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### **Acceptorless Dehydrogenation of Primary and Secondary Benzylic Alcohols Using a Well Defined Phosphine Free Air Stable Mn<sup>II</sup>-Catalyst. Synthesis of Imines via Dehydrogenative Coupling of Alcohols and Amines**

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#### **ABSTRACT**

Acceptor less dehydrogenation of alcohols, in which hydrogen gas is liberated, is an atom-economical and environmentally benign method for the synthesis of useful organic carbonyl compounds in absence of stoichiometric oxidants. The carbonyl compounds, thus synthesized, can be further functionalized to other useful organic compounds like imines, amides or esters in presence of suitable coupling partners. These class of reactions are also of immense interest in the field of energy storage technologies as it offers an opportunity to get H<sub>2</sub> from biomass-derived alcohols and carbohydrates. However, most of the catalysts used for dehydrogenation reaction are mainly based on precious and expensive heavy metals. In this article we report a simple environmentally benign acceptorless dehydrogenation of primary and secondary benzylic alcohols catalyzed by a well defined Mn(II)-complex [Mn<sup>II</sup>(1,10-phen)<sub>2</sub>Cl<sub>2</sub>]. Imines were also synthesized via acceptorless dehydrogenative coupling of alcohols and amines. Several controlled reactions along with deuterium labelling studies were carried out to establish the acceptorless dehydrogenative nature of the reactions.

**KEYWORDS.** Acceptorless dehydrogenation, Alcohol oxidation, H<sub>2</sub> production, Mn-catalyst, Imines

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## INTRODUCTION

Catalytic acceptor less dehydrogenation reactions, particularly, the acceptorless dehydrogenation of alcohols, in which hydrogen gas is liberated, is an atom-economical and environmentally benign method for the synthesis of useful organic carbonyl compounds in absence of stoichiometric oxidants.<sup>1</sup> These reactions are of contemporary interest because of their relevance to chemical energy conversion using renewable resources; it indeed provides an opportunity to get H<sub>2</sub> from biomass-derived alcohols and carbohydrates.<sup>2</sup> Furthermore, the dehydrogenated products, i.e. the ketones or aldehydes can even be further functionalized to other valuable organic compounds like imines, amides, esters and organic heterocycles in presence of suitable coupling partners.<sup>3</sup>

Consequently, a continuous effort is going on to develop new catalysts and catalytic methodologies for acceptorless dehydrogenation reactions. Several homogeneous catalysts were already developed and tested for acceptorless dehydrogenation of alcohols and subsequent chemical transformations. However, these catalysts often contain precious and heavy metals such as Rh, Ir, Ru, and Os.<sup>4-7</sup> Catalysts containing sustainable metals such as iron,<sup>8</sup> cobalt,<sup>9</sup> manganese,<sup>10</sup> and nickel<sup>11</sup> have been much less explored. In recent years, using the non-precious and earth abundant transition metal ions, only a few groups reported the catalytic dehydrogenative oxidation of alcohols and synthesis of imines or amides by direct dehydrogenative coupling of alcohols with amines. For example, Milstein and co-workers, in 2016 reported a Manganese catalyzed synthesis of aldimines via dehydrogenative coupling of alcohols and amines (Figure 1a).<sup>10</sup> In 2015 Hong and co-workers reported a Fe-catalyzed acceptorless dehydrogenation of benzylic alcohols.<sup>8a</sup> Jones and co-workers in 2014 reported a well-defined iron catalyst for the acceptorless dehydrogenation of N-heterocycles.<sup>8b</sup> In 2013, Hanson *et al.* reported a cobalt catalyst featuring a bis (dicyclohexylphosphine) amine (PNP) lig and for the acceptor less dehydrogenation of alcohols.<sup>9a</sup> In the same year, Beller and co-workers demonstrated the hydrogen production from methanol using two octahedral iron complexes and in the presence of KOH.<sup>8d</sup> In contrast to the development of several homogeneous catalysts based on Fe and Co, catalytic dehydrogenative reactions involving Mn-complexes are less developed although manganese is the third most abundant transition metal ions on earth crust.<sup>10,12</sup> Herein acceptorless dehydrogenation of primary and secondary benzylic alcohols and synthesis of imines via direct dehydrogenative coupling of alcohols and amines catalyzed by a simple air stable manganese(II) complex [Mn<sup>II</sup>(1,10-Phen)<sub>2</sub>Cl<sub>2</sub>] is reported. It is noteworthy to mention that imines and their derivatives have been drawing considerable attention over the years; these are frequently used as redox-active ligands in synthetic coordination chemistry.<sup>13</sup> They also found wide applications in the synthesis of dyes, fragrances, fungicides, pharmaceuticals, and agricultural chemicals.<sup>14</sup>

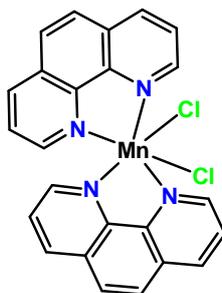


Figure 1. Catalyst used in this study.

## MATERIALS AND METHODS.

**General Information.** All reactions were carried out using standard Schlenk techniques under argon atmosphere. Tetrahydrofuran (THF), toluene, 1,4-dioxane were refluxed over sodium/benzophenone, distilled under argon atmosphere, and stored over 4 Å molecular sieves. All other chemicals were purchased from commercial suppliers and used as received without further purification. Analytical TLC was performed on a Merck 60 F254 silica gel plate (0.25mm thickness) and column chromatography was performed on Merck 60 silica gel (60-120 mesh). During purification of the reaction mixture of some of the controlled experiments preparative TLC was used.  $^1\text{H}$  NMR spectra were recorded on a Bruker DPX-300(300 MHz), Bruker DPX-400(400 MHz) and Bruker DPX-500(500 MHz) spectrometers. TMS (tetramethylsilane) was used as a the internal standard.

**Synthesis of  $[\text{Mn}^{\text{II}}(1,10\text{-Phen})_2\text{Cl}_2]$ .** The catalyst  $[\text{Mn}^{\text{II}}(1,10\text{-Phen})_2\text{Cl}_2]$  was synthesized following the literature procedure via refluxing 1.0 equiv. of  $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$  with 2.0 equiv. of 1,10-Phenanthroline in ethanol for four hours.<sup>15</sup>

**General Procedure for Oxidation of Alcohols.** Under argon atmosphere a mixture of  $[\text{Mn}^{\text{II}}(1,10\text{-Phen})_2\text{Cl}_2]$  (0.03 mmol) and Potassium tert-butoxide (1.0 mmol) was added in a flame-dried Schlenk tube. The tube was capped with a Teflon screw cap, evacuated, and backfilled with argon. The screw cap was replaced with a rubber septum. Alcohol (1.0 mmol) dissolved in 5.0 mL of toluene was added to the Schlenk via a syringe. The Schlenk tube was then placed in an oil bath and heated at 75 °C for a set period. Once the reaction is finished, the resulting mixture was concentrated, volatiles were removed in vacuum and the residue was purified by column chromatography using silica.

**General Procedure for Dehydrogenative Coupling of Alcohols and Amines.** Under argon atmosphere a mixture of  $[\text{Mn}^{\text{II}}(1,10\text{-Phen})_2\text{Cl}_2]$  (0.03 mmol), Potassium tert-butoxide (1.0 mmol) and molecular sieves (4 Å) was added in a flame-dried Schlenk tube. A mixture of alcohol (1.0 mmol) and amine (1.0 mmol) dissolved in 10.0 mL of toluene was added to the Schlenk once

via a syringe. The Schlenk tube was then placed in an oil bath and heated at 110 °C for 48-60 h. After the reaction finished, the resulting mixture was concentrated and the residue was purified by flash chromatography (silica gel) under argon atmosphere. For a few reactions an aliquot of the reaction mixture (100  $\mu$ L) was dissolved in  $\text{CDCl}_3$  and analyzed by  $^1\text{H}$  NMR.

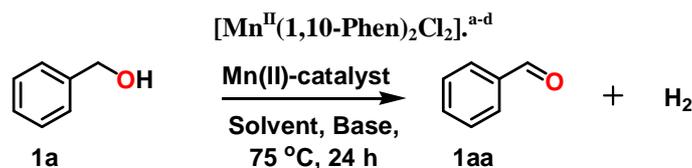
## RESULTS AND DISCUSSION

The catalyst  $[\text{Mn}^{\text{II}}(1,10\text{-Phen})_2\text{Cl}_2]$  was synthesized following the literature procedure via refluxing 1.0 equiv. of  $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$  with 2.0 equiv. of 1,10-Phenanthroline in ethanol for four hours.<sup>15</sup>

Initially benzyl alcohol (**1a**) was chosen as the model substrate to evaluate the optimal reaction conditions for the dehydrogenation reaction using  $[\text{Mn}^{\text{II}}(1,10\text{-Phen})_2\text{Cl}_2]$  as catalyst. Optimization of the reaction conditions revealed that the reaction proceeded most efficiently in nonpolar solvents like toluene, whereas reactions in solvents of high polarities such as MeCN, dioxane, methanol, and DMF afforded poor yields (Table 1, entries 2-4). Among the series of bases examined such as  $\text{K}_3\text{PO}_4$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Cs}_2\text{CO}_3$ ,  $\text{NaO}^t\text{Bu}$ ,  $\text{KO}^t\text{Bu}$ , NaOMe, and NaOH, the best results were obtained with  $\text{KO}^t\text{Bu}$  (Table 1, entries 1–12). Highest conversion of benzyl alcohol to benzaldehyde was achieved when the reaction was carried out at 75 °C in toluene for 24 h in presence of 1.0 equiv. of  $\text{KO}^t\text{Bu}$  using 3.0 mol% of the catalyst (Table 1, entry 1). Lowering the temperature or catalyst loading below 3.0 mol% leads to poor conversion of the alcohols to the corresponding aldehydes or ketones. The stability of the catalytic system was also checked in aerial conditions.  $[\text{Mn}^{\text{II}}(1,10\text{-Phen})_2\text{Cl}_2]$  itself is air stable and excellent conversion of alcohol to aldehyde was achieved when the reaction was carried out in presence of air. However, the yield of the corresponding aldehyde or ketones decreases significantly when the reaction was carried out in a closed schlenk tube (Table 2). This experimental observation is in agreement with the other reported dehydrogenation reactions where the removal of  $\text{H}_2$  from the reaction mixture is essential for the progress of the reaction.<sup>8a</sup>

Controlled experiments showed that no product was obtained in presence of only 1,10-phenanthroline ligand and base. While other manganese(II) sources like  $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (Table 1, entries 13 and 14) only afforded the corresponding aldehydes in trace amounts (<10%).

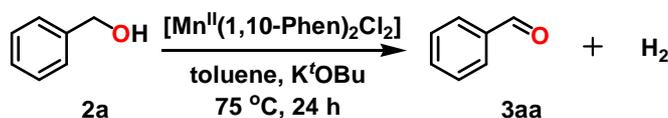
Table 1. Optimization of Reaction Conditions for the Dehydrogenation of Benzyl Alcohol (2a) Catalyzed by



Entry	Mn(II)-catalyst (mol %)	Solvent	Base	Yield (%) <sup>a-d</sup>
1	[Mn <sup>II</sup> (1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	toluene	KO <sup>t</sup> Bu	86
2	[Mn <sup>II</sup> (1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	acetonitrile	KO <sup>t</sup> Bu	trace
3	[Mn <sup>II</sup> (1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	methanol	KO <sup>t</sup> Bu	NR
4	[Mn <sup>II</sup> (1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	ethanol	KO <sup>t</sup> Bu	NR
5	[Mn <sup>II</sup> (1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	THF	KO <sup>t</sup> Bu	75
6	[Mn <sup>II</sup> (1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	toluene	K <sub>2</sub> CO <sub>3</sub>	NR
7 <sup>c</sup>	[Mn <sup>II</sup> (1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	toluene	NaOH	83
8	[Mn(1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	toluene	Na <sub>2</sub> CO <sub>3</sub>	NR
9	[Mn(1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	toluene	NaHCO <sub>3</sub>	NR
10	-	toluene	KO <sup>t</sup> Bu	NR
11	[Mn(1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	toluene	-	NR
12	[Mn(1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (2.0 mol %)	toluene	KO <sup>t</sup> Bu	80
13	MnCl <sub>2</sub> (10.0 mol%)	toluene	KO <sup>t</sup> Bu	NR
14	Mn(ClO <sub>4</sub> ) <sub>2</sub> (10.0 mol%)	toluene	KO <sup>t</sup> Bu	trace

<sup>a</sup>Stoichiometry: benzyl alcohol (1.0 mmol); catalyst (0.03 mmol); base (1.0 mmol, 1.0 equiv.).

<sup>b</sup>Isolated yields after column chromatography. <sup>c</sup>Required time: 48h.

Table 2. Dehydrogenation of Benzyl alcohol (1a) in Open/Closed Systems<sup>a, b</sup>

Entry	Open/Closed	Atmosphere	Yield (%) <sup>a</sup>
1	open	Ar	85
2	open	air	76
3	closed	air/Ar	45

<sup>a</sup>Stoichiometry: benzyl alcohol (1.0 mmol); catalyst (0.03 mmol); base (1.0 mmol, 1.0 equiv.).

<sup>b</sup>Isolated yields after column chromatography.

Various substituted alcohols with different electronic properties and functional groups were tested to explore the substrate scope and versatility of the developed catalytic methodology. As shown in Table 3, excellent yields were obtained with alcohols containing electron donating groups. Reactions also proceeded with electron-withdrawing groups at the *para* position of benzyl alcohols, albeit leading to lower yields. For example, 4- nitro benzyl alcohol (**1c**) produces the corresponding aldehyde in a moderate yield (Table 3, entry 3). Higher yields of the corresponding aldehydes were obtained with alcohols containing electron donating substituents either at *para* or *meta* positions (Table 3, entry 4-6). Secondary alcohols also undergo dehydrogenation to produce the corresponding ketones under the same optimized reaction condition. Diphenyl alcohol or methyl phenyl alcohol

produced benzophenone and acetophenone in high yields (Table 3, entry 7, 8) under the same optimized reaction condition. Pyrene 1-aldehyde or Anthracene - 9- carbaldehyde were also isolated in high yields from their corresponding alcohols (Table 3, entry 9, 10). Heterocyclic alcohols were also found to produce the corresponding aldehydes (Table 3, entry 11-12). For example, 2-Pyridinecarboxaldehyde was obtained in 25% yield from 2-Pyridinemethanol under the optimized reaction condition. Unfortunately, aliphatic alcohols were not dehydrogenated under our catalytic reaction conditions (Table 3, entry 13).

**Table 3. Dehydrogenation of Various Alcohols Catalyzed by  $[\text{Mn}^{\text{II}}(1,10\text{-Phen})_2\text{Cl}_2]$ .<sup>a-c</sup>**

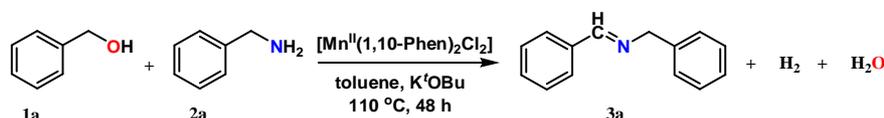
Entry	Alcohol	Product	Yielda (%)
1.	(1a)	(2aa)	86 (2aa)
2.	(1b)	(2bb)	73 (2bb)
3.	(1c)	(2cc)	44 (2cc)
4.	(1d)	(2dd)	84 (2dd)
5.	(1e)	(2ee)	76 (2ee)
6.	(1f)	(2ff)	87 (2ff)
7. <sup>c</sup>	(1g)	(2gg)	86 (2gg)
8.	(1h)	(2hh)	82 (2hh)
9.	(1i)	(2ii)	86 (2ii)
10.	(1j)	(2jj)	81 (2jj)
11.	(1k)	(2kk)	20 (2kk)
12.	(1l)	(2ll)	23 (2ll)
13.	(1m)	(2mm)	NR (2mm)

<sup>a</sup>Stoichiometry: alcohol (1.0 mmol), catalyst (0.03 mmol); KO<sup>t</sup>Bu (1.0 mmol, 1.0 equiv).

<sup>b</sup>Isolated yields after column chromatography. <sup>c</sup>Reaction time: 12 h.

To further expand the scope of the developed catalytic methodology, attempts were made for direct dehydrogenative coupling of alcohols and amines. Reaction of equimolar amounts of benzyl alcohol and benzylamine in presence of 3.0 mol% catalyst and KO<sup>t</sup>Bu as base at 110 °C for 48 h produced the corresponding imine in 85% isolated yield (Table 4, entry 1). Optimization of the reaction conditions by varying the solvents and bases revealed that the highest yield of the imine was obtained in the same reaction condition that is best for dehydrogenation of alcohols; except slightly higher temperature and time is required. Lowering the temperature or catalyst loading below 3.0 mol% leads to poor yields of imines and requires prolonged reaction time (Table 4, entry 12). In polar solvents like acetonitrile or methanol <10% of the corresponding imine was formed (Table 4, entry 2, 3). Addition of molecular sieves (4 Å) further increases the yield and lowers the reaction time slightly (Table 4, entry 13). Notably, the same reaction when carried out in argon atmosphere under closed condition also produce the corresponding imine in 83% yield (Table 4, entry 14). The presence of H<sub>2</sub> in the reaction medium slightly decreases the yield of the imine. Overall, the dehydrogenative coupling of alcohols and amine was found to be clean; no side products, such as amides or esters were observed.

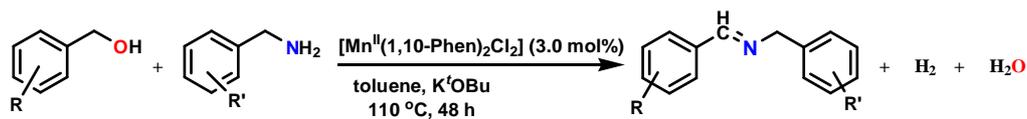
**Table 4. Optimization of Reaction Conditions for the Dehydrogenative Coupling of Benzyl Alcohol and Benzyl Amine Catalyzed by [Mn<sup>II</sup>(1,10-Phen)<sub>2</sub>Cl<sub>2</sub>].<sup>a-e</sup>**



Entry	Mn(II)-catalyst (mol %)	Solvent	Base	Yield(%)
1	[Mn <sup>II</sup> (1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	toluene	KO <sup>t</sup> Bu	85
2	[Mn <sup>II</sup> (1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	acetonitrile	KO <sup>t</sup> Bu	trace
3	[Mn <sup>II</sup> (1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	methanol	KO <sup>t</sup> Bu	NR
4	[Mn <sup>II</sup> (1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	ethanol	KO <sup>t</sup> Bu	NR
5	[Mn <sup>II</sup> (1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	THF	KO <sup>t</sup> Bu	65
6	[Mn <sup>II</sup> (1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	toluene	K <sub>2</sub> CO <sub>3</sub>	NR
7	[Mn <sup>II</sup> (1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	toluene	NaOH	70
8	[Mn <sup>II</sup> (1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	toluene	Na <sub>2</sub> CO <sub>3</sub>	NR
9	[Mn <sup>II</sup> (1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	toluene	NaHCO <sub>3</sub>	NR
10	-	toluene	KO <sup>t</sup> Bu	NR
11	[Mn <sup>II</sup> (1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	toluene	-	NR
12 <sup>c</sup>	[Mn <sup>II</sup> (1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (2.0 mol %)	toluene	KO <sup>t</sup> Bu	76
13 <sup>d</sup>	[Ni <sup>II</sup> (MeTAA)] (3.0 mol %)	toluene	KO <sup>t</sup> Bu	92
14 <sup>c</sup>	[Mn <sup>II</sup> (1,10-Phen) <sub>2</sub> Cl <sub>2</sub> ] (3.0 mol %)	toluene	KO <sup>t</sup> Bu	83

<sup>a</sup>Stoichiometry: benzyl alcohol (1.0 mmol), benzyl amine (1.0 mmol) catalyst (0.03 mmol); KO<sup>t</sup>Bu (1.0 mmol, 1.0 equiv). <sup>b</sup>Isolated yields after column chromatography. <sup>c</sup>Reaction time: 60h. <sup>d</sup>Molecular sieves (4Å) was added. <sup>e</sup>Reaction was carried out in a closed schlenk tube under argon.

Various substituted benzyl alcohols and amines were tested under the optimized conditions to explore the substrate scope of the dehydrogenative coupling reaction. Benzyl alcohol was found to undergo efficient dehydrogenative coupling with a variety of benzylic amines containing both electron donating or withdrawing groups (Table 5, entry 1-11). Presence of electron donating group at the *ortho* or *para* positions of benzylamines resulted in higher yields of the corresponding imines whereas benzyl amines having electron withdrawing substituents produced lower yield of the imine. 4-Methoxybenzylamine and 4-fluorobenzylamine undergoes dehydrogenative coupling with benzyl alcohol under the optimized reaction conditions to produce the corresponding imines in 87 and 71% yield respectively (Table 5, entry 2, 3). Dehydrogenative coupling of cyclohexylamine or hexylamine with benzyl alcohol also produced the corresponding imines in 72 and 57% yield respectively (Table 5, entry 5, 6). Benzyl alcohols bearing either electron donating or -withdrawing substituents were also tested. Reaction of 4-methoxy or 3-methoxy benzyl alcohols with benzylamine produced the corresponding imines in 64 and 66% yield respectively (Table 5, entry 7, 8). Benzyl alcohols with electron withdrawing group at *para* position was also found to undergo the catalytic dehydrogenative coupling reaction to produce the imines. Reaction of 4-nitrobenzyl alcohol with benzylamine produced the corresponding imine in 93% yield (Table 5, entry 10). Presence of electron withdrawing groups in both alcohol and amines also resulted a slight decrease in the yield of the corresponding imine. Reaction of 4-nitrobenzyl alcohol with 4-fluorobenzylamine under the optimized reaction condition yielded the corresponding imine in 85% yield (Table 5, entry 11). Aromatic amines were also found to be suitable for the dehydrogenative coupling; reaction of benzylamine with 4-chloroaniline under the optimized reaction condition produced the corresponding imine in almost quantitative yield.

Table 5. Dehydrogenative Coupling of Various Alcohols and Amines Catalyzed by  $[\text{Mn}^{\text{II}}(1,10\text{-Phen})_2\text{Cl}_2]$ .<sup>a-c</sup>

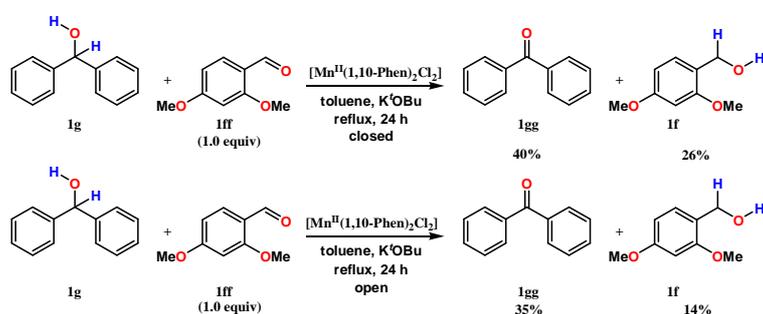
Entry	Alcohol	Amine	Imine	Yield <sup>a,b</sup> (%)
1 <sup>b</sup>				92 (3a)
2 <sup>b</sup>				87 (3b)
3 <sup>b</sup>				71 (3c)
4 <sup>b</sup>				73 (3d)
5 <sup>c</sup>				72 (3e)
6 <sup>c</sup>				57 (3f)
7 <sup>b</sup>				64 (3g)
8 <sup>b</sup>				71 (3h)
9 <sup>c</sup>				66 (3i)
10 <sup>c</sup>				93 (3j)
11 <sup>c</sup>				85 (3k)
12 <sup>b</sup>				>99 (3l)

<sup>a</sup>Stoichiometry: benzyl alcohol (1.0 mmol), benzyl amine (1.0 mmol) catalyst (0.03 mmol); base (1.0 mmol, 1.0 equiv). <sup>b</sup>Isolated yields after column chromatography. <sup>c</sup>NMR yield using 1,4 dioxane as internal standard.

To check the dehydrogenative nature of the catalytic reactions and to confirm  $\text{H}_2$  evolution several controlled reactions were carried out. Intermolecular hydrogen transfer experiments were carried out to make use of the  $\text{H}_2$ , liberated during dehydrogenation of alcohols, to reduce easily reducible substrates (Scheme 1). The dehydrogenation of diphenyl methanol (**1g**) when carried out in presence of 2,4-dimethoxybenzaldehyde (**1ff**) in a closed system, benzophenone (**1gg**) was obtained

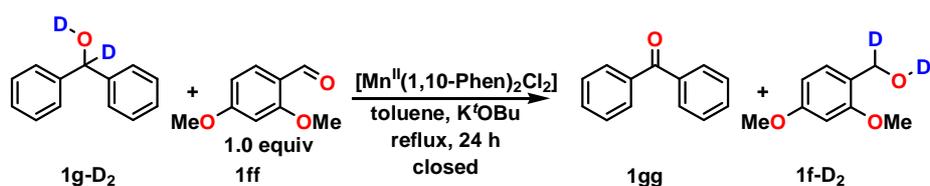
in 40% yield, and (2,4-dimethoxy)benzyl alcohol (**1f**) was obtained as the hydrogenated product of 2,4-dimethoxybenzaldehyde. However, when the reaction was carried out in an open condition under argon atmosphere the dehydrogenation and hydrogen transfer reactions were found to be retarded by some extent. 65% of H<sub>2</sub> was found to be transferred to the corresponding aldehyde when the reaction was carried out in closed condition whereas only 40% H<sub>2</sub> transfer occurs when the reaction was carried out in an open condition under argon atmosphere. The hydrogen transfer efficiency was calculated using a simple equation: [yield of **1f**]/[yield of **1gg**].<sup>8a</sup> This experimental results along with the available literature data indeed conclusively support that dehydrogenative nature of the catalytic methodology developed herein.

### Scheme 1. Controlled Experiments for Intermolecular Hydrogen Transfer.



To further confirm the H<sub>2</sub> evolution, intermolecular transfer hydrogenation reactions were carried out with deuterium labeled compound **1g-D<sub>2</sub>** (Scheme 2). The dehydrogenation of deuterated-diphenyl methanol (**1g-D<sub>2</sub>**) when carried out in presence of 2, 4-dimethoxybenzaldehyde (**1ff**) in a closed system, benzophenone was obtained, and deuterium exchange was observed in (2,4-dimethoxy)benzyl alcohol (**1f**), the deuterated product of 2,4-dimethoxybenzaldehyde (**1f-D<sub>2</sub>**).

### Scheme 2. Deuterium Labeling Study During Intermolecular Hydrogen Transfer.



## CONCLUSION

In summary, an unprecedented acceptorless dehydrogenation of alcohols catalyzed by a earth abundant, air-stable and simple Mn(II)-catalyst is reported. The catalytic methodology has been successfully extended for the synthesis of imines via dehydrogenative coupling of alcohols and amines. A variety of alcohols having different substituents has been found to produce the corresponding carbonyls under the optimized reaction conditions with the evaluation of H<sub>2</sub>. Amines with different substituents undergoes dehydrogenative coupling with alcohols to produce the

corresponding imines in good to excellent yield. Several controlled experiments coupled with deuterium labeling studies confirm the H<sub>2</sub> evolution and dehydrogenative nature of amine alcohol coupling. Further studies are in progress to understand the mechanism and to expand the scope of the dehydrogenative coupling reactions.

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