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α-Alkylation of Nitriles with Alcohols Catalyzed by NNN′ Pincer Ru(II) Complexes Bearing Bipyridyl Imidazoline Ligands

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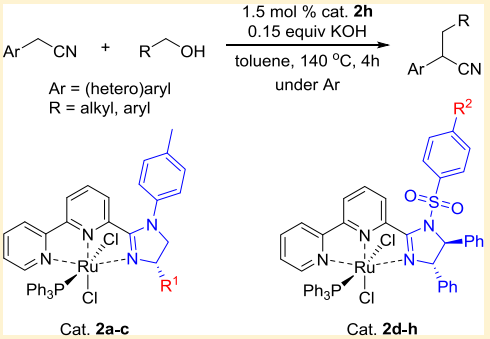
Supporting Information

ABSTRACT: A series of unsymmetrical NNN′ ruthenium(II) complexes supported by a tridentate bipyridyl imidazoline ligand with variable steric hindrance (**2a−c**; R^1 = ^{t}Bu, ^{i}Pr, or Bn) and electronic effect (**2d−h**; R^2 = H, CH_3, OCH_3, Br, or NO_2) were prepared. The molecular structures of ligands **1f** and **1g**, and Ru complex **2a** were further determined by X-ray single-crystal diffraction. The catalytic activity of these eight complexes for α-alkylation of nitriles with alcohols was evaluated, which could be controlled by the substituents on the imidazoline moiety. Ru complex **2h** bearing a strong electron-withdrawing group (R^2 = NO_2) demonstrated the highest catalytic activity, with alkylated nitriles achieved in up to 97% yield.



INTRODUCTION

Alkylation reaction utilizing alcohols as alkylating reagents through a borrow-hydrogen (BH) or hydrogen autotransfer (HA) strategy has emerged as a powerful tool to construct C−C bonds.[1] During these transformations, water is generated as the only byproduct, which is more atom economical and environmentally benign. Until now, α-alkylation of ketones[2] and β-alkylation of secondary alcohols[3] have been well developed. Meanwhile, other substrates including amides, esters,[4] indoles,[5] and methyl-*N*-heteroaromatics[6] have also been successfully achieved. As versatile organic synthons, nitriles can be converted into value-added compounds, including carboxylic derivatives and other biologically active molecules. From this perspective, α-alkylation of nitriles has gained much attention. Transition-metal complexes based on Ir,[7] Rh,[8] Os,[9] and others metals[10] have already been reported to fulfill this conversion. Ru complexes have long been well known for the superior catalytic activity in the BH or HA process. However, Ru-catalyzed α-alkylation of nitriles is usually limited by high temperature, equivalent base, and long reaction time.[11a−d] It is thus highly desirable to develop Ru-based catalytic system with high efficiency.

On the other hand, the chemistry of pincer complexes have underwent tremendous development in organometallic catalysis, organic synthesis, and material science since the pioneering work of Shaw, van Koten, and Noltes.[12] The tridentate coordination mode of pincer ligands enforces a meridional configuration around the metal center, which exhibits unique stability versus reactivity via variations of ligand precursors and transition metals. Especially, organometallic pincer complexes supported by pyridyl-based tridentate NNN ligands, such as terpyridines,[13] bis(oxazolinyl)pyridines,[14] and others,[15] have been widely utilized in (de)hydrogenation and transfer (de)hydrogenation transformations. Recently, unsymmetrical NNN′ pincer metal complexes bearing two different N-donors have underwent tremendous development considering their unique reactivities,[16] which is probably attributed to the hemilabile properties of ligands. As another representative nitrogen donor moiety, imidazolines have also gained much attention because of their facile preparation as well as better steric and electronic tunability.[17] Consequently, a variety of imidazolines-containing pincer complexes have been synthesized.[18,19]

Over the past years, our group has reported a series of symmetrical and unsymmetrical pincer Pt, Pd, Ni, and Rh complexes.[19] Meanwhile, we have recently designed 2,6-bis(imidazo[1,2-*a*]pyridin-2-yl)pyridine-based NNN Ru complexes, which exhibited superior activity in transfer hydrogenation of ketones,[15b] *N*-monoalkylation of amines,[20a] and α-alkylation of ketones.[15d] As an extension, we herein synthesize eight new unsymmetrical NNN′ pincer Ru complexes and explore their catalytic activity in α-alkylation of nitriles. Notably, the current protocol exhibited several advantages, such as low catalyst and base loading, short reaction time, and environmental benign.

RESULTS AND DISCUSSION

Preparation and Characterization of Ligands and Ru Complexes. The synthesis of bipyridyl imidazoline ligands **1a−i** is illustrated in Scheme 1. 2,2′-Bipyridine reacted with

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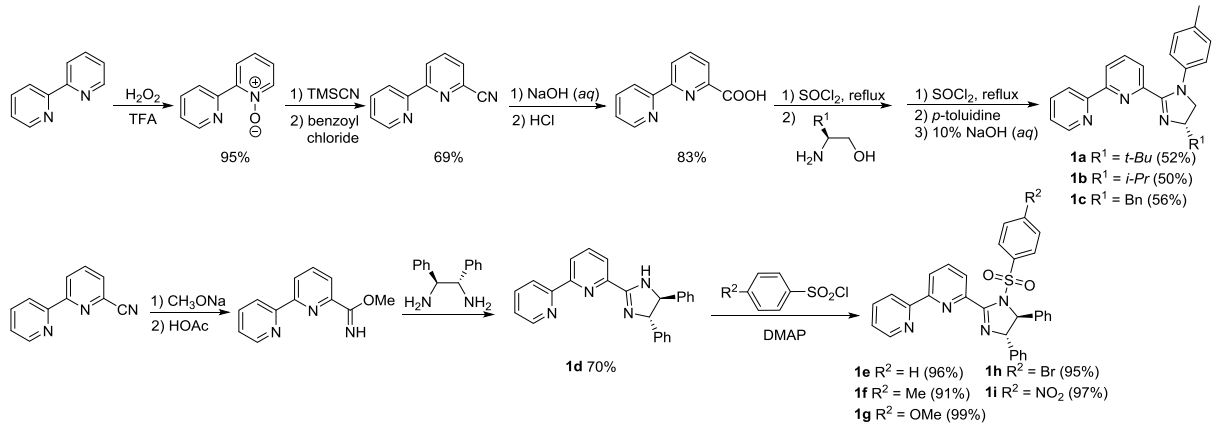
Scheme 1. Preparation of Unsymmetrical NNN′ Precursors 1a−i



hydrogen peroxide in trifluoroacetic acid to give 2,2′-bipyridine-1-oxide, which was converted into 2,2′-bipyridyl-6-carbonitrile in the presence of trimethylsilyl cyanide and benzoyl chloride. To obtain bipyridyl imidazoline ligands **1a−c**, bipyridyl carbonitrile first underwent base-induced hydrolysis in EtOH/H_2O solution to afford 2,2′-bipyridyl-6-carboxylic acid. Also, the desired ligand precursors **1a−c** were obtained in 50−56% yields via formation of amido alcohols and subsequent cyclization according to the previous procedure.[19] On the other hand, addition of bipyridyl carbonitrile into a dilution solution of MeONa followed by neutralization with HOAc provided 2,2′-bipyridyl-6-carboxyimidate without purification. The corresponding ligand **1d** was then obtained by refluxing bipyridyl carboxyimidate with (1*S*,2*S*)-1,2-diphenylethane-1,2-diamine in anhydrous CH_2Cl_2 in 70% yield. Finally, treatment of **1a** with aryl sulfonyl chloride in the presence of dimethylaminopyridine (DMAP) furnished the desired bipyridyl imidazolines **1e−i** in 91−99% yields. The molecular structures of ligands **1f** and **1g** were further confirmed by X-ray crystallography (Figures 1 and 2).

With ligands precursors **1a−c** and **1e−i** in hand, the corresponding cyclometalated ruthenium complexes **2a−h** was

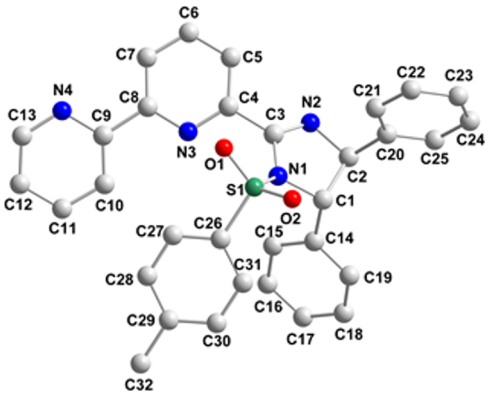


Figure 1. Molecular structure of complex **1f** with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): S(1)−N(1), 1.655(3); S(1)−O(1), 1.422(3); S(1)−O(2), 1.429(3); S(1)−C(26), 1.756(4); N(1)−C(3), 1.411(4); N(1)−C(1), 1.486(4); N(3)−C(4), 1.339(4); N(3)−C(8), 1.343(4); N(4)−C(9), 1.350(5); N(4)−C(13), 1.329(5); N(1)−S(1)−O(1), 106.77(15); N(1)−S(1)−O(2), 107.53(15); N(1)−S(1)−C(26), 103.43(15); N(1)−C(3)−N(2), 115.4(3); C(4)−N(3)−C(8), 116.9(3).

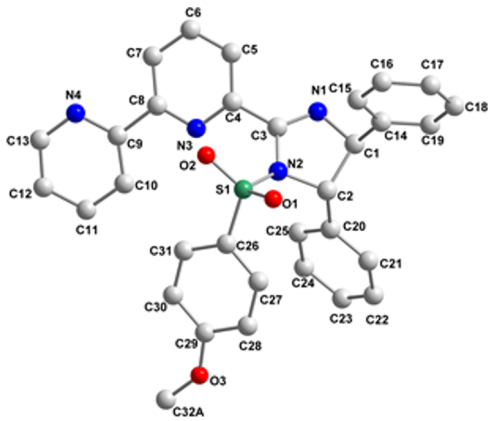


Figure 2. Molecular structure of complex **1g** with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): S(1)−O(1), 1.426(3); S(1)−O(2), 1.421(3); S(1)−N(2), 1.662(3); S(1)−C(26), 1.679(5); O(3)−C(29), 1.328(8); O(3)−C(32A), 1.2875(334); N(2)−C(3), 1.407(5); N(1)−C(3), 1.265(5); N(3)−C(4), 1.329(5); N(3)−C(8), 1.338(4); N(4)−C(9), 1.347(5); N(4)−C(13), 1.331(6); N(2)−S(1)−O(1), 107.64(17); N(2)−S(1)−O(2), 106.90(16); N(2)−S(1)−C(26), 102.9(3); N(1)−C(3)−N(2), 115.1(3); C(4)−N(3)−C(8), 117.3(3).

obtained in 45−70% yields by reaction of ligand precursors with an equimolar amount of $RuCl_2(PPh_3)_3$ in toluene under reflux conditions (Scheme 2). The cycloruthenated complex derived from ligand **1d** is unstable, which could not be isolated in pure form.

Characterization of Ru(II) Complexes 2a−h. All of the obtained Ru(II) complexes **2a−h** are bench-stable and fully characterized. In general, most proton signals on the bipyridyl moiety shifted upfield compared with those of ligand precursors, while a new resonance peak was observed downfield at δ 9.55−9.15 ppm. Meanwhile, the chemical shift of protons on N-Ar or N-SO_2Ar generally moved toward lower fields, which is in accordance with our previous report. In addition, ^{1}H NMR spectra of **2a−c** (δ 7.48−7.37 ppm, δ 7.23−7.16 ppm, and δ 7.14−7.06 ppm) and **2d−h** (δ 7.19−7.09 ppm, δ 7.08−7.16 ppm, and δ 7.14−7.06 ppm) both exhibited three sets of multiplet corresponding to the PPh_3 group. These results indicate that bipyridyl imidazoline-supported NNN′ Ru complexes were formed. For ^{31}P NMR spectra of complexes **2a−h**, the appearance of resonance peaks at δ 42.2, 42.5, 43.2, 36.9, 37.0, 37.0, 36.7, and 36.4 ppm suggests that variations of substituents on the imidazoline

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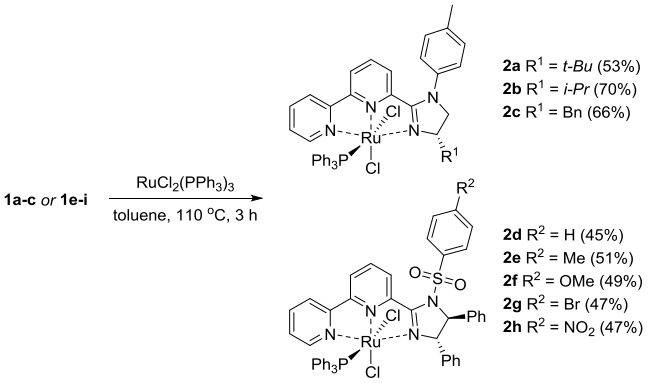
Scheme 2. Preparation of Unsymmetrical NNN′ Pincer Ru Complexes 2a−h



donor probably change the coordination ability of the imidazolyl nitrogen atom.

The molecular structure of pincer Ru(II) complex **2a** was further determined by X-ray analysis (Figure 3). In the solid state, the neutral Ru(II) center is six-coordinated surrounded by the tridentate NNN′ ligand, one PPh_3 group, and two chloride atoms in a distorted pseudo-octahedral geometry. The bond angles of P(1)−Ru(1)−Cl(2) and N(2)−Ru(1)−Cl(1) are 178.310(72)° and 173.633(195)°, respectively, indicating that the PPh_3 ligand is positioned trans to Cl(2) and pyridyl nitrogen N(2) is positioned trans to Cl(1). In complex **2a**, the Cl(1) atom forms two intramolecular CH−Cl hydrogen bonds with the C−H from *t*-Bu group (Cl1···H35 = 2.8291(24) Å) and the pyridyl sidearm (Cl1···H19 = 2.7704(33) Å). Meanwhile, there exist both intramolecular and intermolecular CH−Cl hydrogen bonds between Cl(2) and C−H groups from the *t*-Bu group (Cl2···H35 = 2.7225(17) Å) and PPh_3 ring (Cl2···H4 = 2.8612(21) Å), respectively, which gives a one-dimensional chain structure (Figure 4).

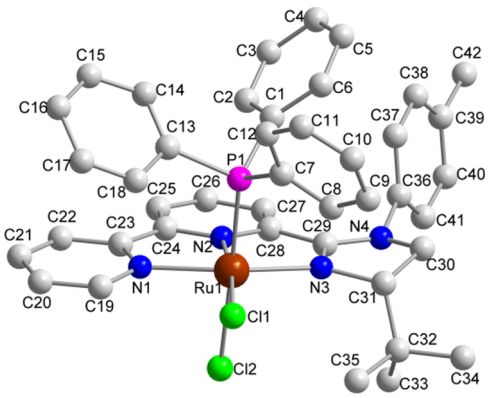
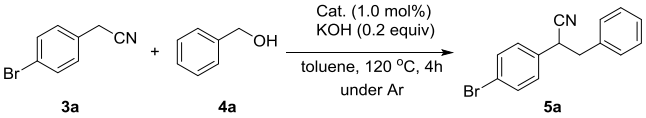


Figure 3. Molecular structure of complex **2a** with hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru(1)−N(1), 2.0687(66); Ru(1)−N(2), 1.9560(64); Ru(1)−N(3), 2.1323(65); Ru(1)−Cl(1), 2.4502(23); Ru(1)−Cl(2), 2.4697(21); Ru(1)−P(1), 2.3073(21); N(2)−Ru(1)−N(3), 78.307(225); P(1)−Ru(1)−Cl(1), 87.872(71); P(1)−Ru(1)−Cl(2), 178.310(72); Cl(1)−Ru(1)−Cl(2), 91.875(69); N(1)−Ru(1)−N(3), 157.379(254); N(2)−Ru(1)−Cl(1), 173.633(195); C(19)−N(1)−C(23), 119.151(713); N(3)−C(29)−N(4), 116.866(757).

Evaluation of Ru(II) Catalysts in α-Alkylation of Nitriles. Initially, the α-alkylation of 4-bromobenzyl cyanide **3a** with benzyl alcohol **4a** was selected as the model reaction to examine the catalytic activity of Ru complexes **2a−h** (Table 1).

Table 1. Optimization of Reaction Conditions Using Ru Complex 2a−h[a]



3a 4a 5a

entry	Catalyst	yield (%)
1	**2a**	20
2	**2b**	15
3	**2c**	14
4	**2d**	37
5	**2e**	37
6	**2f**	33
7	**2g**	40
8	**2h**	65

[a]Reaction conditions: **3a** (0.5 mmol), **4a** (1.0 mmol), Ru catalysts (1.0 mol %), and KOH (0.20 equiv) in toluene (0.8 mL) at 120 °C for 4 h under an Ar atmosphere. Isolated yield.

The reaction was carried out in toluene (0.8 mL) at 120 °C for 4 h using KOH (0.2 equiv) as the base and Ru complexes (1.0 mol %) as the catalyst under an Ar atmosphere. For complexes **2a−c** with different R^1 substituents (^{t}Bu, ^{i}Pr, and Bn), sterically more hindered group ^{t}Bu gave the best result (Table 1, entry 1). When the aryl sulfonyl group was introduced into the imidazoline ring, the reaction efficiency was increased (Table 1, entries 4−8). To our delight, NNN′ Ru complexes **2h** with a strong electron-withdrawing group (NO_2) demonstrated the highest catalytic activity to afford product **5a** in 65% yield (Table 1, entry 8).

To further improve the reaction efficiency, various bases (Table 2, entries 1−8) were examined. Employment of strong bases such as KOH, NaOH, CsOH, $CsOH·H_2O$, KO^{t}Bu, and NaO^{t}Bu resulted in the formation of **5a** in 26−65% yields. When weak base such as K_2CO_3, Na_2CO_3, and Cs_2CO_3 were utilized, the yield of **5a** decreased dramatically. Subsequently,

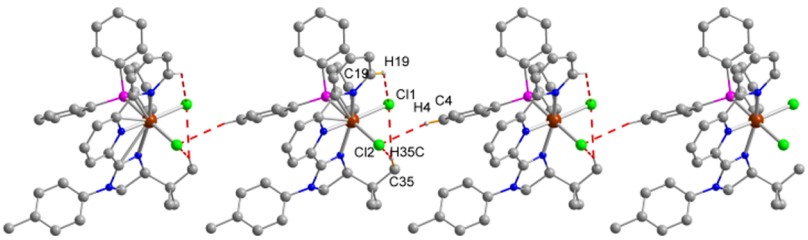


Figure 4. One-dimensional chain structure of complex **2a** formed by CH···Cl hydrogen bonds. Non-hydrogen-bonding H atoms are omitted for clarity.

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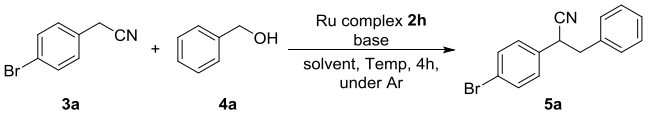
Table 2. Optimization of Reaction Conditions Using Ru Complex 2h[a]



3a 4a 5a

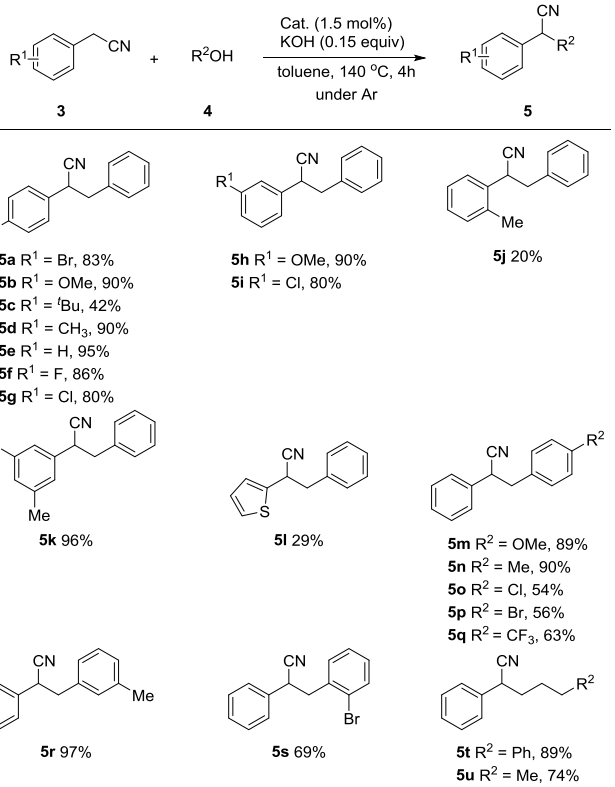
entry	2h (mol %)	base	solvent	temp (°C)	yield (%)
1	1	KOH	toluene	120	65
2	1	NaOH	toluene	120	27
3	1	$CsOH·H_2O$	toluene	120	40
4	1	KO^{t}Bu	toluene	120	61
5	1	NaO^{t}Bu	toluene	120	26
6	1	K_2CO_3	toluene	120	trace
7	1	Na_2CO_3	toluene	120	trace
8	1	Cs_2CO_3	toluene	120	17
9	1	KOH	dioxane	120	48
10	1	KOH	DCE	120	trace
11	1	KOH	xylene	120	9
12	1	KOH	toluene	110	23
13	1	KOH	toluene	130	73
14	1	KOH	toluene	140	74
15	0.5	KOH	toluene	140	68
16	1.5	KOH	toluene	140	76
17	2	KOH	toluene	140	76
18[b]	**1.5**	**KOH**	**toluene**	**140**	**83**
19[c]	1.5	KOH	toluene	140	46

[a]Reaction conditions: **3a** (0.5 mmol), **4a** (1.0 mmol), Ru catalysts **2h**, and base in the solvent heated for 4 h under an Ar atmosphere. Isolated yield. [b]KOH (0.15 equiv). [c]KOH (0.10 equiv).

other solvents such as dioxane, dichloroethylene (DCE), and xylene were also screened, which showed inferior result compared with toluene (Table 2, entries 9−11). Next, when the temperature was elevated at 130 and 140 °C, product **5a** was isolated in 73 and 74% yields, respectively (Table 2, entries 13 and 14). Also, 140 °C was found to be more beneficial when the substrate scope was expanded. Finally, the catalyst and base loading was adjusted (Table 2, entries 15−19), which indicates 1.5 mol % of Ru complex **2h** and 0.15 equiv of KOH is the best choice to deliver the desired product **5a** in 83% yield (Table 2, entry 18).

With the optimized conditions in hand (Table 2, entry 18), the generality of this protocol was investigated (Scheme 3). Initially, a variety of arylacetonitriles reacted with benzyl alcohol **4a** smoothly to deliver alkylated product **5** in good to excellent yield. Para- and meta-substituted nitriles bearing both electron-donating (OMe, ^{t}Bu, and CH_3) and electron-withdrawing (F, Cl, and Br) were well tolerated under the standard conditions. For ortho-substituted nitriles, the corresponding product **5j** was isolated in 20% probably because of the steric hindrance effect. In addition, disubstituted arylacetonitrile was also compatible to afford product **5k** in 96% yield. Moreover, 2-thiopheneacetonitrile was also tested to afford product **5l** in 29% yield. When α-methylphenylacetonitrile was employed, no desired product was detected. Encouraged by the above result, we next sought to the substrate scope of alcohols. Similarly, both electron-rich (OMe and Me) and electron-poor (Cl, Br, and CF_3) benzyl alcohols were proved to be the ideal substrates to deliver products **5m−s** in 54−97% yields. Finally, aliphatic alcohols, including 3-phenyl-1-propanol and 1-butanol, were also evaluated, which provided the corresponding products **5t** and **5u** in 89 and 74% yields, respectively. We

Scheme 3. α-Alkylation of Nitriles with Alcohols Using Ru Complex 2h[a]



[a]Reaction conditions: **3** (0.5 mmol), **4** (1.0 mmol), Ru catalysts **2h** (1.0 mol %), and KOH (0.15 equiv) in toluene (0.8 mL) at 140 °C for 4 h under an Ar atmosphere. Isolated yield.

also tried two secondary alcohols, including 1-phenylethanol and 4-phenyl-2-butanol, which again failed to yield the corresponding product. Pleasingly, vinyl nitriles[21] were obtained when 1-phenylethanol was utilized as the reactant, which was further confirmed by ^{1}H NMR[22] (Figure S4) and MS analysis (Figure S5). The chirality of product **5** was determined using chiral high-performance liquid chromatography, which unfortunately showed no enantioselectivity.

Reaction Mechanism. On the basis of relevant literature and our previous work, a plausible mechanism for Ru(II) **2h**-catalyzed α-alkylation of nitriles was proposed (Scheme 4). Initially, Ru complex **2h** reacts with alcohol **4** in the presence of KOH to generate Ru-alkoxide species **I**, which undergoes β-elimination to give Ru−H species **II** and liberate aldehyde **A**. Next, a KOH-catalyzed condensation between aldehyde **A** and nitrile **3** affords vinyl nitrile **B**, which has been confirmed by ^{1}H NMR and MS analysis. Finally, vinyl nitriles **B** undergoes insertion into Ru−H to afford Ru species **III**, which reacts with the alcohol **4** to provide the desired products **5** and regenerate Ru complex **I**.

CONCLUSIONS

In conclusion, we have successfully prepared eight unsymmetrical NNN′ pincer Ru(II) complexes with tunable steric (**2a−c**) and electronic (**2d−h**) effects on the imidazoline moiety. It was found that the electronic factor played an important role in determining the reaction efficiency in the α-alkylation of nitriles. Also, Ru(II) complex **2h** bearing a strong electron-withdrawing group exhibited the highest catalytic

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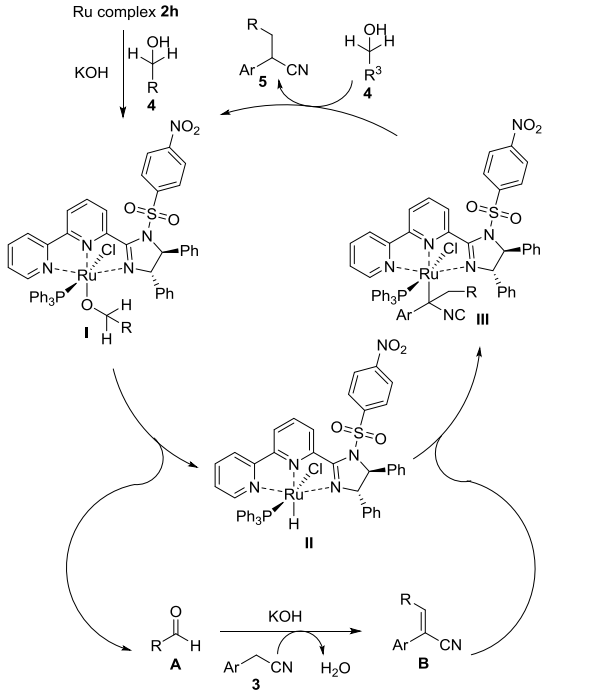
Scheme 4. Proposed Mechanism



activity. The current strategy is featured with several characteristic, including low catalyst and base loading, short reaction time, and environmentally benign.

EXPERIMENTAL SECTION

General Procedures. All air- and moisture-sensitive reactions were carried out under an Ar atmosphere using the standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled prior to use if needed. Column chromatography was performed using 200−300 mesh silica gel. Analytical and preparative thin-layer chromatography (TLC) plates coated with commercial silica gel GF254 were used to monitor the reactions and purify products. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz or 600 MHz using tetramethylsilane as an internal standard. Data are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, and coupling constants (J) in hertz (Hz). HRMS were determined on a Q-Tof Micro MS/MS System ESI spectrometer. The structures of ligands **1f** (CCDC file number 1900520), **1g** (CCDC 1900521), and Ru complex **2a** (CCDC file number 1900522) were further confirmed by X-ray diffraction collected on a diffractometer with graphite-monochromated Cu Kα radiation. Elemental analyses were measured on a Thermo Flash EA 1112 elemental analyzer.

2,2′-Bipyridine-N-oxide.[23] In a 250 mL round-bottom flask was dissolved 2,2-bipyridine (10.0 g, 64.1 mmol) in trifluoroacetic acid (50 mL) at 10 °C. A H_2O_2 solution in H_2O (30 wt %, 10 mL) was added dropwise. The reaction mixture was then stirred at room temperature overnight. CH_2Cl_2 (80 mL) was added and the mixture was extracted with 3 M NaOH (3 × 40 mL) and brine (40 mL). The organic layer was dried over Na_2SO_4, filtered, and evaporated to give the product as a pure yellowish solid. Yield: 10.5 g, 95%. mp 58−60 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.90 (d, J = 8.0 Hz, 1H), 8.73 (d, J = 4.6 Hz, 1H), 8.32 (d, J = 6.5 Hz, 1H), 8.18 (dd, J = 8.0, 2.1 Hz, 1H), 7.83 (td, J = 7.8, 2.1, 1H), 7.39−7.32 (m, 2H), 7.30−7.24 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 149.6, 149.4, 147.3, 140.7, 136.2, 127.9, 125.7, 125.5, 125.3, 124.3. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{10}H_9N_2O$, 173.0709; found, 173.0710.

2,2′-Bipyridyl-6-Carbonitrile.[24] In a three-necked 250 mL round-bottom flask was dissolved 2,2′-bipyridine-*N*-oxide (5.0 g, 29.1 mmol) in anhydrous CH_2Cl_2 (80 mL) under an Ar atmosphere. Trimethylsilyl cyanide (16.7 mL) was added at 0 °C, followed by dropwise addition of benzoyl chloride (6.7 mL). The solution was allowed to warm to room temperature and stirred for four days under an Ar atmosphere. Aqueous Na_2CO_3 solution (10 wt %, 170 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 80 mL). The organic layer was dried over Na_2SO_4, filtered, and evaporated. The residue was purified by silica gel chromatography using PE/EA = 15/1 as the eluent to give the product as a pale yellow solid. Yield: 3.6 g, 69%. mp 132−133 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72−8.65 (m, 2H), 8.47 (d, J = 8.0 Hz, 1H), 7.96 (t, J = 8.0 Hz, 1H), 7.87 (td, J = 7.8, 1.8 Hz, 1H), 7.71 (dd, J = 7.7, 0.9, 1H), 7.38 (ddd, J = 7.5, 4.8, 1.1 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 157.7, 154.0, 149.3, 137.9, 137.2, 133.2, 128.1, 124.8, 124.2, 121.6, 117.4. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{11}H_8N_3$, 182.0713; found, 182.0711.

2,2′-Bipyridine-6-carboxylic Acid.[25] To a 100 mL round-bottom flask was dissolved 2,2′-bipyridyl-6-carbonitrile (1.0 g, 5.5 mmol) and sodium hydroxide (0.85 g, 21.3 mmol) in the ethanol/water mixture (10 mL/10 mL). The reaction was refluxed for 1 h, cooled, and acidified to pH = 3−4 using concentrated HCl until white solid precipitated out. The precipitate was filtered, washed with ice water, and dried under vacuum to give the product as a white solid. Yield: 0.92 g, 83%. mp 133−134 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.29 (s, 1H), 8.72 (d, J = 5.0 Hz, 1H), 8.59 (dd, J = 7.6, 1.3 Hz, 1H), 8.55 (d, J = 7.9 Hz, 1H), 8.17−8.08 (m, 2H), 8.00 (ddd, J = 7.6, 7.6, 1.8 Hz, 1H), 7.51 (ddd, J = 7.6, 4.8, 1.3 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 166.0, 155.2, 154.5, 149.3, 148.0, 138.7, 137.4, 124.8, 124.6, 123.5, 121.1. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{11}H_9N_2O_2$, 201.0659; found, 201.0660.

General Procedure for the Synthesis of Compounds 1a−c. In a 25 mL round-bottom flask was refluxed 2,2′-bipyridine-6-carboxylic acid (2.0 g, 10.0 mmol) in $SOCl_2$ (5 mL, 70 mmol) for 8 h. Then, excess $SOCl_2$ was evaporated under reduced pressure to give crude 2,2′-bipyridine-6-carbonyl chloride, which was dissolved in dry CH_2Cl_2 (20 mL) and added dropwise to a stirred solution of chiral amino alcohol (11 mmol) and Et_3N (4.2 mL, 30 mmol) in dry CH_2Cl_2 (35 mL) under ice bath. The reaction mixture was stirred at room temperature for 12 h. When the reaction was completed, the solvent was evaporated and the solid was dried. Next, the obtained amido alcohol (10 mmol) was refluxed in $SOCl_2$ (5 mL, 70 mmol) for 8 h. After evaporation of excess $SOCl_2$, the residue was dissolved in dry CH_2Cl_2 (15 mL) and added dropwise to a solution of triethylamine (8.4 mL, 60.0 mmol) and *p*-toluidine (1.2 g, 11.0 mmol) in dry CH_2Cl_2 under ice bath. The mixture was stirred at room temperature for 12 h. Aqueous NaOH solution (10 wt %, 35 mL) was added and the mixture was stirred for another 8−12 h. The aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The organic layer was dried over Na_2SO_4, filtered, and evaporated. The residue was purified by silica gel chromatography with PE/EA = 3/1−1/10 as the eluent to give product **1a−c**.

*(S)-6-(4-(tert-Butyl)-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)-2,2′-bipyridine (**1a**).* Brown solid. Yield: 1.9 g, 52%. mp 119−121 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (d, J = 4.7 Hz, 1H), 8.33 (d, J = 7.7 Hz, 1H), 7.99 (d, J = 7.7 Hz, 1H), 7.84 (t, J = 7.7 Hz, 1H), 7.53 (ddd, J = 7.7, 7.7, 1.8 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.19 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H), 6.99 (d, J = 8.0 Hz, 2H), 6.80 (d, J = 8.0 Hz, 2H), 4.23−4.13 (m, 1H), 4.10−4.01 (m, 1H), 3.71 (t, J = 8.4 Hz, 1H), 2.26 (s, 3H), 1.03 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.3, 155.7, 154.8, 149.4, 148.8, 141.6, 137.5, 136.5, 133.3, 129.1, 124.1, 123.7, 123.5, 121.4, 121.3, 74.2, 55.6, 34.3, 26.0, 20.8. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{24}H_{27}N_4$, 371.2230; found, 371.2238.

*(S)-6-(4-iso-Propyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)-2,2′-bipyridine (**1b**).* Brown solid. Yield: 1.8 g, 50%. mp 82−84 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, J = 5.1 Hz, 1H), 8.33 (d, J = 7.5 Hz, 1H), 7.94 (d, J = 7.5 Hz, 1H), 7.84 (t, J = 8.0 Hz, 1H), 7.54 (ddd, J = 7.7, 7.7, 1.8 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.21 (ddd, J = 7.5, 4.9, 1.2 Hz, 1H), 6.99 (d, J = 8.0 Hz, 2H), 6.80 (d, J = 8.0 Hz, 2H), 4.20−4.07 (m, 2H), 3.75−3.65 (m, 1H), 2.26 (s, 3H), 2.01−1.92 (m, 1H), 1.10 (d, J = 6.9 Hz, 3H), 1.00 (d, J = 6.9 Hz, 3H).

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$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.3, 155.6, 154.9, 149.4, 148.8, 141.4, 137.4, 136.5, 133.3, 129.1, 124.1, 123.7, 123.3, 121.5, 121.4, 70.6, 56.9, 33.2, 20.9, 19.1, 18.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{23}H_{25}N_4$, 357.2074; found, 357.2078.

*(S)-6-(4-Benzyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)-2,2′-bipyridine (**1c**).* Brown solid. Yield: 2.3 g, 56%. mp 109−111 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, *J* = 4.7 Hz, 1H), 8.35 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.84 (t, *J* = 7.7 Hz, 1H), 7.53 (ddd, *J* = 7.7, 7.7, 1.8 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.32−7.26 (m, 4H), 7.23−7.16 (m, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.67 (d, *J* = 8.0 Hz, 2H), 4.67−4.57 (m, 1H), 4.07 (t, *J* = 9.5 Hz, 1H), 3.76 (dd, *J* = 9.6, 7.4 Hz, 1H), 3.30 (dd, *J* = 13.6, 4.6 Hz, 1H), 2.90 (dd, *J* = 13.8, 9.0 Hz, 1H), 2.24 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.6, 155.5, 154.9, 148.9, 148.8, 141.0, 138.3, 137.5, 136.6, 133.6, 129.5, 129.1, 128.4, 126.4, 124.2, 123.7, 123.5, 121.6, 121.5, 65.5, 58.7, 42.2, 20.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{25}N_4$, 405.2074; found, 405.2078.

*General Procedure for the Synthesis of Compounds **1d−i**.* In a 50 mL two-necked Schlenk tube was refluxed 6-cyano-2,2′-bipyridine (1.0 g, 5.5 mmol) and NaOMe (0.12 g, 2.2 mmol) in dry MeOH (20 mL) for 30 min. The reaction mixture was cooled to room temperature and adjusted to neutral pH by the addition of glacial HOAc. After removal of the solvent, the solid was dried under vacuum overnight to give dry 2,2′-bipyridyl-6-carboxyimidate without purification. Afterwards, the solution of 2,2′-bipyridyl-6-carboxyimidate and (1*S*,2*S*)-1,2-diphenylethane-1,2-diamine (1.3 g, 6.1 mmol) in dry CH_2Cl_2 (50 mL) was refluxed overnight. After removal of the solvent, the residue was purified by silica gel column chromatography using PE/EA = 1/1 as the eluent to give compound **1d** as a yellow solid. Next, in 50 mL two-necked Schlenk tube was dissolved **1d** (0.377 g, 1.0 mmol) and DMAP (0.367 g, 3.0 mmol) in anhydrous CH_2Cl_2 (20 mL). Aryl sulfonyl chloride (2.2 mmol) was added at 0 °C and the reaction mixture was then stirred at room temperature for 4 h. The reaction mixture was washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, and evaporated. The residue was purified by silica gel chromatography using PE/EA = 1/1 as the eluent to give product **1e−i**.

*6-((4S,5S)-4,5-Diphenyl-4,5-dihydro-1H-imidazol-2-yl)-2,2′-bipyridine (**1d**).* Yellow solid. Yield: 1.5 g, 70%. mp 62−63 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 4.7 Hz, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.42 (d, *J* = 7.8 Hz, 1H), 8.36 (d, *J* = 8.0 Hz, 1H), 7.96 (t, *J* = 7.8 Hz, 1H), 7.80 (td, *J* = 7.8, 1.7 Hz, 1H), 7.46−7.26 (m, 11H), 6.70 (s, 1H), 5.02 (d, *J* = 115.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.6, 155.4, 155.3, 149.3, 147.7, 143.3, 137.8, 136.9, 128.8, 127.7, 126.9, 124.1, 122.84, 122.78, 121.1, 81.4, 70.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{21}N_4$, 377.1761; found, 377.1765.

*6-((4S,5S)-4,5-Diphenyl-1-(phenylsulfonyl)-4,5-dihydro-1H-imidazol-2-yl)-2,2′-bipyridine (**1e**).* White solid. Yield: 0.50 g, 96%. mp 139−140 °C. ^1H NMR (400 MHz, DMSO-d_6): δ 8.75 (d, *J* = 4.8 Hz, 1H), 8.57 (d, *J* = 7.8 Hz, 1H), 8.18 (t, *J* = 7.7 Hz, 1H), 8.02−7.88 (m, 3H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.54−7.42 (m, 7H), 7.42−7.31 (m, 6H), 7.16−7.09 (m, 2H), 5.22 (d, *J* = 4.3 Hz, 1H), 5.18 (d, *J* = 4.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 157.4, 154.5, 154.2, 149.4, 141.0, 140.7, 138.3, 138.2, 137.4, 133.7, 129.13, 129.07, 128.8, 128.2, 127.9, 127.0, 126.1, 124.6, 124.5, 122.0, 120.6, 78.0, 70.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{31}H_{25}N_4O_2S$, 517.1693; found, 517.1694.

*6-((4S,5S)-4,5-Diphenyl-1-tosyl-4,5-dihydro-1H-imidazol-2-yl)-2,2′-bipyridine (**1f**).* White solid. Yield: 0.45 g, 91%. mp 181−182 °C. ^1H NMR (400 MHz, DMSO-d_6): δ 8.75 (d, *J* = 4.7 Hz, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.17 (t, *J* = 7.7 Hz, 1H), 8.02−7.91 (m, 3H), 7.55−7.46 (m, 5H), 7.44−7.39 (m, 1H), 7.37−7.30 (m, 5H), 7.15−7.08 (m, 4H), 5,18 (d, *J* = 4.4 Hz, 1H), 5.15 (d, *J* = 4.4 Hz, 1H), 2.29 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.7, 155.2, 155.1, 149.7, 149.1, 143.6, 141.5, 141.0, 137.6, 136.7, 136.4, 129.7, 129.13, 129.07, 128.98, 128.3, 128.0, 127.6, 126.6, 126.4, 124.6, 123.8, 122.3, 121.5, 78.6, 71.7, 21.5. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{32}H_{27}N_4O_2S$, 531.1849; found, 531.1854.

*6-((4S,5S)-1-((4-Methoxyphenyl)sulfonyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-2-yl)-2,2′-bipyridine (**1g**).* White solid. Yield: 0.54 g, 99%. mp 172−173 °C. ^1H NMR (400 MHz, DMSO-d_6): δ 8.76 (d, *J* = 5.0 Hz, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.17 (t, *J* = 7.7 Hz, 1H), 8.08 (d, *J* = 7.7 Hz, 1H), 8.00−7.93 (m, 2H), 7.55−7.45 (m, 5H), 7.44−7.32 (m, 6H), 7.15−7.09 (m, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.16 (d, *J* = 4.3 Hz, 1H), 5.13 (d, *J* = 4.3 Hz, 1H), 3.75 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 163.1, 157.7, 154.5, 154.3, 149.44, 149.38, 141.4, 140.9, 138.3, 137.3, 129.4, 129.1, 128.8, 128.1, 127.7, 126.1, 126.0, 124.6, 124.5, 121.9, 120.6, 114.3, 78.0, 70.9, 55.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{32}H_{27}N_4O_3S$, 547.1798; found, 547.1802.

*6-((4S,5S)-1-((4-Bromophenyl)sulfonyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-2-yl)-2,2′-bipyridine (**1h**).* White solid. Yield: 0.57 g, 95%. mp 184−186 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, *J* = 4.6 Hz, 1H), 8.53 (dd, *J* = 1.5, 7.5 Hz, 1H), 8.03−7.91 (m, 2H), 7.70 (td, *J* = 1.8, 7.7 Hz, 1H), 7.66−7.60 (m, 1H), 7.49−7.40 (m, 7H), 7.39−7.30 (m, 4H), 7.14−7.04 (m, 4H), 5.55 (d, *J* = 4.6 Hz, 1H), 5.25 (d, *J* = 4.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 158.3, 155.2, 155.0, 149.5, 149.3, 141.1, 140.8, 139.2, 137.8, 136.7, 131.6, 129.3, 129.1, 129.0, 128.6, 128.2, 127.6, 126.8, 126.3, 124.5, 124.1, 122.7, 121.3, 78.5, 71.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{31}H_{24}BrN_4O_2S$, 595.0798; found, 595.0801.

*6-((4S,5S)-1-((4-Nitrophenyl)sulfonyl)-4,5-diphenyl-4,5-dihydro-1H-imidazol-2-yl)-2,2′-bipyridine (**1i**).* White solid. Yield: 0.55 g, 97%. mp 184−185 °C. ^1H NMR (400 MHz, DMSO-d_6): δ 8.73 (d, *J* = 4.6 Hz, 1H), 8.53 (d, *J* = 8.0 Hz, 1H), 8.20 (t, *J* = 7.7 Hz, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.83−7.72 (m, 2H), 7.59−7.43 (m, 8H), 7.42−7.33 (m, 3H), 7.30−7.23 (m, 2H), 5.39 (d, *J* = 3.6 Hz, 1H), 5.29 (d, *J* = 3.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 156.9, 154.7, 154.1, 149.7, 149.5, 148.8, 143.9, 140.5, 140.4, 138.7, 137.0, 129.3, 128.9, 128.5, 128.4, 127.9, 126.2, 126.1, 124.6, 124.5, 124.2, 122.5, 120.5, 77.5, 71.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{31}H_{24}N_5O_4S$, 562.1544; found, 562.1547.

General Procedure for Preparation of Ru Complexes 2a−2h. In a 100 mL two-necked Schlenk tube were dissolved **1** (0.4 mmol) and $RuCl_2(PPh_3)_3$ (0.383 g, 0.4 mmol) in anhydrous toluene (30 mL). The mixture was refluxed under an Ar atmosphere for 3 h. After removal of the solvent, the residue was purified by silica gel chromatography using CH_2Cl_2/MeOH = 50/1 as the eluent to give product **2**.

*Ru Complex **2a**.* Purple solid. Yield: 0.17 g, 53%. mp >300 °C; ^1H NMR (600 MHz, $CDCl_3$): δ 9.55−9.45 (m, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.48−7.37 (m, 7H), 7.25−7.03 (m, 13H), 6.93−6.69 (m, 2H), 6.48 (d, *J* = 7.9 Hz, 1H), 4.07−3.98 (m, 1H), 3.97−3.90 (m, 1H), 3.88−3.77 (m, 1H), 2.38 (s, 3H), 1.27 (s, 9H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 160.3, 157.9, 138.3, 136.8, 134.8, 133.13, 133.11, 131.6, 131.3, 130.1, 128.9, 128.2, 127.7, 127.6, 126.4, 125.0, 121.1, 120.5, 57.1, 35.9, 29.8, 27.4, 21.1. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 42.2 (s, PPh_3). IR (KBr pellets, cm^{-1}) ν: 3053, 2950, 2869, 1739, 1548, 1524, 1511, 1490, 1480, 1426, 1374, 1363, 1296, 1084, 833, 779, 749, 699, 685, 524, 510, 500. HRMS (ESI-TOF) *m/z*: $[M - 2Cl^-]^{2+}$ calcd for $C_{42}H_{41}N_4PRu$, 367.1051; found, 367.1057. Anal. Calcd for $C_{42}H_{41}Cl_2N_4PRu$: C, 62.68; H, 5.14; N, 6.96. Found: C, 62.72; H, 5.49; N, 6.58.

*Ru Complex **2b**.* Purple solid. Yield: 0.22 g, 70%. mp >300 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 9.40−9.34 (m, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.48−7.39 (m, 7H), 7.37−7.29 (m, 1H), 7.21−7.12 (m, 5H), 7.12−7.06 (m, 6H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.94−6.86 (m, 2H), 6.33 (d, *J* = 8.0 Hz, 1H), 4.35−4.20 (m, 1H), 4.09−3.93 (m, 2H), 3.50−3.33 (m, 1H), 2.37 (s, 3H), 1.14 (d, *J* = 6.3 Hz, 3H), 0.95 (d, *J* = 6.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 160.7, 158.1, 153.6, 139.4, 137.2, 134.6, 132.9, 132.8, 132.3, 132.1, 130.2, 128.9, 128.2, 127.8, 127.7, 126.7, 126.1, 124.2, 121.0, 120.1, 55.5, 29.2, 21.1, 20.3, 15.9. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 42.5 (s, PPh_3). IR (KBr pellets, cm^{-1}) ν: 3049, 2963, 2860, 2838, 1552, 1527, 1509, 1485, 1433, 1423, 1373, 1284, 1155, 1087, 1037, 838, 779, 747, 698, 523, 510, 500. HRMS (ESI-TOF) *m/z*: $[M - 2Cl^-]^{2+}$ calcd for $C_{41}H_{39}N_4PRu$, 360.0973; found, 360.0980. Anal.

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Calcd for $C_{41}H_{39}Cl_2N_4PRu$: C, 62.28; H, 4.97; N, 7.09. Found: C, 62.57; H, 5.06; N, 6.87.

Ru Complex ***2c***. Purple solid. Yield: 0.22 g, 66%. mp >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.33 (d, J = 5.3 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.57−7.49 (m, 2H), 7.48−7.42 (m, 6H), 7.39 (d, J = 7.4 Hz, 2H), 7.31 (t, J = 7.4 Hz, 2H), 7.23−7.16 (m, 5H), 7.14−7.08 (m, 8H), 6.98 (d, J = 7.7 Hz, 1H), 6.90−6.81 (m, 2H), 6.35 (d, J = 7.7 Hz, 1H), 4.84−4.75 (m, 1H), 4.57−4.45 (m, 1H), 3.85−3.73 (m, 2H), 3.12−3.01 (m, 1H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 163.3, 161.1, 158.2, 153.9, 153.4, 139.3, 139.2, 137.3, 134.6, 133.1, 133.0, 132.7, 132.3, 130.2, 129.4, 129.0, 128.5, 127.8, 127.7, 126.3, 126.1, 125,8, 124.2, 121.5, 120.4, 67.1, 61.3, 41.6, 21.1. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 43.2 (s, PPh_3). IR (KBr pellets, cm^{-1}) ν: 3054, 2861, 1603, 1551, 1525, 1511, 1482, 1430, 1374, 1293, 1157, 1091, 1039, 827, 777, 754, 744, 697, 527, 514, 496. HRMS (ESI-TOF) m/z: $[M - 2Cl]^{2+}$ calcd for $C_{45}H_{39}N_4PRu$, 384.0973; found, 384.0987. Anal. Calcd for $C_{45}H_{39}Cl_2N_4PRu$: C, 64.44; H, 4.69; N, 6.68. Found: C, 64.25; H, 5.00; N, 6.39.

Ru Complex ***2d***. Purple solid. Yield: 0.17 g, 45%. mp 215−216 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.16 (d, J = 5.4 Hz, 1H), 8.61 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.71−7.64 (m, 3H), 7.51−7.42 (m, 3H), 7.32 (t, J = 7.6 Hz, 2H), 7.26−7.23 (m, 5H), 7.18−7.11 (m, 9H), 7.07−6.89 (m, 12H), 5.09 (d, J = 32.4 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 161.5, 160.5, 158.2, 154.5, 153.9, 140.2, 138.6, 135.5, 134.6, 133.4, 132.9, 132.8, 131.4, 131.1, 129.8, 129.3, 129.2, 129.0, 128.9, 128.5, 128.2, 128.1, 127.94, 127.88, 127.6, 127.0, 126.3, 125.7, 121.3, 120.4, 72.1. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 36.9 (s, PPh_3). IR (KBr pellets, cm^{-1}) ν: 3055, 3029, 1601, 1584, 1496, 1480, 1447, 1434, 1366, 1298, 1171, 1084, 747, 690, 598, 569, 520, 511, 495. HRMS (ESI-TOF) m/z: $[M - 2Cl^-]^{2+}$ calcd for $C_{49}H_{39}N_4O_2PRuS$, 440.0782; found, 440.0789. Anal. Calcd for $C_{49}H_{39}Cl_2N_4O_2PRuS$: C, 61.89; H, 4.13; N, 5.89. Found: C, 62.25; H, 4.21; N, 5.64.

Ru Complex ***2e***. Purple solid. Yield: 0.20 g, 51%. mp 206−208 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.17 (d, J = 5.5 Hz, 1H), 8.56 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 8.0 Hz, 2H), 7.48−7.39 (m, 2H), 7.33 (d, J = 7.5 Hz, 2H), 7.26−7.22 (m, 3H), 7.19−7.11 (m, 9H), 7.07 (d, J = 8.0 Hz, 2H), 7.04−6.89 (m, 12H), 5.17−5.09 (m, 2H), 2.32 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 161.8, 160.4, 158.2, 154.6, 153.9, 145.6, 140.2, 138.5, 137.2, 135.5, 132.9, 132.8, 131.4, 131.1, 130.5, 130.2, 129.3, 129.2, 128.9, 128.5, 128.1, 128.0, 127.93, 127.87, 127.7, 126.7, 126.3, 125.7, 121.4, 120.4, 76.5, 72.0, 21.7. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 37.0 (s, PPh_3). IR (KBr pellets, cm^{-1}) ν: 3053, 3029, 1596, 1480, 1434, 1365, 1301, 1169, 1087, 772, 743, 694, 670, 662, 595, 520, 499. HRMS (ESI-TOF) m/z: $[M - 2Cl^-]^{2+}$ calcd for $C_{50}H_{41}N_4O_2PRuS$, 447.0860; found, 447.0864. Anal. Calcd for $C_{50}H_{41}Cl_2N_4O_2PRuS$: C, 62.24; H, 4.28; N, 5.81. Found: C, 62.56; H, 4.41; N, 5.45.

Ru Complex ***2f***. Purple solid. Yield: 0.19 g, 49%. mp 222−224 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.20 (d, J = 5.6 Hz, 1H), 8.58 (d, J = 8.1 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 7.9 Hz, 1H), 7.56 (d, J = 8.8 Hz, 2H), 7.50 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.38−7.33 (m, 2H), 7.26−7.22 (m, 3H), 7.19−7.11 (m, 9H), 7.06−6.90 (m, 12H), 6.71 (d, J = 8.8 Hz, 2H), 5.17−5.10 (m, 2H), 3.81 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 164.4, 162.0, 160.4, 158.3, 154.7, 154.0, 140.3, 138.7, 135.4, 132.9, 132.8, 131.4, 131.14, 131.08, 129.3, 129.2, 128.9, 128.6, 128.1, 128.0, 127.94, 127.88, 127.7, 126.9, 126.3, 125.7, 124.7, 121.2, 120.3, 115.1, 76.5, 72.0, 55.6. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 37.0 (s, PPh_3). IR (KBr pellets, cm^{-1}) ν: 3054, 3028, 1736, 1593, 1576, 1495, 1481, 1435, 1364, 1262, 1163, 1088, 1025, 743, 694, 672, 600, 553, 520, 499. HRMS (ESI-TOF) m/z: $[M - 2Cl^-]^{2+}$ calcd for $C_{50}H_{41}N_4O_3PRuS$, 455.0835; found, 455.0842. Anal. Calcd for $C_{50}H_{41}Cl_2N_4O_3PRuS$: C, 61.22; H, 4.21; N, 5.71. Found: C, 60.84; H, 4.34; N, 5.46.

Ru Complex ***2g***. Purple solid. Yield: 0.19 g, 47%. mp 218−220 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.24−9.15 (m, 1H), 8.52 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.51−7.46 (m, 3H), 7.44−7.35 (m, 5H), 7.26−7.22 (m, 6H), 7.18−7.11 (m, 6H), 7.05−6.87 (m, 12H), 5.18 (d, J = 24.6 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 161.5, 160.5, 158.1, 154.5, 154.0, 139.8, 138.4, 135.6, 133.1, 132.9, 132.8, 131.9, 131.2, 130.9, 130.5, 130.3, 129.3, 129.2, 129.0, 128.5, 128.4, 128.3, 128.0, 127.9, 127.3, 127.0, 126.4, 125.5, 121.3, 120.3, 76.2, 72.2. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 36.7 (s, PPh_3). IR (KBr pellets, cm^{-1}) ν: 3057, 1573, 1481, 1434, 1369, 1173, 1087, 1068, 742, 696, 616, 583, 522, 500. HRMS (ESI-TOF) m/z: $[M - 2Cl^-]^{2+}$ calcd for $C_{49}H_{38}BrN_4O_2PRuS$, 479.0335; found, 479.0339. Anal. Calcd for $C_{49}H_{38}BrCl_2N_4O_2PRuS$: C, 57.15; H, 3.72; N, 5.44. Found: C, 56.96; H, 3.73; N, 5.08.

Ru Complex ***2h***. Purple solid. Yield: 0.19 g, 47%. mp 206−208 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.21 (d, J = 4.9 Hz, 1H), 8.48 (d, J = 8.1 Hz, 1H), 8.01 (d, J = 8.3 Hz, 2H), 7.88−7.76 (m, 3H), 7.68 (d, J = 8.1 Hz, 1H), 7.57−7.52 (m, 1H), 7.51−7.48 (m, 2H), 7.44 (d, J = 8.1 Hz, 1H), 7.29−7.24 (m, 4H), 7.21−7.18 (m, 1H), 7.17−7.09 (m, 8H), 7.01−6.87 (m, 11H), 5.28 (d, J = 11.3 Hz, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 161.2, 160.5, 158.0, 154.4, 154.1, 151.2, 139.2, 138.4, 137.8, 135.8, 132.83, 132.77, 131.0, 130.7, 130.2, 129.5, 129.3, 129.1, 128.53, 128.46, 128.44, 128.1, 128.04, 127.96, 127.4, 127.2, 126.6, 125.4, 124.8, 121.4, 120.4, 75.7, 72.2. ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$): δ 36.4 (s, PPh_3). IR (KBr pellets, cm^{-1}) ν: 3055, 3025, 1603, 1528, 1480, 1434, 1372, 1346, 1312, 1176, 1086, 849, 738, 694, 680, 625, 584, 522, 499. HRMS (ESI-TOF) m/z: $[M - 2Cl^-]^{2+}$ calcd for $C_{49}H_{38}N_5O_4PRuS$, 462.5708; found, 462.5712. Anal. Calcd for $C_{49}H_{38}Cl_2N_5O_4PRuS$: C, 59.10; H, 3.85; N, 7.03. Found: C, 59.44; H, 3.90; N, 6.75.

General Procedure for α-Alkylation of Arylmethyl Nitriles. In a two-necked 15 mL Schlenk tube were dissolved pincer Ru catalyst **2h** (1.5 mol %), KOH (0.15 equiv), arylmethyl nitriles (0.5 mmol), and alcohol (1.0 mmol) in toluene (0.8 mL). The reaction mixture was stirred at 140 °C for 4 h. After removal of the solvent, the residue was purified by TLC on silica gel plates using PE/EA = 20−30/1 as the eluent to afford the corresponding products **5**.

*2-(4-Bromophenyl)-3-phenylpropanenitrile (****5a****).* White solid. Yield: 119 mg, 83%. mp 80−81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52−7.43 (m, 2H), 7.33−7.26 (m, 3H), 7.14−7.06 (m, 4H), 3.97 (t, J = 7.0 Hz, 1H), 3.18 (dd, J = 13.4, 7.7 Hz, 1H), 3.09 (dd, J = 13.4, 6.7 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 135.8, 134.1, 132.2, 129.2, 128.7, 127.6, 122.3, 119.9, 42.0, 39.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{13}BrN$, 286.0226; found, 286.0228.

*2-(4-Methoxyphenyl)-3-phenylpropanenitrile (****5b****).* White solid. Yield: 107 mg, 90%. mp 63−64 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33−7.22 (m, 3H), 7.14 (dd, J = 8.0, 19.7 Hz, 4H), 6.86 (d, J = 8.0 Hz, 2H), 3.94 (t, J = 8.0 Hz, 1H), 3.80 (s, 3H), 3.16 (dd, J = 13.2, 8.4 Hz, 1H), 3.09 (dd, J = 13.6, 6.5 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 159.4, 136.5, 129.3, 128.65, 128.61, 127.3, 127.2, 120.6, 114.4, 55.3, 42.3, 39.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{15}NNaO$, 260.1046; found, 260.1048.

*2-(4-(tert-Butyl)phenyl)-3-phenylpropanenitrile (****5c****).* White solid. Yield: 55 mg, 42%. mp 124−125 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41−7.35 (m, 2H), 7.34−7.26 (m, 3H), 7.24−7.14 (m, 4H), 3.97 (dd, J = 8.6, 6.4 Hz, 1H), 3.21−3.07 (m, 2H), 1.32 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 151.3, 136.6, 132.3, 129.2, 128.7, 127.3, 127.1, 126.0, 120.5, 42.3, 39.5, 34.6, 31.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{22}N$, 264.1747; found, 264.1749.

*3-Phenyl-2-(p-tolyl)propanenitrile (****5d****).* White solid. Yield: 100 mg, 90%. mp 71−73 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33−7.23 (m, 3H), 7.19−7.08 (m, 6H), 3.96 (dd, J = 8.4, 6.4 Hz, 1H), 3.17 (dd, J = 13.7, 8.4 Hz, 1H), 3.10 (dd, J = 13.7, 6.4 Hz, 1H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.0, 136.5, 132.3, 129.7, 129.2, 128.6, 127.3, 120.6, 42.3, 39.5, 21.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{16}H_{16}N$, 222.1277; found, 222.1278.

*2,3-Diphenylpropanenitrile (****5e****).* White solid. Yield: 99 mg, 95%. mp 52−53 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41−7.19 (m, 8H), 7.17−7.07 (m, 2H), 3.98 (dd, J = 8.4, 6.4 Hz, 1H), 3.17 (dd, J = 13.6, 8.1 Hz, 1H), 3.11 (dd, J = 13.6, 6.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 136.3, 135.3, 129.3, 129.1, 128.7, 128.2, 127.5, 127.4, 120.4, 42.2, 39.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{14}N$, 208.1121; found, 208.1123.

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*2-(4-Fluorophenyl)-3-phenylpropanenitrile (**5f**).* White solid. Yield: 97 mg, 86%. mp 85−86 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33−7.23 (m, 3H), 7.23−7.15 (m, 2H), 7.13−7.06 (m, 2H), 7.06−6.98 (m, 2H), 3.99 (t, *J* = 7.3 Hz, 1H), 3.19 (dd, *J* = 13.3, 8.0 Hz, 1H), 3.10 (dd, *J* = 13.3, 6.6 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 162.5 (d, J_{F-C} = 247.3 Hz), 135.9, 130.95 (d, J_{F-C} = 3.0 Hz), 129.3, 129.2, 128.7, 127.5, 120.2, 116.0 (d, J_{F-C} = 21.9 Hz), 42.2, 39.0. ^{19}F NMR (564 MHz, $CDCl_3$): δ −113.52. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{15}H_{13}FN$, 226.1027; found, 226.1030.

*2-(4-Chlorophenyl)-3-phenylpropanenitrile (**5g**).* White solid. Yield: 97 mg, 80%. mp 79−80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.26 (m, 5H), 7.20−7.13 (m, 2H), 7.12−7.07 (m, 2H), 3.98 (t, *J* = 7.3 Hz, 1H), 3.18 (dd, *J* = 13.6, 8.0 Hz, 1H), 3.10 (dd, *J* = 13.6, 6.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 135.8, 134.3, 133.6, 129.24, 129.20, 128.9, 128.7, 127.5, 120.0, 42.0, 39.1. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{15}H_{13}ClN$, 242.0731; found, 242.0734.

*2-(3-Methoxyphenyl)-3-phenylpropanenitrile (**5h**).* Yellow oil. Yield: 107 mg, 90%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32−7.24 (m, 4H), 7.17−7.12 (m, 2H), 6.85 (d, *J* = 7.7 Hz, 2H), 6.77 (s, 1H), 3.96 (t, *J* = 7.4 Hz, 1H), 3.77 (s, 3H), 3.21−3.15 (m, 1H), 3.13 (dd, *J* = 13.3, 6.4 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 160.0, 136.7, 136.3, 130.1, 129.2, 128.7, 127.4, 120.3, 119.7, 113.8, 113.2, 55.3, 42.1, 39.8. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{16}H_{16}NO$, 238.1226; found, 238.1228.

*2-(3-Chlorophenyl)-3-phenylpropanenitrile (**5i**).* White solid. Yield: 97 mg, 80%. mp 61−63 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33−7.22 (m, 6H), 7.15−7.08 (m, 3H), 3.96 (t, *J* = 7.3 Hz, 1H), 3.17 (dd, *J* = 13.6, 8.3 Hz, 1H), 3.10 (dd, *J* = 13.6, 6.3 Hz, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 137.1, 135.8, 134.9, 130.3, 129.2, 128.8, 128.6, 127.7, 127.6, 125.8, 119.8, 42.0, 39.4. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{15}H_{13}ClN$, 242.0731; found, 242.0734.

*3-Phenyl-2-(o-tolyl)propanenitrile (**5j**).* Colorless oil. Yield: 22 mg, 20%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 (d, *J* = 6.6 Hz, 1H), 7.33−7.26 (m, 3H), 7.25−7.21 (m, 2H), 7.19−7.14 (m, 3H), 4.14 (t, *J* = 6.6 Hz, 1H), 3.19−3.11 (m, 1H), 3.10−3.03 (m, 1H), 2.25 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 136.6, 135.1, 133.7, 131.0, 129.2, 128.7, 128.3, 127.7, 127.4, 126.9, 120.7, 41.0, 36.6, 19.1. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{16}H_{16}N$, 222.1277; found, 222.1279.

*2-(3,5-Dimethylphenyl)-3-phenylpropanenitrile (**5k**).* Yellow oil. Yield: 113 mg, 96%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.22 (m, 3H), 7.21−7.12 (m, 2H), 6.95 (s, 1H), 6.89 (s, 2H), 3.90 (dd, *J* = 9.0, 6.2 Hz, 1H), 3.20−3.04 (m, 2H), 2.30 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.7, 136.7, 135.2, 129.8, 129.2, 128.6, 127.4, 125.2, 120.6, 42.4, 39.9, 21.3. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{17}H_{18}N$, 236.1434; found, 236.1437.

*3-Phenyl-2-(thiophen-2-yl)propanenitrile (**5l**).* Colorless oil. Yield: 31 mg, 29%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34−7.25 (m, 4H), 7.19 (d, *J* = 7.3 Hz, 2H), 7.00−6.97 (m, 1H), 6.97−6.92 (m, 1H), 4.27 (t, *J* = 7.4 Hz, 1H), 3.28−3.20 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 137.2, 136.0, 129.2, 128.8, 127.6, 127.1, 126.5, 125.7, 119.5, 42.3, 34.9. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{13}H_{12}NS$, 214.0685; found, 214.0684.

*3-(4-Methoxyphenyl)-2-phenylpropanenitrile (**5m**).* Yellow solid. Yield: 105 mg, 89%. mp 83−84 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38−7.28 (m, 3H), 7.27−7.22 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 3.95 (t, *J* = 7.1 Hz, 1H), 3.78 (s, 3H), 3.16−3.04 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 158.9, 135.3, 130.3, 129.0, 128.4, 128.1, 127.5, 120.5, 114.0, 55.3, 41.4, 40.1. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{16}H_{16}NO$, 238.1226; found, 238.1220.

*2-Phenyl-3-(p-tolyl)propanenitrile (**5n**).* White solid. Yield: 99 mg, 90%. mp 53−54 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.29 (m, 3H), 7.29−7.22 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 3.96 (dd, *J* = 8.4, 6.8 Hz, 1H), 3.18−3.04 (m, 2H), 2.32 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 137.1, 135.4, 133.3, 129.3, 129.1, 129.0, 128.2, 127.5, 120.4, 41.8, 40.0, 21.1. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{16}H_{16}N$, 222.1277; found, 222.1279.

*3-(4-Chlorophenyl)-2-phenylpropanenitrile (**5o**).* White solid. Yield: 65 mg, 54%. mp 107−108 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42−7.29 (m, 3H), 7.27−7.21 (m, 4H), 7.04 (d, *J* = 7.8 Hz, 2H), 3.98 (t, *J* = 7.4 Hz, 1H), 3.20−3.05 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 134.8, 134.6, 133.4, 130.7, 129.1, 128.8, 128.4, 127.5, 120.1, 41.4, 39.6. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{15}H_{13}ClN$, 242.0731; found, 242.0734.

*3-(4-Bromophenyl)-2-phenylpropanenitrile (**5p**).* White solid. Yield: 80 mg, 56%. mp 106−108 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.38−7.31 (m, 3H), 7.25−7.21 (m, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 3.98 (t, *J* = 7.3 Hz, 1H), 3.17−3.07 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 135.1, 134.8, 131.8, 131.0, 129.1, 128.4, 127.5, 121.5, 120.1, 41.5, 39.5. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{15}H_{13}BrN$, 286.0226; found, 286.0228.

*2-Phenyl-3-(4-(trifluoromethyl)phenyl)propanenitrile (**5q**).* White solid. Yield: 87 mg, 63%. mp 80−81 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.8 Hz, 2H), 7.40−7.32 (m, 3H), 7.28−7.21 (m, 4H), 4.03 (t, *J* = 7.2 Hz, 1H), 3.28−3.16 (m, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 140.1, 134.6, 130.0, 129.7, 129.2, 128.5, 127.4, 125.6 (q, $^3J_{C-F}$ = 3.5 Hz), 124.1 (q, $^1J_{C-F}$ = 271.2 Hz), 119.9, 41.8, 39.3. ^{19}F NMR (564 MHz, $CDCl_3$): δ −62.34. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{16}H_{13}F_3N$, 276.0995; found, 276.0993.

*2-Phenyl-3-(m-tolyl)propanenitrile (**5r**).* Colorless oil. Yield: 107 mg, 97%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37−7.29 (m, 3H), 7.27 (d, *J* = 7.4 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.97−6.90 (m, 2H), 3.98 (dd, *J* = 8.4, 6.3 Hz, 1H), 3.14 (dd, *J* = 13.6, 8.7 Hz, 1H), 3.08 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.31 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 138.3, 136.3, 135.5, 130.0, 129.1, 128.5, 128.2, 128.1, 127.5, 126.2, 120.5, 42.3, 39.9, 21.4. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{16}H_{16}N$, 222.1277; found, 222.1278.

*3-(2-Bromophenyl)-2-phenylpropanenitrile (**5s**).* White solid. Yield: 99 mg, 69%. mp 60−61 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.8 Hz, 1H), 7.41−7.36 (m, 4H), 7.36−7.31 (m, 1H), 7.28−7.22 (m, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 4.20 (t, *J* = 7.8 Hz, 1H), 3.30 (dd, *J* = 13.2, 5.6 Hz, 1H), 3.25−3.18 (m, 1H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 135.8, 135.3, 133.1, 131.9, 129.3, 129.1, 128.3, 127.8, 127.3, 124.4, 120.1, 42.9, 37.7. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{15}H_{13}BrN$, 286.0226; found, 286.0225.

*2,5-Diphenylpentanenitrile (**5t**).* Colorless oil. Yield: 104 mg, 89%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38−7.33 (m, 2H), 7.33−7.25 (m, 5H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 2H), 3.77 (dd, *J* = 8.3, 5.6 Hz, 1H), 2.65 (t, *J* = 7.3 Hz, 2H), 1.99−1.73 (m, 4H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 141.2, 135.8, 129.1, 128.5, 128.4, 128.1, 127.3, 126.1, 120.8, 37.3, 35.3, 35.1, 28.6. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{17}H_{18}N$, 236.1434; found, 236.1433.

*2-Phenylhexanenitrile (**5u**).* Pale yellow oil. Yield: 64 mg, 74%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40−7.28 (m, 5H), 3.76 (t, *J* = 7.3 Hz, 1H), 1.97−1.81 (m, 2H), 1.53−1.31 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 136.1, 129.1, 128.0, 127.2, 121.0, 37.4, 35.7, 29.2, 22.1, 13.8. HRMS (ESI-TOF) *m*/*z*: [M + H]$^+$ calcd for $C_{12}H_{16}N$, 174.1277; found, 174.1274.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00146.

Crystallography of **1f**, **1g**, and **2a**; characterization of vinyl nitrile; and NMR spectra of **1**, **2**, and **5** (PDF)

Accession Codes

CCDC 1900520−1900522 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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REFERENCES

(1) For reviews, please see: (a) Pan, S.; Shibata, T. Recent Advances in Iridium-Catalyzed Alkylation of C-H and N-H Bonds. *ACS Catal.* **2013**, *3*, 704−712. (b) Gunanathan, C.; Milstein, D. Applications of Acceptorless Dehydrogenation and Related Transformations in Chemical Synthesis. *Science* **2013**, *341*, 1229712. (c) Obora, Y. Recent Advances in α-Alkylation Reactions using Alcohols with Hydrogen Borrowing Methodologies. *ACS Catal.* **2014**, *4*, 3972−3981. (d) Werkmeister, S.; Neumann, J.; Junge, K.; Beller, M. Pincer-Type Complexes for Catalytic (De)Hydrogenation and Transfer (De)Hydrogenation Reactions: Recent Progress. *Chem.—Eur. J.* **2015**, *21*, 12226−12250. (e) Nandakumar, A.; Midya, S. P.; Landge, V. G.; Balaraman, E. Transition-Metal-Catalyzed Hydrogen-Transfer Annulations: Access to Heterocyclic Scaffolds. *Angew. Chem., Int. Ed.* **2015**, *54*, 11022−11034. (f) Huang, F.; Liu, Z.; Yu, Z. C-Alkylation of Ketones and Related Compounds by Alcohols: Transition-Metal-Catalyzed Dehydrogenation. *Angew. Chem., Int. Ed.* **2016**, *55*, 862−875. (g) Obora, Y. C-Alkylation by Hydrogen Autotransfer Reactions. *Top. Curr. Chem.* **2016**, *374*, 1−29. (h) Chelucci, G. Ruthenium and osmium complexes in C—C bond-forming reactions by borrowing hydrogen catalysis. *Coord. Chem. Rev.* **2017**, *331*, 1−36. (i) Corma, A.; Navas, J.; Sabater, M. J. Advances in One-Pot Synthesis through Borrowing Hydrogen Catalysis. *Chem. Rev.* **2018**, *118*, 1410−1459. (j) Irrgang, T.; Kempe, R. 3d-Metal Catalyzed N- and C-Alkylation Reactions via Borrowing Hydrogen or Hydrogen Autotransfer. *Chem. Rev.* **2019**, *119*, 2524−2549.

(2) (a) Elangovan, S.; Sortais, J.-B.; Beller, M.; Darcel, C. Iron-Catalyzed α-Alkylation of Ketones with Alcohols. *Angew. Chem., Int. Ed.* **2015**, *54*, 14483−14486. (b) Frost, J. R.; Cheong, C. B.; Akhtar, W. M.; Caputo, D. F. J.; Stevenson, N. G.; Donohoe, T. J. Strategic Application and Transformation of ortho-Disubstituted Phenyl and Cyclopropyl Ketones to Expand the Scope of Hydrogen Borrowing Catalysis. *J. Am. Chem. Soc.* **2015**, *137*, 15664−15667. (c) Peña-López, M.; Piehl, P.; Elangovan, S.; Neumann, H.; Beller, M. Manganese-Catalyzed Hydrogen-Autotransfer C−C Bond Formation: α-Alkylation of Ketones with Primary Alcohols. *Angew. Chem., Int. Ed.* **2016**, *55*, 14967−14971. (d) Schlepphorst, C.; Maji, B.; Glorius, F. Ruthenium-NHC Catalyzed α-Alkylation of Methylene Ketones Provides Branched Products through Borrowing Hydrogen Strategy. *ACS Catal.* **2016**, *6*, 4184−4188. (e) Zhang, G.; Wu, J.; Zeng, H.; Zhang, S.; Yin, Z.; Zheng, S. Cobalt-Catalyzed α-Alkylation of Ketones with Primary Alcohols. *Org. Lett.* **2017**, *19*, 1080−1083. (f) Liu, P.; Liang, R.; Lu, L.; Yu, Z.; Li, F. Use of a Cyclometalated Iridium(III) Complex Containing a N∧C∧N-Coordinating Terdentate Ligand as a Catalyst for the α-Alkylation of Ketones and N-Alkylation of Amines with Alcohols. *J. Org. Chem.* **2017**, *82*, 1943−1950. (g) Chakrabarti, K.; Maji, M.; Panja, D.; Paul, B.; Shee, S.; Das, G. K.; Kundu, S. Utilization of MeOH as a C1 Building Block in Tandem Three-Component Coupling Reaction. *Org. Lett.* **2017**, *19*, 4750−4753. (h) Barman, M. K.; Jana, A.; Maji, B. Phosphine-Free NNN-Manganese Complex Catalyzed α-Alkylation of Ketones with Primary Alcohols and Friedländer Quinoline Synthesis. *Adv. Synth. Catal.* **2018**, *360*, 3233−3238. (i) Das, J.; Vellakkaran, M.; Banerjee, D. Nickel-Catalyzed Alkylation of Ketone Enolates: Synthesis of Monoselective Linear Ketones. *J. Org. Chem.* **2019**, *84*, 769−779.

(3) (a) Freitag, F.; Irrgang, T.; Kempe, R. Cobalt-Catalyzed Alkylation of Secondary Alcohols with Primary Alcohols via Borrowing Hydrogen/Hydrogen Autotransfer. *Chem.—Eur. J.* **2017**, *23*, 12110−12113. (b) Shee, S.; Paul, B.; Panja, D.; Roy, B. C.; Chakrabarti, K.; Ganguli, K.; Das, A.; Das, G. K.; Kundu, S. Tandem Cross Coupling Reaction of Alcohols for Sustainable Synthesis of β-Alkylated Secondary Alcohols and Flavan Derivatives. *Adv. Synth. Catal.* **2017**, *359*, 3888−3893. (c) Liu, T.; Wang, L.; Wu, K.; Yu, Z. Manganese-Catalyzed β-Alkylation of Secondary Alcohols with Primary Alcohols under Phosphine-Free Conditions. *ACS Catal.* **2018**, *8*, 7201−7207. (d) Tan, D.-W.; Li, H.-X.; Zhu, D.-L.; Li, H.-Y.; Young, D. J.; Yao, J.-L.; Lang, J.-P. Ligand-Controlled Copper(I)-Catalyzed Cross-Coupling of Secondary and Primary Alcohols to α-Alkylated Ketones, Pyridines, and Quinolines. *Org. Lett.* **2018**, *20*, 608−611. (e) Wang, Q.; Wu, K.; Yu, Z. Ruthenium(III)-Catalyzed β-Alkylation of Secondary Alcohols with Primary Alcohols. *Organometallics* **2016**, *35*, 1251−1256.

(4) (a) Guo, L.; Ma, X.; Fang, H.; Jia, X.; Huang, Z. A General and Mild Catalytic α-Alkylation of Unactivated Esters Using Alcohols. *Angew. Chem., Int. Ed.* **2015**, *54*, 4023−4027. (b) Deibl, N.; Kempe, R. General and Mild Cobalt-Catalyzed C-Alkylation of Unactivated Amides and Esters with Alcohols. *J. Am. Chem. Soc.* **2016**, *138*, 10786−10789. (c) Jang, Y. K.; Krückel, T.; Rueping, M.; El-Sepelgy, O. Sustainable Alkylation of Unactivated Esters and Amides with Alcohols Enabled by Manganese Catalysis. *Org. Lett.* **2018**, *20*, 7779−7783. (d) Chakraborty, S.; Daw, P.; Ben David, Y.; Milstein, D. Manganese-Catalyzed α-Alkylation of Ketones, Esters, and Amides Using Alcohols. *ACS Catal.* **2018**, *8*, 10300−10305. (f) Midya, S. P.; Rana, J.; Pitchaimani, J.; Nandakumar, A.; Madhu, V.; Balaraman, E. Ni-Catalyzed α-Alkylation of Unactivated Amides and Esters with Alcohols by Hydrogen Auto-Transfer Strategy. *ChemSusChem* **2018**, *11*, 3911−3916.

(5) (a) Siddiki, S. M. A. H.; Kon, K.; Shimizu, K.-i. General and Selective C-3 Alkylation of Indoles with Primary Alcohols by a Reusable Pt Nanocluster Catalyst. *Chem.—Eur. J.* **2013**, *19*, 14416−14419. (b) Jiang, X.; Tang, W.; Xue, D.; Xiao, J.; Wang, C. Divergent Dehydrogenative Coupling of Indolines with Alcohols. *ACS Catal.* **2017**, *7*, 1831−1835. (c) Di Gregorio, G.; Mari, M.; Bartoccini, F.; Piersanti, G. Iron-Catalyzed Direct C3-Benzylation of Indoles with Benzyl Alcohols through Borrowing Hydrogen. *J. Org. Chem.* **2017**, *82*, 8769−8775. (d) Polidano, K.; Allen, B. D. W.; Williams, J. M. J.; Morrill, L. C. Iron-Catalyzed Methylation Using the Borrowing Hydrogen Approach. *ACS Catal.* **2018**, *8*, 6440−6445.

(6) (a) Obora, Y.; Ogawa, S.; Yamamoto, N. Iridium-Catalyzed Alkylation of Methylquinolines with Alcohols. *J. Org. Chem.* **2012**, *77*, 9429−9433. (b) Feng, T.-Y.; Li, H.-X.; Young, D. J.; Lang, J.-P. Ligand-Free $RuCl_3$-Catalyzed Alkylation of Methylazaarenes with Alcohols. *J. Org. Chem.* **2017**, *82*, 4113−4120. (c) Rana, J.; Babu, R.; Subaramanian, M.; Balaraman, E. Ni-Catalyzed Dehydrogenative Coupling of Primary and Secondary Alcohols with Methyl-*N*-Heteroaromatics. *Org. Chem. Front.* **2018**, *5*, 3250−3255.

(7) (a) Löfberg, C.; Grigg, R.; Whittaker, M. A.; Keep, A.; Derrick, A. Efficient Solvent-Free Selective Monoalkylation of Arylacetonitriles with Mono-, Bis-, and Tris-primary Alcohols Catalyzed by a Cp*Ir Complex. *J. Org. Chem.* **2006**, *71*, 8023−8027. (b) Morita, M.; Obora,

DOI: 10.1021/acs.organomet.9b00146
Organometallics XXXX, XXX, XXX−XXX

Y.; Ishii, Y. Alkylation of Active Methylene Compounds with Alcohols Catalyzed by an Iridium Complex. *Chem. Commun.* **2007**, *43*, 2850−2852. (c) Anxionnat, B.; Gomez Pardo, D.; Ricci, G.; Cossy, J. Monoalkylation of Acetonitrile by Primary Alcohols Catalyzed by Iridium Complexes. *Org. Lett.* **2011**, *13*, 4084−4087. (d) Sawaguchi, T.; Obora, Y. Iridium-catalyzed α-Alkylation of Acetonitrile with Primary and Secondary Alcohols. *Chem. Lett.* **2011**, *40*, 1055−1057. (e) Anxionnat, B.; Gomez Pardo, D.; Ricci, G.; Cossy, J. First Intramolecular Alkylation of Nitriles with Primary and Secondary Alcohols Catalyzed by Iridium Complexes. *Eur. J. Org. Chem.* **2012**, *2012*, 4453−4456.

(8) Li, J.; Liu, Y.; Tang, W.; Xue, D.; Li, C.; Xiao, J.; Wang, C. Atmosphere-Controlled Chemoselectivity: Rhodium-Catalyzed Alkylation and Olefination of Alkylnitriles with Alcohols. *Chem.—Eur. J.* **2017**, *23*, 14445−14449.

(9) Buil, M. L.; Esteruelas, M. A.; Herrero, J.; Izquierdo, S.; Pastor, I. M.; Yus, M. Osmium Catalyst for the Borrowing Hydrogen Methodology: α-Alkylation of Arylacetonitriles and Methyl Ketones. *ACS Catal.* **2013**, *3*, 2072−2075.

(10) (a) Liu, Z.; Yang, Z.; Yu, X.; Zhang, H.; Yu, B.; Zhao, Y.; Liu, Z. Methylation of $C(sp^3)$−H/$C(sp^2)$−H Bonds with Methanol Catalyzed by Cobalt System. *Org. Lett.* **2017**, *19*, 5228−5231. (b) Ma, W.; Cui, S.; Sun, H.; Tang, W.; Xue, D.; Li, C.; Fan, J.; Xiao, J.; Wang, C. Iron-Catalyzed Alkylation of Nitriles with Alcohols. *Chem.—Eur. J.* **2018**, *24*, 13118−13123. (c) Jana, A.; Reddy, C. B.; Maji, B. Manganese Catalyzed α-Alkylation of Nitriles with Primary Alcohols. *ACS Catal.* **2018**, *8*, 9226−9231.

(11) (a) Motokura, K.; Nishimura, D.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. A Ruthenium-Grafted Hydrotalcite as a Multifunctional Catalyst for Direct α-Alkylation of Nitriles with Primary Alcohols. *J. Am. Chem. Soc.* **2004**, *126*, 5662−5663. (b) Motokura, K.; Fujita, N.; Mori, K.; Mizugaki, T.; Ebitani, K.; Jitsukawa, K.; Kaneda, K. Environmentally Friendly One-Pot Synthesis of α-Alkylated Nitriles Using Hydrotalcite-Supported Metal Species as Multifunctional Solid Catalysts. *Chem.—Eur. J.* **2006**, *12*, 8228−8239. (c) Cheung, H. W.; Li, J.; Zheng, W.; Zhou, Z.; Chiu, Y. H.; Lin, Z.; Lau, C. P. Dialkylamino cyclopentadienyl ruthenium(ii) complex-catalyzed α-alkylation of arylacetonitriles with primary alcohols. *Dalton Trans.* **2010**, *39*, 265−274. (d) Kuwahara, T.; Fukuyama, T.; Ryu, I. Synthesis of Alkylated Nitriles by $[RuHCl(CO)(PPh_3)_3]$-Catalyzed Alkylation of Acetoni-trile Using Primary Alcohols. *Chem. Lett.* **2013**, *42*, 1163−1165. (e) Thiyagarajan, S.; Gunanathan, C. Facile Ruthenium(II)-Catalyzed *a*-Alkylation of Arylmethyl Nitriles Using Alcohols Enabled by Metal−Ligand Cooperation. *ACS Catal.* **2017**, *7*, 5483−5490.

(12) For reviews, please see: (a) Gunanathan, C.; Milstein, D. Bond Activation and Catalysis by Ruthenium Pincer Complexes. *Chem. Rev.* **2014**, *114*, 12024−12087. (b) Werkmeister, S.; Neumann, J.; Junge, K.; Beller, M. Pincer-Type Complexes for Catalytic (De)-Hydrogenation and Transfer (De)Hydrogenation Reactions: Recent Progress. *Chem.—Eur. J.* **2015**, *21*, 12226−12250. (c) Kumar, A.; Bhatti, T. M.; Goldman, A. S. Dehydrogenation of Alkanes and Aliphatic Groups by Pincer-Ligated Metal Complexes. *Chem. Rev.* **2017**, *117*, 12357−12384. (d) Mukherjee, A.; Milstein, D. Homogeneous Catalysis by Cobalt and Manganese Pincer Complexes. *ACS Catal.* **2018**, *8*, 11435−11469. (e) Junge, K.; Papa, V.; Beller, M. Cobalt-Pincer Complexes in Catalysis. *Chem.—Eur. J.* **2019**, *25*, 122−143.

(13) (a) Wei, C.; He, Y.; Shi, X.; Song, Z. Terpyridine-metal complexes: Applications in catalysis and supramolecular chemistry. *Coord. Chem. Rev.* **2019**, *385*, 1−19. (b) Moore, C. M.; Bark, B.; Szymczak, N. K. Simple Ligand Modifications with Pendent OH Groups Dramatically Impact the Activity and Selectivity of Ruthenium Catalysts for Transfer Hydrogenation: The Importance of Alkali Metals. *ACS Catal.* **2016**, *6*, 1981−1990. (c) Cheng, J.; Zhu, M.; Wang, C.; Li, J.; Jiang, X.; Wei, Y.; Tang, W.; Xue, D.; Xiao, J. Chemoselective Dehydrogenative Esterification of Aldehydes and Alcohols with a Dimeric Rhodium(II) Catalyst. *Chem. Sci.* **2016**, *7*, 4428−4434. (d) Dahl, E. W.; Louis-Goff, T.; Szymczak, N. K. Second Sphere Ligand Modifications Enable a Recyclable Catalyst for Oxidant-Free Alcohol Oxidation to Carboxylates. *Chem. Commun.* **2017**, *53*, 2287−2289. (e) Wang, X.; Wang, C.; Liu, Y.; Xiao, J. Acceptorless Dehydrogenation and Aerobic Oxidation of Alcohols with a Reusable Binuclear Rhodium(II) Catalyst in Water. *Green Chem.* **2016**, *18*, 4605−4610.

(14) (a) Vega, E.; Lastra, E.; Gamasa, M. P. Asymmetric Transfer Hydrogenation of Ketones Catalyzed by Enantiopure Osmium(II) Pybox Complexes. *Inorg. Chem.* **2013**, *52*, 6193−6198. (b) Menéndez-Pedregal, E.; Vaquero, M.; Lastra, E.; Gamasa, P.; Pizzano, A. Highly Enantioselective Hydrogenation ofN-Aryl Imines Derived from Acetophenones by Using Ru-Pybox Complexes under Hydrogenation or Transfer Hydrogenation Conditions in Isopropanol. *Chem.—Eur. J.* **2015**, *21*, 549−553. (c) de Julián, E.; Menéndez-Pedregal, E.; Claros, M.; Vaquero, M.; Díez, J.; Lastra, E.; Gamasa, P.; Pizzano, A. Practical Synthesis of Enantiopure Benzylamines by Catalytic Hydrogenation or Transfer Hydrogenation Reactions in Isopropanol Using a Ru-Pybox Catalyst. *Org. Chem. Front.* **2018**, *5*, 841−849.

(15) (a) Gonzalez-de-Castro, A.; Robertson, C. M.; Xiao, J. Dehydrogenative α-Oxygenation of Ethers with an Iron Catalyst. *J. Am. Chem. Soc.* **2014**, *136*, 8350−8360. (b) Li, K.; Niu, J.-L.; Yang, M.-Z.; Li, Z.; Wu, L.-Y.; Hao, X.-Q.; Song, M.-P. New Type of 2,6-Bis(imidazo[1,2-*a*]pyridin-2-yl)pyridine-Based Ruthenium Complexes: Active Catalysts for Transfer Hydrogenation of Ketones. *Organometallics* **2015**, *34*, 1170−1176. (c) Midya, S. P.; Pitchaimani, J.; Landge, V. G.; Madhu, V.; Balaraman, E. Direct Access to *N*-Alkylated Amines and Imines via Acceptorless Dehydrogenative Coupling Catalyzed by a Cobalt(II)-NNN Pincer Complex. *Catal. Sci. Technol.* **2018**, *8*, 3469−3473. (d) Cao, X.-N.; Wan, X.-M.; Yang, F.-L.; Li, K.; Hao, X.-Q.; Shao, T.; Zhu, X.; Song, M.-P. NNN Pincer Ru(II)-Complex-Catalyzed α-Alkylation of Ketones with Alcohols. *J. Org. Chem.* **2018**, *83*, 3657−3668. (e) Joannou, M. V.; Bezdek, M. J.; Chirik, P. J. Pyridine(diimine) Molybdenum-Catalyzed Hydrogenation of Arenes and Hindered Olefins: Insights into Precatalyst Activation and Deactivation Pathways. *ACS Catal.* **2018**, *8*, 5276−5285.

(16) (a) Chai, H.; Liu, T.; Wang, Q.; Yu, Z. Substituent Effect on the Catalytic Activity of Ruthenium(II) Complexes Bearing a Pyridyl-Supported Pyrazolyl-Imidazolyl Ligand for Transfer Hydrogenation of Ketones. *Organometallics* **2015**, *34*, 5278−5284. (b) Chai, H.; Liu, T.; Yu, Z. NHTs Effect on the Enantioselectivity of Ru(II) Complex Catalysts Bearing a Chiral Bis(NHTs)-Substituted Imidazolyl-Oxazolinyl-Pyridine Ligand for Asymmetric Transfer Hydrogenation of Ketones. *Organometallics* **2017**, *36*, 4136−4144. (c) Shi, J.; Hu, B.; Ren, P.; Shang, S.; Yang, X.; Chen, D. Synthesis and Reactivity of Metal-Ligand Cooperative Bifunctional Ruthenium Hydride Complexes: Active Catalysts for β-Alkylation of Secondary Alcohols with Primary Alcohols. *Organometallics* **2018**, *37*, 2795−2806. (d) Zhang, C.; Zhao, J.-P.; Hu, B.; Shi, J.; Chen, D. Ruthenium-Catalyzed β-Alkylation of Secondary Alcohols and α-Alkylation of Ketones via Borrowing Hydrogen: Dramatic Influence of the Pendant N-Heterocycle. *Organometallics* **2019**, *38*, 654−664.

(17) Liu, H.; Du, D.-M. Recent Advances in the Synthesis of 2-Imidazolines and Their Applications in Homogeneous Catalysis. *Adv. Synth. Catal.* **2009**, *351*, 489−519.

(18) (a) Hyodo, K.; Nakamura, S.; Shibata, N. Enantioselective Aza-Morita−Baylis−Hillman Reactions of Acrylonitrile Catalyzed by Palladium(II) Pincer Complexes having C_2-Symmetric Chiral Bis-(imidazoline) Ligands. *Angew. Chem., Int. Ed.* **2012**, *51*, 10337−10341. (b) Kondo, M.; Nishi, T.; Hatanaka, T.; Funahashi, Y.; Nakamura, S. Catalytic Enantioselective Reaction of α-Amino-acetonitriles Using Chiral Bis(imidazoline) Palladium Catalysts. *Angew. Chem., Int. Ed.* **2015**, *54*, 8198−8202. (c) Weldy, N. M.; Schafer, A. G.; Owens, C. P.; Herting, C. J.; Varela-Alvarez, A.; Chen, S.; Niemeyer, Z.; Musaev, D. G.; Sigman, M. S.; Davies, H. M. L.; Blakey, S. B. Iridium(iii)-bis(imidazolinyl)phenyl catalysts for enantioselective C-H functionalization with ethyl diazoacetate. *Chem. Sci.* **2016**, *7*, 3142−3146. (d) Kondo, M.; Sugimoto, M.;

DOI: 10.1021/acs.organomet.9b00146
Organometallics XXXX, XXX, XXX−XXX

Nakamura, S. Direct Catalytic Enantioselective Mannich-Type Reaction of Dichloroacetonitrile Using Bis(imidazoline)-Pd Catalysts. *Chem. Commun.* **2016**, *52*, 13604−13607. (e) Kondo, M.; Saito, H.; Nakamura, S. Direct catalytic enantioselective Mannich-type reaction of α,α-dithioacetonitriles with imines using chiral bis(imidazoline)-Pd complexes. *Chem. Commun.* **2017**, *53*, 6776−6779.

(19) (a) Shao, D.-D.; Niu, J.-L.; Hao, X.-Q.; Gong, J.-F.; Song, M.-P. Neutral and cationic chiral NCN pincer nickel(ii) complexes with 1,3-bis(2′-imidazolinyl)benzenes: synthesis and characterization. *Dalton Trans.* **2011**, *40*, 9012−9019. (b) Hao, X.-Q.; Xu, Y.-X.; Yang, M.-J.; Wang, L.; Niu, J.-L.; Gong, J.-F.; Song, M.-P. A Cationic NCN Pincer Platinum(II) Aquo Complex with a Bis(imidazolinyl)phenyl Ligand: Studies toward its Synthesis and Asymmetric Friedel-Crafts Alkylation of Indoles with Nitroalkenes. *Organometallics* **2012**, *31*, 835−846. (c) Wang, T.; Niu, J.-L.; Liu, S.-L.; Huang, J.-J.; Gong, J.-F.; Song, M.-P. Chiral NCN Pincer Rhodium(III) Complexes with Bis-(imidazolinyl)phenyl Ligands: Synthesis and Enantioselective Catalytic Alkynylation of Trifluoropyruvates with Terminal Alkynes. *Adv. Synth. Catal.* **2013**, *355*, 927−937. (d) Hao, X.-Q.; Zhao, Y.-W.; Yang, J.-J.; Niu, J.-L.; Gong, J.-F.; Song, M.-P. Enantioselective Hydrophosphination of Enones with Diphenylphosphine Catalyzed by Bis(imidazoline) NCN Pincer Palladium(II) Complexes. *Organometallics* **2014**, *33*, 1801−1811. (e) Yan, J.; Wang, Y.-B.; Zhu, Z.-H.; Li, Y.; Zhu, X.; Hao, X.-Q.; Song, M.-P. Synthesis, Characterization, and Catalytic Studies of Unsymmetrical Chiral NCC Pincer Pd(II) and Ni(II) Complexes Bearing (Imidazolinyl)aryl NHC Ligands. *Organometallics* **2018**, *37*, 2325−2334. (f) Wang, Y.-B.; Liu, Y.-X.; Zhu, Z.-H.; Zhao, X.-M.; Song, B.; Zhu, X.; Hao, X.-Q. Synthesis of Achiral NCN Pincer Pt(II) and Pd(II) Complexes and Catalytic Application in the Suzuki-Miyaura Reaction. *J. Saudi Chem. Soc.* **2019**, *23*, 104−110.

(20) (a) Yang, F.-L.; Zhu, X.; Rao, D.-K.; Cao, X.-N.; Li, K.; Xu, Y.; Hao, X.-Q.; Song, M.-P. Highly Efficient Synthesis of Primary Amides via Aldoximes Rearrangement in Water under Air Atmosphere Catalyzed by An Ionic Ruthenium Pincer Complex. *RSC Adv.* **2016**, *6*, 37093−37098. (b) Yang, F.-L.; Wang, Y.-H.; Ni, Y.-F.; Gao, X.; Song, B.; Zhu, X.; Hao, X.-Q. An Efficient Homogenized Ruthenium-(II) Pincer Complex for N -Monoalkylation of Amines with Alcohols. *Eur. J. Org. Chem.* **2017**, *2017*, 3481−3486.

(21) Chakraborty, S.; Das, U. K.; Ben-David, Y.; Milstein, D. Manganese Catalyzed α-Olefination of Nitriles by Primary Alcohols. *J. Am. Chem. Soc.* **2017**, *139*, 11710−11713.

(22) Maciągiewicz, I.; Dybowski, P.; Skowrońska, A. A General and Stereoselective Method for Synthesis of Tri- and Tetrasubstituted Alkenes. *Tetrahedron* **2003**, *59*, 6057−6066.

(23) Heintz, K.; Imhof, W.; Görls, H. Microwave assisted synthesis of 3-(2,2′-bipyridine-4-yl)-2-propenoic acid ethyl ester. *Monatsh. Chem.* **2017**, *148*, 991−998.

(24) Tse, M. K.; Jiao, H.; Anilkumar, G.; Bitterlich, B.; Gelalcha, F. G.; Beller, M. Synthetic, Spectral and Catalytic Activity Studies of Ruthenium Bipyridine and Terpyridine Complexes: Implications in the Mechanism of the Ruthenium(pyridine-2,6-Bisoxazoline)-(Pyridine-2,6-Dicarboxylate)-Catalyzed Asymmetric Epoxidation of Olefins utilizing H_2O_2. *J. Organomet. Chem.* **2006**, *691*, 4419−4433.

(25) Ryan, P. E.; Guénée, L.; Piguet, C. Monitoring Helical Twists and Effective Molarities in Dinuclear Triple-stranded Lanthanide Helicates. *Dalton Trans.* **2013**, *42*, 11047−11055.

DOI: 10.1021/acs.organomet.9b00146
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