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*J. Org. Chem.*, **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b02957 • Publication Date (Web): 08 Jan 2020

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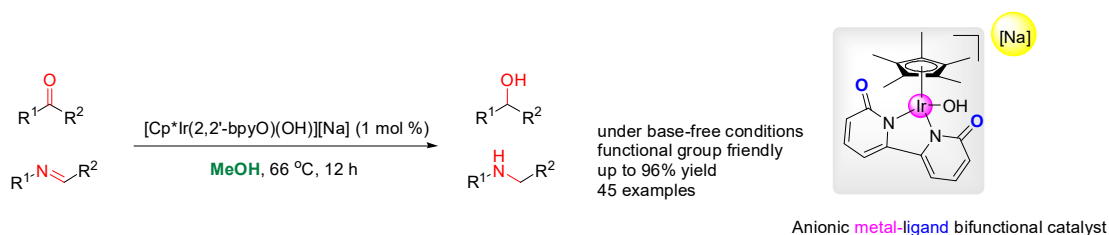
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# Transfer Hydrogenation of Ketones and Imines with Methanol under Base-Free Conditions Catalyzed by an Anionic Metal-Ligand Bifunctional Iridium Catalyst

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## ABSTRACT:

An anionic iridium complex  $[\text{Cp}^*\text{Ir}(2,2'\text{-bpyO})(\text{OH})][\text{Na}]$  was found to be a general and highly efficient catalyst for transfer hydrogenation of ketones and imines with methanol under base-free conditions. Readily reducible or labile substituents, such as nitro, cyano and ester

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6 groups, were tolerated under present reaction conditions. Notably, this study exhibited unique  
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8 potential of anionic metal-ligand bifunctional iridium catalysts for transfer hydrogenation with  
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10 methanol as a hydrogen source.  
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## 12 ■ INTRODUCTION

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16 The reduction of ketones and imines represents one of the most important transformations both  
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18 in the laboratory and in industry. With increasing global environmental concerns, extensive  
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20 effort has been devoted to transition metal-catalyzed transfer hydrogenation of ketones and  
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22 imines using 2-isopropanol, formic acid or its derivatives as hydrogen sources<sup>1</sup> due to that it avoids  
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24 the use of stoichiometric amount of reducing reagents such as LiAlH<sub>4</sub> and NaBH<sub>4</sub>,<sup>2</sup> and  
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26 hazardous molecular hydrogen and high-pressure equipment.<sup>3</sup> Methanol, the simplest alcohol,  
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28 can be from natural gas, coal and, carbon dioxide and renewable biomass. Although methanol  
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30 has been utilized as a fuel, chemical feedstock and energy storage media,<sup>4</sup> it was used as a  
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32 hydrogen source for transition metal-catalyzed transfer hydrogenation remained less explored  
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34 despite excellent hydrogen carrier ability (about 12.5 wt% hydrogen). Compared with higher  
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36 alcohols, the dehydrogenation of methanol required relatively high energy.<sup>5</sup> Recently, Garcia and  
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38 co-workers reported Nickel-catalyzed transfer hydrogenation of  $\alpha,\beta$ -unsaturated enones with  
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40 methanol at 180 °C.<sup>6</sup> Chen and co-worker described transfer hydrogenation of biomass-based  
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42 furfural and 5-hydroxymethylfurfural with methanol over hydrotalcite-derived copper catalysts  
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44 at > 200 °C.<sup>7</sup> More recently, Xiao and co-workers demonstrated transfer hydrogenation of  
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46 aromatic aldehydes with methanol at 90 °C catalyzed by a cyclometalated rhodium complex in  
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48 the presence of 0.5 equiv of base.<sup>8</sup> To the best of our knowledge, Crabtree and workers explored  
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50 the only an example of transfer hydrogenation of ketones and imines with methanol catalyzed by  
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52 a bis-NHC iridium complex bearing CO ligands to date.<sup>9</sup> However, this procedure required high  
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6 catalytic loading (5 mol%), large amount of strong base (KOH, 1-5 equiv), high temperature  
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8 (120 °C) and microwave irradiation, and still suffer from highly limited scope of substrates and  
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10 low yields. Therefore, the development of a general and efficient organometallic catalyst for  
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12 transfer hydrogenation of ketones and imines with methanol under environmentally more  
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14 friendly conditions is still an extreme challenging subject.

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17 In recent years, Fujita and co-workers synthesized a range of iridium complexes bearing a  
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19 bipyridine or a bipyridonate ligand, which were found to be highly efficient catalysts for  
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21 acceptorless dehydrogenation of alcohols and N-heterocycles,<sup>10</sup> and hydrogen production from a  
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23 methanol-water solution under basic conditions.<sup>11</sup> We reported also that these complexes are  
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25 effective metal-ligand bifunctional catalysts for hydrogen auto-transfer process,<sup>12</sup> acceptorless  
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27 dehydrogenative cyclization<sup>13</sup> and transfer hydrogenation of aldehydes with isopropanol.<sup>14</sup> As a  
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29 continuing interest in developing environmentally friendly reaction,<sup>12-15</sup> we herein wish to report  
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31 transfer hydrogenation of ketones and imines with methanol under base-free conditions .  
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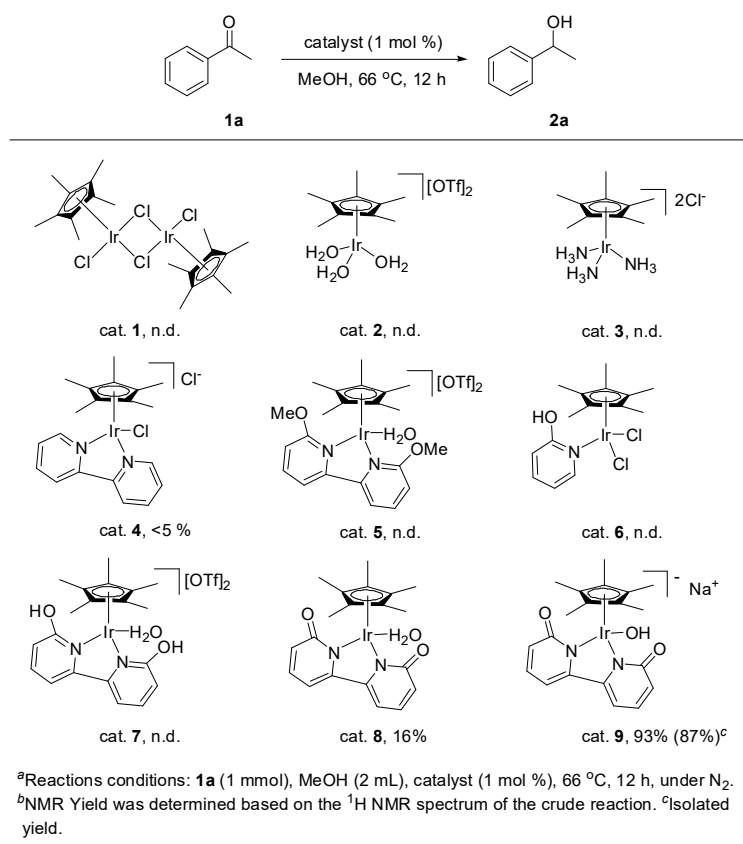
## 37 ■ RESULTS AND DISCUSSION

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40 Initially, the transfer hydrogenation of acetophenone (**1a**) with methanol was selected as a model  
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42 to explore the feasibility of reaction. As shown in Scheme 1, a series of iridium complexes, such  
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44 as  $[\text{Cp}^*\text{IrCl}_2]_2$  ( $\text{Cp}^*$  = pentamethylcyclopentadienyl) (cat. **1**),  $[\text{Cp}^*\text{Ir}(\text{H}_2\text{O})_3][\text{OTf}]_2$  (cat. **2**),  
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46  $[\text{Cp}^*\text{Ir}(\text{NH}_3)_3][\text{Cl}]_2$  (cat. **3**),  $[\text{Cp}^*\text{Ir}(\text{bpy})\text{Cl}][\text{Cl}]$  (cat. **4**),  $[\text{Cp}^*\text{Ir}(6,6'-(\text{OMe})_2-2,2'$   
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48  $\text{bpy})(\text{H}_2\text{O})][\text{OTf}]_2$  (cat. **5**),  $[\text{Cp}^*\text{Ir}(2-(\text{OH})\text{py})\text{Cl}_2]$  (cat. **6**),  $[\text{Cp}^*\text{Ir}(6,6'-(\text{OH})_2-2,2'$   
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50  $\text{bpy})(\text{H}_2\text{O})][\text{OTf}]_2$  (cat. **7**),  $[\text{Cp}^*\text{Ir}(2,2'\text{-bpyO})(\text{H}_2\text{O})]$  (cat. **8**) and  $[\text{Cp}^*\text{Ir}(2,2'\text{-bpyO})(\text{OH})][\text{Na}]$   
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52 (cat. **9**), were examined for their catalytic activity for this model reaction. In the presence of cat.  
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54 **1-7** (1 mol%), the reaction of **1a** (1 mmol) with methanol (2 mL) as both solvent and hydrogen  
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donor was carried out at 66 °C for 12 h, and none of product was detected. When Cp\*Ir complex bearing a bipyridonate ligand [Cp\*Ir(2,2'-bpyO)] (cat. **8**) was used as a catalyst, the reaction gave product **2a** in 16% yield. To our surprise, the product **2a** was obtained in 93% yield when an anionic iridium complex [Cp\*Ir(2,2'-bpyO)(OH)]<sup>-</sup>[Na<sup>+</sup>] (cat. **9**) was used as an alternative catalyst.

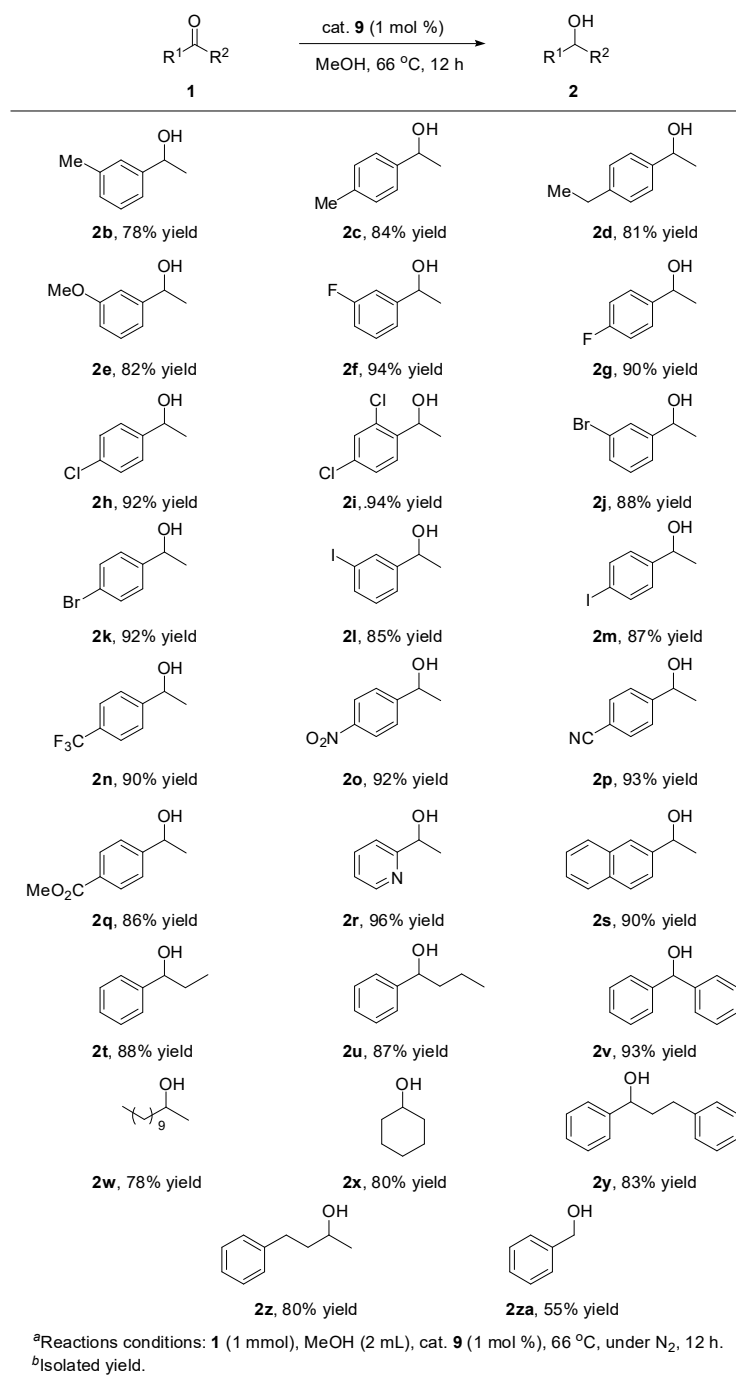
Inspired by above promising result, the scope of reaction with a range of ketones (**1**) under optimal conditions was investigated and these results are shown in Scheme 2. Reactions of acetophenones bearing an electron-donating substituent afforded desired products **2b-2e** in 78-84% yields. As acetophenones bearing one or two halogen were utilized as substrates,

**Scheme 1.** Transfer Hydrogenation of Acetophenone with Methanol using a series of Iridium Catalysts.<sup>a,b</sup>



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6 reactions proceeded to give corresponding products **2f-2m** in 85-94% yields. Strong electron-  
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8 withdrawing substituents, such as trifluoromethyl, nitro, cyano and ester groups, were also  
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10 tolerated and desired products **2n-2q** could be obtained in 87-93% yields. Furthermore, 2-  
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12 acetylpyridine and 2-acetonaphthone were successfully converted to corresponding products **2r**  
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14 and **2s** in 96% and 90% yields, respectively. This catalytic system was also proven to be  
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16 effective to non-methyl ketones, such as propiophenone, butyrophenone and benzophenone,  
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18 affording desired products **2t-2v** in 87-93% yields. For aliphatic ketones, such as 2-dodecanone  
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20 and cyclohexanone, corresponding products **2w** and **2x** were obtained in 78% and 80% yields,  
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22 respectively. Interestingly, when unsaturated ketones, such as (E)-chalcone and (E)-4-Phenyl-3-  
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24 buten-2-one, were conducted, desired products **2y** and **2z** were obtained in 83% and 80% yields,  
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26 respectively, indicating C=O and C=C bonds were simultaneously hydrogenated under present  
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28 conditions. When benzylaldehyde as a substrate was examined, the product **2za** was obtained in  
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30 the 55% yield with methyl benzoate as a by-product (33% yield).<sup>16</sup>  
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**Scheme 2.** Transfer Hydrogenation of a Variety of Ketones with Methanol<sup>a,b</sup>

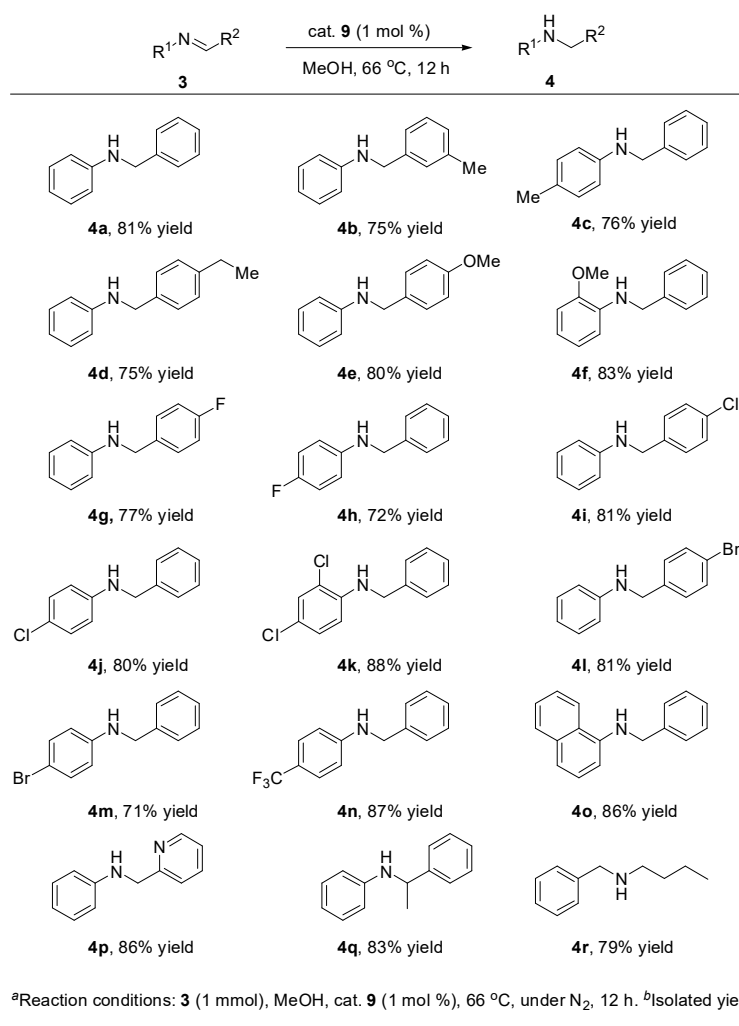


Ttransfer hydrogenation of a series of imines with methanol was then examined (Scheme 3).

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6 The reaction of N-benzylideneaniline afforded the corresponding product **4a** in 81% yield.  
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8 Similarly, N-benzylideneanilines bearing an electron-donating group were converted to desired  
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10 products **4b-4f** in 75-83% yields. This system was also proven to be effective to N-  
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12 benzylideneanilines bearing one or two halogens, or a strong electron-withdrawing substituent,  
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14 affording corresponding products **4g-4n** in 71-88% yield. Furthermore, highly catalytic activities  
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16 were found when (E)-N-benzylidenenaphthalen-1-amine, (E)-N-(pyridin-2-  
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18 ylmethylene)benzenamine, (E)-N-benzylidene(phenyl)methanamine and aliphatic benzylidene-  
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20 butylamine were used as substrates and corresponding products **4o-4r** were obtained in 79%-  
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22 86% yields.  
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56 **Scheme 3.** Transfer Hydrogenation of a Series of Imines with Methanol<sup>a,b</sup>  
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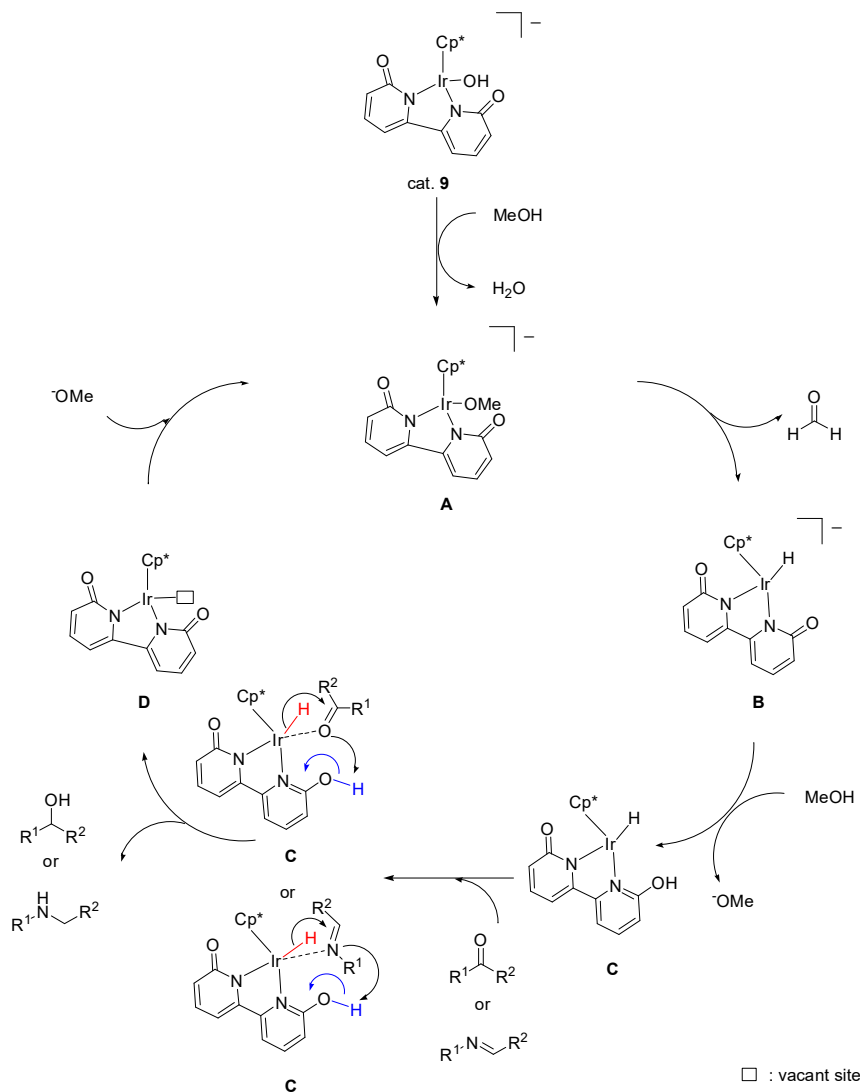




39 A possible mechanism for this transfer hydrogenation of ketones and imines with methanol  
40 under base-free conditions was proposed (Scheme 4). Initially, anionic methoxo species **A** were  
41 **generated** via the reaction of cat. **9** with methanol. With  $\beta$ -hydrogen elimination of species **A**,  
42 **generated** via the reaction of cat. **9** with methanol. With  $\beta$ -hydrogen elimination of species **A**,  
43 **generated** via the reaction of cat. **9** with methanol. With  $\beta$ -hydrogen elimination of species **A**,  
44 **generated** via the reaction of cat. **9** with methanol. With  $\beta$ -hydrogen elimination of species **A**,  
45 iridium hydride species **B** were formed and formaldehyde was released. The protonation of  
46 bipyridonate ligand by methanol afforded neutral hydrido species **C**. Furthermore, simultaneous  
47 transfer of the proton on the hydroxy and the hydride on iridium to C=O or C=N bonds of  
48 ketones or imines took place, resulting in the liberation of alcohols or amines as products and the  
49 formation of unsaturated species **D**.<sup>17</sup> Finally, catalytic species **A** were regenerated by the  
50 reaction of species **D** with methoxide anion. Ligand-promoted simultaneous delivery of proton  
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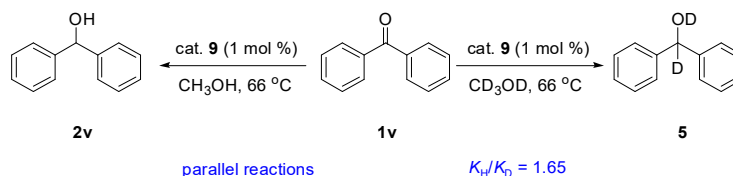
and hydride to ketones or imides was also proposed for other metal-ligand bifunctional catalysts, such as Ru-TsDPEN systems<sup>18</sup> and Shvo's catalyst.<sup>19</sup>

**Scheme 4.** Proposed Reaction Mechanism



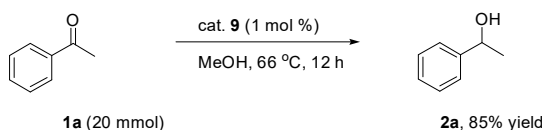
To obtain further the information of reaction mechanism, kinetic studies were undertaken (Scheme 5). Under standard reaction conditions, two parallel reactions of **1v** with CH<sub>3</sub>OH and CD<sub>3</sub>OD were proceeded and kinetic isotope effect (KIE) ( $K_H/K_D = 1.65$ ) was found (Scheme 5). This result suggested that C-H bond cleavage of methanol may be involved in the rate-determining step.

**Scheme 5.** Kinetic Isotope Effect Studies



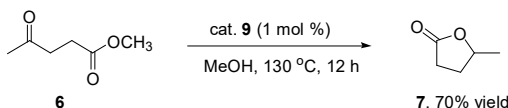
The practical potential of this methodology was explored. The gram-scale hydrogenation of **1a** (20 mmol) was performed in the presence of cat. **9** (0.5 mol %) to give the corresponding product **2a** in 85% yield (Scheme 6).

**Scheme 6.** Large-Scale Hydrogenation of **1a** with Methanol



Furthermore, the synthesis of  $\gamma$ -valerolactone (GVL) via transfer hydrogenation of levulinate ester (LE),<sup>20</sup> one of the important biomass-derived chemicals, with methanol was represented. In the presence of cat. **9** (1 mol %), the reaction of **6** was carried out at 130 °C for 12 h to give the desired product **7** in 70% yield (Scheme 7).

**Scheme 7.** Synthesis of GVL via Transfer Hydrogenation of LE with Methanol



■ CONCLUSIONS

We have demonstrated that an anionic iridium complex  $[\text{Cp}^*\text{Ir}(2,2'\text{-bpyO})(\text{OH})][\text{Na}]$  is a general and highly efficient catalyst for transfer hydrogenation of ketones and imines with methanol under base-free conditions. Readily reducible or labile substituents, such as nitro, cyano and ester groups, were tolerated under present reaction conditions. Furthermore, this catalytic system was also applied to the gram-scale reaction and the biomass conversion. Notably, this study exhibited unique potential of anionic metal-ligand bifunctional iridium catalysts for transfer hydrogenation with methanol as a hydrogen source.

## ■ EXPERIMENTAL SECTION

**General Experimental Details.** Melting points were measured on a X-6 micro-melting apparatus.  $^1\text{H}$  NMR spectra were recorded on a 500 spectrometer. Chemical shifts are reported in delta ( $\delta$ ) units, parts per million (ppm) downfield from tetramethylsilane or ppm relative to the center of the singlet at 7.26 ppm for  $\text{CDCl}_3$ . 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.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a 125 MHz spectrophotometer with broadband  $^1\text{H}$  decoupling. Chemical shifts are reported in delta ( $\delta$ ) units, ppm relative to the center of the triplet at 77.0 ppm for  $\text{CDCl}_3$ . All reactions were run under an atmosphere of nitrogen, unless otherwise indicated. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates.

$[\text{Cp}^*\text{IrCl}_2]_2$  ( $\text{Cp}^*$  = pentamethylcyclopentadienyl) (cat. **1**),<sup>21</sup>  $[\text{Cp}^*\text{Ir}(\text{H}_2\text{O})_3][\text{OTf}]_2$  (cat. **2**),<sup>22</sup>  $[\text{Cp}^*\text{Ir}(\text{NH}_3)_3][\text{Cl}]_2$  (cat. **3**),<sup>23</sup>  $[\text{Cp}^*\text{Ir}(\text{bpy})\text{Cl}][\text{Cl}]$  (cat. **4**),<sup>24</sup>  $[\text{Cp}^*\text{Ir}(6,6'\text{-(OMe)}_2\text{-}2,2'\text{-bpy})(\text{H}_2\text{O})][\text{OTf}]_2$  (cat. **5**),<sup>25</sup>  $[\text{Cp}^*\text{Ir}(2\text{-(OH)py})\text{Cl}_2$  (cat. **6**),<sup>10a</sup>  $[\text{Cp}^*\text{Ir}(6,6'\text{-(OH)}_2\text{-}2,2'\text{-bpy})(\text{H}_2\text{O})][\text{OTf}]_2$  (cat. **7**),<sup>10b</sup>  $[\text{Cp}^*\text{Ir}(2,2'\text{-bpyO})(\text{H}_2\text{O})]$  (cat. **8**)<sup>10c</sup> and  $[\text{Cp}^*\text{Ir}(2,2'\text{-$

bpyO)(OH)][Na] (cat. **9**)<sup>11</sup> were synthesized according the previous reports.

**General procedure for transfer hydrogenation of ketones and imines catalyzed by [Cp\*Ir(2,2'-bpyO)(H<sub>2</sub>O)][Na] (Schemes 1-3).** In a 25-mL Schlenk tube, ketones or imines (1 mmol), methnaol (2 mL), cat. **9** (5.7 mg, 1 mol %) were placed under an N<sub>2</sub> atmosphere, and the reaction mixture was heated at 66 °C in an oil bath for 12 h. The mixture was then cooled to ambient temperature, concentrated in vacuo and purified by flash column chromatography (hexanes/ethyl acetate = 10/1, v/v) to afford the corresponding products.

**1-Phenylethanol (2a).**<sup>26</sup> Light yellow oil; 87% yield (106 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.37-7.33 (m, 4H), 7.28-7.25 (m, 1H), 4.89 (q, *J* = 6.3 Hz, 1H), 1.96 (br s, 1H), 1.49 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 145.8, 128.5, 127.4, 125.3, 70.4, 25.1.

**1-(*m*-Tolyl)ethanol (2b).**<sup>26</sup> Light yellow oil; 78% yield (106 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.24-7.22 (m, 1H), 7.17 (s, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 4.84-4.81 (m, 1H), 2.35 (s, 3H), 2.03 (br s, 1H), 1.47 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 145.8, 138.1, 128.4, 128.1, 126.1, 122.4, 70.3, 25.0, 21.4.

**1-(*p*-Tolyl)ethanol (2c).**<sup>27</sup> Light yellow oil; 84% yield (114 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.25 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 4.95-4.83 (m, 1H), 2.33 (s, 3H), 1.95 (br s, 1H), 1.47 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 142.8, 137.1, 129.1, 125.3, 70.2, 25.0, 21.0.

**1-(4-Ethylphenyl)ethanol (2d).**<sup>26</sup> Light yellow oil; 81% yield (121 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.88-4.86 (m, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.79 (br s, 1H), 1.49 (d, *J* = 6.5 Hz, 3H), 1.23 (t, *J* = 7.6 Hz, 3H); <sup>13</sup>C {1H} NMR (125

MHz, CDCl<sub>3</sub>) δ 143.6, 143.1, 128.0, 125.4, 70.3, 28.5, 25.0, 15.6.

**1-(3-Methoxyphenyl)ethanol (2e).**<sup>26</sup> Light yellow oil; 82% yield (125 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.28-7.25 (m, 1H), 6.94 (s, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 4.89-4.87 (m, 1H), 3.82 (s, 3H), 1.86 (br s, 1H), 1.50 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 159.7, 147.6, 129.4, 117.6, 112.8, 110.9, 70.2, 55.1, 25.1.

**1-(3-Fluorophenyl)ethanol (2f).**<sup>26</sup> Light yellow oil; 94% yield (132 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.32-7.28 (m, 1H), 7.13-7.08 (m, 2H), 6.95 (td, d, *J* = 8.4 and 2.3 Hz, 1H), 4.91-4.86 (m, 1H), 2.02 (br s, 1H), 1.48 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 164.0 (d, *J*<sub>C-F</sub> = 244.5 Hz), 148.5 (d, *J* = 6.4 Hz), 130.0 (d, *J* = 8.1 Hz), 120.9, 114.3 (d, *J* = 21.1 Hz), 112.4 (d, *J* = 21.7 Hz), 69.8, 25.2.

**1-(4-Fluorophenyl)ethanol (2g).**<sup>26</sup> Light yellow oil; 90% yield (126 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.33-7.31 (m, 2H), 7.03-7.00 (m, 2H), 4.87-4.86 (m, 1H), 2.09 (br s, 1H), 1.47 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 163.0 (d, *J*<sub>C-F</sub> = 243.8 Hz), 141.5, 127.0 (d, *J*<sub>C-F</sub> = 8.0 Hz), 115.3 (d, *J*<sub>C-F</sub> = 21.1 Hz), 69.7, 25.2.

**1-(4-Chlorophenyl)ethanol (2h).**<sup>26</sup> Light yellow oil; 92% yield (144 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.32-7.29 (m, 4H), 4.90-4.85 (m, 1H), 1.93 (br s, 1H), 1.47 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 144.2, 133.1, 128.6, 126.8, 68.7, 25.2.

**1-(2,4-Dichlorophenyl)ethanol (2i).**<sup>27</sup> Light yellow oil; 94% yield (179 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.54 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 2.0 Hz, 1H), 7.28-7.26 (m, 1H), 5.24-5.22 (m, 1H), 2.10 (br s, 1H), 1.46 (d, *J* = 6.4 Hz, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 141.7, 133.4, 132.1, 129.1, 127.5, 127.4, 66.6, 23.6.

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6 **1-(3-Bromophenyl)ethanol (2j).**<sup>26</sup> Light yellow oil; 88% yield (176 mg); <sup>1</sup>H NMR (500 MHz,  
7 CDCl<sub>3</sub>) δ 7.53 (s, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H),  
8 4.87-4.85 (m, 1H), 1.95 (br s, 1H), 1.48 (dd, *J* = 6.5 and 1.5 Hz, 3H); <sup>13</sup>C {1H} NMR (125 MHz,  
9 CDCl<sub>3</sub>) δ 148.1, 130.5, 130.1, 128.6, 124.0, 122.6, 69.7, 25.2.

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16 **1-(4-Bromophenyl)ethanol (2k).**<sup>26</sup> Light yellow oil; 92% yield (185 mg); <sup>1</sup>H NMR (500 MHz,  
17 CDCl<sub>3</sub>) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 4.86-4.84 (m, 1H), 2.0 (br s, 1H),  
18 1.46 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 144.7, 131.5, 1127.1, 121.1, 69.7,  
19 25.2.

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26 **1-(3-iodophenyl)ethanol (2l).**<sup>28</sup> Light yellow oil; 85% (211 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  
27 7.7 (s, 1H), 7.58 (d, *J* = 7.85, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.06 (t, *J* = 7.78 Hz, 1H), 4.80 (q, *J* =  
28 6.95 Hz, 1H), 2.80 (s, 1H), 1.42 (d, *J* = 6.50 Hz, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 148.1,  
29 136.3, 134.4, 130.2, 124.6, 94.4, 69.4, 25.1.

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36 **1-(4-Iodophenyl)ethanol (2m).**<sup>29</sup> Light yellow oil, 87% (216 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  
37 δ 7.63-7.61 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 4.75 (m, *J* = 6.0 Hz, 1H), 2.22 (br s,  
38 1H), 1.43 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 145.3, 137.3, 127.3, 92.6,  
39 69.6, 25.1.

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46 **1-(4-(Trifluoromethyl)phenyl)ethanol (2n).**<sup>30</sup> Light yellow oil; 90% yield (171 mg); <sup>1</sup>H NMR  
47 (500 MHz, CDCl<sub>3</sub>) δ 7.59 (d, *J* = 6.7 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 4.92 (q, *J* = 6.5 Hz, 1H),  
48 2.51 (br s, 1H), 1.47 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 149.7, 129.7 (q,  
49 *J*<sub>C-F</sub> = 32.2 Hz), 125.6, 125.4, 123.1 (q, *J*<sub>C-F</sub> = 270.3 Hz), 69.7, 25.2.

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56 **1-(4-Nitrophenyl)ethanol (2o).**<sup>30</sup> Light yellow oil; 92% yield (154 mg); <sup>1</sup>H NMR (500 MHz,  
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6 CDCl<sub>3</sub>) δ 8.21 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 5.04-5.02 (m, 1H), 2.08 (br s, 1H),  
7  
8 1.53 (d, *J* = 6.6 Hz, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 153.0, 147.2, 126.1, 123.7, 69.5,  
9  
10 25.5.

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13 **4-(1-Hydroxyethyl)benzonitrile (2p).**<sup>30</sup> Light yellow oil; 93% yield (136 mg); <sup>1</sup>H NMR (500  
14  
15 MHz, CDCl<sub>3</sub>) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 4.97-4.95 (m, 1H), 2.17 (br s,  
16  
17 1H), 1.50 (d, *J* = 6.6 Hz, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 151.1, 132.3, 126.0, 118.8,  
18  
19 111.0, 69.6, 25.4.

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22 **Methyl 4-(1-hydroxyethyl)benzoate (2q).**<sup>31</sup> Pale yellow oil; 86% yield (157 mg); <sup>1</sup>H NMR (500  
23  
24 MHz, CDCl<sub>3</sub>) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 4.90 (q, *J* = 5.9 Hz, 1H), 3.88 (s,  
25  
26 3H), 2.91 (br s, 1H), 1.46 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 167.0, 151.0,  
27  
28 129.7, 128.8, 125.2, 69.7, 52.0, 25.1.

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31 **1-(Pyridin-2-yl)ethanol (2r).**<sup>31</sup> Light yellow oil; 96% yield (118 mg); <sup>1</sup>H NMR (500 MHz,  
32  
33 CDCl<sub>3</sub>) δ 8.51 (d, *J* = 4.1 Hz, 1H), 7.68 (td, *J* = 7.6 and 1.5 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H),  
34  
35 7.19-7.16 (m, 1H), 4.92-4.87 (m, 1H), 4.63 (br s, 1H), 1.51 (d, *J* = 6.9 Hz, 3H); <sup>13</sup>C {1H} NMR  
36  
37 (125 MHz, CDCl<sub>3</sub>) δ 163.3, 148.0, 136.7, 122.1, 119.7, 68.9, 24.1.

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40 **1-(Naphthalen-2-yl)ethanol (2s).**<sup>26</sup> White solid; 90% yield (154 mg); mp 76-77 °C; <sup>1</sup>H NMR  
41  
42 (500 MHz, CDCl<sub>3</sub>) δ 7.85-7.81 (m, 4H), 7.51-7.46 (m, 3H), 5.10-5.06 (m, 1H), 1.91 (br s, 1H),  
43  
44 1.59 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 143.2, 133.3, 132.9, 128.3, 127.9,  
45  
46 127.6, 126.1, 125.8, 123.78, 123.77, 70.5, 25.1.

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48  
49 **1-Phenylpropan-1-ol (2t).**<sup>26</sup> Light yellow oil; 88% yield (119 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  
50  
51 δ 7.35-7.34 (m, 4H), 7.29-7.26 (m, 1H), 4.61-4.68 (m, 1H), 1.90 (br s, 1H), 1.85-1.72 (m, 2H),  
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0.91 (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C}$  {1H} NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  144.6, 128.4, 127.5, 125.9, 76.0, 31.9, 10.1.

**1-Phenylbutan-1-ol (2u).**<sup>32</sup> Light yellow oil; 87% yield (131 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34-7.33 (m, 4H), 7.28-7.25 (m, 1H), 4.67 (t,  $J = 6.7$  Hz, 1H), 1.91 (br s, 1H), 1.82-1.75 (m, 1H), 1.71-1.64 (m, 1H), 1.47-1.39 (m, 1H), 1.35-1.25 (m, 1H), 0.93 (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C}$  {1H} NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  144.9, 128.4, 127.4, 125.9, 74.4, 41.2, 19.0, 13.9.

**Diphenylmethanol (2v).**<sup>26</sup> White solid; 93% yield (171 mg); mp 65-66 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.31 (m, 8H), 7.27-7.24 (m, 2H), 5.83 (s, 1H), 2.24 (br s, 1H);  $^{13}\text{C}$  {1H} NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.8, 128.5, 127.6, 126.5, 76.3.

**Dodecan-2-ol (2w).**<sup>33</sup> Light yellow oil; 78% yield (145 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.82-3.76 (m, 1H), 1.46-1.40 (m, 4H), 1.31-1.26 (m, 15H), 1.19 (d,  $J = 6.2$  Hz, 3H), 0.88 (t,  $J = 6.9$  Hz, 3H);  $^{13}\text{C}$  {1H} NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  68.3, 39.4, 32.0, 29.8, 29.7 (three peaks overlapping with each other), 29.5, 25.9, 23.5, 22.8. These spectroscopic datas correspond to reported datas.

**Cyclohexanol (2x).**<sup>26</sup> Colorless oil; 80% yield (80 mg);  $^1\text{H}$  NMR (500MHz,  $\text{CDCl}_3$ )  $\delta$  3.57 (m, 1H), 3.20 (br s, 1H), 1.89 (s, 2H), 1.72 (s, 2H), 1.54 (m, 1H), 1.24 (m, 4H), 1.16 (m, 1H);  $^{13}\text{C}$  {1H} NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  69.9, 35.2, 25.3, 24.0.

**1,3-Diphenylpropan-1-ol (2y).**<sup>34</sup> Light yellow oil; 83% yield (176 mg);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.34 (m, 4H), 7.28-7.24 (m, 3H), 7.19-7.16 (m, 3H), 4.69-4.66 (m, 1H), 2.77-2.63 (m, 2H), 2.16-2.00 (m, 2H), 1.92 (br s, 1H);  $^{13}\text{C}$  {1H} NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  144.6, 141.8, 128.5, 128.4, 128.4, 127.6, 125.9, 125.8, 73.9, 40.5, 32.0.

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6 **4-Phenylbutan-2-ol (2z).**<sup>35</sup> Light yellow oil; 80% yield (120 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ  
7  
8 7.29-7.26 (m, 2H), 7.20-7.16 (m, 3H), 3.85-3.79 (m, 1H), 2.78-2.63 (m, 2H), 1.81-1.71 (m, 2H),  
9  
10 1.57 (br s, 1H), 1.23 (d, *J* = 6.2 Hz, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 142.0, 128.3  
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12 (two peaks overlapping with each other), 125.8, 67.4, 40.8, 32.1, 23.5.

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15 These spectroscopic datas correspond to reported datas.

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18 **Phenylmethanol (2xa).**<sup>35</sup> Light yellow oil; 55% yield (59 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  
19  
20 δ 7.35-7.30 (m, 4H), 7.27-7.25 (m, 1H), 4.60 (s, 2H), 2.47 (br s, 1H); <sup>13</sup>C {1H} NMR (125 MHz,  
21  
22 CDCl<sub>3</sub>) δ 140.4, 128.0, 127.0, 126.5, 64.3.

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26 **N-Benzylaniline (4a).**<sup>36</sup> Light yellow oil; 81% yield (148 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ  
27  
28 7.37-7.31 (m, 4H), 7.28-7.25 (m, 1H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.64-  
29  
30 6.62 (d, *J* = 7.9 Hz, 2H), 4.32 (s, 2H), 4.01 (br s, 1H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ  
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32 148.1, 139.4, 129.2, 128.6, 127.5, 127.2, 117.5, 112.8, 48.3.

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36 **N-(3-Methylbenzyl)aniline (4b).**<sup>36</sup> Light yellow oil; 75% yield (148 mg); <sup>1</sup>H NMR (500 MHz,  
37  
38 CDCl<sub>3</sub>) δ 7.23 (d, *J* = 7.5 Hz, 1H), 7.19-7.16 (m, 4H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.71 (t, *J* = 7.3  
39  
40 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 2H), 4.28 (s, 2H), 3.99 (br s, 1H), 2.35 (s, 3H); <sup>13</sup>C {1H} NMR  
41  
42 (125 MHz, CDCl<sub>3</sub>) δ 148.2, 139.3, 138.3, 129.2, 128.5, 128.3, 128.0, 124.6, 117.5, 112.8, 48.3,  
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44 21.4.

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48 **N-Benzyl-4-methylaniline (4c).**<sup>36</sup> Light yellow oil; 76% yield (150 mg); <sup>1</sup>H NMR (500 MHz,  
49  
50 CDCl<sub>3</sub>) δ 7.37-7.31 (m, 4H), 7.26-7.25 (m, 1H), 6.99-6.97 (m, 2H), 6.57-6.55 (m, 2H), 4.30 (s,  
51  
52 2H), 3.89 (br s, 1H), 2.23 (s, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 145.9, 139.6, 129.7,  
53  
54 128.6, 127.5, 127.1, 126.7, 113.0, 48.6, 20.4.

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6 **N-(4-Ethylbenzyl)aniline (4d).**<sup>36</sup> Light yellow oil; 75% yield (158 mg); <sup>1</sup>H NMR (500 MHz,  
7 CDCl<sub>3</sub>) δ 7.29-7.27 (m, 2H), 7.18-7.15 (m, 4H), 6.73-6.69 (m, 1H), 6.64-6.62 (m, 2H), 4.27 (m,  
8 2H), 3.96 (br s, 1H), 2.66-2.61 (m, 2H), 1.26-1.21 (m, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ  
9 148.2, 143.3, 136.6, 129.2, 128.1, 127.6, 117.4, 112.8, 48.1, 28.5, 15.6.

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16 **N-(4-Methoxybenzyl)aniline (4e).**<sup>36</sup> Light yellow solid; 80% yield (171 mg); mp 61-62 °C; <sup>1</sup>H  
17 NMR (500 MHz, CDCl<sub>3</sub>) δ 7.30 (d, *J* = 8.6 Hz, 2H), 7.17 (t, *J* = 7.9 Hz, 2H), 6.89 (d, *J* = 8.6 Hz,  
18 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 2H), 4.25 (s, 2H), 3.94 (br s, 1H), 3.80 (s, 3H);  
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22 <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 158.8, 148.2, 131.4, 129.2, 128.8, 117.5, 114.0, 112.8, 55.3,  
23 47.8.

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28 **N-Benzyl-2-methoxyaniline (4f).**<sup>36</sup> Light yellow oil; 83% yield (177 mg); <sup>1</sup>H NMR (500 MHz,  
29 CDCl<sub>3</sub>) δ 7.38-7.31 (m, 4H), 7.26 (t, *J* = 6.6 Hz, 1H), 6.84-6.77 (m, 2H), 6.68-6.65 (m, 1H), 6.59  
30 (d, *J* = 7.5 Hz, 1H), 4.61 (br s, 1H), 4.34 (s, 2H), 3.83 (s, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>)  
31 δ 146.8, 139.6, 138.1, 128.5, 127.5, 127.1, 121.3, 116.6, 110.0, 109.4, 55.4, 48.0.

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38 **N-(4-Fluorobenzyl)aniline (4g).**<sup>36</sup> Light yellow oil; 77% yield (155 mg); <sup>1</sup>H NMR (500 MHz,  
39 CDCl<sub>3</sub>) δ 7.31 (t, *J* = 6.8 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 6.72 (t, *J* =  
40 6.8 Hz, 1H), 6.62 (d, *J* = 8.5 Hz, 2H), 4.28 (s, 2H), 3.99 (br s, 1H); <sup>13</sup>C {1H} NMR (125 MHz,  
41 CDCl<sub>3</sub>) δ 163.0 (d, *J*<sub>C-F</sub> = 243.6 Hz), 147.9, 135.1, 129.2, 129.0 (d, *J*<sub>C-F</sub> = 7.9 Hz), 117.7, 115.5  
42 (d, *J*<sub>C-F</sub> = 21.2 Hz), 112.8, 47.5.

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50 **N-Benzyl-4-fluoroaniline (4h).**<sup>36</sup> Light yellow oil; 72% yield (145 mg); <sup>1</sup>H NMR (500 MHz,  
51 CDCl<sub>3</sub>) δ 7.36-7.32 (m, 4H), 7.28-7.25 (m, 1H), 6.86 (t, *J* = 8.8 Hz, 2H), 6.55-6.53 (m, 2H), 4.27  
52 (s, 2H), 3.90 (br s, 1H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 156.8 (d, *J*<sub>C-F</sub> = 237.5 Hz), 144.5,  
53 139.2, 128.6, 127.4, 127.3, 115.7 (d, *J*<sub>C-F</sub> = 22.2 Hz), 113.6 (d, *J*<sub>C-F</sub> = 7.3 Hz), 48.9.

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6 **N-(4-Chlorobenzyl)aniline (4i).**<sup>36</sup> Light yellow oil; 81% yield (176 mg); <sup>1</sup>H NMR (500 MHz,  
7 CDCl<sub>3</sub>) δ 7.31-7.27 (m, 4H), 7.16 (t, *J* = 7.9 Hz, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.7 Hz,  
8 2H), 4.29 (s, 2H), 4.04 (br s, 1H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 147.8, 138.0, 132.8,  
9 129.3, 128.7, 128.7, 117.8, 112.8, 47.6.

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16 **N-Benzyl-4-chloroaniline (4j).**<sup>36</sup> Light yellow oil; 80% yield (173 mg); <sup>1</sup>H NMR (500 MHz,  
17 CDCl<sub>3</sub>) δ 7.37-7.29 (m, 5H), 7.13-7.10 (m, 2H), 6.56-6.55 (m, 2H), 4.31 (s, 2H), 4.07 (br s, 1H);  
18 <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 146.7, 138.9, 129.1, 128.7, 127.41, 127.37, 122.1, 113.9,  
19 48.3.

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26 **N-Benzyl-2,4-dichloroaniline (4k).**<sup>37</sup> Light yellow oil; 88% yield (221 mg); <sup>1</sup>H NMR (500 MHz,  
27 CDCl<sub>3</sub>) δ 7.36-7.32 (m, 4H), 7.29-7.25 (m, 2H), 7.03 (dd, *J* = 8.8 and 2.4 Hz, 1H), 6.52 (d, *J* =  
28 8.8 Hz, 1H), 4.71 (br s, 1H), 4.37 (d, *J* = 5.6 Hz, 2H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ  
29 142.5, 138.2, 128.8, 128.7, 127.7, 127.5, 127.1, 121.3, 119.3, 112.0, 47.8.

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36 **N-(4-Bromobenzyl)aniline (4l).**<sup>38</sup> Light yellow solid; 81% yield (213 mg); mp 51-52 °C; <sup>1</sup>H  
37 NMR (500 MHz, CDCl<sub>3</sub>) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.25-7.24 (m, 2H), 7.17 (t, *J* = 7.9 Hz, 2H),  
38 6.72 (t, *J* = 7.3 Hz, 1H), 6.61 (d, *J* = 7.8 Hz, 2H), 4.29 (s, 2H), 4.06 (br s, 1H); <sup>13</sup>C {1H} NMR  
39 (125 MHz, CDCl<sub>3</sub>) δ 147.8, 138.5, 131.6, 129.3, 129.0, 120.9, 117.8, 112.8, 47.6.

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46 **N-Benzyl-4-bromoaniline (4m).**<sup>36</sup> Light yellow oil; 71% yield (184 mg); <sup>1</sup>H NMR (500 MHz,  
47 CDCl<sub>3</sub>) δ 7.35 (d, *J* = 4.5 Hz, 4H), 7.30-7.23 (m, 3H), 6.51 (d, *J* = 8.8 Hz, 2H), 4.30 (s, 2H), 4.08  
48 (br s, 1H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>) δ 147.0, 138.8, 131.9, 128.7, 127.4  
49 (two peaks overlapping with each other), 114.4, 109.1, 48.2.

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55 These spectroscopic datas correspond to reported datas.

**N-Benzyl-4-(trifluoromethyl)aniline (4n).**<sup>38</sup> Light yellow solid; 87% yield (219 mg); mp 53-54 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.38-7.26 (m, 7H), 6.59 (d, *J*<sub>C-F</sub> = 8.6 Hz, 2H), 4.32 (s, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 150.5, 138.4, 128.8, 127.5, 127.3 (q, *J*<sub>C-F</sub> = 3.4 Hz), 126.1 (q, *J*<sub>C-F</sub> = 268.7 Hz), 119.1 (q, *J*<sub>C-F</sub> = 32.2 Hz), 119.9, 47.7.

**N-Benzyl-naphthalen-1-amine (4o).**<sup>36</sup> Light yellow solid; 86% yield (199 mg); mp 69-70 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.77-7.73 (m, 2H), 7.43-7.22 (m, 9H), 6.59 (d, *J* = 7.4 Hz, 1H), 4.62 (br s, 1H), 4.42 (s, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 143.2, 139.0, 134.2, 128.7, 127.7, 127.3, 126.6, 125.7, 124.7, 123.3, 119.9, 117.6, 104.7, 48.5.

**N-(Pyridin-2-ylmethyl)aniline (4p).**<sup>39</sup> Light yellow oil; 86% yield (159 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.57 (d, *J* = 4.6 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 7.18-7.14 (m, 3H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 2H), 4.78 (br s, 1H), 4.44 (s, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 158.5, 149.1, 147.8, 136.5, 129.2, 122.0, 121.5, 117.5, 112.9, 49.2.

**N-(1-Phenylethyl)aniline (4q).**<sup>40</sup> Light yellow oil; 83% yield (163 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.36 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.08 (t, *J* = 7.9 Hz, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 8.1 Hz, 2H), 4.48 (q, *J* = 6.7 Hz, 1H), 4.00 (br s, 1H), 1.51 (d, *J* = 6.8 Hz, 3H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 147.2, 145.2, 129.1, 128.6, 126.8, 125.8, 117.2, 113.2, 53.4, 25.0.

**Benzyl-butyl-amine (4r).**<sup>41</sup> Light yellow oil; 79% yield (130 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.37-7.23 (m, 5 H), 3.80 (s, 2 H), 3.03 (s, 1H), 2.63 (t, *J* = 7.5 Hz, 2 H), 1.53 (q, *J* = 7.4 Hz, 2 H), 1.34 (q, *J* = 7.3 Hz, 2 H), 0.90 (t, *J* = 7.5 Hz, 3 H). <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 139.3, 128.3, 128.2, 127.0, 53.6, 48.7, 31.6, 20.3, 13.9.

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6 **Kinetic Isotope Effect Studies (Scheme 5).** Parallel reactions for the transfer hydrogenation of  
7  
8 **1v** with CH<sub>3</sub>OH and CD<sub>3</sub>OD catalyzed by cat. **9** under standard conditions following the general  
9  
10 procedure. And the progress of the reaction was analysed by <sup>1</sup>H NMR. All the reactions were  
11  
12 repeated twice and the average data were plotted as yield (%) vs time (h).  
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16 **Diphenylmethanol-d<sub>2</sub> (5).**<sup>42</sup> White solid, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.37-7.31 (m, 8H),  
17  
18 7.27-7.23 (m, 2H); <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) δ 143.6, 128.4, 127.5, 126.4, 75.7 (t, *J* =  
19  
20 25 Hz).  
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24 **Procedure for large-scale transfer hydrogenation of acetophenone (1a) with methanol**  
25  
26 **catalyzed by [Cp\*Ir(2,2'-bpyO)(H<sub>2</sub>O)][Na] (Scheme 6).** In a 250 mL Schlenk tube, **1a** (2400  
27  
28 mg, 20 mmol), methanol (30 mL), and cat. **9** (57 mg, 0.1 mmol, 0.5 mol %) were placed under  
29  
30 an N<sub>2</sub> atmosphere, and the reaction mixture was heated at 66 °C in an oil bath for 12 h. The  
31  
32 mixture was then cooled to ambient temperature, concentrated in vacuo, and purified by flash  
33  
34 column chromatography (hexanes/ethyl acetate = 10/1, v/v) to afford the corresponding product  
35  
36 **2a** (2074 mg, 17 mmol, 85% yield).  
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41 **Procedure for the synthesis of  $\gamma$ -valerolactone (GVL) via transfer hydrogenation of**  
42  
43 **levulinate ester (LE) with methanol catalyzed by [Cp\*Ir(2,2'-bpyO)(H<sub>2</sub>O)][Na] (Scheme 7).**  
44  
45 In a 25 mL Schlenk tube, methyl levulate **6** (130 mg, 1 mmol), methanol (2 mL), and cat. **9** (5.7  
46  
47 mg, 1 mol %) were placed under an N<sub>2</sub> atmosphere, and the reaction mixture was heated at 130  
48  
49 °C in an oil bath for 12 h. The mixture was then cooled to ambient temperature, concentrated in  
50  
51 vacuo, and purified by flash column chromatography (hexanes/ethyl acetate = 10/1, v/v) to  
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53 afford the corresponding product.  
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57 **Caution:** This temperature is more than two times to boiling point of the methanol and a reaction  
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6 at this temperature in a low boiling solvent should be conducted in a sealable vessel rated for  
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8 pressure (Teflon sealable flask, pressure tube etc.).  
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11  **$\gamma$ -Valerolactone (7).**<sup>43</sup> Colorless oil; 70% yield (70 mg); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  4.65 (sxt,  
12  
13  $J = 6.6$  Hz, 1H), 2.57-2.53 (m, 2H), 2.37 (sxt,  $J = 6.6$ Hz, 1H), 1.87-1.78 (m, 1H), 1.42 (d,  $J = 6.3$   
14  
15 Hz, 3H); <sup>13</sup>C {1H} NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  176.9, 76.9, 29.3, 28.7, 20.6.  
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## 19 ■ ASSOCIATED CONTENT

### 21 \* Supporting Information

22  
23 The Supporting Information is available free of charge on the  
24 ACS Publications website at DOI: 10.1021/acs.joc.  
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26  
27 <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the products (PDF)  
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45

### 46 Notes

47  
48 The authors declare no competing financial interest.  
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## 51 ■ ACKNOWLEDGEMENTS

52  
53 Financial support from the National Natural Science Foundation of China (21272115), the  
54  
55 Natural Science Foundation of Jiangsu Province (BK20161494) and the State Key Laboratory of  
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6 Fine Chemicals (KF1704) is greatly appreciated.  
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