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Ruthenium-Catalyzed β-Alkylation of Secondary Alcohols and α-Alkylation of Ketones via Borrowing Hydrogen: Dramatic Influence of the Pendant *N*-Heterocycle

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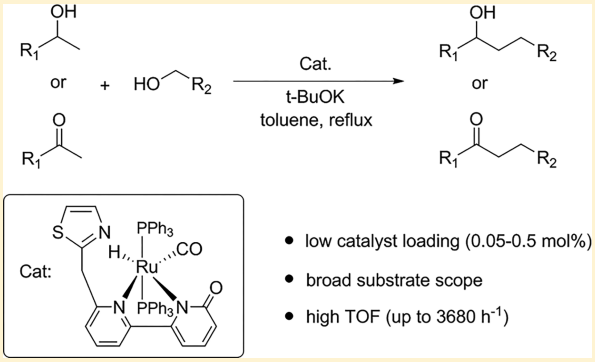
Supporting Information

ABSTRACT: Three bidentate ruthenium(II) complexes with a pyridonate fragment were prepared and fully characterized. These complexes are structurally similar, but differ in their pendant substituents. Complex **1** contains a phenyl unit, whereas complexes **2** and **3** have uncoordinated thienyl and thiazolyl groups, respectively. These complexes were tested as catalysts for β-alkylation of secondary alcohols with primary alcohols, and **3** shows the highest activity, suggesting the thiazolyl ring participates in the catalytic process. Furthermore, **3** is an excellent catalyst for α-alkylation of ketones with primary alcohols. Various α-alkylated ketones were synthesized in high yields, by using 0.05 mol % **3** and 0.25 equiv of *t*-BuOK within 30 min.



INTRODUCTION

Transition metal complexes with 2-hydroxypyridyl (2-HOPy) derivatives are a group of metal−ligand bifunctional catalysts.[1] 2-Hydroxypyridyl is easily deprotonated to its pyridonate form in the presence of a base, which can directly affect the first coordination sphere of the metal and thus the catalytic activity. Such complexes have been widely used for dehydrogenation,[2] (transfer) hydrogenation,[3] hydrofunctionalization,[4] and borrowing hydrogen reactions.[5]

The borrowing hydrogen methodology, also called hydrogen autotransfer, has been developed rapidly in recent years, because it is regarded as an environmentally friendly and an atom-ecomonic tactic.[5,6] For example, many β-alkylated secondary alcohols and α-alkylated ketones were synthesized by following this strategy, and H_2O was the only by-product.[7−21] Direct β-alkylation of secondary alcohols with primary alcohols has been applied under ruthenium,[5d,7] iridium,[8] palladium,[9] copper,[10] manganese,[11] and cobalt[12] catalysis or under transition metal-free conditions.[13] Similarly, various catalysts were also applicable for α-alkylation of ketones with primary alcohols.[5b,f,14−21] Currently, ruthenium complex **A** containing 6,6′-dihydroxy-2,2′-bipyridine is the most effective catalyst for β-alkylation of secondary alcohols, which was reported by Kundu et al, showing TOFs up to 797.6 h^{-1} (Figure 1, **A**).[5d] While for α-alkylation of ketones, the most active catalyst is an iridium *N*-heterocyclic carbene complex developed by Gülcemal's group, revealing TOF values up to 970 h^{-1} (Figure 1, **B**).[19a]

Recently, our group reported ruthenium hydride complex **C** (Figure 1, **C**), based on the NNN ligand with a 2-hydroxypyridyl fragment, for β-alkylation of secondary alcohols with primary alcohols.[22] There is a pendant pyridyl group existing in complex **C**. To investigate the influence of this uncoordinated pyridyl group, and as a part of our interest in developing bifunctional catalysts with a 2-hydroxypyridyl moiety,[23] herein we report the synthesis and catalytic activity of three ruthenium pyridonate complexes (**1**−**3**). When used as the catalyst for α-alkylation of ketones, complex **3** shows TOF values up to 3680 h^{-1} (Figure 1, **3**).

RESULTS AND DISCUSSION

Synthesis and Characterization of Ru Complexes. To explore if the pendant pyridyl group in complex **C** participates in the catalytic cycle (Figure 1, **C**),[22] we first replaced the uncoordinated pyridyl of its ligand by a phenyl group, and synthesized a ligand precursor [HO−C_5H_3N−C_5H_3N−CH_2−C_6H_5] (**L_1**) (Scheme S1 in Supporting Information). Reaction of **L_1** with $RuHCl(PPh_3)_3(CO)$ in refluxing methanol generated a yellow product, [(O−C_5H_3N−C_5H_3N−CH_2−C_6H_5)$RuH(PPh_3)_2(CO)$] (**1**) in 82% yield (Scheme 1).

The ^1H NMR spectrum of **1** in $CDCl_3$ at room temperature exhibits six groups of signals between 7.52 and 6.02 ppm for the pyridyl, phenyl, and PPh_3 groups (41H), one singlet at 3.79

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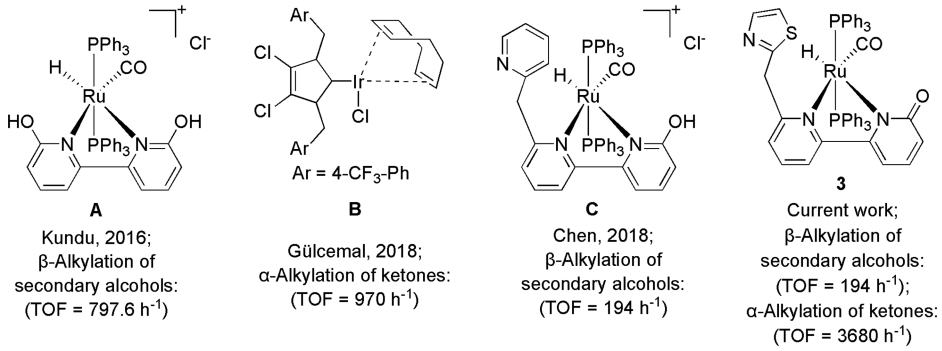
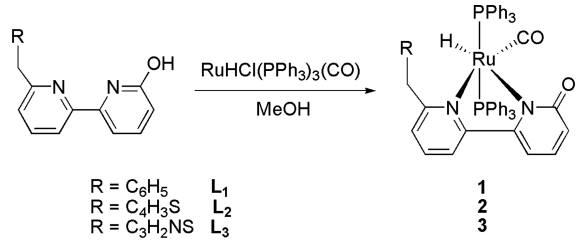


Figure 1. Examples for β-alkylation of secondary alcohols and α-alkylation of ketones.

Scheme 1. Synthesis of Complexes 1−3



ppm for the $-CH_2-$ group (2H), and one triplet at −11.00 ppm for the Ru−H (1H). The ^{31}P NMR shows one singlet for the two PPh_3 groups at 48.00 ppm. The IR displays one strong absorption peak at 1945 cm^{-1} (in KBr) for the terminal CO. The results indicate there are two *trans*-PPh_3, one CO, one hydride, and two pyridyl rings of ligand $\mathbf{L_1}$ coordinating with Ru.

Two similar ligand precusors $[HO-C_5H_3N-C_5H_3N-CH_2-C_4H_3S]$ ($\mathbf{L_2}$) and $[HO\text{-}C_5H_3N-C_5H_3N-CH_2-C_3H_2NS]$ ($\mathbf{L_3}$) were also synthesized (Schemes S2 and S3), and treated with $RuHCl(PPh_3)_3(CO)$ in refluxing methanol. Two bidentate ruthenium products $[(O-C_5H_3N-C_5H_3N-CH_2-C_4H_3S)RuH(PPh_3)_2(CO)]$ (**2**) and $[(O-C_5H_3N-C_5H_3N-CH_2-C_3H_2NS)RuH(PPh_3)_2(CO)]$ (**3**) were formed, respectively (Scheme 1).

Each of the ^1H NMR spectra of **2** and **3** in $CDCl_3$ at room temperature exhibits one singlet for the $-CH_2-$ group (3.90 ppm for **2**; 4.37 ppm for **3**), and one triplet for the Ru−H group (−11.11 ppm for **2**; −11.12 ppm for **3**), similar to those of complex **1**. Their ^{31}P chemical shifts in NMR spectra (47.20 ppm for **2**; 47.93 ppm for **3**) and CO absorption band in IR spectra (1946 cm^{-1} for **2** and 1941 cm^{-1} for **3**) are also comparable to those of **1**. These results suggest they have similar structures.

Complexes **2** and **3** were further identified by X-ray crystallography (Figure 2 and 3). The Ru ion in complex **2** is coordinated in an octahedral geometry. Ligand $\mathbf{L_2}$ coordinates with the Ru atom via its bipyridyl N atoms. The CO ligand is *trans* to the pyridyl ring, and the hydride is *trans* to the pyridonate group. The two PPh_3 groups are in *trans* positions. The C(1)−C(2) distance is 1.434(5) Å, obviously longer than other C−C bonds in the same pyridonate ring, suggesting it has some character as a single bond. The C(1)−O(1) distance (1.251(5) Å) is in the range of a C=O bond.[3d]

Similar to that of complex **2**, the C(1)−C(2) bond in complex **3** is 1.436(3) Å, also much longer than other C−C bonds in the same heterocyclic ring, and the C(1)−O(1) distance (1.259(3) Å) is also in the range of a C=O bond,

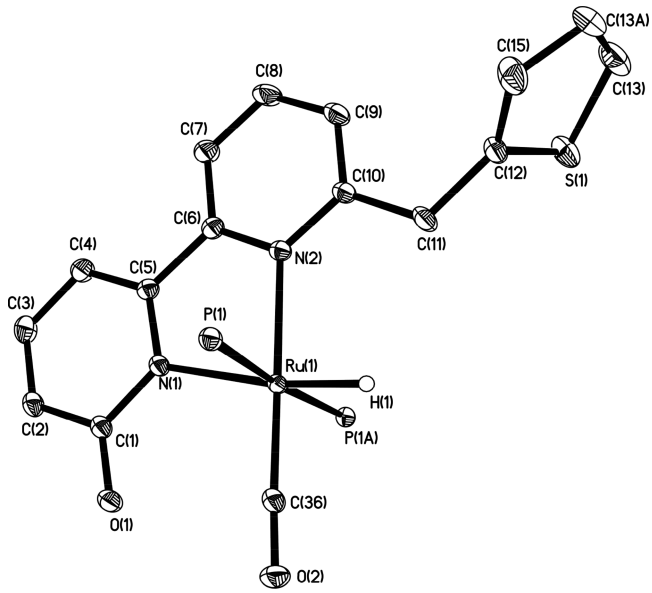


Figure 2. Molecular structure of complex **2**. The thermal ellipsoids are displayed at 30% probability. Hydrogen atoms (except Ru−H), and phenyl rings on PPh_3 ligands have been omitted for clarity. Selected bond distances (Å): Ru(1)−N(1), 2.186(3); Ru(1)−N(2), 2.195(3); Ru(1)−P(1), 2.3614(7); Ru(1)−H(1), 1.509(4); C(1)−N(1), 1.382(4); C(5)−N(1), 1.361(5); C(1)−O(1), 1.251(5). C(1)−C(2), 1.434(5); C(2)−C(3), 1.355(6); C(3)−C(4), 1.400(5); C(4)−C(5), 1.382(5).

suggesting the 2-hydroxypyridyl ring was converted to a pyridonate. It is worth noting that the procedures for synthesizing complexes **1**−**3** are similar to that for complex **C** shown in Figure 1; however, their structures are different. **1**−**3** are neutral complexes with a pyridonate ring, while **C** is a cationic complex with a 2-hydroxypyridyl group. The difference might be caused by the different basicity of the pendant aromatic groups. The uncoordinated pyridyl group in **C** is more basic than phenyl, thienyl, and thiazolyl rings; thus, it might be easier to attract the HCl molecule, so that the ionic form is more stable.

***β*-Alkylation of Secondary Alcohols with Primary Alcohols.** Initially, the coupling of 1-phenylethanol and benzyl alcohol was selected as a model reaction to test the catalytic activity of complexes **1**−**3**. The reactions were conducted in toluene at 110 °C for 60 min. Ruthenium complexes (0.5 mol %) were used as the precatalysts and *t*-BuOK (0.5 equiv) as the base under a N_2 atmosphere, and the results are shown in Table 1. It can be seen that the activity of complex **1** was much

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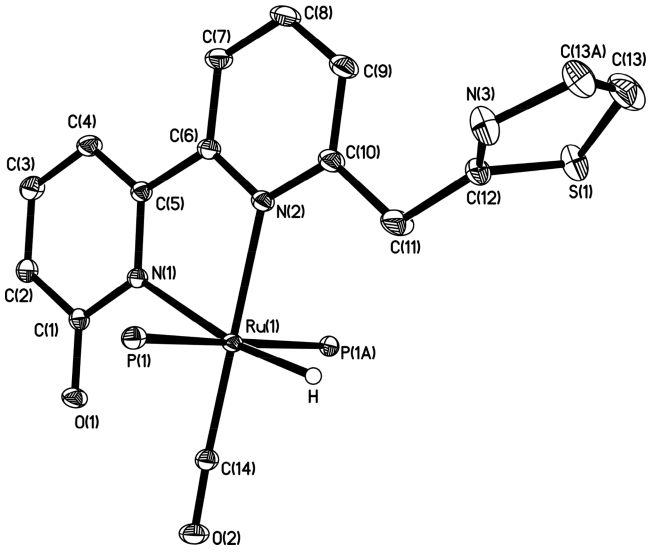


Figure 3. Molecular structure of complex **3**. The thermal ellipsoids are displayed at 30% probability. Hydrogen atoms (except Ru−H), and phenyl rings on PPh_3 ligands have been omitted for clarity. Selected bond distances (Å): Ru(1)−N(1), 2.176(2); Ru(1)−N(2), 2.195(2); Ru(1)−P(1), 2.3643(5); Ru(1)−H, 1.60(4); C(1)−N(1), 1.381(3); C(5)−N(1), 1.360(3); C(1)−O(1), 1.259(3). C(1)−C(2), 1.436(3); C(2)−C(3), 1.362(4); C(3)−C(4), 1.401(4); C(4)−C(5), 1.380(3).

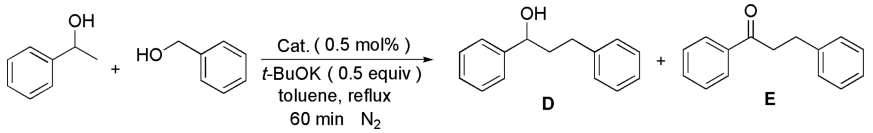
lower than that of complex **C** (entries 1 and 2), suggesting the pyridyl ring of **C** plays a very important role. When complex **2** was used, the conversion was 62% within 60 min, comparable to that of **1** (entry 3). Interestingly, complex **3** also exhibited as high efficiency as **C**, reaching 95% conversion in 60 min (entry 4). These results indicate the pendant *N*-heterocycle rings increase the catalytic activity dramatically, probably due to their participation in the catalytic cycle with the substrates. In fact, this phenomenon is not unusual, because several reactions that the rates could be accelerated by pendant bases have been reported.[24] For example, Beller et al. found the hemilabile pyridyl groups could accelerate the methoxycarbonylation of olefins.[24b] Albrecht's group developed an iridium complex with a pendant pyridyl group, which could act as Lewis base for the stabilization of substrates through hydrogen bonding during oxidative coupling of benzylic amines.[24c] Bera and co-workers synthesized a ruthenium complex for alcohol oxidation, and the uncoordinated pyridyl of the naphthyridine played an important role.[24d]

Subsequently, different bases were tested to optimize the reaction conditions. The results are shown in Table 2. Weak bases gave low conversion during the tested period (entries 1−3). Strong bases such as KOH, NaOH, and *t*-BuOK significantly increased the conversion, and *t*-BuOK was the best (entries 4−6). To optimize the quantity of *t*-BuOK, different amounts were also tested, and 0.5 equiv was optimal (entries 6−10). The reaction could not occur in the absence of a base or catalyst (entries 11 and 12). Thus, the optimized reaction conditions were selected as entry 6 in Table 2, and *β*-alkylation of 1-phenylethanol and its derivatives with a variety of primary alcohols was then performed.

As shown in Table 3, a series of substrates are applicable. When *ortho*-chlorobenzyl alcohol was used as the alkylation reagent with 1-phenylethanol, the conversion and selectivity were lower, compared with those of *meta*-chlorobenzyl alcohol. It might be caused by a steric hindrance effect (entries 1 and 2). Other substituents in *meta* or/and *para* position(s) of benzyl alcohol, either electron-withdrawing or -donating, do not influence the reaction obviously, giving conversions exceeding 90% with satisfied selectivity (entries 3−6). 2-Hydroxymethylnaphthalene is also suitable for this reaction, reaching a conversion of 95%, with a ratio of **D**/**E** as 98:2 (entry 7). An electron-withdrawing group, at the *para* position of 1-phenylethanol, does not obviously influence the reaction, while an electron-donating group, such as methoxyl group, decreases the activity, especially the selectivity, dramatically (entries 8 and 9). Cyclohexylmethanol and 1-butanol can also react with 1-phenylethanol, generating corresponding products in 80 and 81% yields, respectively, with satisfied selectivity (entries 10 and 11).

α-Alkylation of Ketones with Primary Alcohols. *α*-Alkylation of ketones has a similar mechanism as *β*-alkylation of secondary alcohols with primary alcohols. We then tested the catalytic activity of **3** for the reaction of acetophenone and benzyl alcohol. The optimized condition was established as following: **3** (0.05 mol %), *t*-BuOK (0.25 equiv), and 30 min in refluxing toluene (Table 4). Nineteen alkylated ketones were synthesized in the optimized condition, with isolated yields in the range of 60−92%. Whether there is electron-withdrawing or -donating group in benzyl alcohol, the corresponding products could be isolated in high yields (entries 1−10). Especially for *para*-methoxybenzyl alcohol, the product was separated in 92% yield, with a TOF value as 3680 h^{-1} (entry 7). 2-Hydroxymethylnaphthalene also gave an isolated yield as high as 91% (entry 11). Substituted acetophenones were also explored, and except for 1-(4-fluorophenyl)-3-phenylpropan-1-

Table 1. *β*-Alkylation of 1-Phenylethanol with Benzyl Alcohol Using Ru Complexes C and 1−3[a]



entry	catalyst	conversion[b]	D/E ratio[c]
1[d]	**C**	94	95:5
2	**1**	61	83:17
3	**2**	62	89:11
4	**3**	95	95:5

[a]Reaction conditions: catalyst (0.5 mol %), 1-phenylethanol (2.0 mmol), benzyl alcohol (2.0 mmol) and *t*-BuOK (1 mmol) in reflux condition in toluene for 60 min under N_2 atmosphere. [b]Determined by GC analysis based on secondary alcohol. [c]Determined by GC analysis. [d]Data from ref 22.

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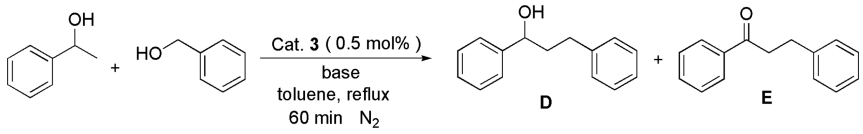
Table 2. β-Alkylation of 1-Phenylethanol with Benzyl Alcohol in the Presence of Different Bases[a]



entry	base [equiv]	conversion [%][b]
1	Na_2CO_3 (0.5 equiv)	4
2	K_2CO_3 (0.5 equiv)	4
3	Cs_2CO_3 (0.5equiv)	8
4	KOH (0.5 equiv)	74
5	NaOH (0.5 equiv)	60
6	*t*-BuOK (0.5 equiv)	95
7	*t*-BuOK (0.4 equiv)	81
8	*t*-BuOK (0.3 equiv)	74
9	*t*-BuOK (0.2 equiv)	62
10	*t*-BuOK (0.1 equiv)	46
11	no base	0
12[c]	*t*-BuOK (0.5 equiv)	0

[a]Reaction conditions: catalyst **3** (0.5 mol %), 1-phenylethanol (2.0 mmol), benzyl alcohol (2.0 mmol), and base in reflux condition in toluene for 60 min under N_2 atmosphere. [b]Determined by GC analysis based on secondary alcohol. [c]No catalyst.

one, other products were isolated in yields higher than 80% (entries 12−15). Other aliphatic alcohols, such as 4-phenyl-1-butanol, cyclohexylmethanol, and 1-butanol, gave corresponding ketones in yields at 66−75% (entries 16−18). The secondary alcohol, 1-phenylethanol, exhibits lower activity, reaching a yield of 60% after 2 h (entry 19). To the best of our knowledge, complex **3** is currently the best catalyst for α-alkylation of ketones, about 4 times as efficient as Gülcemal's iridium complex.[19a]

Reaction Mechanisms. The proposed mechanism for β-alkylation of secondary alcohols with primary alcohols catalyzed by **3**, is shown in Scheme 2. **3** first loses one molecule of PPh_3, to form active intermediate **F** with an open site. Then, the primary and secondary alcohols are both dehydrogenated to corresponding aldehyde and ketone, respectively, releasing two molecules of H_2, and one molecule is absorbed by **F**, transformed to dihydride Ru(II) species **G**. Cross-aldol condensation reaction then occurs between aldehyde and ketone, generating an α,β-unsaturated ketone, which then cooperates with **G** and H_2 to form the final product. The mechanism of α-alkylation of ketones is similar, and the primary alcohol is needed to be oxidized to corresponding aldehyde, with the released H_2 accepted by **F** to afford **G**. The difference is that in this step no extra H_2 is released.

CONCLUSIONS

In summary, three bidentate bifunctional ruthenium complexes, **1**−**3**, with a pridonate fragment were synthesized. These complexes were tested as catalysts for β-alkylation of secondary alcohols, by using primary alcohols as alkylated reagents. Complex **3** with a pendant thiazolyl group shows highest activity, suggesting the uncoordinated *N*-heterocycle interacts with the substrates in the catalytic cycle, which is important for designing new catalysts for such kind of reaction. Complex **3** was further treated as catalyst for α-alkylation of ketones with primary alcohols, revealing exceptionally high TOF values (up to 3680 h^{-1}). To the best of our knowledge, it is the most active catalyst for such transformation reported up to date.

EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out under an inert nitrogen atmosphere using a Schlenk line. Solvents were distilled from appropriate drying agents under N_2 before use. All reagents were purchased from commercial sources. Liquid compounds were degassed by standard freeze−pump−thaw procedures prior to use. $RuHCl(PPh_3)_3(CO)$,[25] ethyl 6′-methoxy-[2,2′-bipyridine]-6-carboxylate,[23c] 6-bromo-6′-methoxy-2,2′-bipyridine,[26] and benzylzinc bromide[27] were prepared as previously described, respectively. The ^1H and ^{31}P NMR spectra were recorded on a Bruker Avance 400 spectrometer. The ^1H NMR chemical shifts were referenced to residual solvent as determined relative to Me_4Si (δ = 0 ppm). The $^{31}P\{^1H\}$ chemical shifts were reported in ppm relative to external 85% H_3PO_4. The $^{13}C\{^1H\}$ chemical shifts were reported in ppm relative to the carbon resonance of $CDCl_3$ (77.0 ppm). Elemental analyses were performed on a PerkinElmer 240C analyzer. The high-resolution mass spectrum (HR-MS) was recorded on a Varian 7.0 T FTICR-MS by the ESI technique. IR spectra were recorded on a Nicolet iS5 FT-IR spectrometer. X-ray diffraction studies were carried out in a SuperNova X-ray single crystal diffractometer or a Bruker D8 Quest X-ray diffractometer. Data collections were performed using four-circle kappa diffractometers equipped with CCD detectors. Data were reduced and then corrected for absorption. Solution, refinement, and geometrical calculations for all crystal structures were performed by SHELXTL. All of the GC measurements were performed on Agilent GC7890A equipment using an Agilent 19091B-102 (25 m, 220 μm) column.

Synthesis of 6-Benzyl-6′-methoxy-2,2′-bipyridine. $Pd(PPh_3)_4$ (0.46 g, 0.40 mmol) and 6-bromo-6′-methoxy-2,2′-bipyridine (2.12 g, 8.00 mmol) were added into benzylzinc bromide (1.98 g, 8.40 mmol) in THF at refluxing overnight. The crude product was purified by column chromatography on silica gel to give the product as a white solid (0.91 g, 41%). Mp: 118 °C. HRMS for $C_{18}H_{16}N_2O$ + H, 277.1341. Found, 277.1343. ^1H NMR (400 MHz, $CDCl_3$, ppm): 8.23 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 7.6 Hz, 1H), 7.72−7.67 (m, 2H), 7.35−7.30 (m, 4H), 7.25−7.21 (m, 1H), 7.08 (d, J = 7.6 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H). 4.25 (s, 2H), 4.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 163.4, 160.2, 155.5, 153.7, 139.7, 139.4, 137.1, 129.2, 128.5, 126.3, 122.9, 118.4, 113.9, 110.9, 99.9, 53.1, 44.8.

Synthesis of L_1: 6′-Benzyl-[2,2′-bipyridin]-6-ol. A solution of 6-benzyl-6′-methoxy-2,2′-bipyridine (0.50 g, 1.81 mmol) in 8 mL of HBr (40% in water) was heated at reflux for 3 h. After cooling to room temperature, the yellow solution was neutralized by slow addition of a saturated aqueous solution of NaOH. The aqueous

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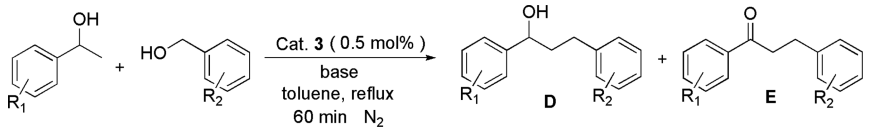
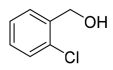
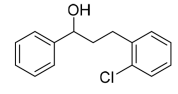
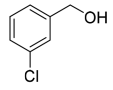
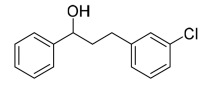
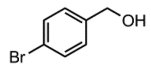
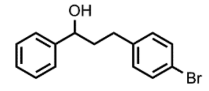
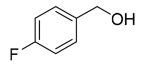
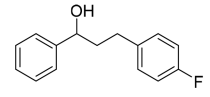
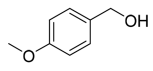
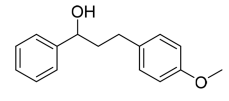
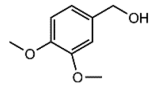
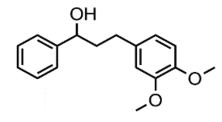
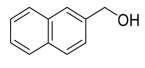
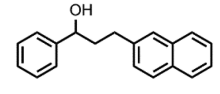
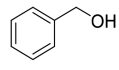
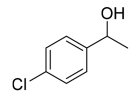
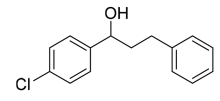
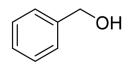
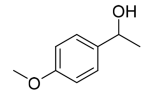
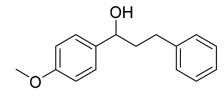
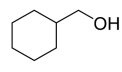
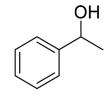
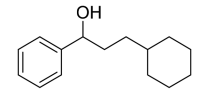
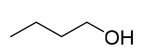
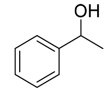
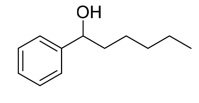
Table 3. β-Alkylation of 1-Phenylethanol and Benzyl Alcohol with Diverse Substitutions[a]



Entry	Primary	Secondary	Product	Conv.[%][b]	D/E Ratio[c]
1				85	75:25
2				96	98:2
3				94	99:1
4				97	98:2
5				93	98:2
6				95	98:2
7				95	98:2
8				90	90:10
9				86	65:35
10				80	90:10
11				81	95:5

[a]Reaction conditions: catalyst **3** (0.5 mol %), 1-phenylethanol (2.0 mmol), benzyl alcohol (2.0 mmol), and *t*-BuOK (1 mmol) under reflux condition in toluene for 60 min under N_2 atmosphere. [b]Determined by GC analysis based on secondary alcohol. [c]Determined by GC analysis.

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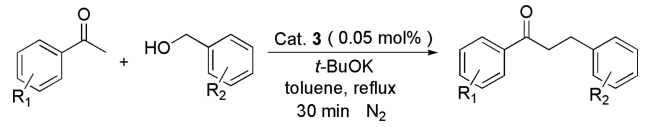
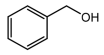
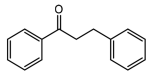
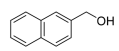
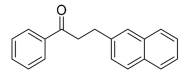
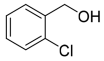
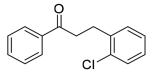
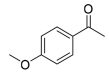
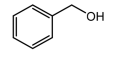
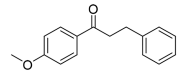
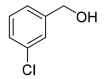
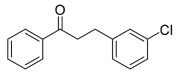
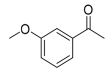
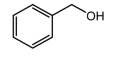
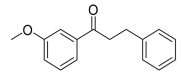
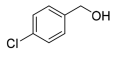
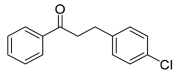
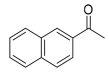
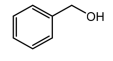
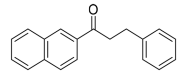
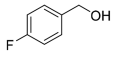
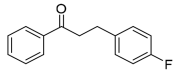
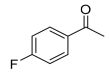
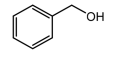
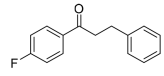
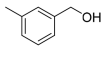
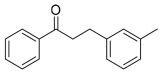
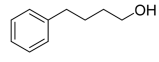
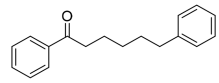
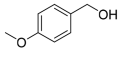
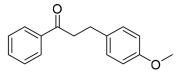
Organometallics XXXX, XXX, XXX−XXX

Table 4. Scope of α-Alkylation of Ketones with Primary Alcohols Catalyzed by Complex 3[a]



Entry	Ketone	Primary Alcohol	Product	Yield[b]	Entry	Ketone	Primary Alcohol	Product	Yield[b]
1				90	11				91
2				85	12				85
3				81	13				80
4				80	14				88
5				90	15				75
6				76	16				75
7				92	17				70
8				80	18				66
9				84	19[c]				60
10				89					

[a]Reaction conditions: catalyst **3** (0.05 mol %), ketone (1.0 mmol), primary alcohol (1.0 mmol), and *t*-BuOK (0.25 mmol) under reflux condition in toluene for 30 min under N_2 atmosphere. [b]Isolated yields. [c]Using 2 h of reflux.

solution was extracted with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated to afford the product as a pale yellow solid (0.4 g, 85%). Mp: 146 °C. HRMS for $C_{17}H_{14}N_2O$ + H, 263.1184. Found, 263.1186. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 10.75 (s, 1H), 7.72−7.63 (m, 2H), 7.50−7.46 (m, 1H), 7.34−7.28 (m, 4H), 7.24−7.22 (m, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 6.79 (d, *J* = 6.8 Hz, 1H), 6.64 (d, *J* = 8.8 Hz, 1H), 4.19 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 162.7, 161.0, 147.1, 141.8, 140.6, 138.7, 137.9, 129.1, 128.8, 126.7, 124.1, 122.0, 117.3, 102.8, 44.5, 29.7.

Synthesis of (6′-Methoxy-[2,2′-bipyridin]-6-yl)(thiophen-2-yl)methanone. Thiophene (0.32 g, 3.85 mmol) in 15 mL of THF was added drop by drop to a solution of *n*-BuLi (1.60 mL, 2.4 M, 3.85 mmol) at −78 °C. After 60 min of stirring at −78 °C, ethyl 6′-methoxy-[2,2′-bipyridine]-6-carboxylate (1.0 g, 3.85 mmol) was added. The mixture was further stirred at −20 °C for 2.5 h. The solution was quenched with dilute HCl (1.0 M) and then neutralized with a solution of NaOH. The mixture was extracted with ethyl acetate, and the solvent was concentrated. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, v/v = 10:1) to give the product as a white solid (0.75 g, 66%). Mp: 100 °C. HRMS for $C_{16}H_{12}N_2O_2S$ + H, 297.0698. Found, 297.0699. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.64 (d, *J* = 8.0 Hz, 1H), 8.42 (d, *J* = 4.0 Hz, 1H), 8.25 (d, *J* = 7.6 Hz, 1H), 8.21 (d, *J* = 7.6 Hz, 1H), 8.00 (t, *J* = 8.0 Hz, 1H), 7.81−7.77 (m, 2H), 7.23 (t, *J* = 4.4 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 4.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 183.3, 163.6, 155.4, 153.2, 152.7, 139.6, 138.9, 138.0, 136.6, 136.5, 127.4, 124.2, 123.6, 114.6, 111.7, 53.3.

Synthesis of 6-Methoxy-6′-(thiophen-2-ylmethyl)-2,2′-bipyridine. To a solution of (6′-methoxy-[2,2′-bipyridin]-6-yl)-

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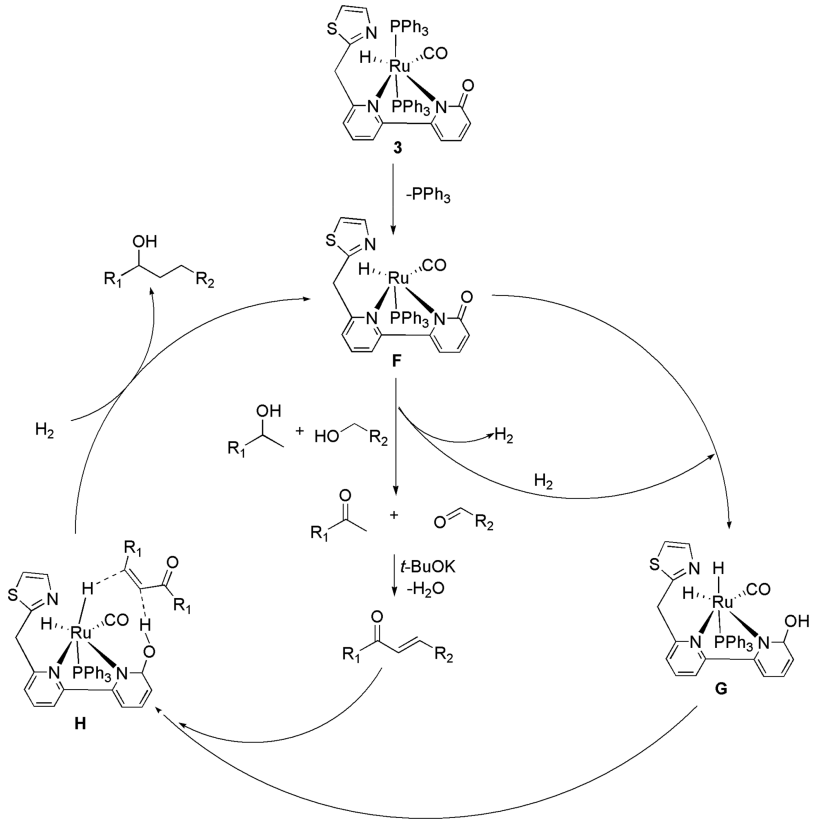
Scheme 2. Proposed Reaction Mechanism



(thiophen-2-yl)methanone (0.5 g, 1.69 mmol) in 10 mL of ethylene glycol was added NaOH (0.75 g) and NH_2NH_2 (10.0 mL, 80% in water). The mixture was heated at 100 °C for 5 h. Water (10 mL) was added and the solution was neutralized by dilute HCl (1.0 M) and extracted with ethyl acetate. The organic phase was dried over Na_2SO_4 and evaporated under vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, v/v = 20:1) to give the product as a white solid (0.3 g, 63%). Mp: 80 °C. HRMS for $C_{16}H_{14}N_2OS$ + H, 283.0905. Found, 283.0908. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.26 (d, J = 7.6 Hz, 1H), 8.14 (d, J = 7.6 Hz, 1H), 7.72 (q, J = 7.6 Hz, 2H), 7.20−7.18 (m, 2H), 6.97−6.95 (m, 2H), 6.78 (d, J = 8.4 Hz, 1H), 4.43 (s, 2H), 4.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 162.4, 158.1, 154.5, 152.5, 140.8, 138.3, 136.3, 125.7, 124.6, 123.4, 121.4, 117.6, 112.9, 109.9, 52.1, 37.8.

Synthesis of L_2: 6′-(Thiophen-2-ylmethyl)-[2,2′-bipyridin]-6-ol. A solution of 6-methoxy-6′-(thiophen-2-ylmethyl)-2,2′-bipyridine (0.30 g, 1.06 mmol) in 5 mL of HBr (40% in water) was heated at reflux for 3 h. After cooling to room temperature, the brown solution was neutralized by slow addition of a saturated aqueous solution of NaOH. The aqueous solution was extracted with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated to afford the product as a yellow solid (0.25 g, 89%). Mp: 138 °C. HRMS for $C_{15}H_{12}N_2OS$ + H, 269.0749. Found, 269.0753. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 11.05 (s, 1H), 7.77−7.68 (m, 2H), 7.56−7.52 (m, 1H), 7.28 (s, 1H), 7.20 (dd, J = 5.2, 1.2 Hz, 1H), 6.97−6.87 (m, 3H), 6.69 (d, J = 9.2 Hz, 1H), 4.40 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 161.9, 158.9, 146.2, 140.7, 139.7, 139.5, 137.1, 126.0, 125.0, 123.8, 122.7, 121.0, 116.6, 102.1, 37.5.

Synthesis of (6′-Methoxy-[2,2′-bipyridin]-6-yl)(thiazol-2-yl)-methanone. 2-Bromothiazole (0.63 g, 3.85 mmol) in 15 mL THF was added drop by drop to a solution of *n*-BuLi (1.60 mL, 2.4 M, 3.85 mmol) at −78 °C. After 60 min of stirring at −78 °C, ethyl 6′-methoxy-[2,2′-bipyridine]-6-carboxylate (1.0 g, 3.85 mmol) was added. The mixture was further stirred at −20 °C for 2.5 h. The solution was quenched with dilute HCl (1.0 M) and then neutralized with a solution of NaOH. The mixture was extracted with ethyl acetate, and the solvent was concentrated. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, v/v = 1:1) to give the product as a yellow solid (0.80 g, 70%). Mp: 120 °C. HRMS for $C_{15}H_{11}N_3O_2S$ + H, 298.0650. Found, 298.0655. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.69 (d, J = 3.6 Hz, 1H), 8.33 (d, J = 7.6 Hz, 1H), 8.24−8.21 (m, 2H), 8.05 (t, J = 7.6 Hz, 1H), 7.83 (d, J = 3.2 Hz, 1H), 7.79 (t, J = 7.6 Hz, 1H), 6.85 (d, J = 8.0 Hz, 1H), 4.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 180.7, 163.7, 159.7, 155.8, 152.3, 151.9, 144.8, 139.6, 138.2, 127.6, 125.1, 124.3, 114.8, 111.9, 53.4.

Synthesis of 2-((6′-Methoxy-[2,2′-bipyridin]-6-yl)methyl)-thiazole. To a solution of (6′-methoxy-[2,2′-bipyridin]-6-yl)-(thiazol-2-yl)methanone (0.5 g, 1.68 mmol) in 10 mL of ethylene glycol was added NaOH (0.75 g) and NH_2NH_2 (10.0 mL, 80% in water). The mixture was heated at 100 °C for 5 h. Water (10 mL) was added, and the solution was neutralized by dilute HCl (1.0 M) and extracted with ethyl acetate. The organic phase was dried over Na_2SO_4 and evaporated under vacuum. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, v/v = 2:1) to give the product as an orange oil liquid (0.35 g, 74%). HRMS for $C_{15}H_{13}N_3OS$ + H, 284.0858. Found, 284.0860. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.32 (d, J = 7.6 Hz, 1H), 8.14 (d, J = 7.6 Hz, 1H), 7.78−7.70 (m, 3H), 7.30 (d, J = 7.6 Hz, 1H), 7.26 (d, J = 3.2 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 4.63 (s, 2H), 4.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): 168.0, 163.5, 156.6, 155.9, 153.3, 142.1, 139.3, 137.5, 123.0, 119.5, 119.2, 114.0, 110.9, 53.1, 42.1.

Synthesis of L_3: 6′-(Thiazol-2-ylmethyl)-[2,2′-bipyridin]-6-ol. A solution of 2-((6′-methoxy-[2,2′-bipyridin]-6-yl)methyl)-thiazole (0.30 g, 1.06 mmol) in 5 mL of HBr (40% in water) was heated at reflux for 3 h. After cooling to room temperature, the brown solution was neutralized by slow addition of a saturated aqueous solution of NaOH. The aqueous solution was extracted with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated to afford the product as a brown solid (0.24 g, 86%).

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Mp: 135 °C. HRMS for $C_{14}H_{11}N_3OS$ + H, 270.0701. Found, 270.0702. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 10.69 (s, 1H), 7.81−7.71 (m, 3H), 7.49 (t, J = 8.0 Hz, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.28 (d, J = 3.2 Hz, 1H), 6.81 (d, J = 6.8 Hz, 1H), 6.64 (d, J = 9.2 Hz, 1H), 4.59 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 166.5, 162.7, 157.3, 147.5, 142.6, 141.5, 140.5, 138.3, 124.3, 122.3, 119.6, 118.0, 103.0, 41.7.

Synthesis of 1. A solution of $\mathbf{L_1}$ (0.17 g, 0.63 mmol) and $RuHCl(PPh_3)_3(CO)$ (0.58 g, 0.63 mmol) was heated in refluxing methanol (200 mL) for 24 h. The mixture was allowed to cool to room temperature, and the organic phase was evaporated under vacuum. The crude product was recrystallized with dichloromethane/*n*-hexane to give **1** as a yellow powder (0.48 g, 82%). Single crystals suitable for X-ray crystallographic determination were grown with CH_2Cl_2/CH_3OH/*n*-hexane at ambient temperature. Mp: 145 °C. Anal. Calcd for $C_{54}H_{44}N_2P_2O_2Ru$: C, 70.81; H, 4.84; N, 3.06. Found: C, 70.92; H, 4.82; N, 3.00. IR (ν_{CO}, KBr, cm^{-1}): 1945 (s). IR (ν_{Ru-H}, KBr, cm^{-1}): 1911 (s). ^{1}H NMR (500 MHz, $CDCl_3$, ppm, r.t.): 7.52−7.49 (m, 13H), 7.33 (br s, 1H), 7.29−7.28 (m, 4H), 7.21−7.13 (m, 17H), 6.90 (br s, 1H), 6.36−6.31 (m, 2H), 6.05−6.02 (m, 3H), 3.79 (s, 2H), −11.00 (t, J = 19.5 Hz, 1H). ^{1}H NMR (400 MHz, $CDCl_3$, ppm, −50 °C): 8.11 (s, 1H), 7.52−7.28 (m, 16H), 7.24−7.09 (m, 18H), 6.90 (t, J = 7.6 Hz, 1H), 6.42 (d, J = 8.4 Hz, 1H), 6.28 (d, J = 7.2 Hz, 1H), 5.96 (d, J = 8.0 Hz, 1H), 5.81 (d, J = 7.2 Hz, 2H), 3.60 (s, 2H), −10.87 (t, J = 19.6 Hz, 1H). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): 48.00. ^{13}C NMR (100 MHz, $CDCl_3$): 206.0 (CO), 163.7, 151.7, 137.6, 136.1, 134.7, 134.5, 134.0, 133.9, 133.9, 133.8, 133.8, 133.7, 133.5, 133.3, 133.1, 130.1, 129.9, 129.3, 129.1, 128.5, 128.4, 128.0, 127.9, 127.8, 126.6, 122.9, 119.5, 105.8, 65.9, 53.5, 50.6, 49.3 (CH_2).

Synthesis of 2. A solution of $\mathbf{L_2}$ (0.17 g, 0.63 mmol) and $RuHCl(PPh_3)_3(CO)$ (0.58 g, 0.63 mmol) was heated in refluxing methanol (200 mL) for 24 h. The mixture was allowed to cool to room temperature, and the organic phase was evaporated under vacuum. The crude product was recrystallized with dichloromethane/*n*-hexane to give **2** as a yellow powder (0.48 g, 83%). Single crystals suitable for X-ray crystallographic determination were grown with CH_2Cl_2/CH_3OH/*n*-hexane at ambient temperature. Mp: 220 °C. Anal. Calcd for $C_{52}H_{42}N_2O_2P_2RuS$: C, 67.74; H, 4.59; N, 3.04. Found: C, 67.45; H, 4.62; N, 2.97. IR (ν_{CO}, KBr, cm^{-1}): 1946 (s). IR (ν_{Ru-H}, KBr, cm^{-1}): 1912 (s). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 7.49 (br s, 13H), 7.37−7.36 (m, 2H), 7.28−7.27 (m, 5H), 7.21−7.18 (m, 13H), 7.12 (d, J = 5.0 Hz, 1H), 6.90−6.85 (m, 1H), 6.34 (d, J = 5.5 Hz, 2H), 6.19 (d, J = 7.0 Hz, 1H), 5.92 (s, 1H), 3.90 (s, 2H), −11.11 (t, J = 20 Hz, 1H). ^{1}H NMR (400 MHz, $CDCl_3$, ppm, −50 °C): 8.12 (s, 1H), 7.55−7.28 (m, 17H), 7.20−7.11 (m, 15H), 6.92 (t, J = 7.6 Hz, 1H), 6.83 (t, J = 3.6 Hz, 1H), 6.42 (d, J = 8.4 Hz, 1H), 6.32 (d, J = 7.2 Hz, 1H), 6.13 (d, J = 6.8 Hz, 1H), 5.73 (d, J = 2.4 Hz, 1H), 3.71 (s, 2H), −10.97 (t, J = 20.0 Hz, 1H). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): 47.20.

Synthesis of 3. A solution of $\mathbf{L_3}$ (0.17 g, 0.63 mmol) and $RuHCl(PPh_3)_3(CO)$ (0.58 g, 0.63 mmol) was heated in refluxing methanol (200 mL) for 24 h. The mixture was allowed to cool to room temperature, and the organic phase was evaporated under vacuum. The crude product was recrystallized with dichloromethane/*n*-hexane to give **3** as a yellow powder (0.48 g, 83%). Single crystals suitable for X-ray crystallographic determination were grown with CH_2Cl_2/CH_3OH/*n*-hexane at ambient temperature. Mp: 180 °C. Anal. Calcd for $C_{51}H_{41}N_3O_2P_2RuS$: C, 66.37; H, 4.48; N, 4.55. Found: C, 66.61; H, 4.51; N, 4.56. IR (ν_{CO}, KBr, cm^{-1}): 1941 (s). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 7.61 (d, J = 3.0 Hz, 1H), 7.56−7.52 (m, 12H), 7.28−7.23 (m, 8H), 7.19−7.16 (m, 12H), 7.11 (d, J = 3.0 Hz, 1H), 6.91 (t, J = 7.0 Hz, 1H), 6.37 (s, 2H), 6.25 (d, J = 6.0 Hz, 1H), 4.37 (s, 2H), −11.19 (t, J = 19.5 Hz, 1H). ^{1}H NMR (400 MHz, $CDCl_3$, ppm, −50 °C): 7.60−7.30 (m, 15H), 7.26−6.89 (m, 20H), 6.43 (d, J = 8.4 Hz, 1H), 6.32 (d, J = 6.4 Hz, 1H), 6.22 (d, J = 6.8 Hz, 1H), 4.22 (s, 2H), −11.05 (t, J = 19.6 Hz, 1H). ^{31}P NMR (162 MHz, $CDCl_3$, ppm): 47.93.

General Procedure for β-Alkylation of Secondary Alcohols with Primary Alcohols. The catalytic β-alkylation of secondary alcohol reaction was carried out in a 10 mL Schlenk tube under nitrogen conditions. Initially, catalyst **3** (0.5 mol %) and *t*-BuOK (0.5 equiv) were taken as solid, and then under nitrogen conditions, secondary alcohol (1 equiv), primary alcohol (1 equiv), and toluene (3 mL) were added and the resulting mixture heated at 110 °C (oil bath temperature) for 60 min. After cooling to room temperature, the toluene was evaporated under reduced pressure, and the resulting mixture was purified by silica gel column chromatography using ethyl acetate and hexane as eluent to afford the desire product.

General Procedure for the α-Alkylation of Ketones with Primary Alcohols to Give α-Alkylated Ketones. To a 10 mL Schlenk tube were added ketone (1 equiv), primary alcohol (1 equiv), catalyst **3** (0.05 mol %), and *t*-BuOK (0.25 equiv) in toluene (3 mL) under a nitrogen atmosphere. The reaction mixture was stirred at 130 °C (oil bath temperature) for 30 min. After the reaction was completed, the reaction mixture was evaporated and the residue was purified by TLC on silica gel plates using EA/PE as eluent to afford the corresponding ketone product.

1,3-Diphenylpropan-1-ol.[5d] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.35−7.18 (m, 10H), 4.68 (t, J = 7.2 Hz, 1H), 2.78−2.62 (m, 2H), 2.17−1.98 (m, 2H), 1.86 (s, 1H).

3-(2-Chlorophenyl)-1-phenylpropan-1-ol.[5d] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.38−7.10 (m, 9H), 4.72 (dd, J = 7.6, 5.2 Hz, 1H), 2.93−2.73 (m, 2H), 2.14−1.99 (m, 2H), 1.89 (s, 1H).

3-(3-Chlorophenyl)-1-phenylpropan-1-ol.[5d] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.37−7.14 (m, 8H), 7.07−7.05 (m, 1H), 4.66 (dd, J = 7.6, 5.2 Hz, 1H), 2.76−2.60 (m, 2H), 2.14−1.95 (m, 2H), 1.92 (s, 1H).

3-(4-Bromophenyl)-1-phenylpropan-1-ol.[5d] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.39−7.24 (m, 7H), 7.04 (d, J = 8 Hz, 2H), 4.64 (dd, J = 7.6, 5.2 Hz, 1H), 2.72−2.57 (m, 2H), 2.13−1.92 (m, 3H).

3-(4-Fluorophenyl)-1-phenylpropan-1-ol.[5d] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.37−7.24 (m, 5H), 7.15−7.10 (m, 2H), 6.98−6.92 (m, 2H), 4.65 (dd, J = 8.0, 5.6 Hz, 1H), 2.75−2.59 (m, 2H), 2.14−1.95 (m, 2H), 1.91 (s, 1H).

3-(4-Methoxyphenyl)-1-phenylpropan-1-ol.[5d] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.35−7.26 (m, 5H), 7.11 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 4.67 (dd, J = 7.6, 5.6 Hz, 1H), 3.78 (s, 3H), 2.73−2.57 (m, 2H), 2.15−1.95 (m, 2H), 1.86 (s, 1H).

3-(3,4-Dimethoxyphenyl)-1-phenylpropan-1-ol.[28] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.38−7.25 (m, 5H), 6.79−6.70 (m, 3H), 4.68 (dd, J = 7.6, 5.2 Hz, 1H), 3.85 (s, 6H), 2.74−2.58 (m, 2H), 2.16−1.96 (m, 2H), 1.90 (s, 1H).

3-(Naphthalen-2-yl)-1-phenylpropan-1-ol.[29] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.80−7.75 (m, 3H), 7.62 (s, 1H), 7.46−7.39 (m, 2H), 7.36−7.23 (m, 6H), 4.70 (dd, J = 8.0, 5.6 Hz, 1H), 2.94−2.79 (m, 2H), 2.26−2.06 (m, 2H), 1.89 (s, 1H).

1-(4-Chlorophenyl)-3-phenylpropan-1-ol.[5d] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.36−7.25 (m, 6H), 7.21−7.17 (m, 3H), 4.66 (dd, J = 7.6, 5.2 Hz, 1H), 2.76−2.62 (m, 2H), 2.14−1.94 (m, 2H), 1.86 (s, 1H).

1-(4-Methoxyphenyl)-3-phenylpropan-1-ol.[5d] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.28−7.23 (m, 4H), 7.18−7.15 (m, 3H), 6.89−6.85 (m, 2H), 4.60 (dd, J = 7.6, 6.0 Hz, 1H), 3.78 (s, 3H), 2.74−2.58 (m, 2H), 2.16−1.94 (m, 3H).

3-Cyclohexyl-1-phenylpropan-1-ol.[5d] ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 7.36−7.27 (m, 5H), 4.63 (t, J = 6.5 Hz, 1H), 1.84−1.61 (m, 8H), 1.36−1.29 (m, 1H), 1.26−1.10 (m, 5H), 0.89−0.82 (m, 2H).

1-Phenylhexan-1-ol.[5d] ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 7.35−7.25 (m, 5H), 4.64 (t, J = 7.0 Hz, 1H), 1.89 (s, 1H), 1.82−1.75 (m, 1H), 1.72−1.66 (m, 1H), 1.46−1.36 (m, 1H), 1.32−1.23 (m, 5H), 0.88−0.85 (m, 3H).

1,3-Diphenylpropan-1-one.[14a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.97−7.95 (m, 2H), 7.57−7.54 (m, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.32−7.19 (m, 5H), 3.31 (t, J = 7.2 Hz, 2H), 3.07 (t, J = 8.0 Hz, 2H).

3-(2-Chlorophenyl)-1-phenylpropan-1-one.[19a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.99 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.2 Hz,

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1H), 7.47 (t, J = 7.6 Hz, 2H), 7.39−7.33 (m, 2H), 7.23−7.16 (m, 2H), 3.34 (t, J = 7.2 Hz, 2H), 3.20 (t, J = 7.6 Hz, 2H).

3-(3-Chlorophenyl)-1-phenylpropan-1-one.[30] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.96 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 8.0 Hz, 2H), 7.26−7.13 (m, 4H), 3.30 (t, J = 7.6 Hz, 2H), 3.05 (t, J = 7.6 Hz, 2H).

3-(4-Chlorophenyl)-1-phenylpropan-1-one.[14a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.96 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.47 (t, J = 8.0 Hz, 2H), 7.28−7.26 (m, 2H), 7.21−7.19 (m, 2H), 3.30 (t, J = 7.2 Hz, 2H), 3.06 (t, J = 7.6 Hz, 2H).

3-(4-Fluorophenyl)-1-phenylpropan-1-one.[14a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.95 (d, J = 8.8 Hz, 2H), 7.56 (t, J = 8.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.23−7.19 (m, 2H), 6.98 (t, J = 8.8 Hz, 2H), 3.29 (t, J = 7.2 Hz, 2H), 3.05 (t, J = 7.6 Hz, 2H).

1-Phenyl-3-(m-tolyl)propan-1-one.[14a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.98 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.6 Hz, 1H), 7.09−7.03 (m, 3H), 3.31 (t, J = 7.6 Hz, 2H), 3.05 (t, J = 8.0 Hz, 2H), 2.35 (s, 3H).

3-(4-Methoxyphenyl)-1-phenylpropan-1-one.[14a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.96 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 8.0 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2H), 3.79 (s, 3H), 3.28 (t, J = 7.2 Hz, 2H), 3.02 (t, J = 8.0 Hz, 2H).

3-(4-Bromophenyl)-1-phenylpropan-1-one.[14a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.96−7.94 (m, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.48−7.40 (m, 4H), 7.13 (d, J = 8.0 Hz, 2H), 3.28 (t, J = 7.2 Hz, 2H), 3.03 (t, J = 7.6 Hz, 2H).

3-(3-Methoxyphenyl)-1-phenylpropan-1-one.[14a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.97−7.95 (m, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 8.0 Hz, 2H), 7.25−7.20 (m, 1H), 6.85−6.74 (m, 3H), 3.79 (s, 3H), 3.30 (t, J = 7.6 Hz, 2H), 3.05 (t, J = 8.0 Hz, 2H).

3-(3,4-Dimethoxyphenyl)-1-phenylpropan-1-one.[14a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.97−7.95 (m, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 6.82−6.78 (m, 3H), 3.86 (d, J = 4.8 Hz, 6H), 3.29 (t, J = 7.2 Hz, 2H), 3.02 (t, J = 8.0 Hz, 2H).

3-(Naphthalen-2-yl)-1-phenylpropan-1-one.[31] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.99−7.97 (m, 2H), 7.82−7.78 (m, 3H), 7.70 (s, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.48−7.39 (m, 5H), 3.40 (t, J = 7.2 Hz, 2H), 3.24 (t, J = 8.0 Hz, 2H).

1-(4-Methoxyphenyl)-3-phenylpropan-1-one.[14a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.96−7.93 (m, 2H), 7.32−7.19 (m, 5H), 6.94−6.90 (m, 2H), 3.86 (s, 3H), 3.25 (t, J = 7.2 Hz, 2H), 3.06 (t, J = 8.0 Hz, 2H).

1-(3-Methoxyphenyl)-3-phenylpropan-1-one.[14a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.57−7.51 (m, 2H), 7.39−7.23 (m, 6H), 7.12 (dd, J = 8.4, 2.4 Hz, 1H), 3.86 (s, 3H), 3.31 (t, J = 7.2 Hz, 2H), 3.09 (t, J = 8.0 Hz, 2H).

1-(Naphthalen-2-yl)-3-phenylpropan-1-one.[14a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.34 (s, 1H), 7.93 (dd, J = 8.8, 1.6 Hz, 1H), 7.82−7.73 (m, 3H), 7.49−7.40 (m, 2H), 7.23−7.18 (m, 4H), 7.14−7.10 (m, 1H), 3.32 (t, J = 7.2 Hz, 2H), 3.02 (t, J = 8.0 Hz, 2H).

1-(4-Fluorophenyl)-3-phenylpropan-1-one.[14a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.00−7.97 (m, 2H), 7.32−7.23 (m, 5H), 7.12 (t, J = 8.4 Hz, 2H), 3.28 (t, J = 7.2 Hz, 2H), 3.07 (t, J = 8.0 Hz, 2H).

1,6-Diphenylhexan-1-one.[32] ^{1}H NMR (500 MHz, $CDCl_3$, ppm): 7.71 (d, J = 8.0 Hz, 2H), 7.53 (t, J = 6.5 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 7.26 (t, J = 8.0 Hz, 2H), 7.17 (d, J = 7.0 Hz, 3H), 2.94 (t, J = 7.5 Hz, 2H), 2.62 (t, J = 7.5 Hz, 2H), 1.80−1.74 (m, 2H), 1.70−1.64 (m, 2H), 1.45−1.39 (m, 2H).

1-Phenylhexan-1-one.[14a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.96−7.94 (m, 2H), 7.56−7.51 (m, 1H), 7.47−7.42 (m, 2H), 2.97−2.92 (m, 2H), 1.75−1.72 (m, 2H), 1.37−1.35 (m, 4H), 0.91−0.90 (m, 3H).

3-Cyclohexyl-1-phenylpropan-1-one.[14a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.96 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 2.98 (t, J = 7.6 Hz, 2H), 1.78−1.61 (m, 7H), 1.26−1.14 (m, 4H), 0.99−0.91 (m, 2H).

1,3-Diphenylbutan-1-one.[14a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.93−7.91 (m, 2H), 7.56−7.45 (m, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.32−7.23 (m, 4H), 7.21−7.15 (m, 1H), 3.56−3.44 (m, 1H), 3.33−3.15 (m, 2H), 1.34 (d, J = 6.8 Hz, 3H).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00847.

Crystallographic details for complexes **2** and **3**, screening reactions, synthetic routes of complexes **1**−**3**, and IR and NMR spectra of the new compounds (PDF)

Accession Codes

CCDC 1879634−1879635 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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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Hale, L. V. A.; Szymczak, N. K. Hydrogen Transfer Catalysis beyond the Primary Coordination Sphere. *ACS Catal.* **2018**, *8*, 6446−6461. (b) Sordakis, K.; Tang, C.; Vogt, L. K.; Junge, H.; Dyson, P. J.; Beller, M.; Laurenczy, G. Homogeneous Catalysis for Sustainable Hydrogen Storage in Formic Acid and Alcohols. *Chem. Rev.* **2018**, *118*, 372−433. (c) Moore, C. M.; Dahl, E. W.; Szymczak, N. K. Beyond H_2: Exploiting 2-Hydroxypyridine as a Design Element from [Fe]-Hydrogenase for Energy-Relevant Catalysis. *Curr. Opin. Chem. Biol.* **2015**, *25*, 9−17. (d) Khusnutdinova, J. R.; Milstein, D. Metal-Ligand Cooperation. *Angew. Chem., Int. Ed.* **2015**, *54*, 12236−12273.

(2) For selected examples, see (a) Fujita, K.; Wada, T.; Shiraishi, T. Reversible Interconversion between 2,5-Dimethylpyrazine and 2,5-Dimethylpiperazine by Iridium-Catalyzed Hydrogenation/Dehydrogenation for Efficient Hydrogen Storage. *Angew. Chem., Int. Ed.* **2017**, *56*, 10886−10889. (b) Fujita, K.; Tamura, R.; Tanaka, Y.; Yoshida, M.; Onoda, M.; Yamaguchi, R. Dehydrogenative Oxidation of Alcohols in Aqueous Media Catalyzed by a Water-Soluble Dicationic Iridium Complex Bearing a Functional N-Heterocyclic Carbene Ligand without Using Base. *ACS Catal.* **2017**, *7*, 7226−7230. (c) Iguchi, M.; Zhong, H.; Himeda, Y.; Kawanami, H. Effect of the *ortho*-Hydroxyl Groups on a Bipyridine Ligand of Iridium Complexes for the High-Pressure Gas Generation from the Catalytic Decom-

DOI: 10.1021/acs.organomet.8b00847
Organometallics XXXX, XXX, XXX−XXX

position of Formic Acid. *Chem. - Eur. J.* **2017**, *23*, 17788−17793. (d) de Boer, S. Y.; Korstanje, T. J.; La Rooij, S. R.; Kox, R.; Reek, J. N.; van der Vlugt, J. I. Ruthenium PNN(O) Complexes: Cooperative Reactivity and Application as Catalysts for Acceptorless Dehydrogenative Coupling Reactions. *Organometallics* **2017**, *36*, 1541−1549. (e) Fujita, K.; Kawahara, R.; Aikawa, T.; Yamaguchi, R. Hydrogen Production from a Methanol-Water Solution Catalyzed by an Anionic Iridium Complex Bearing a Functional Bipyridonate Ligand under Weakly Basic Conditions. *Angew. Chem., Int. Ed.* **2015**, *54*, 9057−9060. (f) Chakraborty, S.; Piszel, P. E.; Brennessel, W. W.; Jones, W. D. A Single Nickel Catalyst for the Acceptorless Dehydrogenation of Alcohols and Hydrogenation of Carbonyl Compounds. *Organometallics* **2015**, *34*, 5203−5206. (g) Wang, W.-H.; Ertem, M. Z.; Xu, S.; Onishi, N.; Manaka, Y.; Suna, Y.; Kambayashi, H.; Muckerman, J. T.; Fujita, E.; Himeda, Y. Highly Robust Hydrogen Generation by Bioinspired Ir Complexes for Dehydrogenation of Formic Acid in Water: Experimental and Theoretical Mechanistic Investigations at Different pH. *ACS Catal.* **2015**, *5*, 5496−5504. (h) Fujita, K.; Tanaka, Y.; Kobayashi, M.; Yamaguchi, R. Homogeneous Perdehydrogenation and Perhydrogenation of Fused Bicyclic N-heterocycles Catalyzed by Iridium Complexes Bearing a Functional Bipyridonate Ligand. *J. Am. Chem. Soc.* **2014**, *136*, 4829−4832.

(3) For selected examples, see (a) Wang, R.; Tang, Y.; Xu, M.; Meng, C.; Li, F. Transfer Hydrogenation of Aldehydes and Ketones with Isopropanol under Neutral Conditions Catalyzed by a Metal-Ligand Bifunctional Catalyst [Cp*Ir(2,2′-bpyO)(H_2O)]. *J. Org. Chem.* **2018**, *83*, 2274−2281. (b) Siek, S.; Burks, D. B.; Gerlach, D. L.; Liang, G.; Tesh, J. M.; Thompson, C. R.; Qu, F.; Shankwitz, J. E.; Vasquez, R. M.; Chambers, N.; Szulczewski, G. J.; Grotjahn, D. B.; Webster, C. E.; Papish, E. T. Iridium and Ruthenium Complexes of N-Heterocyclic Carbene- and Pyridinol-Derived Chelates as Catalysts for Aqueous Carbon Dioxide Hydrogenation and Formic Acid Dehydrogenation: The Role of the Alkali Metal. *Organometallics* **2017**, *36*, 1091−1106. (c) Dubey, A.; Nencini, L.; Fayzullin, R. R.; Nervi, C.; Khusnutdinova, J. R. Bio-Inspired Mn(I) Complexes for the Hydrogenation of CO_2 to Formate and Formamide. *ACS Catal.* **2017**, *7*, 3864−3868. (d) 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. (e) Onishi, N.; Xu, S.; Manaka, Y.; Suna, Y.; Wang, W.-H.; Muckerman, J. T.; Fujita, E.; Himeda, Y. CO_2 Hydrogenation Catalyzed by Iridium Complexes with a Proton-Responsive Ligand. *Inorg. Chem.* **2015**, *54*, 5114−5123. (f) Moore, C. M.; Szymczak, N. K. 6,6′-Dihydroxy Terpyridine: a Proton-Responsive Bifunctional Ligand and Its Application in Catalytic Transfer Hydrogenation of Ketones. *Chem. Commun.* **2013**, *49*, 400−402. (g) Hull, J. F.; Himeda, Y.; Wang, W.-H.; Hashiguchi, B.; Periana, R.; Szalda, D. J.; Muckerman, J. T.; Fujita, E. Reversible Hydrogen Storage Using CO_2 and a Proton-Switchable Iridium Catalyst in Aqueous Media under Mild Temperatures and Pressures. *Nat. Chem.* **2012**, *4*, 383−388.

(4) Geri, J. B.; Szymczak, N. K. A Proton-Switchable Bifunctional Ruthenium Complex that Catalyzes Nitrile Hydroboration. *J. Am. Chem. Soc.* **2015**, *137*, 12808−12814.

(5) (a) Maji, M.; Chakrabarti, K.; Paul, B.; Roy, B. C.; Kundu, S. Ruthenium(II)-NNN-Pincer-Complex-Catalyzed Reactions Between Various Alcohols and Amines for Sustainable C−N and C−C Bond Formation. *Adv. Synth. Catal.* **2018**, *360*, 722−729. (b) 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. (c) Wang, R.; Fan, H.; Zhao, W.; Li, F. Acceptorless Dehydrogenative Cyclization of o-Aminobenzyl Alcohols with Ketones to Quinolines in Water Catalyzed by Water-Soluble Metal-Ligand Bifunctional Catalyst [Cp*(6,6′-$(OH)_2$bpy)(H_2O)][$OTf]_2$. *Org. Lett.* **2016**, *18*, 3558−3561. (d) Roy, B. C.; Chakrabarti, K.; Shee, S.; Paul, S.; Kundu, S. Bifunctional Ru(II)-Complex-Catalysed Tandem C-C Bond Formation: Efficient and Atom Economical Strategy for the Utilisation of Alcohols as Alkylating Agents. *Chem. - Eur. J.* **2016**, *22*, 18147−18155. (e) Chakraborty, S.; Piszel, P. E.; Hayes, C. E.; Baker, R. T.; Jones, W. D. Highly Selective Formation of n-Butanol from Ethanol through the Guerbet Process: A Tandem Catalytic Approach. *J. Am. Chem. Soc.* **2015**, *137*, 14264−14267. (f) Wang, R.; Ma, J.; Li, F. Synthesis of α-Alkylated Ketones via Tandem Acceptorless Dehydrogenation/α-Alkylation from Secondary and Primary Alcohols Catalyzed by Metal-Ligand Bifunctional Iridium Complex [Cp*Ir(2,2′-bpyO)(H_2O)]. *J. Org. Chem.* **2015**, *80*, 10769−10776.

(6) (a) Corma, A.; Navas, J.; Sabater, M. J. Advances in One-Pot Synthesis through Borrowing Hydrogen Catalysis. *Chem. Rev.* **2018**, *118*, 1410−1459. (b) Crabtree, R. H. Homogeneous Transition Metal Catalysis of Acceptorless Dehydrogenative Alcohol Oxidation: Applications in Hydrogen Storage and to Heterocycle Synthesis. *Chem. Rev.* **2017**, *117*, 9228−9246. (c) 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. (d) Yang, Q.; Wang, Q.; Yu, Z. Substitution of Alcohols by N-nucleophiles *via* Transition Metal-Catalyzed Dehydrogenation. *Chem. Soc. Rev.* **2015**, *44*, 2305−2329. (e) Obora, Y. Recent Advances in α-Alkylation Reactions using Alcohols with Hydrogen Borrowing Methodologies. *ACS Catal.* **2014**, *4*, 3972−3981. (f) Gunanathan, C.; Milstein, D. Applications of Acceptorless Dehydrogenation and Related Transformations in Chemical Synthesis. *Science* **2013**, *341*, 1229712.

(7) (a) Roy, B. C.; Debnath, S.; Chakrabarti, K.; Paul, B.; Maji, M.; Kundu, S. *Ortho*-Amino Group Functionalized 2,2′-Bipyridine based Ru(II) Complex Catalysed Alkylation of Secondary Alcohols, Nitriles and Amines using Alcohols. *Org. Chem. Front.* **2018**, *5*, 1008−1018. (b) Tseng, K.-N. T.; Lin, S.; Kampf, J. W.; Szymczak, N. K. Upgrading Ethanol to 1-Butanol with a Homogeneous Air-Stable Ruthenium Catalyst. *Chem. Commun.* **2016**, *52*, 2901−2904. (c) Wang, Q. F.; Wu, K.; Yu, Z. Ruthenium(III)-Catalyzed β-Alkylation of Secondary Alcohols with Primary Alcohols. *Organometallics* **2016**, *35*, 1251−1256.

(8) (a) Jiménez, M. V.; Fernández-Tornos, J.; Modrego, F. J.; Pérez-Torrente, J. J.; Oro, L. A. Oxidation and β-Alkylation of Alcohols Catalysed by Iridium(I) Complexes with Functionalised N-Heterocyclic Carbene Ligands. *Chem. - Eur. J.* **2015**, *21*, 17877−17889. (b) Ruiz-Botella, S.; Peris, E. Unveiling the Importance of π-Stacking in Borrowing-Hydrogen Processes Catalysed by Iridium Complexes with Pyrene Tags. *Chem. - Eur. J.* **2015**, *21*, 15263−15271.

(9) Kose, O.; Saito, S. Cross-Coupling Reaction of Alcohols for Carbon-Carbon Bond Formation using Pincer-Type NHC/Palladium Catalysts. *Org. Biomol. Chem.* **2010**, *8*, 896−900.

(10) (a) 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. (b) Liao, S.; Yu, K.; Li, Q.; Tian, H.; Zhang, Z.; Yu, X.; Xu, Q. Copper-Catalyzed C-Alkylation of Secondary Alcohols and Methyl Ketones with Alcohols Employing the Aerobic Relay Race Methodology. *Org. Biomol. Chem.* **2012**, *10*, 2973−2978.

(11) 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.

(12) 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.

(13) (a) Xu, Q.; Chen, J.; Liu, Q. Aldehyde-Catalyzed Transition Metal-Free Dehydrative β-Alkylation of Methyl Carbinols with Alcohols. *Adv. Synth. Catal.* **2013**, *355*, 697−704. (b) Allen, L. J.; Crabtree, R. H. Green Alcohol Couplings without Transition Metal Catalysts: Base-Mediated β-Alkylation of Alcohols in Aerobic Conditions. *Green Chem.* **2010**, *12*, 1362−1364.

(14) (a) 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**,

DOI: 10.1021/acs.organomet.8b00847
Organometallics XXXX, XXX, XXX−XXX

83, 3657−3668. (b) Liu, S.-Y.; Xu, L.-Y.; Liu, C.-Y.; Ren, Z.-G.; Young, D. J.; Lang, J.-P. Efficient Alkylation of Ketones with Primary Alcohols Catalyzed by Ruthenium(II)/P, N Ligand Complexes. *Tetrahedron* **2017**, *73*, 2374−2381. (c) Chang, W.; Gong, X.; Wang, S.; Xiao, L.-P.; Song, G. Acceptorless Dehydrogenation and Dehydrogenative Coupling of Alcohols Catalysed by Protic NHC Ruthenium Complexes. *Org. Biomol. Chem.* **2017**, *15*, 3466−3471. (d) Kuwahara, T.; Fukuyama, T.; Ryu, I. $RuHCl(CO)(PPh_3)_3$-Catalyzed α-Alkylation of Ketones with Primary Alcohols. *Org. Lett.* **2012**, *14*, 4703−4705.

(15) Piehl, P.; Peña-López, M.; Frey, A.; Neumann, H.; Beller, M. Hydrogen Autotransfer and Related Dehydrogenative Coupling Reactions using a Rhenium(I) Pincer Catalyst. *Chem. Commun.* **2017**, *53*, 3265−3268.

(16) 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.

(17) 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.

(18) 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.

(19) (a) Genç, S.; Günnaz, S.; Çetinkaya, B.; Gülcemal, S.; Gülcemal, D. Iridium(I)-Catalyzed Alkylation Reactions To Form α-Alkylated Ketones. *J. Org. Chem.* **2018**, *83*, 2875−2881. (b) Wang, D.; Zhao, K.; Ma, P.; Xu, C.; Ding, Y. Direct α-alkylation of Ketones with Primary Alcohols Catalyzed by Iridium-CNP Complex. *Tetrahedron Lett.* **2014**, *55*, 7233−7235.

(20) Mamidala, R.; Samser, S.; Sharma, N.; Lourderaj, Y.; Venkatasubbaiah, K. Isolation and Characterization of Regioisomers of Pyrazole-Based Palladacycles and Their Use in α-Alkylation of Ketones Using Alcohols. *Organometallics* **2017**, *36*, 3343−3351.

(21) Xu, Q.; Chen, J.; Tian, H.; Yuan, X.; Li, S.; Zhou, C.; Liu, J. Catalyst-Free Dehydrative α-Alkylation of Ketones with Alcohols: Green and Selective Autocatalyzed Synthesis of Alcohols and Ketones. *Angew. Chem., Int. Ed.* **2014**, *53*, 225−229.

(22) 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.

(23) (a) Deng, D.; Hu, B.; Yang, M.; Chen, D. Methylation of Amines and Ketones with Methanol Catalyzed by an Iridium Complex Bearing a 2-Hydroxypyridylmethylene Fragment. *Organometallics* **2018**, *37*, 3353−3359. (b) Deng, D.; Hu, B.; Yang, M.; Chen, D. NNN-Ruthenium Catalysts for the Synthesis of Pyridines, Quinolines, and Pyrroles by Acceptorless Dehydrogenative Condensation. *Organometallics* **2018**, *37*, 2386−2394. (c) Shi, J.; Shang, S.; Hu, B.; Chen, D. Ruthenium NNN Complexes with a 2-Hydroxypyridylmethylene Fragment for Transfer Hydrogenation of Ketones. *Appl. Organomet. Chem.* **2018**, *32*, No. e4100. (d) Shi, J.; Hu, B.; Chen, X.; Shang, S.; Deng, D.; Sun, Y.; Shi, W.; Yang, X.; Chen, D. Synthesis, Reactivity, and Catalytic Transfer Hydrogenation Activity of Ruthenium Complexes Bearing NNN Tridentate Ligands: Influence of the Secondary Coordination Sphere. *ACS Omega* **2017**, *2*, 3406−3416. (e) Shi, J.; Hu, B.; Gong, D.; Shang, S.; Hou, G.; Chen, D. Ruthenium Complexes Bearing an Unsymmetrical Pincer Ligand with a 2-Hydroxypyridylmethylene Fragment: Active Catalysts for Transfer Hydrogenation of Ketones. *Dalton Trans* **2016**, *45*, 4828−4834.

(24) (a) Liu, T.; Guo, M.; Orthaber, A.; Lomoth, R.; Lundberg, M.; Ott, S.; Hammarström, L. Accelerating Proton-Coupled Electron Transfer of Metal Hydrides in Catalyst Model Reactions. *Nat. Chem.* **2018**, *10*, 881−887. (b) Dong, K.; Sang, R.; Wei, Z.; Liu, J.; Dühren, R.; Spannenberg, A.; Jiao, H.; Neumann, H.; Jackstell, R.; Franke, R.; Beller, M. Cooperative Catalytic Methoxycarbonylation of Alkenes: Uncovering the Role of Palladium Complexes with Hemilabile Ligands. *Chem. Sci.* **2018**, *9*, 2510−2516. (c) Valencia, M.; Pereira, A.; Müller-Bunz, H.; Belderraín, T. R.; Pérez, P. J.; Albrecht, M. Triazolylidene-Iridium Complexes with a Pendant Pyridyl Group for Cooperative Metal-Ligand Induced Catalytic Dehydrogenation of Amines. *Chem. - Eur. J.* **2017**, *23*, 8901−8911. (d) Sarbajna, A.; Dutta, I.; Daw, P.; Dinda, S.; Rahaman, S. M. W.; Sarkar, A.; Bera, J. K. Catalytic Conversion of Alcohols to Carboxylic Acid Salts and Hydrogen with Alkaline Water. *ACS Catal.* **2017**, *7*, 2786−2790. (e) Ghatak, T.; Sarkar, M.; Dinda, S.; Dutta, I.; Rahaman, S. M. W.; Bera, J. K. Olefin Oxygenation by Water on an Iridium Center. *J. Am. Chem. Soc.* **2015**, *137*, 6168−6171.

(25) Jasimuddin, S.; Thakurata, D. G. Synthesis and Characterization of Stable Thiazolylazo Anion Radical Complexes of Ruthenium(II). *Transition Met. Chem.* **2009**, *34*, 937−942.

(26) Yoshinaga, Y.; Yamamoto, T.; Suginome, M. Chirality-Switchable 2, 2′-Bipyridine Ligands Attached to Helical Poly (quinoxaline-2,3-diyl)s for Copper-Catalyzed Asymmetric Cyclopropanation of Alkenes. *ACS Macro Lett.* **2017**, *6*, 705−710.

(27) Huang, W.; Ye, J. L.; Zheng, W.; Dong, H.-Q.; Wei, B.-G. Radical Migration-Addition of N-tert-Butanesulfinyl Imines with Organozinc Reagents. *J. Org. Chem.* **2013**, *78*, 11229−11237.

(28) Yang, J.; Liu, X.; Meng, D.-L.; Chen, H.-Y.; Zong, Z.-H.; Feng, T.-T.; Sun, K. Efficient Iron-Catalyzed Direct β-Alkylation of Secondary Alcohols with Primary Alcohols. *Adv. Synth. Catal.* **2012**, *354*, 328−334.

(29) Cheung, H. W.; Lee, T. Y.; Lui, H. Y.; Yeung, C. H.; Lau, C. P. Ruthenium-Catalyzed β-Alkylation of Secondary Alcohols with Primary Alcohols. *Adv. Synth. Catal.* **2008**, *350*, 2975−2983.

(30) Xu, J.; Yue, H.; Liu, S.; Wang, H.; Du, Y.; Xu, C.; Dong, W.; Liu, C. Cu-Ag/Hydrotalcite Catalysts for Dehydrogenative Cross-Coupling of Primary and Secondary Benzylic Alcohols. *RSC Adv.* **2016**, *6*, 24164−24174.

(31) Huang, S.; Wu, S.-P.; Zhou, Q.; Cui, H.-Z.; Hong, X.; Lin, Y.-J.; Hou, X.-F. Iridium(III)-Benzoxazolyl and Benzothiazolyl Phosphine Ligands Catalyzed Versatile Alkylation Reactions with Alcohols and the Synthesis of Quinolines and Indole. *J. Organomet. Chem.* **2018**, *868*, 14−23.

(32) Kong, W.; Yu, C.; An, H.; Song, Q. Photoredox-Catalyzed Decarboxylative Alkylation of Silyl Enol Ethers to Synthesize Functionalized Aryl Alkyl Ketones. *Org. Lett.* **2018**, *20*, 349−352.

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