyrrole products. Treatment of hexane-2,5-diol (**5e**) with **6a** (2 equiv) in refluxing toluene afforded dipyrrole **10** in 56% yield, depicting a potential application of the method for dipyrrole

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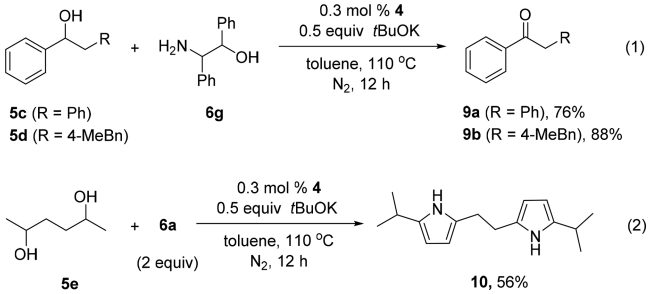
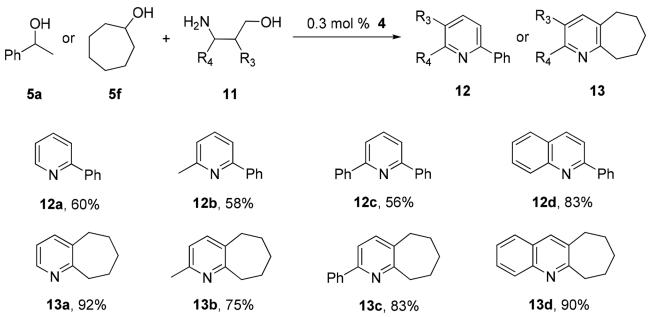


synthesis (eq 2). It is noteworthy that the reaction mechanism for pyrrole synthesis was investigated in a fashion similar to those employed in Kempe's and Milstein's work[12,16] (see the Supporting Information for details). Initially, a secondary alcohol was dehydrogenated to generate the corresponding ketone by means of ruthenium complex **4** as the catalyst. Subsequent formation of the imine intermediate was achieved by condensation of the in situ generated ketone and the amino alcohol substrate. A second dehydrogenation followed by intramolecular base-promoted cyclization leads to a substituted pyrrole or pyridine product. However, other pathways could not be ruled out.[17]

Synthesis of Pyridines. In a similar fashion, the reactions of secondary alcohol **5a** and cycloheptanol (**5f**) with γ-amino alcohols were conducted (Table 4). In general, 1-phenylethanol

Table 4. Scope of γ-Amino Alcohols (11)[a]



[a]Conditions: **5a** or **5f** (2 mmol), **11** (2 mmol), catalyst **4** (0.006 mmol), *t*BuOK (1 mmol), toluene (2 mL), 110 °C, 0.1 MPa N_2, 12 h. Yields refer to the isolated products.

(**5a**) exhibited a reactivity inferior to that of compound **5f**. Thus, **5a** and **5f** reacted with 3-aminopropan-1-ol to afford pyridine products **12a** (60%) and **13a** (92%), and the reactions using 3-aminobutan-1-ol gave products **12b** (58%) and **13b** (75%), respectively. It is noted that phenyl-substituted 3-amino-3-phenylpropan-1-ol exhibited a decent reactivity to interact with these secondary alcohols to generate **12c** (56%) and **13c** (83%). The potential application of the protocol for the synthesis of quinolines was also tested. The reactions of 2-aminobenzyl alcohol with secondary alcohols **5a** and **5f** yielded 2-phenylquinoline (**12d**; 83%) and 7,8,9,10-tetrahydro-6*H*-cyclohepta[*b*]quinoline (**13d**; 90%), respectively.

CONCLUSIONS

In conclusion, direct synthesis of multisubstituted pyrroles and pyridines was efficiently achieved by using a versatile pincer Ru(II)-NNP complex catalyst. The present work provides an alternative method to construct highly active transition-metal complex catalysts.

EXPERIMENTAL SECTION

General Considerations. ^{1}H and $^{13}C\{^1H\}$ NMR spectra were recorded on a 400 MHz spectrometer, and all chemical shift values refer to $CDCl_3$ ($\delta(^1H)$ 7.26 ppm and $\delta(^{13}C)$ 77.16 ppm) and CD_3OD ($\delta(^1H)$ 3.30 ppm and $\delta(^{13}C)$ 49.00 ppm). High-resolution mass spectra (HRMS) were measured on a GC-TOF mass spectrometer. All of the melting points were measured and uncorrected. X-ray crystallographic analysis was achieved by the Analysis Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Analytical TLC plates were viewed by UV light (254 nm). Column chromatographic purifications were performed on silica gel 160. All of the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated.

X-ray Crystallographic Studies. Single-crystal X-ray diffraction studies for complex **4** were carried out on a SMART APEX diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package.

General Procedure for the Synthesis of Substituted Pyrroles and Pyridines. Under a nitrogen atmosphere a mixture of secondary alcohol (2.0 mmol), amino alcohol (2.0 mmol), complex **4** (2.9 mg, 0.006 mmol), and *t*BuOK (112 mg, 1.0 mmol) in 2 mL of toluene was stirred at 110 °C for 12 h. After the mixture was cooled to ambient temperature, 10 mL water was added and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic phase was concentrated under reduced pressure. The resultant residue was subject to purification by column chromatography on silica gel (eluent petroleum ether (60−90 °C)/ethyl acetate 200 1, v/v) to afford the target product.

Synthesis of Compound 2. To a mixture of 2-bromo-6-(1-methyl-1*H*- pyrazol-3-yl)pyridine (**1**; 490 mg, 2.0 mmol), Cu_2O (42 mg, 0.3 mmol), DMEDA (54 mg, 0.6 mmol), and K_2CO_3 (84 mg, 0.6 mmol) in glycol (4 mL) in a sealed tube was added an excess amount of aqueous ammonia (28%, 4 mL). The resulting mixture was stirred at 110 °C for 12 h. After this mixture was cooled to ambient temperature, 10 mL of water was added and the aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic phase was washed with brine (20 mL) and dried over anhydrous Na_2SO_4. The crude product was subject to purification by silica gel column chromatography (eluent petroleum ether (60−90 °C)/ethyl acetate 2/1, v/v), affording **2** as a white solid (250 mg, 70%). Mp: 160−162 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 (t, J = 7.8 Hz, 1 H, 4-H), 7.36 and 6.74 (d each, J = 2.0 and 2.1 Hz, 1:1 H, 5′-H and 4′-H), 7.19 and 6.42 (d each, J = 7.5 and 8.1 Hz, 1:1 H, 5-H and 3-H), 4.58 (br, 2 H, NH_2), 3.96 (s, 3 H, N-CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 158.3 (Cq), 151.8 (Cq), 150.6 (Cq), 138.3, 131.3, 110.5, 107.4, 104.4, 39.2 (N-CH_3). HRMS: calcd for $C_9H_{10}N_4$ 174.0905, found 174.0900.

Synthesis of Ligand 3. To a suspension of 6-(1-methyl-1*H*-pyrazol- 3-yl)pyridin-2-amine (**2**; 174 mg, 1.0 mmol) in toluene (5 mL) was added NEt_3 (0.17 mL, 1.2 mmol). The mixture was cooled to −78 °C, and then *n*BuLi (0.5 mL, 2.4 M solution in hexane, 1.2 mmol) was slowly added with stirring. After 20 min, tBu_2PCl (0.23 mL, 1.2 mmol) was added dropwise at −78 °C. The mixture was warmed to ambient temperature, and stirring was continued at 80 °C overnight. After the reaction mixture was quenched with methanol (1.0 mL), all of the volatiles were removed under reduced pressure. The resultant residue was subject to purification by silica gel column chromatography (eluent petroleum ether (60−90 °C)/ethyl acetate 5/1, v/v), affording **3** as a white solid (223 mg, 70%). Mp: 149−151 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 (t, J = 7.8 Hz, 1 H, 4-H), 7.35 and 6.70 (d and br, J = 1.6 Hz, 1:1 H, 5′-H and 4′-H), 7.14 (m, 2 H, 5-H and 3-H), 5.17 (d, J = 11.0 Hz, 2 H, NH_2), 3.96 (s, 3 H, N-CH_3), 1.16 and 1.13 (s each, 18 H, C-$(CH_3)_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100

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MHz): δ 161.2 (Cq, d, J = 21.5 Hz), 152.1 (Cq), 150.5 (Cq), 138.0, 131.3, 111.1, 107.8 (d, J = 20.3 Hz), 104.6, 39.3 (N-CH_3), 34.2 (d, J = 18.8 Hz, C-$(CH_3)_3$), 28.3 (d, J = 15.0 Hz, C-$(CH_3)_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 59.4 (tBu_2P). HRMS: calcd for $C_{17}H_{27}N_4P$ 318.1973, found 318.1968.

Synthesis of Complex 4. Under a nitrogen atmosphere, a mixture of $RuHCl(CO)(PPh_3)_3$ (314 mg, 0.3 mmol) and ligand **3** (105 mg, 0.3 mmol) in 1,4-dioxane (5 mL) was refluxed for 2 h, forming a yellow solution. After the mixture was cooled to ambient temperature, the resultant precipitates were filtered off, washed with diethyl ether (3 × 5 mL), and dried under vacuum to afford complex **4** as a yellow crystalline solid (122 mg, 76%). Single crystals suitable for X-ray crystallographic determination were grown from recrystallization in $CHCl_2/CH_3OH$/*n*-hexane (1/0.5/3, v/v/v) at 25 °C. Mp: >320 °C dec. ^1H NMR (CD_3OD, 400 MHz): δ 7.93 and 6.95 (br each, 1:1 H, 5′-H and 4′-H), 7.75 (t, J = 7.9 Hz, 1 H, 4-H), 7.31 and 7.02 (d each, J = 7.5 and 8.4 Hz, 1:1 H, 5-H and 3-H), 4.25 (s, 3 H, N-CH_3), 1.44 and 1.30 (d each, J = 14.5 and 14.4 Hz, 9:9 H, C-$(CH_3)_3$), −19.40 (d, J = 27.7 Hz, 1 H, Ru-H). $^{13}C\{^1H\}$ NMR (CD_3OD/CD_2Cl_2, 100 MHz): δ 205.3 (Cq, d, J = 7.1 Hz, CO), 161.6 (Cq, d, J = 7.1 Hz), 152.8 (Cq), 149.9 (Cq, d, J = 1.6 Hz), 139.8, 134.3 (d, J = 1.6 Hz), 110.3, 108.5 (d, J = 6.8 Hz), 104.2, 39.4 (N-CH_3), 39.3 and 39.1 (d each, J = 9.4, 11.7 Hz, C-$(CH_3)_3$), 28.1 and 27.7 (d each, J = 5.6, 4.6 Hz, C-$(CH_3)_3$). $^{31}P\{^1H\}$ NMR (CD_3OD, 162 MHz): δ 156.9 (tBu_2P). IR (KBr pellets, cm^{-1}): 2024 (ν_{Ru-H}), 1929 (ν_{CO}). Anal. Calcd for $C_{18}H_{28}ClN_4OPRu$: C, 44.67; H, 5.83; N, 11.58. Found: C, 44.60; H, 6.00; N, 11.48.

2-Isopropyl-5-phenyl-1*H*-pyrrole (7a): 333 mg, 90% yield, colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.17 (s, br, 1 H), 7.50−7.47 (m, 2 H), 7.41−7.36 (m, 2 H), 7.23−7.19 (m, 1 H), 6.48−6.47 (m, 1 H), 6.05- 6.04 (m, 1 H), 3.07−2.96 (m, 1 H), 1.36 (d, J = 6.9 Hz, 3:3 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 140.4, 133.1, 130.6, 128.9, 125.8, 123.6, 105.9, 105.1, 27.3, 22.8.

2-Isopropyl-5-(*o*-tolyl)-1*H*-pyrrole (7b): 339 mg, 85% yield, colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.10 (s, br, 1 H), 7.49−7.47 (m, 1 H), 7.40−7.33 (m, 2 H), 7.32−7.28 (m, 1 H), 6.41 (t, J = 3.0 Hz, 1 H), 6.18- 6.17 (m, 1 H), 3.15−3.08 (m, 1 H), 2.62 (s, 3 H), 1.46 (d, J = 6.9 Hz, 6 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 139.3, 134.8, 133.1, 131.1, 129.7, 127.5, 126.3, 126.1, 108.8, 104.2, 27.1, 22.7, 21.5. HRMS: calcd for $C_{14}H_{17}N$ 199.1361, found 199.1362.

2-Isopropyl-5-(3-methoxyphenyl)-1*H*-pyrrole (7c): 280 mg, 65% yield, yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.05 (s, br, 1 H), 7.17 (t, J = 7.9 Hz, 1 H), 6.96−6.94 (m, 1 H), 6.90 (t, J = 2.1 Hz, 1 H), 6.66−6.63 (m, 1 H), 6.33 (t, J = 3.1 Hz, 1 H), 5.91−5.89 (m, 1 H), 3.75 (s, 3 H), 2.92−2.85 (m, 1 H), 1.22 (d, J = 6.9 Hz, 6 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 160.1, 140.5, 134.6, 130.4, 129.9, 116.2, 111.1, 109.5, 106.2, 105.1, 55.4, 27.3, 22.8. HRMS: calcd for $C_{14}H_{17}NO$ 215.1310, found 215.1311.

2-Isopropyl-5-(4-methoxyphenyl)-1*H*-pyrrole (7d): 301 mg, 70% yield, white solid, mp 79−81 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.08 (s, br, 1 H), 7.42−7.38 (m, 2 H), 6.95−6.91 (m, 2 H), 6.33 (t, J = 3.0 Hz, 1 H), 6.01−5.99 (m, 1 H), 3.84 (s, 3 H), 3.02−2.96 (m, 1 H), 1.33 (d, J = 6.9 Hz, 6 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 158.0, 139.7, 130.6, 126.3, 125.0, 114.4, 104.8, 104.7, 55.4, 27.3, 22.8. HRMS: calcd for $C_{14}H_{17}NO$ 215.1310, found 215.1309.

2-(2-Chlorophenyl)-5-isopropyl-1*H*-pyrrole (7e): 325 mg, 74% yield, colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.76 (s, br, 1 H), 7.47−7.45 (m, 1 H), 7.29 (d, J = 8.0 Hz, 1 H), 7.15 (t, J = 7.6 Hz, 1 H), 7.03−6.99 (m, 1 H), 6.43 (t, J = 3.1 Hz, 1 H), 5.93 (t, J = 3.0 Hz, 1 H), 2.96−2.86 (m, 1 H), 1.23 (d, J = 6.9 Hz, 6 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 140.6, 131.3, 130.9, 129.4, 129.0, 127.5, 127.2, 126.8, 109.5, 104.5, 27.3, 22.7. HRMS: calcd for $C_{13}H_{14}ClN$ 219.0815, found 219.0814.

2-(3-Fluorophenyl)-5-isopropyl-1*H*-pyrrole (7f): 325 mg, 80% yield, colorless oil, ^1H NMR ($CDCl_3$, 400 MHz): δ 8.10 (s, br, 1 H), 7.28−7.22 (m, 1 H), 7.18−7.16 (m, 1 H), 7.10−7.07 (m, 1 H), 6.84−6.79 (m, 1 H), 6.42 (t, J = 3.1 Hz, 1 H), 5.98 (t, J = 2.9 Hz 1 H), 2.99−2.89 (m, 1 H), 1.28 (d, J = 6.9 Hz, 6 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 163.5 (d, J = 243.0 Hz), 141.1, 135.3 (d, J = 8.3 Hz), 130.4 (d, J = 7.0 Hz), 129.4 (d, J = 2.7 Hz), 119.0 (d, J = 2.6 Hz), 112.3 (d, J = 21.3 Hz), 110.2 (d, J = 22.4 Hz), 107.0, 105.4, 27.3, 22.7. HRMS: calcd for $C_{13}H_{14}FN$ 203.1110, found 203.1107.

2-(4-Bromophenyl)-5-isopropyl-1*H*-pyrrole (7g): 380 mg, 72% yield, white solid, mp 57−59 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.08 (s, br, 1 H), 7.44−7.42 (m, 2 H), 7.29−7.27 (m, 2 H), 6.40 (t, J = 3.0 Hz, 1 H), 5.98 (t, J = 3.3 Hz, 1 H), 3.00−2.89 (m, 1 H), 1.29 (d, J = 6.9 Hz, 6 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 141.0, 132.1, 132.0, 129.4, 125.0, 119.2, 106.6, 105.4, 27.4, 22.8. HRMS: calcd for $C_{13}H_{14}BrN$ 263.0310, found 263.0314.

2-Isopropyl-5-(4-(trifluoromethyl)phenyl)-1*H*-pyrrole (7h): 284 mg, 56% yield, white solid, mp 88−90 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.22 (s, br, 1 H), 7.60 (d, J = 8.2 Hz, 2 H), 7.53 (d, J = 8.2 Hz, 2 H), 6.55 (t, J = 2.6 Hz, 1 H), 6.06 (t, J = 2.6 Hz, 1 H), 3.06−2.96 (m, 1 H), 1.34 (d, J = 6.9 Hz, 6 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 141.9, 136.3, 129.0, 124.6 (q, J = 269.9 Hz), 127.3 (q, J = 32.3 Hz), 126.0 (q, J = 3.8 Hz), 123.2, 107.9, 105.8, 27.4, 22.7. HRMS: calcd for $C_{14}H_{14}F_3N$ 253.1078, found 253.1075.

2-Isopropyl-5-(naphthalen-2-yl)-1*H*-pyrrole (7i): 400 mg, 85% yield, white solid, mp 71−73 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.37 (s, br, 1 H), 7.92−7.88 (m, 4 H), 7.75 (d, J = 8.7 Hz, 1 H), 7.58−7.49 (m, 2 H), 6.69 (t, J = 3.0 Hz, 1 H), 6.18 (t, J = 2.8 Hz, 1 H), 3.14−3.04 (m, 1 H), 1.44 (d, J = 6.9 Hz, 3:3 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 140.9, 133.9, 131.9, 130.5, 128.5, 127.8, 127.6, 126.4, 125.2, 123.2, 120.3, 106.7, 105.3, 27.3, 22.8. HRMS: calcd for $C_{17}H_{17}N$ 235.1361, found 235.1359.

2-(5-Isopropyl-1*H*-pyrrol-2-yl)pyridine (7j): 197 mg, 53% yield, yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 9.48 (s, br, 1 H), 8.43−8.42 (m, 1 H), 7.60−7.56 (m, 1 H), 7.51−7.49 (m, 1 H), 7.00−6.96 (m, 1 H), 6.64−6.62 (m, 1 H), 6.02−6.00 (m, 1 H), 3.03−2.93 (m, 1 H), 1.31 (d, J = 6.9 Hz, 6 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 150.9, 148.7, 141.8, 136.5, 129.9, 120.0, 117.9, 107.6, 105.5, 27.4, 22.7. HRMS: calcd for $C_{12}H_{14}N_2$ 186.1157, found 186.1153.

2-Cyclopropyl-5-isopropyl-1*H*-pyrrole (7k): 260 mg, 87% yield, colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.86 (s, br, 1 H), 5.89 (t, J = 2.9 Hz, 1 H), 5.85 (t, J = 2.9 Hz, 1 H), 3.03−2.93 (m, 1 H), 1.91−1.85 (m, 1 H), 1.36 (d, J = 6.9 Hz, 6 H), 0.92−0.87 (m, 2 H), 0.74−0.70 (m, 2 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 137.6, 132.8, 103.4, 102.6, 27.1, 22.7, 8.2, 6.4. HRMS: calcd for $C_{10}H_{15}N$ 149.1204, found 149.1200.

2-Isopropyl-5-propyl-1*H*-pyrrole (7l): 242 mg, 80% yield, colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.60 (s, br, 1 H), 5.81−5.78 (m, 2 H), 2.92−2.85 (m, 1 H), 2.54 (t, J = 7.7 Hz, 2 H), 1.69−1.60 (m, 2 H), 1.25 (d, J = 6.9 Hz, 3:3 H), 0.98 (t, J = 7.3 Hz, 3 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 137.4, 131.3, 104.5, 102.7, 30.1, 27.1, 23.1, 22.8, 14.2. HRMS: calcd for $C_{10}H_{17}N$ 151.1361, found 151.1354.

2-Heptyl-5-isopropyl-1*H*-pyrrole (7m): 344 mg, 83% yield, colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.73 (s, br, 1 H), 5.93−5.90 (m, 2 H), 3.03−2.96 (m, 1 H), 2.67 (t, J = 7.8 Hz, 2 H), 1.78−1.70 (m, 2 H), 1.48−1.42 (m, 8 H), 1.36 (d, J = 6.9 Hz, 6 H), 1.02 (t, J = 6.9 Hz, 3 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 137.3, 131.3, 104.3, 102.6, 31.9, 29.7, 29.5, 29.2, 27.9, 27.1, 22.7, 14.2. HRMS: calcd for $C_{14}H_{25}N$ 207.1987, found 207.1989.

2-Isopropyl-1,4,5,6,7,8-hexahydrocyclohepta[*b*]pyrrole (7n): 248 mg, 70% yield, yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.42 (s, br, 1H), 5.66 (d, J = 2.9 Hz, 1 H), 2.88−2.81 (m, 1 H), 2.65−2.62 (m, 2 H), 2.55−2.52 (m, 2 H), 1.78−1.75 (m, 2 H), 1.70−1.68 (m, 4 H), 1.23 (t, J = 6.9 Hz, 3:3 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 134.8, 128.5, 121.0, 105.2, 32.0, 29.5, 29.4, 28.6, 28.2, 26.9, 22.8.

2-Isopropyl-4,5,6,7,8,9,10,11,12,13-decahydro-1*H*-cyclododeca[*b*]pyrrole (7o): 322 mg, 65% yield, colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.35 (s, br, 1 H), 5.65 (d, J = 2.5 Hz, 1 H), 2.89−2.80 (m, 1 H), 2.55 (t, J = 6.8 Hz, 2 H), 2.37 (t, J = 6.9 Hz, 2 H), 1.61 (m, 4 H), 1.41−1.38 (m, 4 H), 1.33−1.32 (m, 4 H), 1.28−1.25 (m, 4 H), 1.23 (t, J = 6.9 Hz, 3:3 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 137.2, 126.6, 119.7, 102.9, 31.0, 29.1, 28.3, 27.1, 24.9, 24.8, 24.8, 24.5, 22.7, 22.5, 22.5, 22.2. HRMS: calcd for $C_{17}H_{29}N$ 247.2300, found 247.2299.

2-Isopropyl-4,5-dihydro-1*H*-benzo[*g*]indole (7p): 338 mg, 80% yield, colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.92 (s, br,

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1 H), 7.05−6.96 (m, 3 H), 6.88 (t, J = 7.3 Hz, 1 H), 5.73 (m, 1 H), 2.84−2.78 (m, 3 H), 2.61−2.57 (m, 2 H), 1.18 (d, J = 6.9 Hz, 3:3 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 140.1, 134.4, 129.6, 128.3, 126.4, 126.2, 124.4, 120.3, 117.8, 103.3, 30.1, 27.4, 22.8, 22.0. HRMS: calcd for $C_{15}H_{17}N$ 211.1361, found 211.1356.

2-Methyl-5-phenyl-1*H*-pyrrole (7q): 289 mg, 92% yield, colorless solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.14 (s, br, 1 H), 7.49−7.47 (m, 2 H), 7.41−7.37 (m, 2 H), 7.25−7.21 (m, 1 H), 6.49−6.47 (t, J = 3.0 Hz, 1 H), 6.04−6.02 (m, 1 H), 2.37 (s, 3 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 133.0, 130.9, 129.2, 128.9, 125.7, 123.4, 108.0, 106.3, 13.2.

2-Methyl-5-phenyl-1*H*-pyrrole (7r): 312 mg, 91% yield, colorless solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.16 (s, br, 1 H), 7.48 (d, J = 7.9 Hz, 2 H), 7.39 (t, J = 7.7 Hz, 2 H), 7.22 (t, J = 7.3 Hz, 1 H), 6.48 (t, J = 2.9 Hz, 1 H), 6.05−6.04 (m, 1 H), 2.73 (q, J = 7.6 Hz, 2 H), 1.34 (t, J = 7.6 Hz, 3 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 135.8, 133.1, 130.7, 128.9, 125.8, 123.5, 106.4, 106.1, 21.1, 13.7.

2-(*tert*-Butyl)-5-phenyl-1*H*-pyrrole (7s): 352 mg, 88% yield, white solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.17 (s, br, 1 H), 7.49−7.47 (m, 2 H), 7.40−7.36 (m, 2 H), 7.22−7.18 (m, 1 H), 6.45−6.44 (m, 1 H), 6.05- 6.03 (m, 1 H), 1.39 (s, 9 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 143.4, 133.2, 130.5, 128.9, 125.8, 123.6, 105.8, 104.6, 31.6, 30.7.

2-Benzyl-5-phenyl-1*H*-pyrrole (7t): 397 mg, 85% yield, colorless solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.10 (s, br, 1 H), 7.48−7.33 (m, 9 H), 7.27−7.23 (m, 1 H), 6.56 (t, J = 3.0 Hz, 1 H), 6.16−6.15 (m, 1 H), 4.10 (s, 2 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 139.4, 132.9, 132.1, 131.6, 128.9, 128.8, 128.7, 126.6, 125.9, 123.5, 108.7, 106.2, 34.3.

2,5-Diphenyl-1*H*-pyrrole (7u): 347 mg, 79% yield, colorless solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.44 (s, br, 1 H), 7.41 (d, J = 7.7 Hz, 4 H), 7.27 (t, J = 7.7 Hz, 4 H), 7.12 (t, J = 7.0 Hz, 2 H), 6.48 (d, J = 2.3 Hz, 2 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 133.2, 132.6, 129.0, 126.5, 123.9, 108.0.

2,3,5-Triphenyl-1*H*-pyrrole (7v): 384 mg, 65% yield, white solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.38 (s, br, 1 H), 7.53 (d, J = 7.5 Hz, 2 H), 7.40−7.18 (m, 13 H), 6.69 (d, J = 2.7 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 136.5, 133.2, 132.3, 129.1, 128.8, 128.5, 128.5, 127.6, 127.1, 126.7, 126.1, 123.9, 123.9, 108.7.

5-(Naphthalen-2-yl)-2,3-diphenyl-1*H*-pyrrole (7w): 484 mg, 70% yield, colorless solid. mp 187−189 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.54 (s, br, 1 H), 7.90−7.80 (m, 4 H), 7.72−7.70 (m, 1 H), 7.51−7.43 (m, 6 H), 7.36−7.21 (m, 6 H), 6.82 (d, J = 2.8 Hz, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 136.4, 133.9, 133.1, 132.4, 129.9, 129.7, 128.9, 128.8, 128.6, 128.5, 127.9, 127.8, 127.7, 127.2, 126.7, 126.1, 125.7, 124.1, 123.1, 121.2, 109.4. HRMS:calcd for $C_{26}H_{19}N$ 345.1517, found 345.1515.

3,5-Dimethyl-2-phenyl-1*H*-pyrrole (8a): 274 mg, 80% yield, colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.81 (s, br, 1 H), 7.40−7.37 (m, 4 H), 7.23−7.19 (m, 1 H), 5.85 (s, 1 H), 2.31 (s, 3 H), 2.25 (s, 3 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 134.0, 128.8, 127.6, 126.9, 126.0, 125.6, 116.6, 110.4, 13.1, 12.6.

5-Ethyl-3-methyl-2-phenyl-1*H*-pyrrole (8b): 315 mg, 85% yield, colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.74 (s, br, 1 H), 7.33−7.27 (m, 4 H), 7.14−7.10 (m, 1 H), 5.78 (d, J = 2.6 Hz, 1 H), 2.56 (q, J = 7.4 Hz, 2 H), 2.17 (s, 3 H), 1.19 (t, J = 7.6 Hz, 3 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 134.1, 128.8, 128.1, 126.7, 126.1, 125.6, 116.4, 108.7, 21.0, 13.7, 12.7.

5-Isopropyl-3-methyl-2-phenyl-1*H*-pyrrole (8c): 327 mg, 82% yield, colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.91 (s, br, 1 H), 7.51−7.46 (m, 4 H), 7.32−7.28 (m, 1 H), 5.98 (d, J = 2.7 Hz, 1 H), 3.08−2.97 (m, 1 H), 2.36 (s, 3 H), 1.39 (d, J = 6.9 Hz, 6 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 138.8, 134.1, 128.7, 126.6, 126.1, 125.6, 116.1, 107.4, 27.2, 22.8, 12.7.

5-(*tert*-Butyl)-3-methyl-2-phenyl-1*H*-pyrrole (8d): 324 mg, 76% yield, colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.74 (s, br, 1 H), 7.32−7.26 (m, 4 H), 7.12−7.08 (m, 1 H), 5.78 (d, J = 2.9 Hz, 1 H), 2.16 (s, 3 H), 1.23 (s, 9 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 141.7, 134.1, 128.7, 126.5, 126.1, 125.6, 115.9, 106.9, 31.4, 30.7, 12.6. HRMS: calcd for $C_{15}H_{19}N$ 213.1517, found 213.1514.

5-Benzyl-3-methyl-2-phenyl-1*H*-pyrrole (8e): 297 mg, 60% yield, colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.65 (s, br, 1 H), 7.28 (m, 2 H), 7.25−7.23 (m, 3 H), 7.19−7.09 (m, 5 H), 5.83 (d, J = 2.8 Hz, 1 H), 3.90 (s, 2 H), 2.17 (s, 3 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 139.4, 133.9, 130.7, 128.9, 128.8, 128.8, 127.6, 126.6, 126.1, 125.7, 116.5, 110.9, 34.3, 12.7.

3-Methyl-2,5-diphenyl-1*H*-pyrrole (8f): 378 mg, 81% yield, white solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.30 (s, br, 1 H), 7.53−7.50 (m, 4 H), 7.47−7.43 (m, 2 H), 7.41−7.37 (m, 2 H), 7.31−7.27 (m, 1 H), 7.25−7.21 (m, 1 H), 6.48 (d, J = 2.8 Hz, 1 H), 2.33 (s, 3 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 133.6, 132.6, 131.6, 129.5, 129.0, 128.9, 126.5, 126.4, 126.3, 123.8, 118.3, 110.1, 12.7.

3-Methyl-2,4,5-triphenyl-1*H*-pyrrole (8g): 427 mg, 69% yield, white solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.24 (s, br, 1 H), 7.62 (m, 2 H), 7.54 (t, J = 7.5 Hz, 2 H), 7.47−7.31 (m, 11 H), 2.31 (s, 3 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 136.2, 133.5, 133.1, 130.7, 128.9, 128.7, 128.4, 126.9, 126.8, 126.5, 126.3, 124.5, 117.1, 11.4.

1,2-Diphenylethanone (9a): 300 mg, 76% yield, white solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.91 (d, J = 7.6 Hz, 2 H), 7.45−7.42 (m, 1 H), 7.36−7.32 (m, 2 H), 7.24−7.13 (m, 5 H), 4.17 (s, 2 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 197.7, 136.7, 134.6, 133.2, 129.5, 128.7, 128.7, 128.7, 127.0, 45.6.

1-Phenyl-3-(*p*-tolyl)propan-1-one (9b): 395 mg, 88% yield, white solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.85 (d, J = 7.4 Hz, 2 H), 7.45−7.42 (m, 1 H), 7.35−7.31 (m, 2 H), 7.05−6.99 (m, 4 H), 3.17 (t, J = 7.7 Hz, 2 H), 2.92 (t, J = 7.7 Hz, 2 H), 2.2 (s, 3 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 199.4, 138.3, 136.9, 135.7, 133.1, 129.3, 128.7, 128.4, 128.1, 40.7, 29.8, 21.1.

1,2-Bis(5-isopropyl-1*H*-pyrrol-2-yl)ethane (10): 274 mg, 56% yield, yellow oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.60 (s, br, 2 H), 5.90 (t, J = 2.8 Hz, 2 H), 5.85 (t, J = 2.7 Hz, 2 H), 2.91 (s, 4 H), 2.88−2.83 (m, 2 H), 1.24 (d, J = 6.9 Hz, 6:6 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 137.9, 130.5, 105.0, 102.7, 28.2, 27.1, 22.8. HRMS: calcd for $C_{16}H_{24}N_2$ 244.1939, found 244.1934.

2-Phenylpyridine (12a): 186 mg, 60% yield, colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.71−8.69 (m, 1 H), 8.01−7.99 (m, 2 H), 7.74−7.72 (m, 2 H), 7.50−7.46 (m, 2 H), 7.44−7.41 (m, 1 H), 7.24−7.20 (m, 1 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 157.5, 149.7, 139.5, 136.8, 129.0, 128.8, 127.0, 122.2, 120.7.

2-Methyl-6-phenylpyridine (12b): 196 mg, 58% yield, colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.88−7.86 (m, 2 H), 7.48 (t, J = 7.7 Hz, 1 H), 7.39−7.32 (m, 3 H), 7.29−7.25 (m, 1 H), 6.95 (d, J = 7.6 Hz, 1 H), 2.51 (s, 3 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 158.4, 157.0, 139.8, 136.9, 128.7, 128.7, 127.0, 121.6, 117.6, 24.8.

2,6-Diphenylpyridine (12c): 259 mg, 56% yield, white solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.21−8.19 (m, 4 H), 7.84−7.80 (m, 1 H), 7.71 (d, J = 7.6 Hz, 2 H), 7.56−7.52 (m, 4 H), 7.48−7.45 (m, 2 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 156.9, 139.6, 137.6, 129.1, 128.8, 127.1, 118.7.

2-Phenylquinoline (12d): 341 mg, 83% yield, white solid. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.04 (d, J = 8.4 Hz,1 H),8.01−7.99 (m, 2 H), 7.93 (d, J = 8.6 Hz, 1 H), 7.62 (d, J = 8.6 Hz, 1 H), 7.58−7.51 (m, 2 H), 7.36−7.27 (m, 4 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 157.3, 148.3, 139.6, 136.7, 129.7, 129.6, 129.3, 128.8, 127.6, 127.5, 127.1, 126.2, 118.9.

6,7,8,9-Tetrahydro-5*H*-cyclohepta[*b*]pyridine (13a): 271 mg, 92% yield, colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.21 (dd, J = 4.9, 1.5 Hz, 1 H), 7.29 (dd, J = 7.4, 1.2 Hz, 1 H), 6.95−6.92 (m, 1 H), 2.99−2.96 (m, 2 H), 2.70−2.68 (m, 2 H), 1.83−1.77 (m, 2 H), 1.66−1.56 (m, 4 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 163.2, 146.1, 138.1, 136.4, 121.1, 39.4, 35.3, 32.5, 27.9, 26.4.

2-Methyl-6,7,8,9-tetrahydro-5*H*-cyclohepta[*b*]pyridine (13b): 242 mg, 75% yield, colorless oil. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.19 (d, J = 7.6 Hz, 1 H), 6.79 (d, J = 7.6 Hz, 1 H), 2.95−2.92 (m, 2 H), 2.67−2.64 (m, 2 H), 2.41 (s, 3 H), 1.82−1.76 (m, 2 H), 1.63−1.55 (m, 4 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 162.6, 154.5, 137.0, 134.9, 120.6, 39.5, 35.0, 32.7, 28.2, 26.7, 24.1.

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2-Phenyl-6,7,8,9-tetrahydro-5*H*-cyclohepta[*b*]pyridine (13c): 371 mg, 83% yield, colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.03−8.00 (m, 2 H), 7.49−7.37 (m, 5 H), 3.18−3.15 (m, 2 H), 2.83−2.80 (m, 2 H), 1.94−1.89 (m, 2 H), 1.80−1.69 (m, 4 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 163.1, 154.0, 139.8, 137.2, 136.6, 128.6, 128.3, 126.8, 117.9, 39.8, 35.0, 32.6, 28.1, 26.7.

7,8,9,10-Tetrahydro-6*H*-cyclohepta[*b*]quinoline (13d): 355 mg, 90% yield, white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97 (d, J = 8.5 Hz, 1 H), 7.65 (s, 1 H), 7.60−7.58 (m, 1 H), 7.55−7.51 (m, 1 H), 7.37−7.33 (m, 1 H), 3.14−3.12 (m, 2 H), 2.81−2.79 (m, 2 H), 1.82−1.76 (m, 2 H), 1.73−1.68 (m, 2 H), 1.64−1.62 (m, 2 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 164.5, 146.1, 136.3, 134.4, 128.3, 128.3, 127.2, 126.7, 125.6, 39.9, 35.2, 32.1, 28.7, 26.9.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00774.

NMR spectra of the new compounds and X-ray crystallographic data for **4** (PDF)

Cartesian coordinates of the calculated structures (XYZ)

Accession Codes

CCDC 1563982 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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