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α-Alkylation of Ketones with Primary Alcohols Catalyzed by a Cp*Ir Complex Bearing a Functional Bipyridonate Ligand

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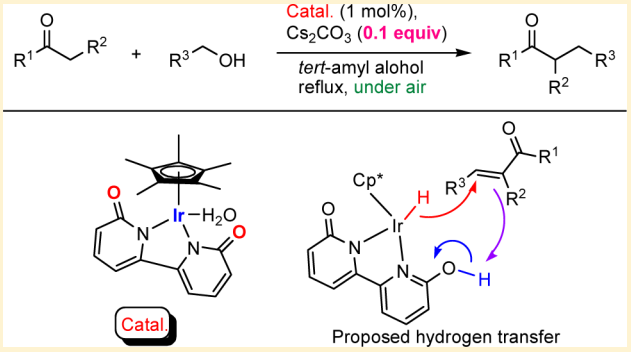
Supporting Information

ABSTRACT: A Cp*Ir complex bearing a functional bipyridonate ligand was found to be a highly effective and versatile catalyst for the α-alkylation of ketones with primary alcohols under extremely environmentally benign and mild conditions (0.1 equiv of Cs_2CO_3 per substrate, reflux in *tert*-amyl alcohol under an air atmosphere for 6 h). Furthermore, this complex also exhibited a high level of catalytic activity for the α-methylation of ketones with methanol. The mechanistic investigation revealed that the carbonyl group on the ligand is of critical importance for catalytic hydrogen transfer. Notably, the results of this study revealed the unique potential of Cp*Ir complexes bearing a functional bipyridonate ligand for the development of C−C bond-forming reactions with the activation of primary alcohols as electrophiles.



INTRODUCTION

The α-alkylation of ketones is one of the most important C−C bond-forming reactions in organic synthesis. Such reactions are traditionally performed using alkyl halides as alkylating agents in the presence of at least stoichiometric amounts of strong bases.[1] In recent years, considerable attention has been directed to the α-alkylation of ketones with primary alcohols that are more environmentally benign alkylating agents than alkyl halides; these reactions have been based on the hydrogen-autotransfer (or hydrogen-borrowing) process,[2] using ruthenium,[3] iridium,[4] palladium,[5] and other transition-metal complexes[6] as catalysts. In this process, primary alcohols are initially dehydrogenated to afford aldehyde and metal hydride species, followed by cross-aldol condensation between the resulting aldehydes and ketones to afford α,β-unsaturated ketones that undergo transfer hydrogenation by the metal hydride species (generated during the alcohol dehydrogenation step) to afford α-alkylated ketones. Although considerable effort has been devoted to this research, the α-alkylation of ketones with primary alcohols can be efficiently catalyzed only by the known transition-metal complexes in the presence of a considerable amount of a strong inorganic base (typically KOH) under a nitrogen atmosphere. Recently, Ryu and co-workers demonstrated that this transformation could be catalyzed by $RuHCl(CO)(PPh_3)_3$ in the presence of carbonate.[7] Despite significant advancements, this procedure still has obvious limitations, and it requires more than the stoichiometric amount of Cs_2CO_3 (1.5 equiv per substrate), a high temperature (140 °C), a nitrogen atmosphere, and a long reaction time (20 h). Moreover, the addition of extra 1,10-phenanthroline as the ligand is required for an α-alkylation reaction that uses aliphatic alcohols. Therefore, the development of a new type of organometallic catalyst for the α-alkylation of ketones with primary alcohols under more environmentally benign and mild conditions is highly desirable.

Very recently, we reported the *N*-alkylation of sulfonamides with alcohols in water, catalyzed by a water-soluble Cp*Ir complex bearing a functional 6,6′-dihydroxy-2,2′-bipyridine (6,6′-$(OH)_2$bpy) ligand ($[Cp^*Ir(6,6'\text{-}(OH)_2bpy)(H_2O)][OTf]_2$).[8,9] The catalytically active species was proposed to be an iridium complex bearing a functional 2,2′-bipyridonate (2,2′-bpyO) ligand and a water ligand ($[Cp^*Ir(2,2'\text{-}bpyO)(H_2O)]$).[8] Fujita, Yamaguchi, and co-workers demonstrated that such iridium complexes are highly efficient catalysts for the acceptorless dehydrogenative oxidation of alcohols and bicyclic *N*-heterocycles.[10] As part of our continuing interest in the development of iridium-catalyzed transformations with the activation of alcohols as electrophiles,[11,12] we herein report the unique potential of Cp*Ir complexes bearing a functional bipyridonate ligand for the α-alkylation of ketones with primary alcohols.

RESULTS AND DISCUSSION

Initially, the α-alkylation of acetophenone (**1a**) with benzyl alcohol (**2a**) was selected as a model reaction. In the presence of $[Cp^*Ir(2,2'\text{-}bpyO)(H_2O)]$ (catalyst (cat.) **1**, 1 mol %) and Cs_2CO_3 (1 equiv per substrate), the reaction was performed in

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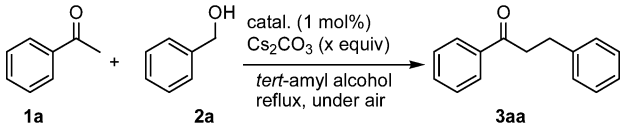
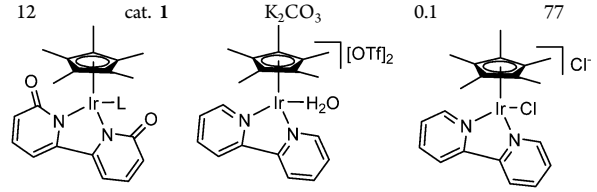
tert-amyl alcohol under reflux under an air atmosphere for 6 h to afford α-alkylated product **3aa** in 92% yield (Table 1, entry 1). Next, the reaction conditions were optimized. Surprisingly, the yield of **3aa** remained at 92% even in the presence of Cs_2CO_3 (0.1 equiv per substrate) at 110 °C (Table 1, entry 2). Analogous catalyst complexes **2** and **3**, which contained pyridine or aniline, respectively, as an alternative ligand to water, exhibited similar catalytic activity for this transformation (Table 1, entries 3 and 4). When other iridium complexes, including $[Cp^*Ir(bpy)(H_2O)][OTf]_2$ (cat. **4**), $[Cp^*Ir(bpy)Cl)][Cl]$ (cat. **5**), $[Cp^*Ir(2\text{-phenylpyridine-}kC,N)]Cl$ (cat. **6**), $[Cp^*Ir(H_2O)_3][OTf]_2$ (cat. **7**), $[Cp^*Ir(NH_3)_3][Cl]_2$ (cat. **8**), $[Cp^*IrCl_2]_2$ (cat. **9**), and $[Ir(cod)Cl]_2$ (cat. **10**) were used as catalysts under the same reaction conditions, product **3aa** could be obtained in ≤18% yield (Table 1, entries 5–11). In the presence of cat. **1** and K_2CO_3 (0.1 equiv), the reaction afforded **3aa** in 77% yield (Table 1, entry 12).

Table 1. α-Alkylation of Acetophenone (1a) with Benzyl Alcohol (2a) under Various Conditions[a]

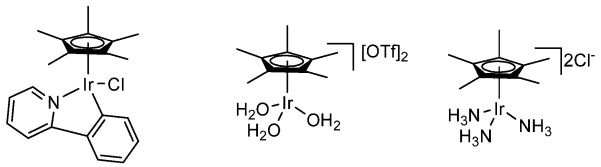


1a 2a 3aa

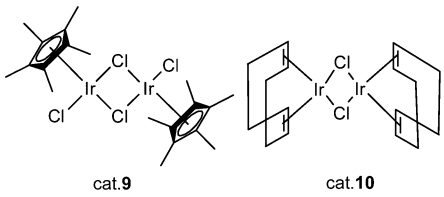
entry	catalyst	base	x	yield (%)
1	cat. **1**	Cs_2CO_3	1.0	92
2	cat. **1**	Cs_2CO_3	0.1	92
3	cat. **2**	Cs_2CO_3	0.1	90
4	cat. **3**	Cs_2CO_3	0.1	89
5	cat. **4**	Cs_2CO_3	0.1	9
6	cat. **5**	Cs_2CO_3	0.1	18
7	cat. **6**	Cs_2CO_3	0.1	
8	cat. **7**	Cs_2CO_3	0.1	
9	cat. **8**	Cs_2CO_3	0.1	8
10	cat. **9**	Cs_2CO_3	0.1	7
11	cat. **10**	Cs_2CO_3	0.1	
12	cat. **1**	K_2CO_3	0.1	77



cat.4 cat.5



cat.6 cat.7 cat.8



cat.9 cat.10

[a]Reaction conditions: **1a** (1 mmol), **2a** (1.1 mmol), cat. (1 mol %), base (x equiv), *tert*-amyl alcohol (1 mL), reflux, 6 h.

Having established the optimal catalyst system and conditions (Table 1, entry 2), the α-alkylation of acetophenone (**1a**) with a variety of alcohol **2** derivatives was conducted. These results are summarized in Table 2. Reactions with benzylic alcohols bearing one or two halogen atoms, such as fluorine (**2b**), chlorine (**2c–d**), dichlorine (**2e**), and bromine (**2f**), afforded corresponding products **3ab–3af** in yields of 86–91% (Table 2, entries 1–5). Similarly, transformations of benzylic alcohols bearing a strong electron-withdrawing substituent, such as a trifluoromethyl (**2g**) or trifluoromethoxy (**2h**) group, afforded desired products **3ag** and **3ah** in 84 and 85% yields, respectively (Table 2, entries 6 and 7). With benzylic alcohols bearing one or two electron-donating substituents, such as a methyl (**2i**), methoxy (**2j**), or dimethoxy (**2k**) group, α-alkylated products **3ai–3ak** were also obtained in high yields (Table 2, entries 8–10). Furthermore, 1-naphthalenemethanol (**2l**), 2-furyl alcohol (**2m**), and ferrocenemethanol (**2n**) could be successfully converted to corresponding products **3al–3an** in yields of 82–85% (Table 2, entries 11–13). Aliphatic alcohols, such as 1-butanol (**2o**), 1-hexanol (**2p**), and cyclohexylmethanol (**2q**), were demonstrated to be suitable alkylating agents, and desired products **3ao–3aq** were obtained in yields of 84–87% (Table 2, entries 14–16).

The α-alkylation of a range of ketone **1** derivatives with benzyl alcohol (**2a**) was investigated to explore further the scope of the reaction (Table 3). Transformations of acetophenones bearing a halogen atom, such as fluorine (**1b**), chlorine (**1c**), or bromine (**1d**), afforded corresponding products **3ba–3da** in yields of 86–90% (Table 3, entries 1–3). For acetophenones bearing an even stronger electron-withdrawing substituent such as a trifluoromethyl group (**1e**), the reaction proceeded smoothly to afford desired product **3ea** in 87% yield (Table 3, entry 4). Furthermore, when α-alkylation was applied to acetophenones bearing an electron-donating substituent group, such as a methyl (**1f–g**), ethyl (**1h**), or methoxy (**1i**) group, corresponding products **3fa–3ia** were afforded in yields of 87–93% (Table 3, entries 5–8). High levels of catalytic activity were also observed when 2-acetylthiophene (**1j**) and 2-acetonaphthone (**1k**) were used as the substrates (Table 3, entries 9 and 10). In the case of nonmethyl ketones, such as propiophenone (**1l**) and 1-indanone (**1m**), desired products **3la** and **3ma** were obtained in 83 and 79% yields, respectively (Table 3, entries 11 and 12). In addition to aromatic ketones, aliphatic ketones, such as 1-cyclopropylethanone (**1n**) and 3,3-dimethyl-2-butanone (**1o**), were also found to be suitable substrates, and corresponding products **3na** and **3oa** could be obtained in 83 and 85% yields, respectively (Table 3, entries 13 and 14).

Very recently, Donohoe and co-workers reported the α-methylation of ketones with the activation of methanol[13] as the methylating agent for the corresponding α-methylated products catalyzed by $[Cp^*RhCl_2]_2$.[14] Subsequently, Obora and co-workers also described such transformations catalyzed by $[Cp^*IrCl_2]_2$.[15] However, these two procedures required 5 mol % catalyst loadings and 5 equiv of Cs_2CO_3 or 0.5 equiv of KOH per substrate. To further explore the potential of cat. **1**, the α-methylation of a series of ketones with methanol was examined (Table 4). The reaction of propiophenone (**1l**) with methanol (**2r**) in the presence of cat. **1** (2 mol %) and Cs_2CO_3 (0.3 equiv per substrate) was carried out for 12 h to obtain

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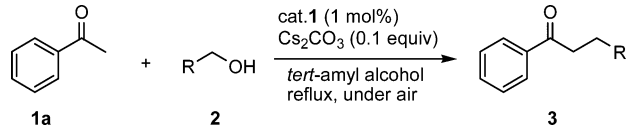
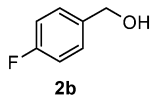
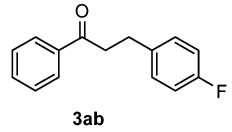
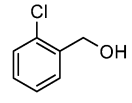
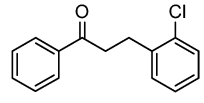
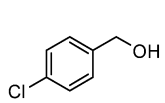
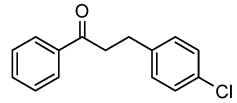
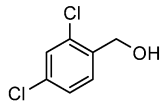
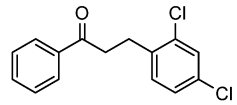
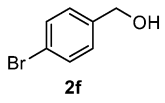
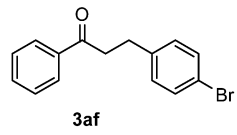
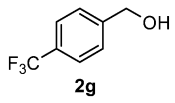
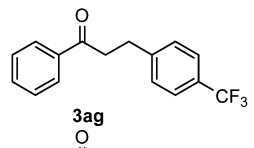
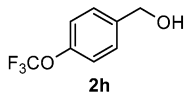
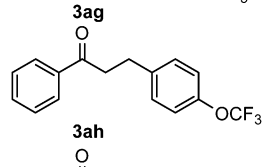
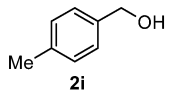
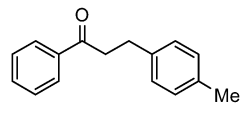
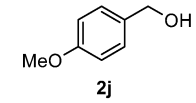
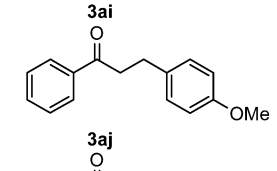
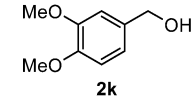
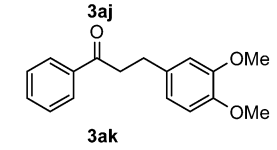
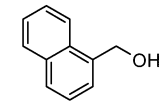
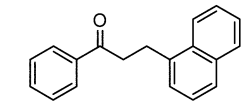
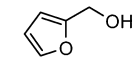
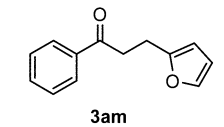
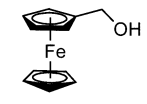
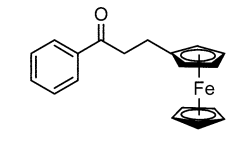
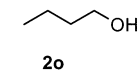
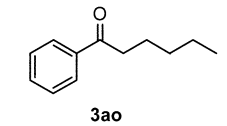
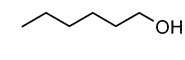
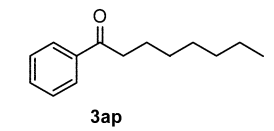
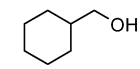
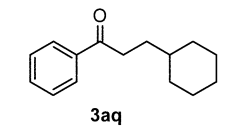
Table 2. α-Alkylation of Acetophenone (1a) with a Variety of Alcohol 2 Derivatives[a]



entry	alcohol	product	yield (%)
1	 **2b**	 **3ab**	88
2	 **2c**	 **3ac**	87
3	 **2d**	 **3ad**	91
4	 **2e**	 **3ae**	90
5	 **2f**	 **3af**	86
6	 **2g**	 **3ag**	84
7	 **2h**	 **3ah**	85
8	 **2i**	 **3ai**	88
9	 **2j**	 **3aj**	90
10	 **2k**	 **3ak**	85
11	 **2l**	 **3al**	83
12	 **2m**	 **3am**	85
13	 **2n**	 **3an**	82
14	 **2o**	 **3ao**	84
15	 **2p**	 **3ap**	87
16	 **2q**	 **3aq**	85

[a]Reaction conditions: **1a** (1 mmol), **2** (1.1 mmol), cat. **1** (1 mol %), Cs_2CO_3 (0.1 equiv), *tert*-amyl alcohol (1 mL), reflux, 6 h.

desired product **3lr** in 85% yield (Table 4, entry 1). Similarly, propiophenones bearing a substituent (**1p**−**r**) were also converted to corresponding products **3pr**−**3rr** in yields of 79−83% (Table 4, entries 2−4). When 1-indanone (**1m**) was used as the substrate, desired product **3mr** was isolated in 80% yield (Table 4, entry 5).

A plausible mechanism is proposed in Scheme 1 to explain the α-alkylation of ketones with alcohols. In the initial step for the activation of alcohols, the bipyridonate ligand accepted a proton, resulting in the generation of an alkoxy iridium species (**B**), which underwent β-hydrogen elimination to afford an iridium hydride species (**C**) and aldehydes.[9c,10a] Base-mediated cross-aldol condensation between the resulting aldehydes and ketones produced α,β-unsaturated ketones as intermediates. Finally, the functional ligand-promoted transfer from the hydroxyl proton on the ligand and the hydride on the iridium to the C=C bond of the α,β-unsaturated ketones occurred to release α-alkylated ketones as the reaction products accompanied by the regeneration of catalytic species **A**.[16−18]

The catalytic hydrogen transfer between an α,β-unsaturated ketone with an alcohol as the hydrogen source was investigated to support the proposed mechanism. As shown in Scheme 2, in the presence of cat. **1** (1 mol %) and Cs_2CO_3 (0.1 equiv), the reaction of (*E*)-chalcone (**4**) with benzyl alcohol (**2a**) proceeded under reflux for 6 h to afford corresponding product **3aa** in 90% yield. When cat. **4** and cat. **5** were used as alternative catalysts, product **3aa** could be obtained only in 8 and 10% yields, respectively.[19] Clearly, the carbonyl group in

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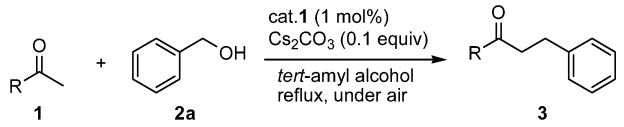
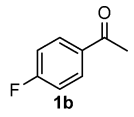
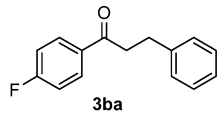
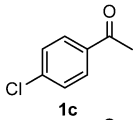
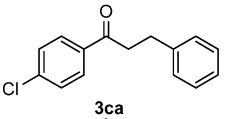
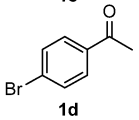
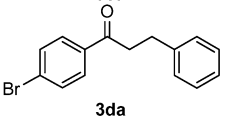
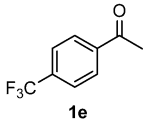
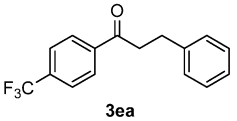
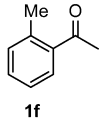
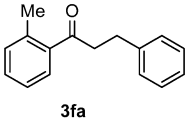
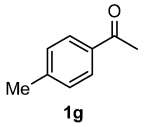
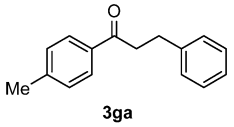
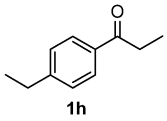
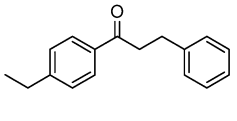
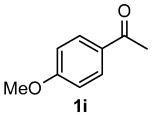
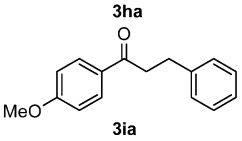
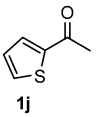
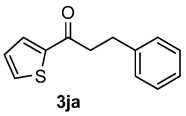
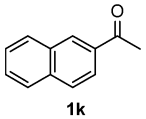
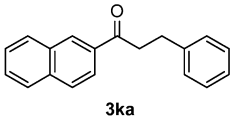
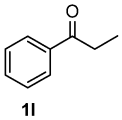
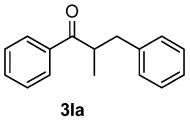
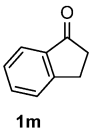
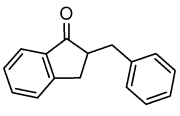
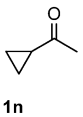
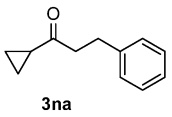
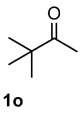
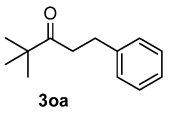
Table 3. α-Alkylation of a Range of Ketone 1 Derivatives with Benzyl Alcohol (2a)[a]



entry	ketone	product	yield (%)
1	 1b	 3ba	86
2	 1c	 3ca	90
3	 1d	 3da	88
4	 1e	 3ea	87
5	 1f	 3fa	89
6	 1g	 3ga	93
7	 1h		87

entry	ketone	product	yield (%)
8	 1i	 3ha 3ia	91
9	 1j	 3ja	85
10	 1k	 3ka	83
11	 1l	 3la	83
12	 1m	 3ma	79
13	 1n	 3na	83
14	 1o	 3oa	85

[a]Reaction conditions: **1** (1 mmol), **2a** (1.1 mmol), cat. **1** (1 mol %), Cs_2CO_3 (0.1 equiv), *tert*-amyl alcohol (1 mL), reflux, 6 h.

the ligand is critically important for catalytic hydrogen transfer, and thus cat. **1** may be regarded as a metal−ligand bifunctional catalyst.

Furthermore, the reaction of a ketone with an aldehyde in the presence of a hydrogen donor under catalytic conditions was investigated. The reaction of acetophenone (**1a**), benzaldehyde (**5**), and 2-propanol (**6**) (3 equiv) was performed in the presence of cat. **1** (1 mol %) and Cs_2CO_3 (0.1 equiv) in *tert*-amyl alcohol under reflux for 6 h to afford product **3aa** in 87% yield (Scheme 3). Apparently, cross-aldol condensation between **1a** and **5** occurred to afford (*E*)-chalcone (**4**), which was further hydrogenated by 2-propanol (**6**) to afford product **3aa**. These experiments strongly support the proposed mechanism in Scheme 1.

■ CONCLUSIONS

We have demonstrated that a Cp*Ir complex bearing a functional bipyridonate ligand is a highly effective and versatile catalyst for the α-alkylation of ketones with primary alcohols under environmentally benign and mild conditions (0.1 equiv of Cs_2CO_3, reflux in *tert*-amyl alcohol under an air atmosphere for 6 h). Furthermore, this complex also exhibited high levels of catalytic activity for the α-methylation of ketones with methanol. The mechanistic investigation revealed that the carbonyl group in the ligand is crucial for catalytic hydrogen transfer. Notably, the results of this study revealed the unique potential of Cp*Ir complexes bearing a functional bipyridonate ligand for the development of C−C bond-forming reactions with the activation of primary alcohols as electrophiles.

■ EXPERIMENTAL SECTION

Experimental Details. High-resolution mass spectra (HRMS) were obtained on a HPLC-Q-ToF MS (Micro) spectrometer and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M + Na]^+$. Melting points were measured on an X-6 micromelting apparatus. ^1H NMR spectra were recorded on a 500 MHz spectrometer. Chemical shifts are reported in delta (δ) units (parts per million (ppm) downfield from tetramethylsilane or ppm relative to the center of the singlet at 7.26 ppm for $CDCl_3$). Coupling constants (J) are reported in hertz (Hz), and the splitting patterns were designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. $^{13}C\{^1H\}$ NMR spectra were recorded on a 125 MHz spectrophotometer with broadband ^1H decoupling. Chemical shifts for $^{13}C\{^1H\}$ NMR spectra are reported in δ units, ppm relative to the center of the triplet at 77.0 ppm for $CDCl_3$. Analytical thin-layer

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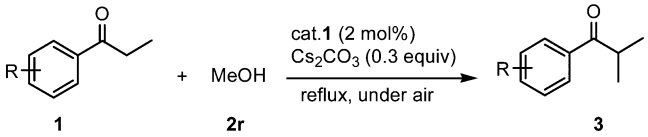
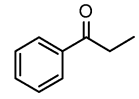
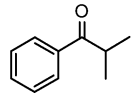
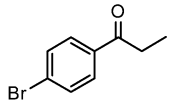
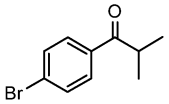
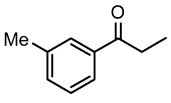
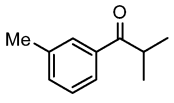
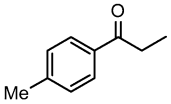
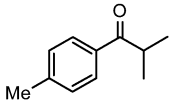
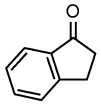
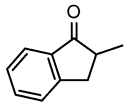
Table 4. α-Methylation of Ketone 1 Derivatives with Methanol 2r[a]



1 2r 3

Entry	Ketone	Product	Yield (%)
1	 1l	 3lr	85
2	 1p	 3pr	79
3	 1q	 3qr	81
4	 1r	 3rr	83[b]
5	 1m	 3mr	80

[a]Reaction conditions: **1** (1 mmol), **2r** (1 mL), cat. **1** (2 mol %), Cs_2CO_3 (0.3 equiv), reflux, 12 h. [b]Reaction time: 18 h.

chromatography (TLC) was carried out using commercial silica-gel plates (0.2 mm).

[Cp*Ir(2,2′-bpyO)(H_2O)] (cat. **1**),[10a] [Cp*Ir(2,2′-bpyO)(pyridine)] (cat. **2**),[10a] [Cp*Ir(2,2′-bpyO)(aniline)] (cat. **3**),[10b] Cp*Ir(bpy)(H_2O)][$OTf]_2$ (cat. **4**),[20] [Cp*Ir(bpy)Cl)][Cl] (cat. **5**),[21] [Cp*Ir(2-phenylpyridine-*k*C,N)]Cl (cat. **6**),[22] [Cp*Ir(H_2O)$_3$][$OTf]_2$ (cat. **7**),[23] [Cp*Ir(NH_3)$_3$][$Cl]_2$ (cat. **8**),[24] [Cp*$IrCl_2]_2$ (cat. **9**),[25] and [Ir(cod)$Cl]_2$ (cat. **10**)[26] were synthesized according to previous reports.

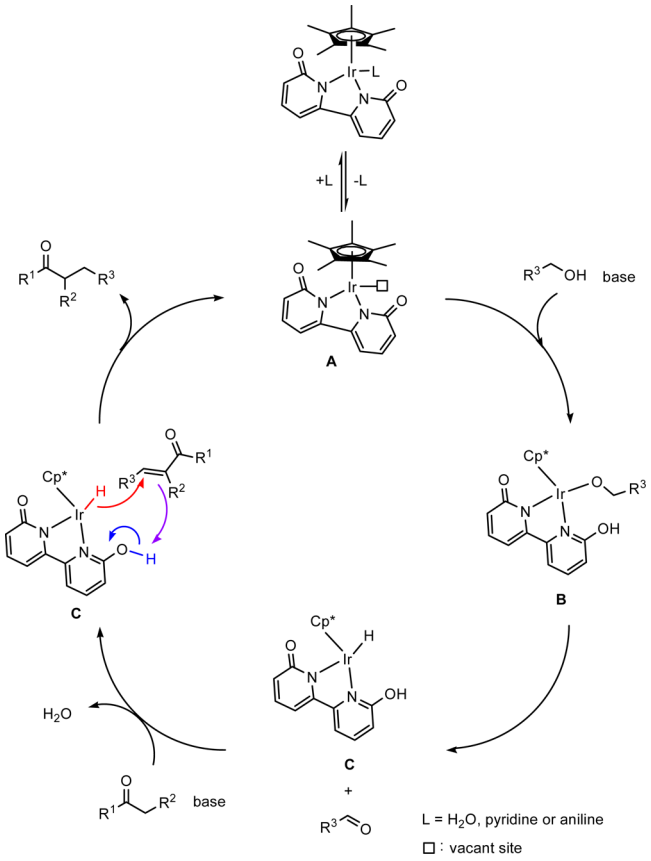
*General Procedure for the α-Alkylation of Ketones with Alcohols Catalyzed by [Cp*Ir(2,2′-bpyO)(H_2O)] (Cat. 1) (Tables 1–3).* In a round-bottomed flask with a condenser tube, ketone (1 mmol), alcohol (1.1 mmol, 1.1 equiv), cat. **1** (5.3 mg, 0.01 mmol, 1 mol %), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.1 equiv), and *tert*-amyl alcohol (1 mL) were placed under an air atmosphere. The reaction mixture was heated under reflux in an oil bath for 6 h. The reaction mixture was cooled to ambient temperature, concentrated in vacuo, and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding product.

*1,3-Diphenylpropan-1-one (**3aa**).*[7] White solid; 92% yield (193 mg); mp 69–70 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 6.9 Hz, 1H), 7.45 (t, *J* = 6.9 Hz, 2H), 7.34–7.23 (m, 4H), 7.20 (t, *J* = 6.7 Hz, 1H), 3.30 (t, *J* = 7.3 Hz, 2H), 3.07 (t, *J* = 7.3 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.2, 141.3, 136.9, 133.0, 128.6, 128.5, 128.4, 128.0, 126.1, 40.4, 30.1.

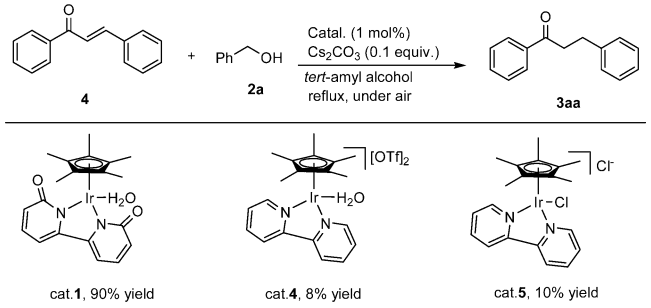
*3-(4-Fluorophenyl)-1-phenylpropan-1-one (**3ab**).*[27] White solid; 88% yield (201 mg); mp 65–66 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.5 Hz 2H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 6.1 Hz, 2H), 6.98 (t, *J* = 8.2 Hz, 2H), 3.28 (t, *J* = 7.3 Hz, 2H), 3.05 (t, *J* = 7.3 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.0, 161.4 (d, J_{C-F} = 242.8 Hz), 136.8, 136.7, 133.1, 129.8 (d, J_{C-F} = 7.6 Hz), 128.6, 128.0, 115.2 (d, J_{C-F} = 20.8 Hz), 40.4, 29.2.

*3-(2-Chlorophenyl)-1-phenylpropan-1-one (**3ac**).*[28] White solid; 87% yield (213 mg); mp 45–46 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.23–7.13 (m, 2H), 3.32 (t, *J* = 7.6 Hz, 2H), 3.18 (t, *J* = 7.6 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.0, 138.8, 136.7, 133.9, 133.1, 130.8, 129.5, 128.6, 128.0, 127.7, 126.9, 38.4, 28.3.

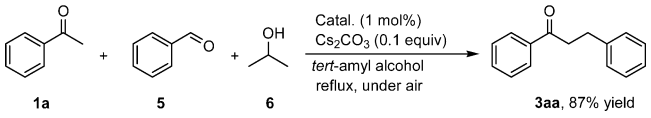
Scheme 1. Proposed Reaction Mechanism



Scheme 2. Hydrogen Transfer between α,β-Unsaturated Ketone 4 and Alcohol 2a



Scheme 3. Reaction of Ketone 1a, Aldehyde 5, and 2-Propanol (6)



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3-(4-Chlorophenyl)-1-phenylpropan-1-one (**3ad**).[29] White solid; 91% yield (222 mg); mp 53−54 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 7.5 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 3.29 (t, J = 7.6 Hz, 2H), 3.05 (t, J = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.8, 139.7, 136.7, 133.1, 131.8, 129.8, 128.6, 128.5, 128.0, 40.1, 29.3.

3-(2,4-Dichlorophenyl)-1-phenylpropan-1-one (**3ae**).[27] White solid; 90% yield (251 mg); mp 64−65 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.3 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.38 (d, J = 2.0 Hz, 1H), 7.26 (d, J = 8.2 Hz, 1H), 7.18 (dd, J = 8.2 and 2.0 Hz, 1H), 3.30 (t, J = 7.5 Hz, 2H), 3.15 (t, J = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.6, 137.4, 136.6, 134.5, 133.2, 132.6, 131.6, 129.3, 128.6, 128.0, 127.2, 38.1, 27.6.

3-(4-Bromophenyl)-1-phenylpropan-1-one (**3af**).[28] White solid; 86% yield (249 mg); mp 63−64 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 3.28 (t, J = 7.5 Hz, 2H), 3.03 (t, J = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.8, 140.2, 136.7, 133.1, 131.5, 130.2, 128.6, 128.0, 119.9, 40.0, 29.4.

1-Phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (**3ag**).[27] White solid; 84% yield (233 mg); mp 47−48 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98−7.92 (m, 2H), 7.60−7.52 (m, 3H), 7.46 (t, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 1H), 3.33 (t, J = 7.5 Hz, 2H), 3.14 (t, J = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.5, 145.4, 136.7, 133.2, 128.8, 128.6, 128.2 (q, J_{C-F} = 32.2 Hz), 128.0, 125.4 (q, J_{C-F} = 3.6 Hz), 124.3 (q, J_{C-F} = 270.5 Hz), 39.8, 29.7.

1-Phenyl-3-(4-(trifluoromethoxy)phenyl)propan-1-one (**3ah**). Pale-yellow oil; 85% yield (251 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98−7.92 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.27(d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 3.30 (t, J = 7.5 Hz, 2H), 3.08 (t, J = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.7, 147.6, 140.0, 136.8, 133.1, 129.7, 128.6, 128.0, 121.0, 120.5 (q, J_{C-F} = 255.1 Hz), 40.1, 29.3; HRMS (ESI) calcd for $C_{16}H_{13}O_2F_3$ + Na^+ $[M + Na]^+$ m/z, 317.0765; found, 317.0754.

1-Phenyl-3-p-tolylpropan-1-one (**3ai**).[7] White solid; 88% yield (198 mg); mp 33−34 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 6.4 Hz, 2H), 7.55 (t, J = 7.1 Hz, 1H), 7.45 (t, J = 7.4 Hz, 2H), 7.21−7.05 (m, 4H), 3.28 (t, J = 7.2 Hz, 2H), 3.03 (t, J = 7.2 Hz, 2H), 2.32 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.3, 138.2, 136.9, 135.6, 133.0, 129.2, 128.6, 128.3, 128.0, 40.6, 29.7, 21.0.

3-(4-Methoxyphenyl)-1-phenylpropan-1-one (**3aj**).[7] White solid; 90% yield (216 mg); mp 64−65 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.5 Hz, 2H), 7.55 (t, J = 7.1 Hz, 1H), 7.45 (t, J = 7.4 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 6.84 (d, J = 8.0 Hz, 2H), 3.79 (s, 3H) 3.27 (t, J = 7.5 Hz, 2H), 3.01 (t, J = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.3, 157.9, 136.8, 133.3, 133.0, 129.3, 128.5, 128.0, 113.9, 55.2, 40.7, 29.2.

3-(3,4-Dimethoxyphenyl)-1-phenylpropan-1-one (**3ak**).[30] White solid; 85% yield (230 mg); mp 65−66 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.1 Hz, 2H), 7.56 (t, J = 6.8 Hz, 1H), 7.46 (t, J = 7.0 Hz, 2H), 6.85−6.72 (m, 3H), 3.86 (d, J = 4.9 Hz, 6H), 3.29 (t, J = 7.0 Hz, 2H), 3.02 (t, J = 7.0 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.3, 148.9, 147.4, 136.9, 133.9, 133.0, 128.5, 128.0, 120.1, 111.8, 111.3, 55.9, 55.8, 40.6, 29.8.

3-(Naphthalen-1-yl)-1-phenylpropan-1-one (**3an**).[31] White solid; 83% yield (216 mg); mp 51−52 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 7.5 Hz, 1H), 7.87 (d, J = 7.7 Hz, 1H), 7.74 (t, J = 4.1 Hz, 1H), 7.59−7.47 (m, 3H), 7.47−7.35 (m, 4H), 3.54 (t, J = 7.4 Hz, 2H), 3.43 (t, J = 7.4 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.2, 137.3, 136.8, 133.9, 133.1, 131.6, 128.9, 128.6, 128.0, 127.0, 126.11, 126.05, 125.61, 125.57, 123.5, 39.7, 27.2.

3-(Furan-2-yl)-1-phenylpropan-1-one (**3al**).[7] Brown oil; 85% yield (169 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 7.4 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.31 (s, 1H), 6.31−6.26 (m, 1H), 6.08−6.03 (m, 1H), 3.34 (t, J = 7.5 Hz, 2H), 3.09 (t, J = 7.5 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.6, 154.7, 141.1, 136.7, 133.1, 128.6, 128.0, 110.2, 105.3, 36.9, 22.5.

3-Ferrocenyl-1-phenylpropan-1-one (**3am**).[32] Yellow solid; 82% yield (260 mg); mp 91−92 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 4.18−4.09 (m, 7H), 4.07 (s, 2H), 3.20 (t, J = 7.7 Hz, 2H), 2.79 (t, J = 7.7 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.5, 136.9, 133.0, 128.6, 128.0, 88.0, 68.5, 68.1, 67.3, 40.3, 24.1.

1-Phenylhexan-1-one (**3ao**).[33] Pale-yellow oil; 84% yield (147 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.4 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 2.96 (t, J = 7.4 Hz, 2H), 1.74 (quintet, J = 7.3 Hz, 2H), 1.41−1.33 (m, 4H), 0.91 (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 200.5, 137.0, 132.8, 128.5, 128.0, 38.5, 31.5, 24.0, 22.5, 13.9.

1-Phenyloctan-1-one (**3ap**).[34] Pale-yellow oil; 87% yield (178 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.4 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 2.96 (t, J = 7.4 Hz, 2H), 1.74 (quintet, J = 7.4 Hz, 2H), 1.40−1.26 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 200.6, 137.1, 132.8, 128.5, 128.0, 38.6, 31.7, 29.3, 29.1, 24.4, 22.6, 14.0.

3-Cyclohexyl-1-phenylpropan-1-one (**3aq**).[7] White solid; 85% yield (184 mg); mp 39−40 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H,), 7.46 (t, J = 7.6 Hz, 2H), 2.98 (t, J = 7.7 Hz, 2H), 1.78−1.68 (m, 4H), 1.68−1.61 (m, 3H), 1.35−1.28 (m, 1H), 1.28−1.13 (m, 3H), 1.00−0.90 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 200.8, 137.1, 132.8, 128.5, 128.0, 37.4, 36.1, 33.2, 31.8, 26.5, 26.3.

1-(4-Fluorophenyl)-3-phenylpropan-1-one (**3ba**).[35] White solid; 86% yield (196 mg); mp 38−39 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05−7.90 (m, 2H), 7.30 (t, J = 7.1 Hz, 2H), 7.27−7.18 (m, 3H), 7.12 (t, J = 7.5 Hz, 2H), 3.28 (t, J = 6.8 Hz, 2H), 3.06 (t, J = 6.9 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 197.6, 165.7 (d, J_{C-F} = 253.1 Hz), 141.1, 133.2, 130.6 (d, J_{C-F} = 8.9 Hz), 128.5, 128.4, 126.2,115.6 (d, J_{C-F} = 22.3 Hz), 40.3, 30.0.

1-(4-Chlorophenyl)-3-phenylpropan-1-one (**3ca**).[29] White solid; 90% yield (220 mg); mp 73−74 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 6.5 Hz, 2H), 7.42 (d, J = 6.5 Hz, 2H), 7.35−7.17 (m, 5H), 3.27 (t, J = 6.7 Hz, 2H), 3.06 (t, J = 6.7 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 197.9, 141.0, 139.5, 135.2, 129.4, 128.9, 128.5, 128.4, 126.2, 40.4, 30.0.

1-(4-Bromophenyl)-3-phenylpropan-1-one (**3da**).[36] White solid; 88% yield (255 mg); mp 98−99 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 7.9 Hz, 2H), 7.59 (d, J = 7.9 Hz, 2H), 7.35−7.18 (m, 5H), 3.27 (t, J = 7.3 Hz, 2H), 3.06 (t, J = 7.2 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.1, 141.0, 135.5, 131.9, 129.5, 128.5, 128.4, 128.2, 126.2, 40.4, 30.0.

3-Phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (**3ea**).[37] White solid; 87% yield (242 mg); mp 46 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.28−7.19 (m, 3H), 3.33 (t, J = 7.6 Hz, 2H), 3.08 (t, J = 7.6 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.2, 140.8, 139.5 134.4 (q, J_{C-F} = 32.6 Hz), 128.6, 128.4, 128.3, 126.3, 125.7, 123.6 (q, J_{C-F} = 271.2 Hz), 40.7, 29.9.

3-Phenyl-1-o-tolylpropan-1-one (**3fa**).[38] Colorless oil; 89% yield (199 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62−7.58 (m, 1H), 7.38−7.33 (m, 1H), 7.29 (t, J = 7.5 Hz, 2H), 7.26−7.17 (m, 5H), 3.23 (t, J = 7.7 Hz, 2H), 3.04 (t, J = 7.7 Hz, 2H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 203.3, 141.1, 138.0, 137.9, 131.9, 131.2, 128.5, 128.4, 128.3, 126.1, 125.6, 43.2, 30.3, 21.2.

3-Phenyl-1-p-tolylpropan-1-one (**3ga**).[39] White solid; 93% yield (209 mg); mp 68−69 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 7.4 Hz, 2H), 7.35−7.15 (m, 7H), 3.28 (t, J = 7.3 Hz, 2H), 3.06 (t, J = 7.2 Hz, 2H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.8, 143.8, 141.4, 134.3, 129.2, 128.5, 128.4, 128.1, 126.1, 40.3, 30.2, 21.6.

1-(4-Ethylphenyl)-3-phenylpropan-1-one (**3ha**). White solid; 87% yield (207 mg); mp 64−65 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 7.8 Hz, 2H), 7.35−7.24 (m, 6H), 7.21 (t, J = 6.8 Hz, 1H), 3.28 (t, J = 7.7 Hz, 2H), 3.06 (t, J = 7.6 Hz, 2H), 2.70 (quart, J = 7.5 Hz, 2H), 1.25 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.9, 150.0, 141.4, 134.6, 128.5, 128.4, 128.2, 128.1, 126.1, 40.3, 30.2,

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28.9, 15.2; HRMS (ESI) calcd for $C_{17}H_{18}O$ + Na^+ $[M + Na]^+$ m/z, 261.1255; found, 261.1262.

*1-(4-Methoxyphenyl)-3-phenylpropan-1-one (**3ia**).*[40] White solid; 91% yield (219 mg); mp 95−96 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 8.8 Hz, 2H), 7.30 (t, J = 7.4 Hz, 2H), 7.26 (d, J = 7.0 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 6.92 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H), 3.25 (t, J = 7.8 Hz, 2H), 3.06 (t, J = 7.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 197.8, 163.4, 141.4, 130.3, 129.9, 128.5, 128.4, 126.0, 113.7, 55.4, 40.1, 30.3.

*3-Phenyl-1-(thiophen-2-yl)propan-1-one (**3ja**).*[40] Brown solid; 85% yield (183 mg); mp 44−45 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, J = 3.8 and 0.6 Hz, 1H), 7.62 (dd, J = 4.9 and 0.7 Hz, 1H), 7.30 (t, J = 7.5 Hz, 2H), 7.27−7.23 (m, 2H), 7.21 (t, J = 7.2 Hz, 1H), 7.13−7.09 (m, 1H), 3.23 (t, J = 7.8 Hz, 2H), 3.07 (t, J = 7.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 192.1, 144.1, 141.0, 133.5, 131.8, 128.5, 128.4, 128.0, 126.2, 41.1, 30.3.

*1-(Naphthalen-2-yl)-3-phenylpropan-1-one (**3ka**).*[38] White solid; 83% yield (216 mg); mp 93−94 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.88 (t, J = 8.9 Hz, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.55 (t, J = 7.3 Hz, 1H), 7.37−7.27 (m, 4H), 7.22 (t, J = 6.6 Hz, 1H), 3.45 (t, J = 7.6 Hz, 2H), 3.13 (t, J = 7.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 199.1, 141.3, 135.5, 134.1, 132.5, 129.7, 129.5, 128.5, 128.4, 127.7, 126.7, 126.1, 123.8, 40.5, 30.2.

*2-Methyl-1,3-diphenylpropan-1-one (**3la**).*[41] Pale-yellow oil; 83% yield (186 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 7.5 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.26 (t, J = 7.5 Hz, 2H), 7.22−7.15 (m, 3H), 3.75 (sextet, J = 7.0 Hz, 1H), 3.17 (dd, J = 13.7 and 6.3 Hz, 1H), 2.69 (dd, J = 13.7 and 7.9 Hz, 1H), 1.20 (d, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 203.7, 140.0, 136.5, 132.9, 129.1, 128.6, 128.3, 128.2, 126.2, 42.7, 39.4, 17.4.

*2-Benzyl-2,3-dihydroinden-1-one (**3ma**).*[42] Yellow oil; 79% yield (176 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 7.7 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.40 (d, J = 7.7 Hz, 1H), 7.37 (t, J = 7.4 Hz, 1H), 7.30 (t, J = 7.5 Hz, 2H), 7.27−7.19 (m, 3H), 3.40 (dd, J = 14.0 and 4.3 Hz, 1H), 3.17 (dd, J = 17.2 and 7.8 Hz, 1H), 3.05−2.96 (m, 1H), 2.86 (dd, J = 17.2 and 4.0 Hz, 1H), 2.67 (dd, J = 14.0 and 10.5 Hz, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 207.7, 153.6, 139.6, 136.5, 134.8, 128.9, 128.5, 127.4, 126.5, 126.3, 124.0, 48.9, 37.0, 32.2.

*1-Cyclopropyl-3-phenylpropan-1-one (**3na**).*[43] Pale-yellow oil; 83% yield (145 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.31−7.26 (m, 2H), 7.22−7.16 (m, 3H), 2.95−2.85 (m, 4H), 1.95−1.87 (m, 1H), 1.05−0.99 (m, 2H), 0.88−0.83 (m, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 209.9, 141.2, 128.4, 128.3, 126.0, 44.9, 29.9, 20.5, 10.7.

*4,4-Dimethyl-1-phenylpentan-3-one (**3oa**).*[32] Pale-yellow oil; 85% yield (162 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.31−7.24 (m, 2H), 7.22−7.15 (m, 3H), 2.91−2.83 (m, 2H), 2.83−2.77 (m, 2H), 1.10 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 214.8, 141.5, 128.4, 128.3, 125.9, 44.0, 38.4, 30.0, 26.3.

*General Procedure for the α-Methylation of Ketones Using Methanol (**2r**) and [Cp*Ir(2,2′-bpyO)(H_2O)] as a Catalyst (Table 4).* In a round-bottomed flask with a condenser tube, ketone (1 mmol), methanol (**2r**) (1 mL), cat. **1** (10.6 mg, 0.02 mmol, 2 mol %), and Cs_2CO_3 (97.8 mg, 0.3 mmol, 0.3 equiv) were placed under an air atmosphere. The reaction mixture was heated under reflux in an oil bath for 12 h. The reaction mixture was cooled to ambient temperature, concentrated in vacuo, and purified by flash column chromatography with hexanes/ethyl acetate to afford the corresponding product.

*2-Methyl-1-phenylpropan-1-one (**3lr**).*[14] Colorless oil; 85% yield (126 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 3.56 (septet, J = 6.9 Hz, 1H), 1.22 (d, J = 6.9 Hz, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 204.5, 136.2, 132.7, 128.6, 128.3, 35.3, 19.1.

*1-(4-Bromophenyl)-2-methylpropan-1-one (**3pr**).*[14] Yellow oil; 79% yield (179 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.3 Hz, 2H), 3.49 (septet, J = 6.9 Hz, 1H), 1.21 (d, J = 6.9 Hz, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 203.3, 134.9, 131.9, 129.8, 127.9, 35.4, 19.0.

*2-Methyl-1-m-tolylpropan-1-one (**3qr**).*[15] Yellow oil; 81% yield (131 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.79−7.72 (m, 2H), 7.39−7.31 (m, 2H), 3.55 (septet, J = 6.8 Hz, 1H), 2.41 (s, 3H), 1.21 (d, J = 6.9 Hz, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 204.7, 138.3, 136.3, 133.5, 128.8, 128.4, 125.5, 35.3, 21.3, 19.2.

*2-Methyl-1-p-tolylpropan-1-one (**3rr**).*[15] Pale-yellow oil; 83% yield (135 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 3.54 (septet, J = 6.9 Hz, 1H), 2.41 (s, 3H), 1.21 (d, J = 6.9 Hz, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 204.1, 143.4, 133.7, 129.2, 128.4, 35.1, 21.5, 19.2.

*2-Methyl-2,3-dihydroinden-1-one (**3mr**).*[44] Pale-yellow oil; 80% yield (117 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 7.7 Hz, 1H), 7.58 (t, J = 7.4 Hz, 1H), 7.45 (d, J = 7.7 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 3.40 (quad, J = 8.8 Hz, 1H), 2.76−2.67 (m, 2H), 1.32 (d, J = 7.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 209.4, 153.4, 136.3, 134.6, 127.3, 126.5, 123.9, 42.0, 34.9, 16.2.

*Hydrogen Transfer between α,β-unsaturated Ketone **4** and Alcohol **2a** (Scheme 2).* In a round-bottomed flask with a condenser tube, (*E*)-chalcone (**4**) (1 mmol), benzyl alcohol (**2a**) (1.1 mmol), cat. **1** (5.3 mg, 0.01 mmol, 1 mol %), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.1 equiv), and *tert*-amyl alcohol (1 mL) were placed under an air atmosphere. The resulting mixture was then heated under reflux in an oil bath for 6 h, at which point the reaction mixture was allowed to cool to ambient temperature. The reaction mixture was concentrated in vacuo and purified by flash column chromatography with hexanes/ethyl acetate to afford product **3aa** in 90% yield (188 mg).

*Procedure for the Reaction of Ketone **1a**, Aldehyde **5**, and 2-Propanol (**6**) Using Catalyst **1** (Scheme 3).* In a round-bottomed flask with a condenser tube, ketone **1a** (1 mmol), aldehyde **5** (1.1 mmol), cat. **1** (5.3 mg, 0.01 mmol, 1 mol %), 2-propanol (**6**) (3 mmol, 3 equiv), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.1 equiv), and *tert*-amyl alcohol (1 mL) were placed under an air atmosphere. The reaction mixture was heated under reflux in an oil bath for 6 h. The reaction mixture was cooled to ambient temperature, concentrated in vacuo, and purified by flash column chromatography with hexanes/ethyl acetate to afford product **3aa** in 87% yield (183 mg).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H and ^{13}C NMR spectra of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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