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Ambient-pressure hydrogenation of ketones and aldehydes by a metal-ligand bifunctional catalyst [$Cp^*Ir(2,2'\text{-}bpyO)(H_2O)$] without using base

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ABSTRACT

An efficient catalytic system for hydrogenation of ketones and aldehydes using a Cp*Ir complex [$Cp^*Ir(2,2'\text{-}bpyO)(H_2O)$] bearing a bipyridine-based functional ligand as catalyst has been developed. A wide variety of secondary and primary alcohols were synthesized by the catalyzed hydrogenation of ketones and aldehydes under facile atmospheric-pressure without a base. The catalyst also displays an excellent chemoselectivity towards other carbonyl functionalities and unsaturated motifs. This catalytic system exhibits high activity for hydrogenation of ketones and aldehydes with H_2 gas.

1. Introduction

The reduction of ketones and aldehydes is of great relevance for organic synthesis, as well as industrial application in the production of flavours, fragrances, fine chemicals and pharmaceutical compounds [1]. Typically, the stoichiometric amount of toxic reducing agents such as $NaBH_4$, boranes, and $LiAlH\text{-}(OR)_3$ are used for this transformation [2], and a large number of environmentally unfriendly by-products are produced in these reactions. The catalytic hydrogenation has been realized as an excellent method that resolves this problem by using H_2 gas as a clean and green reagent. A wide variety of highly productive catalysts based on metals ions (Ru [3], Rh [4], Ir [5], Fe [6], and Co [7]) have been developed for this purpose. However, these hydrogenation reactions were achieved using an inorganic/organic base and high-pressure H_2 gas. A facile self-aldol side reaction unavoidably occurred under the basic conditions limits application of the catalytic hydrogenation. In addition, the specialized experimental setup was required for security with the presence of high-pressure H_2 gas. Recently, Hanson [8] and Do[5b] reported two catalysts for the hydrogenation of ketones and aldehydes under 1 atm H_2 pressure and base-free conditions. However, only a few examples were reported in this condition, and high-pressure H_2 gas, higher reaction temperature and longer reaction time were required for aliphatic aldehydes. Thus, the development of an efficient and general organometallic catalyst for the hydrogenation of ketones and aldehydes at atmospheric pressure of H_2 as well as under base-free conditions is highly desirable.

Recently, a series of metal-ligand bifunctional iridium complexes containing a functional bipyridine or a bipyridonate ligand were reported by Fujita and Yamaguchi [9]. It was demonstrated that they are very active catalysts for acceptorless dehydrogenation of alcohols and the dehydrogenative cyclization for the construction of quinazolinones [10a,10b]. More recently, we developed the highly efficient transfer hydrogenation of aldehydes and chemoselective transfer hydrogenation of unsaturated aldehydes with isopropyl alcohol under neutral conditions using [$Cp^*Ir(2,2'$-

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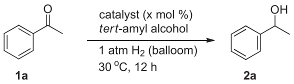
bpyO)(H_2O)] complexes [10c]. Within this context, to further explore the catalytic activity of the metal-ligand bifunctional iridium complexes, we applied this kind of catalysts to catalytic hydrogenation of ketones and aldehydes under 1 atm H_2 pressure and base-free conditions.

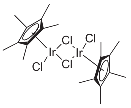
2. Results and discussion

The reaction conditions were optimized by using acetophenone (**1a**) as the model substrate (Table 1). Various catalysts were initially evaluated in the model hydrogenation reaction of acetophenone (**1a**) in *tert*-amyl alcohol for 12 h at 30 °C. When [Cp*$IrCl_2$]$_2$ (Cp* = pentamethylcyclopentadienyl) (cat. **1**), [Cp*Ir(H_2O)$_3$][OTf]$_2$ (cat. **2**), [Cp*Ir(bpy)Cl)][Cl] (cat. **3**) and [Cp*Ir(6,6′-(OMe)$_2$bpy)(H_2O)] [OTf]$_2$ (cat. **4**) were screened, the desired product **2a** was only obtained in ≤20% yield. Interestingly, it is clear from Table 1, that the yield of **2a** could be obviously increased with the presence of [Cp*Ir(2-(OH)py)]Cl_2 (cat. **5**), [Cp*Ir(6,6′−(OH)$_2$−2,2′-bpy)(H_2O)] [OTf]$_2$ (cat. **6**) and [Cp*Ir(2,2′-bpyO)(H_2O)] (cat. **7**) bearing a functional pyridine, bipyridine or bipyridonate ligand. The yield of product **2a** could reach up to 96%, when the hydrogenation reaction was performed in the presence of cat. **7**. From the above results, it can be inferred that the functional ligands play a crucial role in improving the activity of catalysts. When the reaction was performed in the presence of [Cp*Rh(2,2′-bpyO)(H_2O)] (cat. **8**) or [(*p*-cymene)Ru(2,2′-bpyO)(H_2O)] (cat. **9**) as

Table 1
Hydrogenation of acetophenone (**1a**) in *tert*-amyl alcohol under 1 atm H_2 at 30 °C using a range of catalysts.[a, b]



entry	catalyst	x (mol %)	yield (%)[c]
1	cat. **1**	0.5	*20*
2	cat. **2**	0.5	*12*
3	cat. **3**	0.5	n.d.
4	cat. **4**	0.5	8
5	cat. **5**	0.5	32
6	cat. **6**	0.5	79
7	cat. **7**	0.5	>98 (96[d])
8	cat. **8**	0.5	35
9	cat. **9**	0.5	6
10	cat. **7**	0.2	86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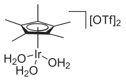
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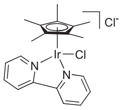
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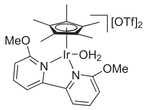
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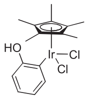
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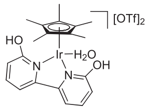
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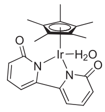
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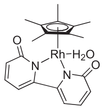
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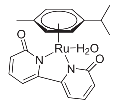
cat. **9**

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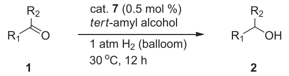
[a] Reaction conditions: **1a** (1 mmol), 1 atm H_2 (balloon), catalyst (x mol %), *tert*-amyl alcohol (1 mL), 30 °C, 12 h.
[b] Catalyst structures.
[c] Yield was determined on the basis of ^{1}H NMR spectrum of the crude reaction.
[d] Isolated yield.

Table 2
Hydrogenation of ketones in *tert*-amyl alcohol under 1 atm H_2 at 30 °C by cat. **7**.[a]



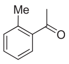
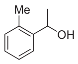
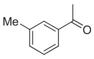
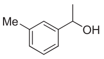
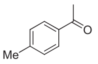
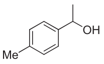
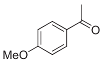
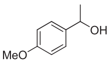
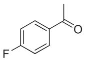
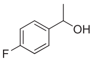
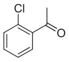
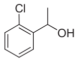
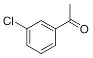
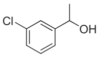
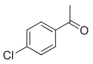
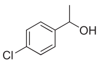
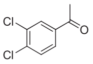
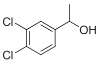
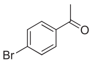
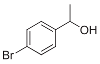
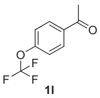
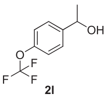
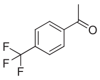
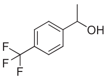
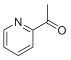
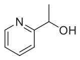
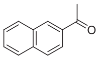
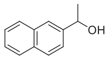
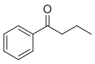
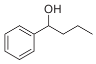
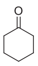
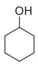
Entry	Ketone	Product	Yield (%)[b]
1	 **1b**	 **2b**	95
2	 **1c**	 **2c**	94
3	 **1d**	 **2d**	94
4	 **1e**	 **2e**	93
5	 **1f**	 **2f**	96
6	 **1g**	 **2g**	96
7	 **1h**	 **2h**	92
8	 **1i**	 **2i**	96
9	 **1j**	 **2j**	94
10	 **1k**	 **2k**	96
11	 **1l**	 **2l**	97
12	 **1m**	 **2m**	96
13	 **1n**	 **2n**	96
14	 **1o**	 **2o**	95
15	 **1p**	 **2p**	94
16	 **1q**	 **2q**	89

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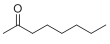
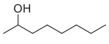
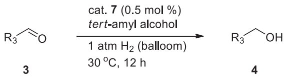
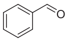
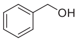
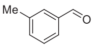
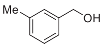
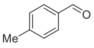
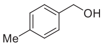
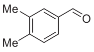
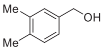
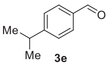
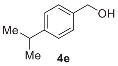
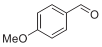
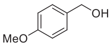
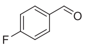
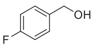
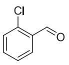
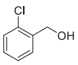
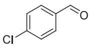
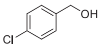
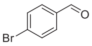
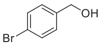
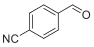
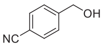
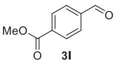
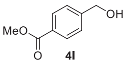
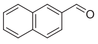
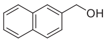
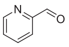
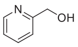
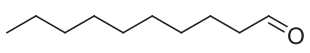
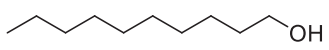
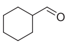
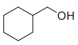
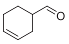
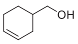
Table 2 (*continued*)

Entry	Ketone	Product	Yield (%)[b]
17	 **1r**	 **2r**	87

[a] Reaction conditions: **1** (1 mmol), 1 atm H_2 (balloon), cat. **7** (0.5 mol %), *tert*-amyl alcohol (1 mL), 30 °C, 12 h.
[b] Isolated yield.

Table 3
Hydrogenation of aldehydes in *tert*-amyl alcohol under 1 atm H_2 at 30 °C by cat. **7**.[a]



Entry	Aldehyde	Product	Yield (%)[b]
1	 **3a**	 **4a**	96
2	 **3b**	 **4b**	94
3	 **3c**	 **4c**	92
4	 **3d**	 **4d**	96
5	 **3e**	 **4e**	93
6	 **3f**	 **4f**	94
7	 **3g**	 **4g**	95
8	 **3h**	 **4h**	83
9	 **3i**	 **4i**	96
10	 **3j**	 **4j**	97
11	 **3k**	 **4k**	94
12	 **3l**	 **4l**	95
13	 **3m**	 **4m**	94
14	 **3n**	 **4n**	96
15	 **3o**	 **4o**	96
16	 **3p**	 **4p**	91
17	 **3q**	 **4q**	92

[a] Reaction conditions: **3** (1 mmol), 1 atm H_2 (balloon), cat. **7** (0.5 mol %), *tert*-amyl alcohol (1 mL), 30 °C, 12 h.
[b] Isolated yield.

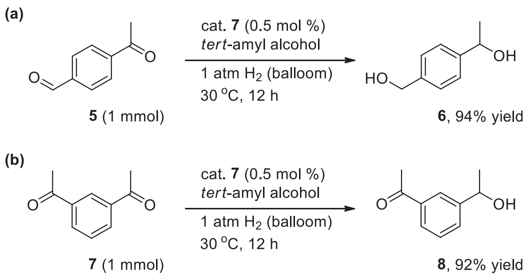
an alternative catalyst, we obtained only 35% and 6% yields of the target product **2a**, respectively. However, the yield of **2a** is lower in the presence of cat. **7** with a loading of 0.2 mol %.

The optimized condition (Table 1, entry 7) was then applied to various ketones to extend the scope of the method. The results are summarized in Table 2. The reactions with aromatic ketones bearing electron-donating substituents at the aromatic ring, such as methyl and methoxy, proceeded to give the corresponding products (**2b**-**2e**) in good to excellent yields (entries 1–4). Halogen atoms were well tolerated, as demonstrated by high yields of the fluoro-, chloro-, bromo-substituted aromatic alcohols (**2f**-**2k**, entries 5–10). Furthermore, the strong electron-withdrawing phenyl rings in **1l** and **1m** survived from the reduction in 97% and 96% yields (entries 11–12). 2-acetylpyridine (**1n**) and 2-acetonaphthone (**1o**) also underwent hydrogenation readily and delivered excellent yields of alcohols in 96% and 95% yields (entries 13–14). For the reaction of butyrophenone (**1p**), the corresponding product **2p** could be obtained in high yield (entry 15). Fused aliphatic ketones **1q** and **1r** also underwent the hydrogenation to yield the desired products in 89% and 87% yields (entries 16–17), respectively.

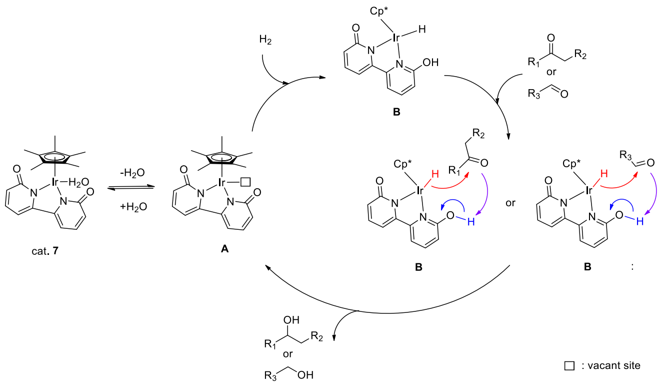
Under the same conditions, hydrogenation of various aldehydes was carried out using complex **7** as the catalyst (Table 3). In addition to benzaldehyde (**3a**), other electron-rich aldehydes such as 3-methylbenzaldehyde (**3b**), 4-methylbenzaldehyde (**3c**), 3,4- dimethylbenzaldehyde (**3d**), 4-isopropylbenzaldehyde (**3e**), and 4-methoxybenzaldehyde (**3f**), were readily reduced to corresponding alcohols efficiently in 92–96% yields (entries 1–6). Similarly, fluoro, chloro and bromo substituents were tolerant in this catalytic system and the desired products **4g**-**4j** were obtained in 83–97% yield (entries 7–10). Strong electron-withdrawing substituents, such as cyano and ester group, were also converted to the corresponding primary alcohols (**4k**-**4l**) in 94% and 95% yields (entries 11–12). Other aromatic aldehydes such as 2-naphthaldehyde (**3m**) and 2-pyridinecarboxaldehyde (**3n**) could be also used as suitable substrates and the corresponding products **4m**-**4n** were obtained in 94% and 96% yields, respectively (entries 13–14). The present catalytic system was also applicable to aliphatic aldehydes, such as decanal (**3o**) and cyclohexanecarbaldehyde (**3p**), and the yields of corresponding aliphatic alcohols were high (entries 15–16). Furthermore, when the unsaturated aliphatic aldehyde **3q** served as a substrate, the C=C bond remained unreacted and the product **4q** was obtained in 92% yield (entry 17).

On the basis of the above results, chemoselectivity was investigated with aromatic substrates containing two ketone groups or one aldehyde and one ketone group in the presence of cat. **7** (Scheme 1). The hydrogenation of 4-acetylbenzaldehyde (**5**) was accomplished, but only product **6** was obtained in 94% yield (Scheme 1, a). Both of aldehyde and ketone groups were hydrogenated to alcohols. Interestingly, while 1,3-diacetylbenzene (**7**) with two ketone groups was tested, only one ketone group was selectively hydrogenated and the corresponding product **8** was obtained in 92% yield (Scheme 1, b).

Considering the above experimental results, a plausible mechanism was proposed for the present hydrogenation of ketones or aldehydes with H_2 catalyzed by cat. **7** (Scheme 2). This mechanism is closely related to the proposed mechanism of the transfer hydrogenation of aldehydes with isopropyl alcohol [10c]. The initial step of the reaction involves elimination of H_2O from the catalyst cat. **7** to afford an unsaturated species A bearing a 2-pyridonate-



Scheme 1. Chemoselective hydrogenation of ketones. Isolated yield.



Scheme 2. Proposed hydrogenation mechanism.

based ligand. Then, the reaction of H$_2$ with the species A would occur to afford iridium hydride species B. Finally, the simultaneous transfer of the hydride on iridium with the hydroxyl proton on the functional ligand to C=O bond of ketones or aldehydes would occur to give the corresponding alcohols accompanied by the regeneration of A.

3. Conclusions

In conclusion, we have developed an efficient iridium catalyst [Cp*Ir(2,2′-bpyO)(H$_2$O)] bearing a functional bipyridonate ligand for the hydrogenation of ketones and aldehydes in *tert*-amyl alcohol under 1 atm H$_2$ at 30 °C. It does not require base or high-pressure hydrogen condition, offering an operationally simple and green procedure. Of significance is the good tolerance of a wide variety of functional groups, such as electron-rich or deficient groups, cyano, ester, and halide groups. Notably, the research exhibits new potential of metal-ligand bifunctional catalysts for hydrogenation.

4. Experimental

4.1. General

Authors Melting points were measured on a RY-1 micro-melting apparatus. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 400 MHz using a 400 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 values are reported in Hertz (Hz), and the splitting patterns were designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. Analytical thin-layer chromatography (TLC) was carried out using 0.2-mm commercial silica gel plates. [Cp*IrCl$_2$]$_2$ (cat. **1**) [11], [Cp*Ir(H$_2$O)$_3$] [OTf]$_2$ (cat. **2**) [12], [Cp*Ir(bpy)Cl)] [Cl] (cat. **3**) [13], [Cp*Ir(6,6′-(OMe)$_2$bpy)(H$_2$O)] [OTf]$_2$ (cat. **4**) [14], [Cp*Ir(2-(OH)py)] Cl$_2$ (cat. **5**) [9e], [Cp*Ir(6,6′−(OH)$_2$−2,2′-bpy)(H$_2$O)] [OTf]$_2$ (cat. **6**) [9h], [Cp*Ir(2,2′-bpyO)(H$_2$O)] (cat. **7**) [15], [Cp*Rh(2,2′-bpyO)(H$_2$O)] (cat. **8**) [16], [(*p*-cymene)Ru(2,2′-bpyO)(H$_2$O)] (cat. **9**) [17] were synthesized according the previous reports.

*4.2. General procedure for catalytic hydrogenation of **2***

To an oven-dried 5 mL round-bottom flask were added ketone (1 mmol), cat. **7** (2.7 mg, 0.5 mol %) and *tert*-amyl alcohol (1 mL). Next, vacuum was applied to the flask followed by filling with H$_2$ gas and keeping the flask attached to a balloon filled with H$_2$ gas. The mixture was heated at 30 °C for 12 h. After completion of the reaction, the solvent was removed by evaporation under reduced pressure. The alcohols were isolated and purified by filtering a hexanes/ethyl acetate (5:1) solution of the crude product through a pad of silica gel, and then removing the solvent under reduced pressure. The conversion and purity of the alcohol products was assessed using NMR spectroscopy.

*4.3. Characterization date of **2***

*4.3.1. 1-Phenylethanol (**2a**). [18]*

Light yellow oil; 96% yield (117 mg); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31–7.30 (m, 4H), 7.26–7.20 (m, 1H), 4.80 (q, *J* = 6.5 Hz, 1H), 2.66 (br s, 1H), 1.43 (d, *J* = 6.5 Hz, 3H).

*4.3.2. 1-o-Tolylethanol (**2b**). [18]*

Light yellow soil; 95% yield (129 mg); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, *J* = 7.6 Hz, 1H), 7.22–7.09 (m, 3H), 5.06 (q, *J* = 6.4 Hz, 1H), 2.30 (s, 3H), 2.24 (br s, 1H), 1.42 (d, *J* = 6.4 Hz, 3H).

*4.3.3. 1-(m-Tolyl)ethanol (**2c**). [18]*

Light yellow oil; 94% yield (128 mg); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.21 (t, *J* = 7.5 Hz, 1H), 7.16–7.12 (m, 2H), 7.08 (s, 1H), 4.81 (q, *J* = 6.5 Hz, 1H), 2.34 (s, 3H), 2.19 (br s, 1H), 1.46 (d, *J* = 6.5 Hz, 3H).

*4.3.4. 1-(p-Tolyl)ethanol (**2d**). [18]*

Light yellow oil; 94% yield (128 mg); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.18 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 4.76 (q, *J* = 6.4 Hz, 1H), 2.26 (s, 3H), 1.97 (br s, 1H), 1.39 (d, *J* = 6.5 Hz, 3H).

*4.3.5. 1-(4-Methoxyphenyl)ethanol (**2e**). [18]*

Light yellow oil; 93% yield (141 mg); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.82 (q, *J* = 6.4 Hz, 1H), 3.78 (s, 3H), 2.16 (br s, 1H), 1.46 (d, *J* = 6.5 Hz, 3H).

*4.3.6. 1-(4-Fluorophenyl)ethanol (**2f**). [18]*

Light yellow oil; 96% yield (134 mg); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30–7.26 (m, 2H), 7.62–6.98 (m, 2H), 4.82 (q, *J* = 6.4 Hz, 1H), 2.61 (br s, 1H), 1.43 (d, *J* = 6.5 Hz, 3H).

*4.3.7. 1-(2-Chlorophenyl)ethanol (**2g**). [18]*

Light yellow oil; 96% yield (151 mg); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60 (d, *J* = 7.3 Hz, 1H), 7.33–7.28 (m, 2H), 7.22–7.18 (m, 1H), 5.30 (q, *J* = 6.3 Hz, 1H), 2.11 (br s, 1H), 1.49 (d, *J* = 6.4 Hz, 3H).

*4.3.8. 1-(3-Chlorophenyl)ethanol (**2h**). [18]*

Light yellow oil; 92% yield (144 mg); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38 (s, 1H), 7.27–7.23 (m, 3H), 4.88 (q, *J* = 6.4 Hz, 1H), 1.93 (br s, 1H), 1.49 (d, *J* = 4.5 Hz, 3H).

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4.3.9. 1-(4-Chlorophenyl)ethanol (**2i**). [18]

Light yellow oil; 96% yield (151 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (m, 4H), 4.83 (q, $J = 6.4$ Hz, 1H), 2.38 (br s, 1H), 1.44 (d, $J = 6.4$ Hz, 3H).

4.3.10. 1-(3,4-Dichlorophenyl)ethanol (**2j**). [19]

Light yellow oil; 94% yield (180 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42–7.36 (m, 2H), 7.14–7.12 (dd, 2.0 and 8.2 Hz, 1H), 4.80 (q, $J = 6.5$ Hz, 1H), 2.79 (br s, 1H), 1.42 (d, $J = 6.5$ Hz, 3H).

4.3.11. 1-(4-Bromophenyl)ethanol (**2k**). [18]

Light yellow oil; 96% yield (193 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, $J = 8.4$ Hz, 2H), 7.23 (d, $J = 8.3$ Hz, 2H), 4.83 (q, $J = 6.4$ Hz, 1H), 2.23 (br s, 1H), 1.45 (d, $J = 6.5$ Hz, 3H).

4.3.12. 1-(4-(Trifluoromethoxy)phenyl)ethanol (**2l**). [20]

Light yellow oil; 97% yield (200 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, $J = 8.6$ Hz, 2H), 7.19 (d, $J = 8.1$ Hz, 2H), 4.88 (q, $J = 6.4$ Hz, 1H), 2.34 (br s, 1H), 1.47 (d, $J = 6.5$ Hz, 3H).

4.3.13. 1-(4-(Trifluoromethyl)phenyl)ethanol (**2m**). [21]

Light yellow soil; 96% yield (183 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, $J = 8.1$ Hz, 2H), 7.42 (d, $J = 8.1$ Hz, 2H), 4.87 (q, $J = 6.5$ Hz, 1H), 2.95 (br s, 1H), 1.44 (d, $J = 6.6$ Hz, 3H).

4.3.14. 1-(Pyridin-2-yl)ethanol (**2n**). [22]

Light yellow oil; 96% yield (118 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, $J = 4.7$ Hz, 1H), 7.70–7.66 (td, $J = 1.6$ and 7.7 Hz, 1H), 7.34 (d, $J = 7.9$ Hz, 1H), 7.19–7.16 (m, 1H), 4.90 (q, $J = 6.5$ Hz, 1H), 4.71 (br s, 1H), 1.51 (d, $J = 6.6$ Hz, 3H).

4.3.15. 1-(Naphthalen-2-yl)ethanol (**2o**). [18]

Light yellow solid; 95% yield (163 mg); mp 74–75 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86–7.82 (m, 4H), 7.53–7.46 (m, 3H), 5.11–5.06 (m, 1H), 1.89 (br s, 1H), 1.60 (d, $J = 6.4$ Hz, 3H).

4.3.16. Phenylbutan-1-ol (**2p**). [23]

Light yellow oil; 94% yield (141 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.33 (m, 4H), 7.28–7.25 (m, 1H), 4.66 (t, $J = 6.6$ Hz, 1H), 1.96 (br s, 1H), 1.83–1.62 (m, 2H), 1.49–1.23 (m, 2H), 0.92 (t, $J = 6.5$ Hz, 3H).

4.3.17. Cyclohexanol (**2q**). [18]

Light yellow oil; 89% yield (89 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 3.61–3.56 (m, 1H), 2.47 (br s, 1H), 1.90–1.88 (m, 2H), 1.75–1.72 (m, 2H), 1.56–1.53 (m, 1H), 1.27–1.14 (m, 5H).

4.3.18. 2-Octanol (**2r**). [24]

Light yellow oil; 87% yield (113 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 3.82–3.74 (m, 1H), 1.46–1.29 (m, 10H), 1.21–1.17 (m, 4H), 0.89 (t, $J = 6.6$ Hz, 1H).

4.4. General procedure for catalytic hydrogenation of **4**

To an oven-dried 5 mL round-bottom flask were added aldehyde (1 mmol), cat. **7** (2.7 mg, 0.5 mol %) and *tert*-amyl alcohol (1 mL). Next, vacuum was applied to the flask followed by filling with H_2 gas and keeping the flask attached to a balloon filled with H_2 gas. The mixture was heated at 30 °C for 12 h. After completion of the reaction, the solvent was removed by evaporation under reduced pressure. The alcohols were isolated and purified by filtering a hexanes/ethyl acetate (5:1) solution of the crude product through a pad of silica gel, and then removing the solvent under reduced pressure. The conversion and purity of the alcohol products was assessed using NMR spectroscopy.

4.5. Characterization date of **4**

4.5.1. Phenylmethanol (**4a**) [21]

Light yellow oil; 96% yield (104 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.31 (m, 4H), 7.29–7.26 (m, 1H), 4.62 (s, 2H), 2.32 (br s, 1H).

4.5.2. m-Tolylmethanol (**4b**) [25]

Light yellow oil; 94% yield (115 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.24–7.20 (m, 1H), 7.14–7.07 (m, 3H), 4.58 (s, 2H), 2.43 (br s, 2H), 2.33 (s, 3H).

4.5.3. p-Tolylmethanol (**4c**). [21]

Yellow soil; 92% yield (112 mg); mp 59–61 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, $J = 7.8$ Hz, 2H), 7.16 (d, $J = 7.8$ Hz, 2H), 4.59 (s, 2H), 2.34 (s, 3H), 2.12 (br s, 1H).

4.5.4. (3,4-Dimethylphenyl)methanol (**4d**). [26]

Light yellow oil; 96% yield (131 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.13–7.07 (m, 3H), 4.60 (s, 2H), 2.26 (s, 3H), 2.25 (s, 3H), 1.79 (br s, 1H).

4.5.5. (4-Isopropylphenyl)methanol (**4e**). [25]

Light yellow oil; 93% yield (140 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, $J = 8.0$ Hz, 2H), 7.26 (d, $J = 6.0$ Hz, 2H), 4.66 (s, 2H), 2.96–2.86 (m, 1H), 1.26 (d, $J = 6.9$ Hz, 6H).

4.5.6. (4-Methoxyphenyl)methanol (**4f**). [21]

Light yellow oil; 94% yield (130 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, $J = 8.6$ Hz, 2H), 6.88 (d, $J = 8.6$ Hz, 2H), 4.5 (s, 2H), 3.78 (s, 3H), 2.20 (br s, 1H).

4.5.7. (4-Fluorophenyl)methanol (**4g**). [21]

Light yellow oil; 95% yield (120 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34–7.26 (m, 4H), 4.66 (s, 2H), 1.97 (br s, 1H).

4.5.8. (2-Chlorophenyl)methanol (**4h**). [27]

Light yellow soil; 83% yield (118 mg); mp 71–72 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, $J = 7.3$ Hz, 1H), 7.37 (d, $J = 8.6$ Hz, 1H), 7.30–7.21 (m, 2H), 4.77 (s, 2H), 2.33 (br s, 1H).

4.5.9. (4-Chlorophenyl)methanol (**4i**). [21]

White soil; 96% yield (137 mg); mp 69–70 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-.7.26 (m, 4H), 4.64 (s, 2H), 2.01 (br s, 1H).

4.5.10. (4-Bromophenyl)methanol (**4j**). [21]

Yellow soil; 97% yield (181 mg); mp 63–64 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, $J = 8.2$ Hz, 2H), 7.24 (d, $J = 8.2$ Hz, 2H), 4.64 (s, 2H), 1.87 (br s, 1H).

4.5.11. 4-(Hydroxymethyl)benzonitrile (**4k**). [21]

White soil; 94% yield (125 mg); mp 41–42 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, $J = 8.2$ Hz, 2H), 7.49 (d, $J = 8.1$ Hz, 2H), 4.78 (s, 2H), 2.16 (br s, 1H).

4.5.12. Methyl-4-(hydroxymethyl)benzoate (**4l**). [25]

White solid; 95% yield (158 mg); mp 48–49 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, $J = 8.2$ Hz, 2H), 7.45 (d, $J = 8.2$ Hz, 2H), 4.78 (s, 2H), 3.92 (s, 3H), 1.88 (br s, 1H).

4.5.13. Naphthalen-1-ylmethanol (**4m**). [28]

Light yellow soil; 94% yield (149 mg); mp 58–59 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, $J = 8.2$ Hz, 1H), 7.89 (d, $J = 7.6$ Hz, 1H), 7.82 (d, $J = 8.1$ Hz, 1H), 7.57–7.49 (m, 3H), 7.44 (t, $J = 7.6$ Hz, 1H), 5.14 (s, 2H), 1.86 (br s, 1H).

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4.5.14. *Pyridin-2-ylmethanol (**4n**).* [21]

Light yellow oil; 96% yield (105 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, $J = 4.8$ Hz, 1H), 7.68 (td, $J = 1.6$ and 7.7 Hz, 1H), 7.33 (d, $J = 7.8$ Hz, 1H), 7.19 (t, $J = 6.2$ Hz, 1H), 4.80 (br s, 1H), 4.76 (s, 2H).

4.5.15. *Decan-1-ol (**4o**).* [29]

Light yellow oil; 96% yield (152 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.61 (t, $J = 6.7$ Hz, 2H), 2.44 (br s, 1H), 1.59–1.52 (m, 2H), 1.31–1.27 (m, 14H), 0.88 (t, $J = 6.8$ Hz, 3H).

4.5.16. *Cyclohexylmethanol (**4p**).* [30]

Light yellow oil; 91% yield (104 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.43 (d, $J = 6.4$ Hz, 2H), 2.32 (br s, 1H), 1.77–1.66 (m, 5H), 1.51–1.42 (m, 1H), 1.30–1.14 (m, 3H), 0.97–0.87 (m, 2H).

4.5.17. *3-Cyclohexene-1-methanol (**4q**).* [31]

Light yellow soil; 92% yield (103 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71–5.65 (m, 2H), 3.55–3.50 (m, 2H), 2.31 (br s, 1H), 2.13–2.05 (m, 3H), 1.84–1.73 (m, 3H), 1.29–1.23 (m, 1H).

4.5.18. *1-(4-(hydroxymethyl)phenyl)ethanol (**6**).* [32]

Light yellow soil; 94% yield (143 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (m, 4H), 4.74 (q, $J = 6.4$ Hz, 1H), 4.47 (s, 2H), 3.67 (br s, 2H), 1.37 (d, $J = 6.5$ Hz, 3H).

4.5.19. *1-(3-(1-hydroxyethyl)phenyl)ethanone (**8**).* [33]

Light yellow soil; 92% yield (151 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.88 (d, $J = 7.7$ Hz, 1H), 7.61 (d, $J = 7.7$ Hz, 1H), 7.46 (t, $J = 7.7$ Hz, 1H), 4.99 (q, $J = 6.5$ Hz, 1H), 2.62 (s, 3H), 1.54 (d, $J = 6.4$ Hz, 3H).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2019.07.021.

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