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Use of a Cyclometalated Iridium(III) Complex Containing a N^C^N-Coordinating Terdentate Ligand as a Catalyst for the α-Alkylation of Ketones and *N*-Alkylation of Amines with Alcohols

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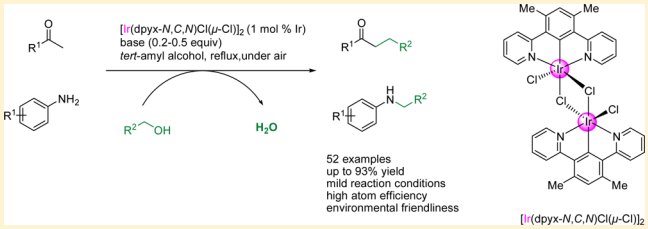
Supporting Information

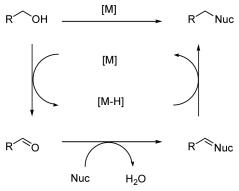
ABSTRACT: A cyclometalated iridium(III) complex containing a N^C^N-coordinating terdentate ligand [Ir(dpyx-*N*,*C*,*N*)-Cl(μ-Cl)]$_2$ was found to be a general and highly effective catalyst for the α-alkylation of ketones and *N*-alkylation of amines with alcohols. In the presence of catalyst (1 mol % Ir) and base (0.2−0.5 equiv), a variety of desirable products were obtained in good yields under an air atmosphere. Notably, this research exhibited the new potential of Ir(III) complexes bearing non-Cp* ligand and will facilitate the progress of the hydrogen autotransfer process.



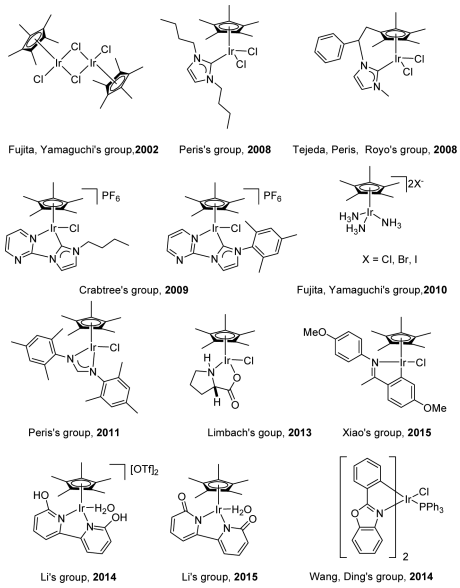
INTRODUCTION

Alkylation represents a class of the most important reactions for the construction of C−C and C−N bonds in organic synthesis.[1] Traditionally, alkylation is performed with alkyl halides as alkylating agents in the presence of a stoichiometric or excess amount of bases. In recent years, much attention has been paid to the alkylation with alcohols as alkylating agents based on a transition-metal-catalyzed hydrogen autotransfer process (or hydrogen-borrowing strategy).[2] In this process, alcohols are first dehydrogenated to form aldehydes, followed by the condensation of the resulting aldehydes with nucleophilic agents, which affords imine intermediates that are further hydrogenated by metal hydride species generated in the step of the dehydrogenation of alcohols to give alkylated products (Scheme 1). Such methodology is attractive because of the low toxicity of alcohols, high atom efficiency, and the formation of water as the only side product. Over the past decade, ruthenium,[3] iridium,[4,5] and other transition-metal complexes[6] have been developed as catalysts for the hydrogen autotransfer process. Especially, the half-sandwich iridium(III) complexes having a pentamethylcyclopentadienyl ligand, e.g. Cp*Ir(III), have emerged as one of the most effective and promising catalysts. As outlined in Scheme 2, representative examples includ [Cp*IrCl$_2$]$_2$ (Fujita, Yamaguich's group),[4a−c] Cp*Ir(III) complexes bearing a ligand such as *N*-heterocyclic carbene ligands (Peris's group, Crabtree's group),[4d−f] ammonias (Fujita,

Scheme 1. Transition-Metal-Catalyzed Hydrogen Autotransfer Process



Scheme 2. Representative Ir(III) Complexes as Catalysts for the Hydrogen Autotransfer Process



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Yamaguchi's group),[4g] bis(2,4,6-trimethylphenyl)formamidine (Peris's group),[4h] carbonate (Limbach's),[4i] and chelating ketimine (Xiao's group).[4j] More recently, we demonstrated that Cp*Ir(III) complexes bearing a functional bihydroxypyridine or bipyridonate ligand are metal−ligand bifunctional catalysts for the *N*-alkylation of sulfonamides in water and the α-alkylation of ketones with alcohols.[7,8] On the other hand, Ir(III) complexes bearing a non-Cp* ligand have obtained a wide application in recent years. They have been used as efficient catalysts for water oxidation,[9] CO_2 hydrogenation,[10] and organic photoredox reactions.[11] However, the potential of such complexes as catalysts for the alkylation with alcohols remains rarely explored. In 2014, Wang and co-workers reported a class of benzoxazolyl iridium(III) complexes which exhibited highly catalytic activities for the α-alkylation of ketones and *N*-alkylation of amines with alcohols.[12] However, it is necessary to add expensive $AgNTf_2$ to activate benzoxazolyl iridium(III) complexes. Moreover, these reactions required the presence of a stoichiometric amount of base and a nitrogen atmosphere. From both synthetic and environmental point of views, the development of a new type of Ir(III) complexes bearing a non-Cp* ligand as catalysts for the alkylation with alcohols under more environmentally benign conditions is apparently highly desirable.

We reported a series of environmentally friendly reactions based on the hydrogen autotransfer process catalyzed by Cp*Ir(III) complexes.[7,13] As part of our continuing effort in this field, we are interested in exploring the α-alkylation of ketones and *N*-alkylation of amines with alcohols catalyzed by air-stable cyclometalated complexes containing N^C^N-coordinating terdentate ligands. Such complexes were originally developed by Williams and co-workers[14] and used as organic light-emitting devices,[15] organic light-emitting diodes (OLEDs),[16,17] and catalysts for water photoreduction.[18]

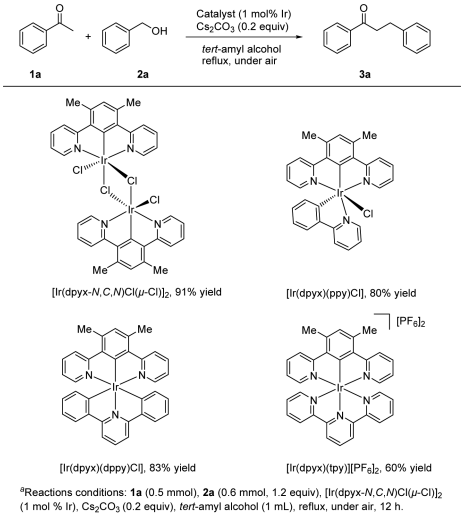
RESULTS AND DISCUSSION

Our initial investigation focused on the α-alkylation of acetophenone (**1a**) with benzylic alcohol (**2a**). As shown in Scheme 3, a range of cyclometalated iridium(III) complexes containing a N^C^N-coordinating terdentate ligand were chosen as catalysts for this model reaction. In the presence of dichlorobridged dimer complex $[Ir(dpyx\text{-}N,C,N)Cl(\mu\text{-}Cl)]_2$ (dpyx: 1,3-di(2-pyridyl)-4,6-dimethylbenzene) (1 mol % Ir) and Cs_2CO_3 (0.2 equiv), the reaction proceeded in *tert*-amyl alcohol at reflux under air atmosphere for 12 h to afford the desired α-alkylated product **3a** in 91% yield. Using neutral bisterdentate complexes [Ir(dpyx)(ppy)Cl] (ppy: 2-phenylpyridine) and [Ir(dpyx)(dppy)Cl] (dppy: 2,6-diphenylpyridine) as alternative catalysts, the product **3a** was also obtained in 80 and 83% yields, respectively. When a cationic bisterdentate complex $[Ir(dpyx)(tpy)][PF_6]_2$ (tpy: 2-(6-(pyridin-2-yl)pyridin-2-yl)pyridine) was examined, the reaction gave the product **3a** in only 60% yield.

Inspired by the above promising results, we examined the scope of α-alkylation with respect to alcohols catalyzed by $[Ir(dpyx\text{-}N,C,N)Cl(\mu\text{-}Cl)]_2$, and these results are outlined in Scheme 4. The α-alkylation of **1a** with benzylic alcohols bearing an electron-donating substituent such as methyl, isopropyl, and methoxy groups afforded the corresponding products **3b−f** in 80−89% yields. Similarly, benzylic alcohols bearing an electron-withdrawing group such as fluoro, chloro, bromo and trifluoromethyl groups were converted to the desired products **3g−k** in 82−88% yields. Transformations of 2-thiophenemethanol, ferrocenemethanol, and 2-naphthylmethanol gave the corresponding products **3l−n** in 77−87% yields as well. When aliphatic alcohols such as 1-hexanol, 2-methyl-1-butanol, 1-octanol, and 2-ethylhexan-1-ol were utilized, the desired products **3o−3r** were obtained in 75−78% yields.

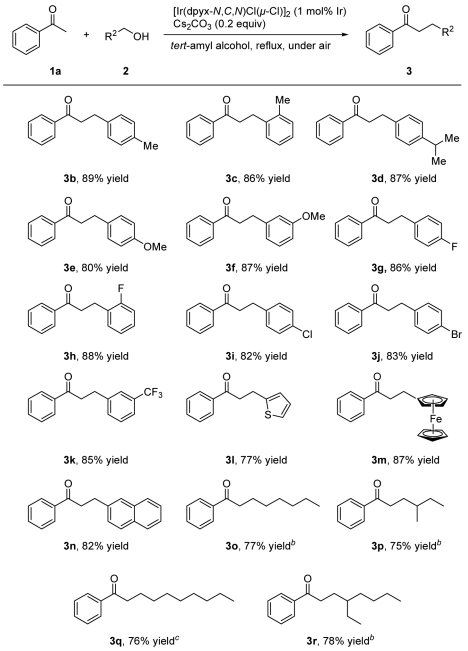
As shown in Scheme 5, the scope of α-alkylation with respect to ketones was then investigated. The α-alkylation of acetophenones (**1**) bearing an electron-donating or electron-withdrawing group with **2a** proceeded smoothly to give the corresponding products **4a−g** in 83−91% yields. For 1-indanone and 1-tetralone, reactions afforded the desired

Scheme 3. α-Alkylation of Acetophenone with Benzyl Alcohol as a Model Reaction



[a]Reactions conditions: **1a** (0.5 mmol), **2a** (0.6 mmol, 1.2 equiv), $[Ir(dpyx\text{-}N,C,N)Cl(\mu\text{-}Cl)]_2$ (1 mol % Ir), Cs_2CO_3 (0.2 equiv), *tert*-amyl alcohol (1 mL), reflux, under air, 12 h.

Scheme 4. α-Alkylation of Acetophenone with Various Alcohols



[a]Reactions conditions: **1a** (0.5 mmol), **2** (0.6 mmol, 1.2 equiv), $[Ir(dpyx\text{-}N,C,N)Cl(\mu\text{-}Cl)]_2$ (1 mol % Ir), Cs_2CO_3 (0.2 equiv), *tert*-amyl alcohol (1 mL), reflux, under air, 12 h. [b]**2** (2 equiv), Cs_2CO_3 (0.5 equiv). [c]**2** (2 equiv), KOH (0.3 equiv).

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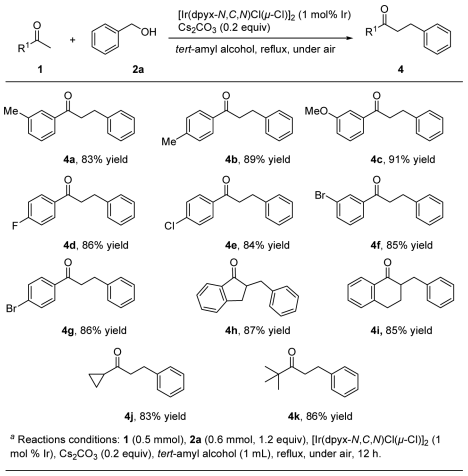
J. Org. Chem. 2017, 82, 1943−1950

Scheme 5. α-Alkylation of a Series of Ketones with Benzyl Alcohols

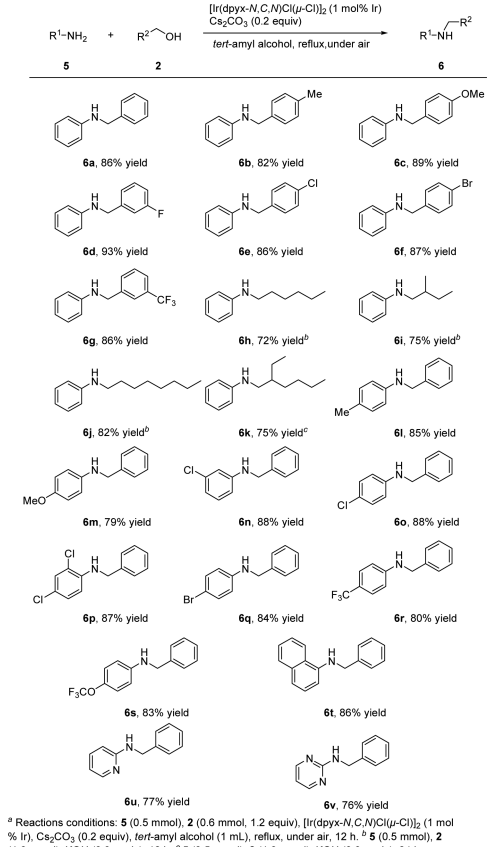


[a] Reactions conditions: **1** (0.5 mmol), **2a** (0.6 mmol, 1.2 equiv), [Ir(dpyx-*N,C,N*)Cl(μ-Cl)]$_2$ (1 mol % Ir), Cs_2CO_3 (0.2 equiv), *tert*-amyl alcohol (1 mL), reflux, under air, 12 h.

products **4h** and **4i** in 87 and 85% yields, respectively. In the case of aliphatic ketones, the desired products **4j** and **4k** were isolated in 83 and 86% yields, respectively.

To further expand the generality of catalytic system, the *N*-alkylation of amines with alcohols was then investigated (Scheme 6). Reactions of aniline with benzyl alcohols and benzylic alcohols bearing an electron-donating or electron-withdrawing group afforded the desired products **6a**−**g** in 82−93% yields. For aliphatic alcohols, the desired products **6h**−**k** were also obtained in 72−82% yields. Transformations of

Scheme 6. *N*-alkylation of Amines with Alcohols



[a] Reactions conditions: **5** (0.5 mmol), **2** (0.6 mmol, 1.2 equiv), [Ir(dpyx-*N,C,N*)Cl(μ-Cl)]$_2$ (1 mol % Ir), Cs_2CO_3 (0.2 equiv), *tert*-amyl alcohol (1 mL), reflux, under air, 12 h. [b] **5** (0.5 mmol), **2** (1.0 mmol), KOH (0.3 equiv), 12 h. [c] **5** (0.5 mmol), **2** (1.0 mmol), KOH (0.3 equiv), 24 h.

anilines bearing a variety of substituents with **2a** gave the corresponding products **6l**−**s** in 79−89% yields. The system was also applied to naphthylamine and heterocyclic anilines, giving the desired products **6t**−**v** in 76−86% yields.

A plausible mechanism is proposed to account for the α-alkylation of ketones and *N*-alkylation of amines with alcohols catalyzed by [Ir(dpyx-*N,C,N*)Cl(μ-Cl)]$_2$ (Scheme 7). The initial step of reaction involved the formation of alkoxo iridium species **A** by the reaction of iridium species with alcohols under the acceleration of base. Accompanied by the β-hydrogen elimination of alkoxo iridium species **A**, the iridium hydride species **B** coordinated with aldehydes were generated. Subsequently, the condensation between resulting **B** and ketones (or amines) occurred to give iridium hydride species **C** (or **E**) coordinated with α,β-unsaturated ketones (or imines). The addition of iridium hydride into the C═C bond of α,β-unsaturated ketones (or C═N bond of imines) afforded the carbanion-iridium species **D** (or amido-iridium species **F**). Finally, α-alkylated ketones (or *N*-alkylated amines) were released as products and the catalytically active alkoxo iridium species **A** were regenerated via the reaction of species **D** (or **F**) with alcohols.

To support the proposed mechanism shown in Scheme 7, the hydrogen transfer between an α,β-unsaturated ketone (or an unsaturated imine), which was formed by the condensation between a ketone (or a amine), an aldehyde, and an alcohol was conducted (Scheme 8). In the presence of [Ir(dpyx-*N,C,N*)-Cl(μ-Cl)]$_2$ (1 mol % Ir) and Cs_2CO_3 (0.2 equiv), the reaction of (*E*)-chalcone (**7**) with **2a** was carried out under reflux for 12 h to give the product **3a** in 88% yield. Similarly, the transformation of (*E*)-*N*-benzylidenebenzenamine (**8**) with **2a** gave the product **6a** in 86% yield.

The present catalytic system was also applied to direct synthesis of a biologically active molecule donepezil (a well-known acetylcholinesterase inhibitor used clinically to treat cognitive dysfunction in Alzheimer's disease) (Scheme 9).[19] In the presence of [Ir(dpyx-*N,C,N*)Cl(μ-Cl)]$_2$ (1 mol % Ir) and Cs_2CO_3 (0.2 equiv), the reaction of 5,6-dimethoxy-2,3-dihydroinden-1-one (**9**) with 2-((1-benzylpiperidin-4-yl)-methyl)-5,6-dimethoxy-2,3-dihydroinden-1-one (**10**) was performed at reflux for 12 h to give the desired product **11** in 85% yield.

■ CONCLUSION

In summary, we demonstrated that a cyclometalated iridium(III) complex containing a N^C^N-coordinating terdentate ligand [Ir(dpyx-*N,C,N*)Cl(μ-Cl)]$_2$ is a general and highly effective catalyst for the α-alkylation of ketones and *N*-alkylation of amines with primary alcohols. In the presence of catalyst (1 mol % Ir) and base (0.2−0.5 equiv), a variety of desirable products were obtained in good yields under an air atmosphere. Notably, this research exhibited the new potential of Ir(III) complexes bearing non-Cp* ligand and will facilitate the progress of the hydrogen autotransfer process.

■ EXPERIMENTAL SECTION

Experimental Details. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 500 MHz. Chemical shifts are reported in δ units and 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 values) 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 NMR spectra were

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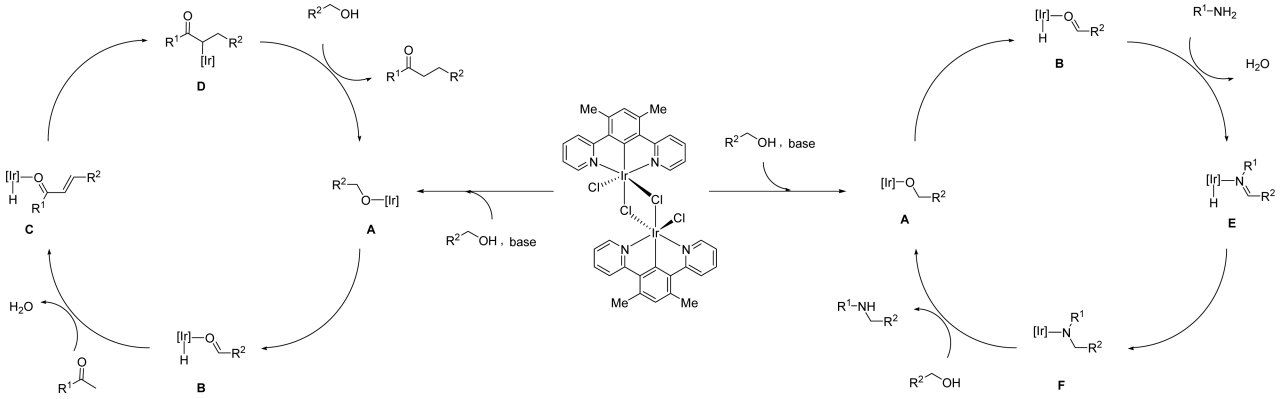
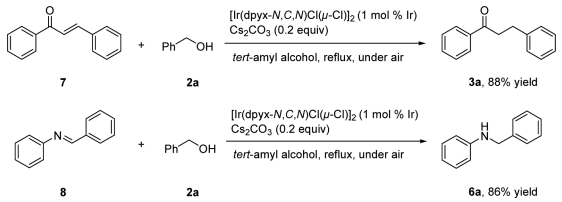
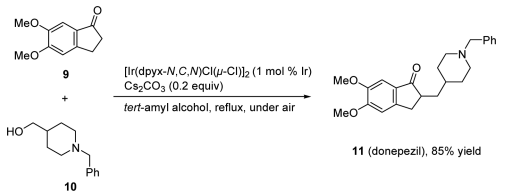
Scheme 7. Proposed Reaction Mechanism



Scheme 8. Transfer Hydrogenation of an Unsaturated Intermediate with an Alcohol



Scheme 9. Synthesis of Biologically Active Molecule Donepezil



recorded at 125 MHz. Chemical shifts are reported in δ units, ppm relative to the center of the triplet at 77.0 ppm for $CDCl_3$. ^{13}C NMR spectra were routinely run with broadband decoupling.

$[Ir(dpyx\text{-}N,C,N)Cl(\mu\text{-}Cl)]_2$, [Ir(dpyx)(ppy)Cl], [Ir(dpyx)(dppy)-Cl], and $[Ir(dpyx)(tpy)][PF_6]_2$ were synthesized according to previous reports.[14]

General Procedure for α-Alkylated Ketones with Alcohols Catalyzed by [Ir(dpyx-N,C,N)Cl(μ-Cl)]2 (Schemes 3 and 4). In a round-bottomed flask with a condenser tube, ketone (0.5 mmol), alcohol (0.6 mmol, 1.2 equiv), $[Ir(dpyx\text{-}N,C,N)Cl(\mu\text{-}Cl)]_2$ (2.6 mg, 0.0025 mmol, 1 mol % Ir), Cs_2CO_3 (33 mg, 0.1 mmol, 0.2 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 12 h. The reaction mixture was cooled to ambient temperature, concentrated in vacuo, and purified by flash column chromatography with hexane/ethyl acetrate to afford the corresponding product.

*1,3-Diphenylpropan-1-one (**3a**).*[3b] White solid; 86% yield (91 mg); mp 69−70 °C; ^1H 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); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 199.1, 141.2, 136.8, 133.0, 128.5, 128.5, 128.4, 128.0, 126.1, 40.4, 30.1.

*1-Phenyl-3-p-tolylpropan-1-one (**3b**).*[3b] White solid; 89% yield (100 mg); mp 33−34 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.3 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.15 (d, J = 8.1 2H), 7.11 (d, J = 8.0 Hz, 2H), 3.28 (t, J = 7.7 Hz, 2H), 3.03 (t, J = 7.7 Hz, 2H), 2.32 (s, 3H); $^{13}C\{1H\}$ 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.

*1-Phenyl-3-o-tolylpropan-1-one (**3c**).*[6c] Pale yellow oil; 86% yield (96 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.19−7.11 (m, 4H) 3.24 (t, J = 7.9 Hz, 2H), 3.05 (t, J = 7.8 Hz, 2H), 2.35 (s, 3H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 199.3, 139.4, 136.9, 136.0, 133.1, 130.4, 128.7, 128.6, 128.1, 126.3.126.2, 39.1, 27.5, 19.3.

*3-(4-Isopropylphenyl)-1-phenylpropan-1-one (**3d**).*[20] Pale yellow oil; 87% yield (110 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.2, 2H), 7.55 (t, J = 7.4, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.19−7.15 (m, 4H), 3.29 (t, J = 7.8 Hz, 2H), 3.04 (t, J = 7.8 Hz, 2H), 2.91−2.85 (m, 1H), 1.24 (d, J = 6.9 Hz, 6H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 199.3, 146.6, 138.5, 136.9, 132.9, 128.5, 128.3, 128.0, 40.5, 33.7, 29.7, 24.0.

*3-(4-Methoxyphenyl)-1-phenylpropan-1-one (**3e**).*[3b] White solid; 80% yield (96 mg); mp 64−65 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.17 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H), 3.27 (t, J = 7.7 Hz, 2H), 3.01 (t, J = 7.7 Hz, 2H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 199.3, 157.9, 136.9, 133.2, 132.9, 129.3, 128.5, 128.0, 113.9, 55.2, 40.6, 29.2.

*3-(3-Methoxyphenyl)-1-phenylpropan-1-one (**3f**).*[21] White solid; 87% yield (104 mg); mp 68−69 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.22(t, J = 7.9 Hz, 1H), 6.85 (d, J = 7.6 Hz, 1H), 6.80 (s, 1H), 6.76 (dd, J = 8.2 and 2.2 Hz, 1H), 3.80 (s, 3H) 3.30 (t, J = 7.7 Hz, 2H), 3.05 (t, J = 7.7 Hz, 2H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 199.0, 159.7, 142.8, 136.8, 132.9, 129.4, 128.5, 127.9,120.6, 114.2, 111.3, 55.0, 40.2, 30.1

*3-(4-Fluorophenyl)-1-phenylpropan-1-one (**3g**).*[22] White solid; 86% yield (98 mg); mp 65−66 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.20 (dd, J = 8.5 and 5.6 Hz, 2H), 6.97 (t, J = 8.7 Hz, 2H), 3.28 (t, J = 7.6 Hz, 2H), 3.05 (t, J = 7.6 Hz, 2H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 198.9, 161.4 (d, J_{C-F} = 243.9 Hz), 136.8, 136.8, 133.0, 129.8 (d, J_{C-F} = 7.7 Hz), 128.6, 128.0, 115.2 (d, J_{C-F} = 21.2 Hz), 40.3, 29.2.

*3-(2-Fluorophenyl)-1-phenylpropan-1-one (**3h**).*[23] Pale yellow oil, 88% yield (100 mg); ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.29−7.25 (m, 1H), 7.21−7.17 (m, 1H), 7.08−7.01 (m, 2H), 3.32 (t, J = 7.6 Hz, 2H), 3.18 (t, J = 7.6 Hz, 2H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 199.0, 161.2 (d, J_{C-F} = 243.9 Hz), 136.7, 133.1, 130.9 (d, J_{C-F} = 4.8 Hz), 128.6, 128.0, 127.9, 127.9,124.1 (d, J_{C-F} = 3.0 Hz), 115.3 (d, J_{C-F} = 22.1 Hz), 38.8, 23.9.

*3-(4-Chlorophenyl)-1-phenylpropan-1-one (**3i**).*[24] White solid; 82% yield (100 mg); mp 52−53 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.21 (dd, J = 8.5 and 5.5 Hz, 2H), 6.97 (t, J = 7.8 Hz, 2H), 3.28 (t, J = 7.6 Hz, 2H), 3.05 (t, J = 7.5 Hz, 2H); $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 198.8, 139.7, 136.7, 133.1, 131.8, 129.8, 128.6, 128.6, 128.0, 40.1, 29.3.

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J. Org. Chem. 2017, 82, 1943−1950

3-(4-Bromophenyl)-1-phenylpropan-1-one (**3j**).[25] White solid; 83% yield (120 mg); mp 63−64 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 7.3 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.3 Hz, 2H), 3.28 (t, J = 7.6 Hz, 2H), 3.03 (t, J = 7.5 Hz, 2H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 198.7, 140.2, 136.7, 133.1, 131.5, 130.2, 128.6, 127.9, 119.8, 40.0, 29.4.

1-Phenyl-3-(3-(trifluoromethyl)phenyl)propan-1-one (**3k**).[21] White solid; 85% yield (118 mg); mp 57−58 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.3 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.22 (t, J = 7.9 Hz, 1H), 6.85 (d, J = 7.6 Hz, 1H), 6.80 (s, 1H), 6.76 (dd, J = 8.2 and 2.2 Hz, 1H), 3.80 (s, 3H), 3.30 (t, J = 7.7 Hz, 2H), 3.05 (t, J = 7.7 Hz, 2H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 198.5, 142.2, 136.6, 133.2, 131.9, 130.8 (q, J_{C-F} = 32.0 Hz), 128.9, 128.6,128.0, 128.6, 128.0, 125.1 (d, J_{C-F} = 3.4 Hz), 124.2 (q, J_{C-F} = 272.1 Hz), 123.0 (d, J_{C-F} = 3.4 Hz), 39.9, 29.7.

3-(Thiophen-2-yl)-1-phenylpropan-1-one (**3l**).[21] White solid; 77% yield (83 mg); mp 46−47 °C; ^{1}H NMR (500 MHz,$CDCl_3$) δ 7.96 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.11 (dd, J = 5.1 and 1.0 Hz, 1H), 6.92−6.90 (m, 1H), 6.86−6.85 (m, 1H), 3.35 (t, J = 7.0 Hz, 2H), 3.29 (t, J = 7.0 Hz, 2H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 198.5, 143.8, 136.7, 133.1,128.6, 128.0, 126.8, 124.6, 123.3, 40.5, 24.2.

3-Ferrocenyl-1-phenylpropan-1-one (**3m**).[26] Red solid; 87% yield (138 mg); mp 90−91 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 4.13 (s, 5H), 4.11 (t, J = 1.7 Hz, 2H), 4.07 (t, J = 1.7 Hz, 2H), 3.20 (t, J = 7.7 Hz, 2H), 2.79 (t, J = 7.7 Hz, 2H); ^{13}C{1H} 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.

3-(Naphthalen-2-yl)-1-phenylpropan-1-one (**3n**).[21] White solid; 82% yield (107 mg); mp 65−66 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.2 Hz, 1H), 7.79 (t, J = 8.6 Hz, 3H), 7.68 (s,1H), 7.54 (t, J = 7.3 Hz, 1H), 7.46−7.38 (m, 5H), 3.38 (t, J = 7.7 Hz, 2H), 3.23 (t, J = 7.6 Hz, 2H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 199.1, 138.8, 136.8, 133.6, 133.0, 132.1, 128.6, 128.1, 128.0, 127.6, 127.5, 127.2, 126.5, 126.0, 125.3, 40.3, 30.2.

1-Phenyloctan-1-one (**3o**).[27] Pale yellow oil; 77% yield (79 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.3 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 2.96 (t, J = 7.4 Hz, 2H), 1.76−1.70 (m, 2H), 1.37−1.29 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 200.6, 137.1, 132.8, 128.5, 128.0, 38.6, 31.7, 29.3, 29.1, 24.3, 22.5, 14.0.

4-Methyl-1-phenylhexan-1-one (**3p**).[3b] Pale yellow oil; 75% yield (71 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.9 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.4 Hz, 2H), 3.02−2.90 (m, 2H), 1.81−1.74 (m, 1H), 1.58−1.51 (m, 1H), 1.46−1.36 (m, 2H), 1.26−1.16 (m, 1H), 0.93−0.88 (m, 6H); ^{13}C{1H} NMR (125 MHz,$CDCl_3$) δ 200.8, 137.1, 132.8, 128.5, 128.0, 36.3, 34.2, 30.9, 29.3, 19.0, 11.3.

1-Phenyldecan-1-one (**3q**).[28] Yellow oil; 76% yield (88 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 = 7.6 Hz, 2H), 2.96 (t, J = 7.4 Hz, 2H), 1.75−1.72 (m, 2H), 1.38−1.27 (m, 12H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 200.5, 137.1, 132.8, 128.5, 128.0, 38.6, 31.8, 29.4, 29.2, 24.3, 22.6, 14.0.

4-Ethyl-1-phenyloctan-1-one (**3r**).[5a] Yellow oil; 78% yield (90 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 7.3 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 2.94 (t, J = 7.8 Hz, 2H), 1.72−1.67(m, 2H), 1.35−1.25 (m, 9H), 0.90−0.86 (m, 6H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 200.9, 137.1, 132.8, 128.5, 128.0, 38.6, 36.1, 32.7, 28.9, 27.7, 25.7, 23.1,14.1, 10.9.

3-Phenyl-1-m-tolylpropan-1-one (**4a**).[29] Pale yellow oil; 83% yield (93 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79−7.77 (m, 2H), 7.39−7.35 (m, 2H), 7.32 (t, J = 7.4 Hz, 2H), 7.28−7.26 (m, 2H), 7.23 (t, J = 7.1 Hz, 1H), 3.31(t, J = 7.7 Hz, 2H), 3.08 (t, J = 7.7 Hz, 2H), 2.42 (s, 3H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 199.3, 141.3, 138.3, 136.9, 133.7, 128.6, 128.5, 128.4, 128.3, 126.0, 125.2, 40.4, 30.1, 21.3.

3-Phenyl-1-p-tolylpropan-1-one (**4b**).[29] White solid; 89% yield (100 mg); mp 67−68 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 7.5 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.26−7.24 (m, 4H), 7.21 (t, J = 7.2 Hz, 2H), 3.28 (t, J = 7.8 Hz, 2H), 3.06 (t, J = 7.7 Hz, 2H), 2.41 (s, 3H); ^{13}C{1H} 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-(3-Methoxyphenyl)-3-phenylpropan-1-one (**4c**).[23] Pale yellow oil; 91% yield (109 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, J = 7.7 Hz, 2H), 7.49 (m, 1H), 7.35 (t, J = 8.0 Hz, 1H) 7.30 (t, J = 7.4 Hz, 2H), 7.25−7.24 (m, 2H), 7.20 (t, J = 7.2 Hz, 1H), 7.09 (dd, J = 8.2 and 2.5 Hz, 1H), 3.84 (s, 3H), 3.29 (t, J = 7.8 Hz, 2H), 3.06 (t, J = 7.7 Hz, 2H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 199.0, 159.8, 141.2, 138.2, 129.6, 128.4, 126.1, 120.6, 119.5, 112.3, 55.4, 40.5, 30.2.

1-(4-Fluorophenyl)-3-phenylpropan-1-one (**4d**).[30] Gray solid; 86% yield (98 mg); mp 38−39 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (m, 2H), 7.30 (t, J = 7.4 Hz, 2H), 7.24 (d, J = 7.1 Hz, 2H), 7.21 (t, J = 7.3 Hz, 1H), 7.12 (t, J = 8.6 Hz, 2H), 3.27 (t, J = 7.7 Hz, 2H), 3.06 (t, J = 7.7 Hz, 2H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 197.6, 165.7 (d, J_{C-F} = 254.5 Hz), 141.1, 133.3, 130.6 (d, J_{C-F}= 9.3 Hz), 128.5, 128.4, 126.2, 115.6 (d, J_{C-F} = 21.9 Hz), 40.3, 30.1.

1-(4-Chlorophenyl)-3-phenylpropan-1-one (**4e**).[24] White solid; 84% yield (103 mg); mp 73−74 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.25−7.20 (m, 3H), 3.27 (t, J = 7.6 Hz, 2H), 3.06 (t, J = 7.6 Hz, 2H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 197.9, 141.0, 139.4, 135.1, 129.4, 128.9, 128.5, 128.3, 126.2, 40.3, 30.0.

1-(3-Bromophenyl)-3-phenylpropan-1-one (**4f**).[31] Pale yellow oil; 85% yield (122 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (t, J = 1.7 Hz, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.69−7.67 (m, 1H), 7.35−7.29 (m, 3H), 7.25−7.20 (m, 3H), 3.27 (t, J = 7.7 Hz, 2H), 3.06 (t, J = 7.6 Hz, 2H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 197.8, 140.9, 138.6, 135.9, 131.1, 130.2, 128.6, 128.4, 126.5, 126.2, 123.0, 40.5, 30.0.

1-(4-Bromophenyl)-3-phenylpropan-1-one (**4g**).[32] White solid; 86% yield (124 mg); mp 98−99 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.5 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.25−7.20 (m, 3H), 3.27 (t, J = 7.6 Hz, 2H), 3.06 (t, J = 7.6 Hz, 2H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 198.6, 140.4, 136.6, 132.9, 132.7, 130.6, 128.4, 127.9, 127.8, 127.5, 124.2, 38.4.3, 30.6.

2-Benzyl-2,3-dihydroinden-1-one (**4h**).[33] Yellow oil; 87% yield (97 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 7.6 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.40−7.35 (m, 2H), 7.29 (t, J = 7.4 Hz, 2H), 7.25−7.20 (m, 3H), 3.40 (dd, J = 14.0 and 4.2 Hz, 1H), 3.16 (dd, J = 17.1 and 7.3 Hz, 1H), 3.03−2.97 (m, 1H), 2.85 (dd, J = 17.2 and 4.1 Hz, 1H), 2.66 (dd, J = 13.9 and 10.5 Hz, 1H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 207.8, 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.

2-Benzyltetralin-1-one (**4i**).[34] Yellow oil; 85% yield (100 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 7.8 Hz, 1H), 7.45 (t, J = 7.4 Hz, 1H), 7.32−7.29 (m, 3H), 7.25−7.20 (m, 4H), 7.25−7.20 (m, 3H), 3.50 (dd, J = 13.8 and 4.0 Hz, 1H), 3.16 (dd, J = 17.1 and 7.3 Hz, 1H), 3.03−2.97 (m, 1H), 2.85 (dd, J = 17.2 and 4.1 Hz, 1H), 2.97−2.88 (m, 1H), 2.78−2.72 (m, 1H), 2.64 (dd, J = 13.8 and 9.0 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.3, 144.0, 140.0, 133.2, 132.5, 129.2, 128.7, 128.4, 127.5, 126.6, 126.1, 49.4, 35.7, 28.6, 27.7.

1-Cyclopropyl-3-phenylpropan-1-one (**4j**).[35] Pale yellow oil; 83% yield (72 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29−7.24 (m, 2H), 7.20−7.17 (m, 3H), 2.94−2.85 (m, 4H), 1.92−1.87 (m, 1H), 1.03−1.00 (m, 2H), 0.86−0.83 (m, 2H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 209.9, 141.1, 128.4, 128.3, 126.0, 44.9, 29.9, 20.5, 10.6.

4,4-Dimethyl-1-phenylpentan-3-one (**4k**).[3b] Pale yellow oil; 86% yield (82 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29−7.26 (m, 2H), 7.19−7.18 (m, 3H), 2.87 (t, J = 7.2 Hz, 2H), 2.79 (t, J = 7.1 Hz, 2H), 1.10 (s, 9H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 214.9, 141.6, 128.4, 128.3, 126.0, 44.1, 38.5, 30.1, 26.3.

General Procedure for the N-Alkylation of Amines with Alcohols Catalyzed by [Ir(dpyx-N,C,N)Cl(μ-Cl)]$_2$ (Scheme 5). In a round-bottomed flask with a condenser tube, amine (0.5 mmol), alcohol (0.6 mmol, 1.2 equiv), [Ir(dpyx-*N,C,N*)Cl(μ-Cl)]$_2$ (2.6 mg, 0.0025 mmol, 1 mol % Ir), Cs_2CO_3 (33 mg, 0.1 mmol, 0.2 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 12 h. The reaction mixture was cooled to ambient temperature, concentrated in vacuo, and purified by flash column chromatography with hexane/ethyl acetate to afford the corresponding product.

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J. Org. Chem. 2017, 82, 1943−1950

N-Benzylaniline (**6a**).[12] Pale yellow oil; 86% yield (79 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38−7.32 (m, 4H), 7.27 (t, J = 7.1 Hz, 1H), 7.17 (t, J = 7.9 Hz, 2H), 6.71 (t, J = 7.3 Hz, 1H), 6.63 (d, J = 7.7 Hz, 2H), 4.33 (s, 2H), 4.01 (brs, 1H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 148.2, 139.4, 129.3, 128.6, 127.5, 127.2, 117.6, 112.8, 48.3.

N-(4-Methylbenzyl)aniline (**6b**).[12] Pale yellow oil; 82% yield (81 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, J = 7.2 Hz, 2H), 7.18−7.14 (m, 4H), 6.71 (t, J = 7.3 Hz, 2H), 6.63 (d, J = 7.8 Hz, 2H), 4.28 (s, 2H), 3.97 (brs, 1H), 2.34 (s, 3H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 148.2, 136.8, 136.3, 129.3, 129.2, 127.5, 117.4, 112.8, 48.0, 21.1.

N-(4-Methoxybenzyl)aniline (**6c**).[12] Pale yellow solid; 89% yield (95 mg); mp 61−62 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, J = 7.3 Hz, 2H), 7.17−7.15 (m, 2H), 6.87 (d, J = 6.9 Hz, 2H), 6.70 (t, J = 7.5 Hz, 1H), 6.62 (d, J = 7.5 Hz, 2H), 4.23 (s, 2H), 3.92 (brs, 1H), 3.78 (s, 3H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 158.8, 148.2, 131.4, 129.2, 128.7, 117.4, 114.0, 112.8, 55.2, 47.7.

N-(3-Fluorobenzyl)aniline (**6d**).[36] Pale yellow oil; 93% yield (93 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (dd, J = 13.8 and 7.9 Hz, 1H), 7.19−7.13 (m, 3H), 7.08 (d, J = 9.8 Hz, 1H), 6.95 (td, J = 8.4 and 2.2 Hz, 1H), 6.73 (t, J = 7.3 Hz, 1H), 6.61 (d, J = 7.7 Hz, 2H), 4.34 (s, 2H), 4.09 (brs, 1H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 163.1 (d, J_{C-F} = 246.5 Hz), 147.8, 142.3 (d, J_{C-F} = 6.6 Hz), 130.0 (d, J_{C-F} = 8.2 Hz), 129.2, 122.7, 114.0 (d, J_{C-F} = 15.7 Hz), 113.9 (d, J_{C-F} = 15.2 Hz), 112.8, 47.7.

N-(4-Chlorobenzyl)aniline (**6e**).[12] Pale yellow solid; 86% yield (93 mg), mp 50−51 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (s, 4H), 7.16 (t, J = 7.9 Hz, 2H), 6.72 (t, J = 7.4 Hz, 1H), 6.60 (d, J = 7.7 Hz, 2H), 4.29 (s, 2H), 4.03 (brs, 1H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 147.8, 138.0, 132.8, 129.2, 128.7, 128.6, 117.8, 112.9, 46.60.

N-(4-Bromobenzyl)aniline (**6f**).[36] Pale yellow solid; 87% yield (114 mg); mp 51−52 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 7.19 (t, J = 7.6 Hz, 1H), 6.75 (t, J = 7.6 Hz, 1H), 6.62 (d, J = 7.9 Hz, 2H), 4.29 (s, 2H), 4.05 (brs, 1H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 147.7, 138.5, 131.6, 129.2, 129.0, 120.8, 127.70, 117.7, 112.8, 47.6.

N-(3-Trifluoromethylbenzyl)aniline (**6g**).[37] Pale yellow oil; 86% yield (108 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.55−7.51 (m, 2H), 7.43 (t, J = 7.7 Hz, 2H), 7.17 (t, J = 8.0 Hz, 2H), 6.73 (t, J = 7.3 Hz, 1H), 6.60 (d, J = 7.7 Hz, 2H), 4.37 (s, 2H), 4.07 (brs, 1H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 147.7, 140.6, 130.9 (q, J_{C-F} = 32.2 Hz), 130.6, 129.3, 129.1, 124.1 (q, J_{C-F} = 272.3 Hz), 124.1, 118.0, 112.9, 47.9.

N-Hexylaniline (**6h**).[38] Pale yellow oil; 72% yield (64 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (t, J = 7.8 Hz, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.60 (d, J = 8.1 Hz, 2H), 3.58 (brs, 1H), 3.10 (t, J = 7.2 Hz, 2H), 1.61 (p, J = 7.3 Hz, 2H), 1.43−1.37 (m, 2H), 1.33−1.31 (m, 4H), 0.90 (t, J = 6.6 Hz, 3H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 148.5, 129.2, 117.0, 112.7, 44.0, 31.6, 29.5, 26.8, 22.6, 14.0.

N-(2-Methylbutyl)aniline (**6i**).[39] Pale yellow oil; 75% yield (61 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (t, J = 7.9 Hz, 2H), 6.67 (t, J = 7.3 Hz, 1H), 6.58 (d, J = 7.7 Hz, 2H), 3.65 (brs, 1H), 3.06−3.02 (m, 1H), 2.90−2.86 (m, 1H), 1.69−1.63 (m, 1H), 1.53−1.45 (m, 1H), 1.25−1.16 (m, 1H), 0.96−0.91 (m, 6H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 148.6, 129.2, 116.9, 112.6, 49.9, 34.5, 27.3, 17.5, 11.3.

N-Octylaniline (**6j**).[40] Yellow oil; 82% yield (84 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (t, J = 7.8 Hz, 2H), 6.68 (t, J = 7.3 Hz, 2H), 6.59 (d, J = 8.4 Hz, 2H), 3.58 (brs, 1H), 3.09 (t, J = 7.2 Hz, 2H), 1.62−1.59 (m, 2H), 1.30−1.28 (m, 8H), 0.90−0.87 (m, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 148.5, 129.2, 117.0, 112.6, 44.0, 31.8, 29.6, 29.4, 29.3, 27.2, 22.6, 14.1.

N-(2-Ethylhexyl)aniline (**6k**).[12] Yellow oil; 75% yield (77 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (t, J = 7.7 Hz, 2H), 6.67 (t, J = 7.8 Hz, 1H), 6.60 (d, J = 8.0 Hz, 2H), 3.60 (brs, 1H), 3.01 (d, J = 6.8 Hz, 2H), 1.57−1.53 (m, 1H), 1.43−1.38 (m, 2H), 1.35−1.30 (m, 6H), 0.92−0.89 (m, 6H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 148.7, 129.1, 116.9, 112.6, 47.0, 39.1, 31.3, 29.0, 24.5, 23.2, 14.1, 10.9.

N-Benzyl-4-methylaniline (**6l**).[36] Pale yellow oil; 85% yield (84 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35−7.30 (m, 4H), 7.25 (t, J = 7.3 Hz, 1H), 6.97 (d, J = 8.2 Hz, 2H), 6.54 (d, J = 8.3 Hz, 2H), 4.28 (s, 2H), 3.87 (brs, 1H), 2.22 (s, 3H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 145.9, 139.6, 129.7, 128.6, 127.4, 127.1, 126.7,112.9, 48.9, 20.4.

N-Benzyl-4-methoxyaniline (**6m**).[12] Pale yellow oil; 79% yield (84 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36−7.30 (m, 4H), 7.25 (t, J = 7.0 Hz, 1H), 6.76 (d, J = 8.9 Hz, 2H), 6.58 (d, J = 8.9 Hz, 2H), 4.26 (s, 2H), 3.71 (s, 3H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 152.1, 142.4, 139.6, 128.5, 127.5, 127.1, 114.9, 114.0, 55.7, 49.2.

N-Benzyl-3-chloroaniline (**6n**).[12] Pale yellow oil; 88% yield (96 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 5.1 Hz, 4H), 7.29−7.26 (m, 1H), 7.04 (t, J = 8.0 Hz, 1H), 6.68 (dd, J = 7.9 and 1.3 Hz, 1H), 6.62 (s, 1H), 6.49 (dd, J = 8.2 and 1.6 Hz, 1H), 4.29 (s, 1H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 148.5, 138.3, 135.0, 130.2, 128.7, 127.6, 127.5, 117.9, 113.0, 112.6, 48.4.

N-Benzyl-4-chloroaniline (**6o**).[12] Pale yellow oil; 88% yield (96 mg), mp 46−45 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 4.3 Hz, 4H), 7.29−7.27 (m, 1H), 7.10 (d, J = 8.3 Hz, 4H), 6.53 (d, J = 8.2 Hz, 4H), 4.29 (s, 2H), 4.07 (brs, 1H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 146.6, 138.9, 129.0, 128.7, 127.4,127.3,122.0, 113.9, 48.3.

N-Benzyl-2,4-dichloroaniline (**6p**).[41] Pale yellow oil; 87% yield (109 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36−7.31 (m, 4H), 7.29−7.25 (m, 2H), 7.02 (dd, J = 8.7 and 2.3 Hz, 1H), 6.50 (d, J = 8.3 Hz, 1H), 4.71 (brs, 1H), 4.35 (d, J = 4.5 Hz, 1H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 142.5, 138.2, 128.7, 128.7, 127.7,127.5,127.1, 121.3, 119.3, 112.0, 47.8.

N-Benzyl-4-bromoaniline (**6q**).[36] Pale yellow oil; 84% yield (110 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 4.5 Hz, 4H), 7.29−7.26 (m, 1H), 7.23 (d, J = 8.4 Hz, 4H), 6.49 (d, J = 8.7 Hz, 4H), 4.28 (s, 2H), 4.06 (brs, 1H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 147.0, 138.8, 131.9, 128.7, 127.4, 114.4, 109.1, 48.2.

N-Benzyl-4-trifluoromethylaniline (**6r**).[42] White solid; 80% yield (100 mg); mp 53−54 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 8.6 Hz, 2H), 7.34−7.31 (m, 4H), 7.29−7.26 (m, 1H), 6.59 (d, J = 8.6 Hz, 2H), 4.33 (s, 2H), 4.11 (brs, 1H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 150.4, 138.4, 128.8, 127.5, 127.3, 126.6 (d, J_{C-F} = 3.4 Hz), 124.9 (q, J_{C-F} = 270.2 Hz), 119.0 (q, J_{C-F} = 32.5 Hz), 111.9, 47.8.

N-Benzyl-4-trifluoromethoxyaniline (**6s**).[43] Pale yellow oil; 83% yield (111 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37−7.29 (m, 5H), 7.02 (d, J = 8.3 Hz, 2H), 6.58 (d, J = 9.0 Hz, 2H), 4.32 (s, 2H), 4.11 (brs, 1H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 146.9, 140.6, 138.9, 128.7, 127.4, 122.4, 120.7 (q, J_{C-F} = 255.1 Hz), 113.0, 113.0, 48.4.

N-Benzylnaphthalen-1-amine (**6t**).[12] White solid; 86% yield (100 mg); mp 69−70 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85−7.81 (m, 2H), 7.48−7.25 (m, 9H), 6.65 (d, J = 7.4 Hz, 1H), 4.71 (brs, 1H), 4.52 (s, 2H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 143.2, 139.1, 134.2, 128.7, 127.7, 127.3, 126.6, 125.7, 124.7, 123.3, 119.9, 117.6, 104.7, 48.5.

2-Benzylaminopyridine (**6u**).[12] White solid; 77% yield (71 mg); mp 92−93 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 4.9 Hz, 1H), 7.38−7.30 (m, 5H), 7.25(t, J = 7.7 Hz, 1H), 6.55 (dd, J = 6.9 and 5.7 Hz, 1H), 6.34 (d, J = 8.4 Hz,1H), 5.12 (brs, 1H), 4.48 (d, J = 5.9 Hz, 2H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 158.6, 148.1, 139.1, 137.4, 128.5, 127.3, 127.1, 113.0, 106.7, 46.2.

N-Benzyl-(2-pyrimidyl)amine (**6v**).[44] White solid; 76% yield (70 mg); mp 78−79 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, J = 4.5 Hz, 2H), 7.37−7.32 (m, 4H), 7.29−7.26 (m, 1H), 6.54 (t, J = 9.7 Hz, 1H), 5.59 (brs, 1H), 4.64 (d, J = 5.9 Hz, 2H); ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 162.3, 158.0, 139.1, 128.6, 127.5, 127.2, 110.7, 45.4.

Hydrogen Transfer between an α,β-Unsaturated Ketone and an Alcohol (Scheme 7). In a round-bottomed flask with a condenser tube, **7** (104 mg, 0.5 mmol), **2a** (65 mg, 0.6 mmol), [Ir(dpyx-*N,C,N*)Cl(μ-Cl)]$_2$ (2.6 mg, 0.0025 mmol, 1 mol % Ir), Cs_2CO_3 (33 mg, 0.1 mmol, 0.2 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 12 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 **3a** in 88% yield (92 mg).

Hydrogen Transfer between an Imine and an Alcohol (Scheme 8). In a round-bottomed flask with a condenser tube, **8** (91 mg, 0.5 mmol), **2a** (65 mg, 0.6 mmol), [Ir(dpyx-*N,C,N*)Cl(μ-Cl)]$_2$ (2.6 mg,

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J. Org. Chem. 2017, 82, 1943−1950

0.0025 mmol, 1 mol % Ir), Cs_2CO_3 (33 mg, 0.1 mmol, 0.2 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 12 h, at which point the reaction mixture was allowed to cool to ambient temperature. 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 hexane/ethyl acetate to afford product **6a** in 86% yield (79 mg).

Procedure for the Synthesis of Donepezil (Scheme 9). In a round-bottomed flask with a condenser tube, **9** (96 mg, 0.5 mmol),**10** (123 mg, 0.6 mmol, 1.2 equiv), $[Ir(dpyx\text{-}N,C,N)Cl(\mu\text{-}Cl)]_2$ (2.6 mg, 0.0025 mmol, 1 mol % Ir), Cs_2CO_3 (33 mg, 0.1 mmol, 0.2 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 12 h. The reaction mixture was cooled to ambient temperature, concentrated in vacuo, and purified by flash column chromatography with hexane/ethyl acetate to afford the corresponding product.

2-((1-Benzylpiperidin-4-yl)methyl)-5,6-dimethoxy-2,3-dihydroinden-1-one (11).[45] Pale yellow oil; 85% yield (162 mg); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.32−7.22 (m, 5H), 7.06−7.05 (m, 2H), 3.85 (s, 3H), 3.78 (s, 3H), 3.42 (s, 2H), 3.22−3.17 (dd, J = 17.6 and 8.1 Hz, 1H), 2.80−2.75 (m, 2H), 2.65−2.62 (m, 2H), 1.91−1.87 (m, 2H), 1.72−1.67 (m 2H), 1.60−1.57 (m, 1H), 1.46−1.38 (m, 1H), 1.26−1.10 (m, 3H); ^{13}C{1H} NMR (125 MHz, DMSO-d_6) δ 206.5, 155.2, 149.0, 148.6, 138.6, 128.7, 128.3, 128.0, 126.7, 108.1, 103.9, 62.5, 55.8, 55.5, 53.2, 44.7, 38.2, 33.8, 32.6, 31.4.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02758.

^{1}H NMR and ^{13}C NMR spectra of the products (PDF)

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Notes

The authors declare no competing financial interest.

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