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Phosphine-Free Well-Defined Mn(I) Complex-Catalyzed Synthesis of Amine, Imine, and 2,3-Dihydro-1*H*-perimidine via Hydrogen Autotransfer or Acceptorless Dehydrogenative Coupling of Amine and Alcohol

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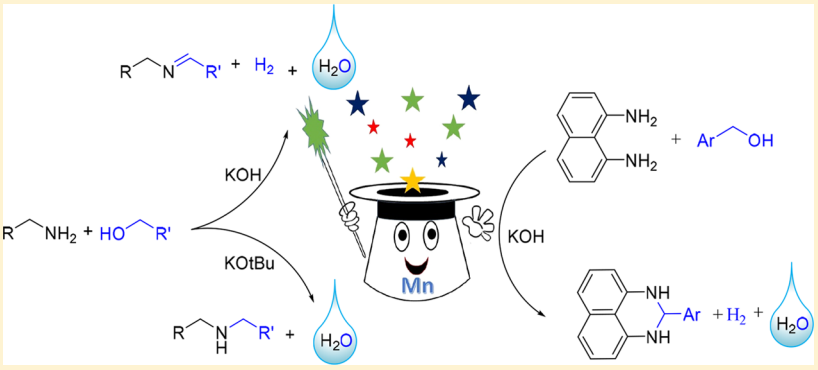
Supporting Information



ABSTRACT: The application of nontoxic, earth-abundant transition metals in place of costly noble metals is a paramount goal in catalysis and is especially interesting if the air- and moisture-stable ligand scaffold is used. Herein, we report the synthesis of amines/imines directly from alcohol and amines via hydrogen autotransfer or acceptorless dehydrogenation catalyzed by well-defined phosphine-free Mn complexes. Both imines and amines can be obtained from the same set of alcohols and amines using the same catalyst, only by tuning the reaction conditions. The amount and nature of the base are found to be a highly important aspect for the observed selectivity. Both the primary and secondary amines have been employed as substrates for the N-alkylation reaction. As a highlight, we showed the chemoselective synthesis of resveratrol derivatives. Furthermore, the Mn-catalyzed dehydrogenative synthesis of structurally important 2,3-dihydro-1*H*-perimidines has also been demonstrated. Density functional theory calculations were also carried out to model the reaction path and to calculate the reaction profile.

INTRODUCTION

Nitrogenous compounds such as amine and imines are known for their valuable application in chemistry.[1] They are ubiquitous in many natural products and widely used as dyes, pharmaceuticals, agrochemicals, lubricants, and surfactants.[2] Thus, the development of an environmentally benign, atom-economical catalytic approach for construction of the C−N bond is a paramount aim in catalysis.[3] The most important processes to synthesize amines are the Buchwald−Hartwig amination[4] and Ullmann reactions.[5] Although the high significance and wide application of these processes proved their efficacy in the organic synthesis, they often suffer from the generation of substantial amounts of side products or wastes. The usage of alcohols as starting materials has attracted significant attention in view of recent sustainable developments, as the alcohols are easily available either by different industrial processes or can be obtained renewably from lignocellulose.[6] The conventional approach for the construction of the C−N bond from alcohols is converting first the alcohol functionality to a suitable leaving group such as halides, triflates, tosylates, or mesylates and then reacting with primary amines to get the N-alkylated product.[7] These multistep strategies use hazardous reagents and lengthy work-up procedures, which generates a large amount of waste.[8] They also suffer from poor atom economy[9] and a low level of selectivity. To overcome these drawbacks, new catalytic protocols involving direct N-alkylation of amines by alcohol using "hydrogen autotransfer" (HA) or "borrowing hydrogen"(BH) strategies have been developed.[10] The catalytic cycle (Scheme 1) consists of three steps: (i) dehydrogenation of alcohol to form aldehyde/ketone, (ii) imine generation, and (iii) hydrogenation of imine to form amine (hydrogen autotransfer).

The process is completely environmentally benign as water is the only byproduct. Although the pioneering works on the N-alkylation of amines by alcohols were described independently by Watanabe[11] and Grigg[12] at the beginning of 1980s,

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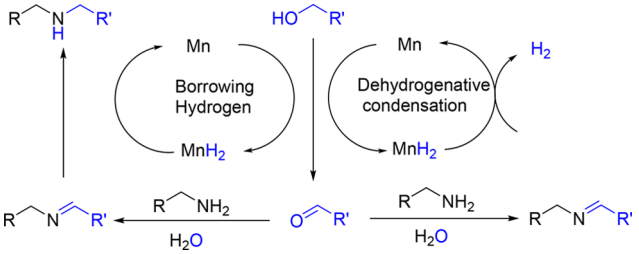
Scheme 1. Synthesis of Imines/Amines via Borrowing Hydrogen/Dehydrogenative Condensation



the significant progress has been achieved only after 2000 using precious metals.[13−17] The replacement of precious noble metal catalysts by eco-friendly, inexpensive earth-abundant metals is a key challenge in the homogeneous catalysis. In recent years, explosive growth in the catalysis by base metals has been observed.[18] Since 2016, manganese, being the third most abundant transition metal in the earth's crust, has attracted considerable attention toward the de(hydrogenative) synthesis of complex organic molecules from renewable starting materials.[19] However, the N-alkylation of alcohols with amine or the dehydrogenative synthesis of imines from alcohol and amine using environmentally benign, nontoxic Mn is still in the nascent stage (Figure 1).[20] Beller and co-workers

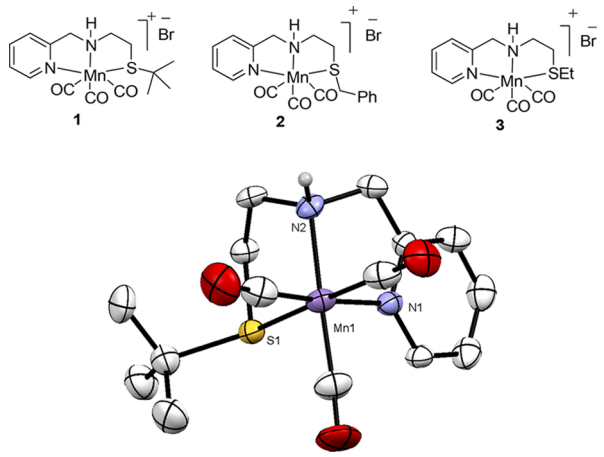


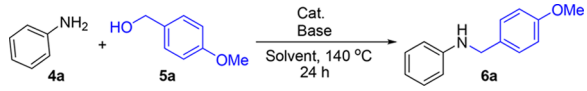
Figure 1. Phosphine-free Mn complexes and the molecular structure of complex **1** with a thermal ellipsoid at the 30% probability level (all the hydrogens except N2 and the counter ion are not shown for clarity).

first demonstrated the efficient N-alkylation of alcohol using the Mn-PNP pincer complex.[20a] Milstein and co-workers reported the first imine synthesis through the dehydrogenative coupling of alcohols and amines catalyzed by the pyridine-based Mn-PNP pincer complex.[20b] Although phosphine ligands are known for their significant applications in the homogeneous catalysis, still, there are some drawbacks associated with their air and moisture sensitivities, complex synthetic procedures, and relatively high cost. Thus, catalysis using phosphine-free, earth-abundant metal complexes are highly desirable in terms of sustainability and cost-effectiveness. Herein, we report first phosphine-free well-defined Mn complex (Figure 1) catalyzed N-alkylation of amines with alcohol and the dehydrogenative synthesis of imine. The selective synthesis of N-alkylated amines or imines is achieved by using a single precatalyst, only by tuning the reaction condition. In addition, the first dehydrogenative synthesis of structurally important 2,3-dihydro-1*H*-perimidine derivatives using the Mn complex has also been demonstrated under the phosphine-free condition.

RESULTS AND DISCUSSION

Initially, we investigated the catalytic applicability of complexes **1**−**3**[21] toward the N-alkylation reaction of amine with alcohol. Aniline and 4-methoxybenzyl alcohol were taken as a model substrate to optimize the reaction condition. When a toluene solution containing aniline (1 mmol), 4-methoxybenzyl alcohol (1.1 mmol), and potassium *tert*-butoxide (tBuOK) (1.2 mmol) was refluxed for 24 h in the presence of 5 mol % catalyst **1**, *N*-(4-methoxybenzyl)aniline was obtained in a 79% yield (Table 1, entry 1). Keeping the other conditions unaltered when xylene was used, the yield of the N-alkylated product was dropped to a 31% yield (Table 1, entry 2). Next, we studied the catalytic activity of the catalyst **2**; under the similar reaction condition using the toluene solvent, catalyst **2** gave only a 48% desired product yield (Table 1, entry 3). Gratifyingly, catalyst **3** gave a yield of 85% of the N-

Table 1. Optimization of the Reaction Conditions for the N-Alkylation Reaction of Amine with Alcohols[a]



entry	catalyst	solvent	base (mmol)	amine:alcohol (mmol)	yield (%)[b]
1	**1**	toluene	tBuOK (1.2)	1:1.1	79
2	**1**	xylene	tBuOK (1.2)	1:1.1	31
3	**2**	toluene	tBuOK (1.2)	1:1.1	48
4	**2**	xylene	tBuOK (1.2)	1:1.1	14
5	**3**	toluene	tBuOK (1.2)	1:1.1	85
6	**3**	xylene	tBuOK (1.2)	1:1.1	34
7	**3**	toluene	tBuOK (1.2)	1:1.2	98
8	**3**	toluene	tBuOK (1.2)	1:1.3	96
9	**3**	toluene	tBuOK (1.0)	1:1.2	77
10	**3**	toluene	tBuOK (0.75)	1:1.2	49
11	**3**	toluene	tBuOK (1.5)	1:1.2	42
12[c]	**3**	toluene	tBuOK (1.2)	1:1.2	71
13[d]	**3**	toluene	tBuOK (1.2)	1:1.2	80
14[e]	**3**	toluene	tBuOK (1.2)	1:1.2	33
15	**3**	toluene	KOH (1.2)	1:1.2	50
16	**3**	toluene	K_2CO_3 (1.2)	1:1.2	27
17	$Mn(CO)_5Br$	toluene	tBuOK (1.2)	1:1.2	20

[a]Reaction conditions: aniline (1 mmol), 4-methoxy benzyl alcohol (1.1−1.3 mmol), catalyst (5 mol %), base (0.75−1.5 mmol), 140 °C (oil bath temperature), 24 h, solvent (2 mL). [b]NMR yield using CH_3CN as internal standard. [c]2.5 mol %. [d]12 h. [e]100 °C loading.

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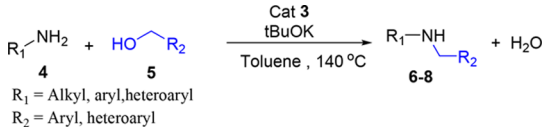
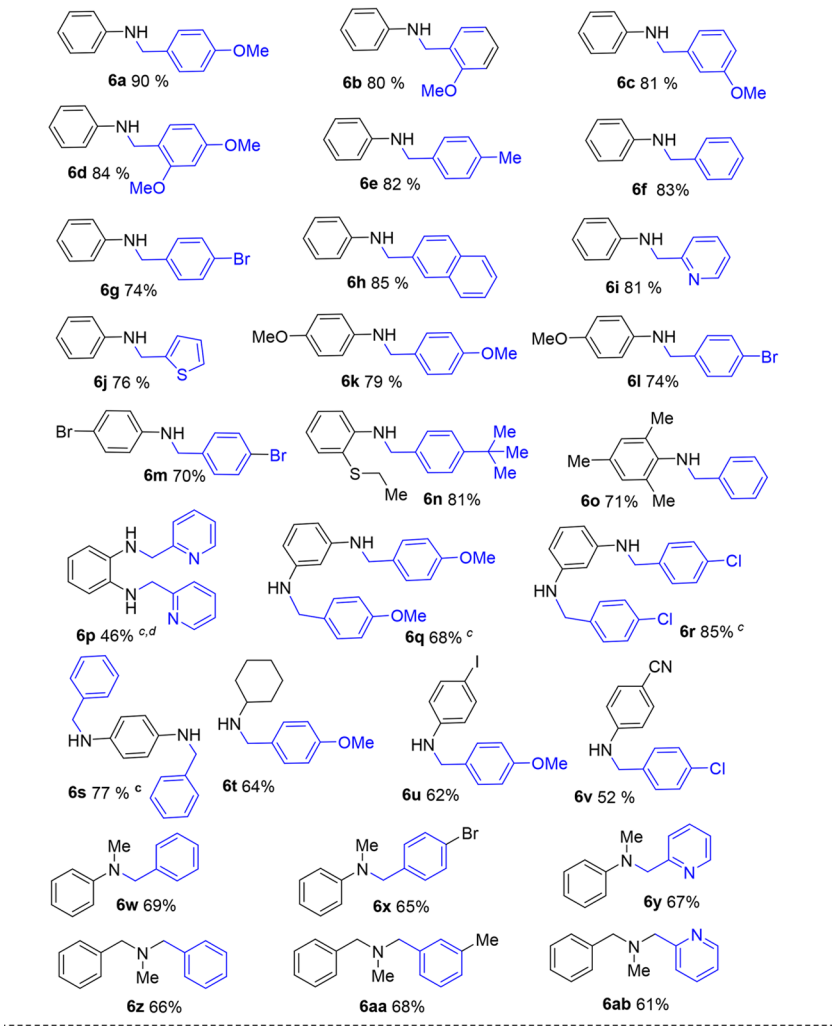
Table 2. Scope of N-Alkylation Reaction of Primary and Secondary Amines with Different Primary Alcohol[a,b]





[a]Reaction conditions: amine (1 mmol), alcohol (1.2 mmol), catalyst **3** (5 mol %), tBuOK (1.2 mmol), 140 °C (oil bath temperature), 24 h, toluene (2 mL). [b]Isolated yield. [c]Diaminobenzene (0.5 mmol), alcohol (1.5 mmol), 36 h. [d]18 h.

alkylated product, which was further improved to 98% when aniline and 4-methoxybenzyl alcohol were taken in a 1:1.2 ratio yield (Table 1, entries 5 and 7). The amine:alcohol ratio (1:1.2) used in our protocol is relatively lower than the previously reported PNP-Mn(I) complex[20c] or nickel complex.[18o] The yield of desired *N*-(4-methoxybenzyl)aniline was decreased with a lower amount of tBuOK (Table 1, entries 9 and 10) or by using a weaker base such as KOH or K_2CO_3 (Table 1, entries 15 and 16).

Thus, when 1.2 mmol of a weaker base such as KOH was used, only a yield of 48% of the desired N-alkylated product was obtained (Table 1, entry 15) together with a 41% yield of imine, although decreasing the amount of tBuOK (0.75) selectivity toward the desired amine was dropped to 49% (Table 1, entry 10). Thus, the nature and stoichiometry of the base are crucial for the observed selectivity. The lower temperature or the shorter reaction time is found to have a detrimental effect on the yield of the reaction (Table 1, entries 13 and 14). $MnBr(CO)_5$ gave only a yield of 20% of the desired amine under the optimized reaction condition (Table 1, entry 17).

After establishing the optimal reaction condition, we investigated a wide range of the substrate scope to demonstrate the generality of the reaction (Table 2). At the outset, different substituted aniline and alcohols were tested. Substrates having the electron-donating or electron-withdrawing group in the aryl group of aniline or benzyl alcohols were reacted smoothly under the optimized condition to afford the N-monoalkylated product in high yields. Even the sterically hindered anilines such as 2-(ethylthio)aniline and 2,4,6-trimethylaniline underwent N-alkylation smoothly, affording the corresponding N-monoalkylated product in good yields. Alcohols possessing heteroaromatic moieties or naphthyl moieties have also worked well. Furthermore, we investigated the N-alkylation of diaminobenzene. There is a possibility of formation of the dialkylated (N-alkylation of

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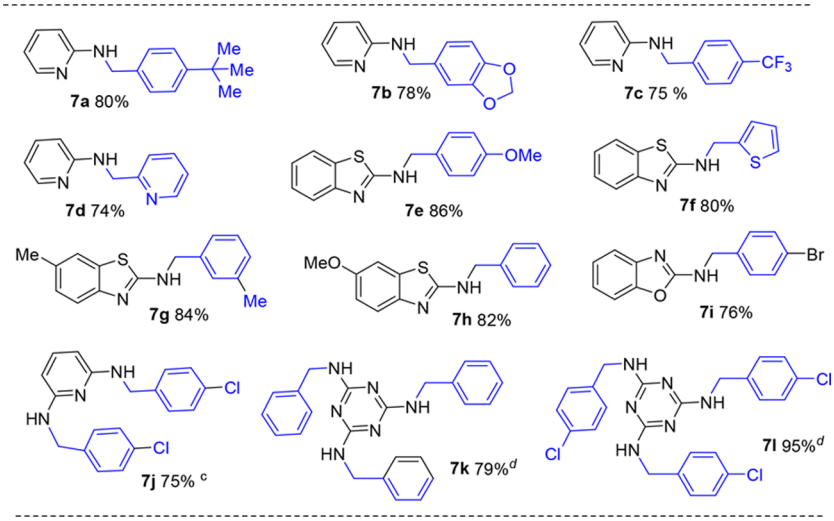
Table 3. Scope of N-Alkylation Reaction of Heterocyclic Amines[a,b]



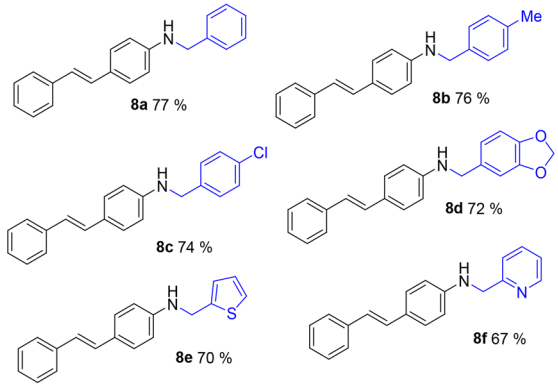
[a]Reaction conditions: amine (1 mmol), alcohol (1.2 mmol), catalyst **3** (5 mol %), base (1.2 mmol), 140 °C (oil bath temperature), 24 h, toluene (2 mL). [b]Isolated yield. [c]Diaminobenzene (0.5 mmol), alcohol (1.5 mmol), 36 h. [d]Melamine (0.5 mmol), alcohol (2.25 mmol), catalyst **3** (0.08 mmol), tBuOK (1.6 mmol), 52 h.

both NH_2) and mono-alkylated (N-alkylation of one of NH_2) product. Indeed, when 1,3-diaminobenzene and 4-chlorobenzyl alcohol were taken in a 1:2.4 ratio, the mixtures of mono- and dialkylated products were formed 30 and 40%, respectively. Increasing the ratio to 1:3, the dialkylated product was isolated to an 85% yield after 36 h. In the case of 1,2-diaminobenzene, only a 46% yield of the desired dialkylated product was obtained due to the formation of 1,2-disubstituted benzimidazole.[21a] Pure aliphatic amine such as cyclohexyl amine has reacted smoothly under the reaction condition. To demonstrate the usefulness of our protocol, we explored the N-alkylation of secondary amine to synthesize unsymmetrically substituted tertiary amine. The challenging substrates such as *N*-methylaniline[18o] and less basic *N*-methylbenzylamine have reacted well with different benzylic and heteroaryl alcohols, which, to the best of our knowledge, are not yet reported with any manganese catalyst.

To illustrate the synthetic utility, the scope of the N-alkylation reaction with regard to different heterocyclic amines was investigated further (Table 3). 2-(*N*-alkylamino)-benzothiazoles are structurally important units in many bioactive compounds[22] and have a broad range of physiological and pharmacological activities.[23] Thus, initially, we explored the N-alkylation of 2-aminobenzothiazole with different alcohols, gratifyingly N-exosubstituted 2-(*N*-alkylamino)benzothiazoles were obtained in a high yield. The reaction catalyzed by the Mn complex is completely regioselective toward N-exosubstituted 2-(*N*-alkylamino)-benzothiazoles, although N-alkylation of 2-aminobenzothiazoles with alkyl halides give N-endosubstituted 3-alkyl-2-iminobenzothiazolines.[24] Next, we investigated the N-alkylation of aminopyridines as the selective N-alkylation of aminopyridine is a challenging role as amides can be formed as byproducts.[25] To our delight, the N-alkylation of amino pyridines proceeds well to afford the desired N-alkylated product in a good yield. Next, we were interested in the tri-N-alkylation of melamine as substituted *s*-triazine derivatives are known to have different biological activities.[26] Thus, we studied the reaction of melamine with different benzyl alcohols. Upon refluxing melamine (0.5 mmol) with 4-chlorobenzyl alcohol (2.25 mmol) in toluene led to the formation of the corresponding trialkyalted product in a 58% yield after 36 h, which was further improved to 95%, only by increasing the reaction time (52 h).

Resveratrol-derived amines are known for their activity toward the treatment of Alzheimer's disease.[27] Thus, we have applied our protocol for the chemoselective N-alkylation of 4-aminostilbene with different alcohols to afford resveratrol derivatives in a good isolated yield (Scheme 2).

Scheme 2. Synthesis of Resveratrol Derivatives[a,b]



[a]Reaction conditions: 4-aminostilbene (1 mmol), alcohol (1.2 mmol), catalyst **3** (0.05 mmol), t-BuOK (1.2 mmol), toluene (2 mL), 140 °C (oil bath temperature), 24 h. [b]Isolated yield.

Next, we are interested to synthesize imine directly from the alcohol and amines using our Mn complexes, only by tuning the reaction condition (Table 4). In 2016, Milstein and co-workers first reported the Mn-catalyzed dehydrogenative synthesis of imines,[20b] and very recently, Kempe and co-workers demonstrated sustainable imine formation using the triazine-based PNP-Mn complex.[20c] Thus, the dehydrogen-

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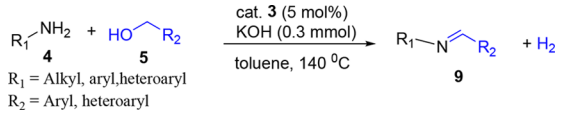
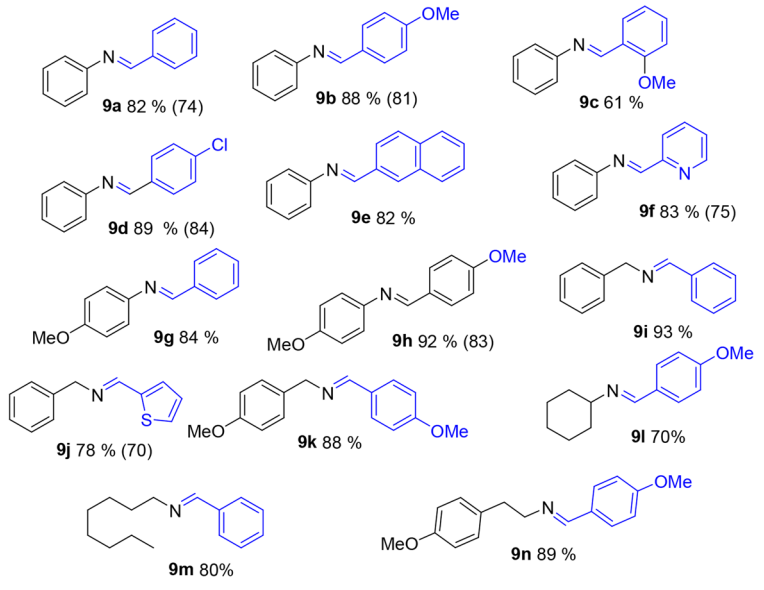
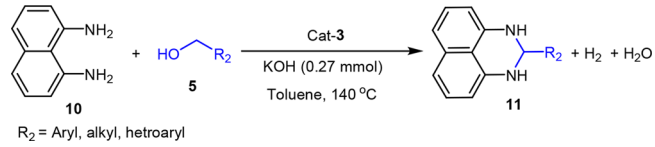
Table 4. Dehydrogenative Condensation Reaction of Alcohol and Amine[a,b]

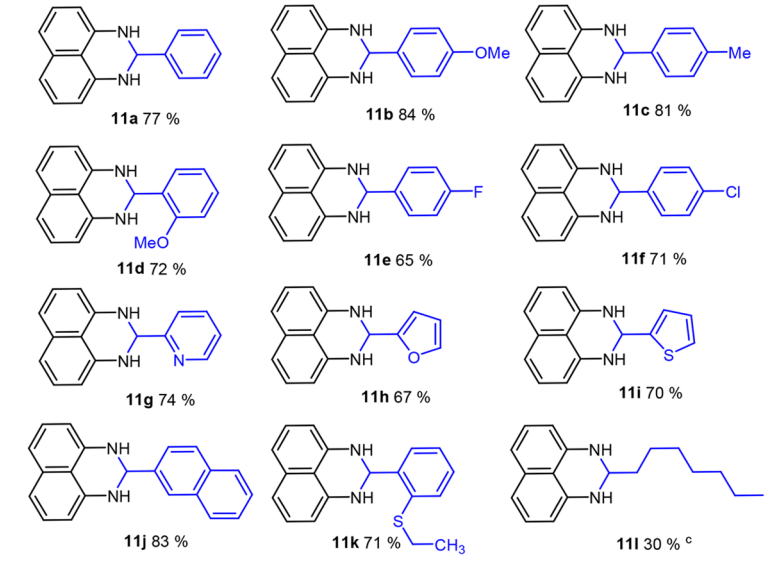




[a]Reaction conditions: amine (1 mmol), alcohol (1.2 mmol), catalyst **3** (5 mol %), KOH (0.3 mmol), 140 °C (oil bath temperature), 24 h, toluene (2 mL). [b]NMR yield (the yield in the parenthesis is the isolated yield).

Table 5. Scope of the Reaction To Synthesize 2,3-Dihydro-1*H*-Perimidine Derivatives[a,b]





[a]Reaction conditions: catalyst (5 mol %), 1,8-diaminonaphthalene (1 mmol), alcohol (1.2 mmol), base (0.3 mmol), 140 °C (oil bath temperature), 24 h, toluene (2 mL). [b]Isolated yield. [c]Alcohol (2.0 mmol), base (0.5 mmol), 72 h.

ative condensation of alcohol and amine using phosphine-free Mn complexes is highly desirable. Hence, when a toluene solution having aniline (1 mmol) and 4-methoxybenzyl alcohol (1.2 mmol) was refluxed in the presence of KOH (0.3 mmol) and 5 mol % catalyst **3** under argon flow, the desired imine was obtained in an 88% yield.

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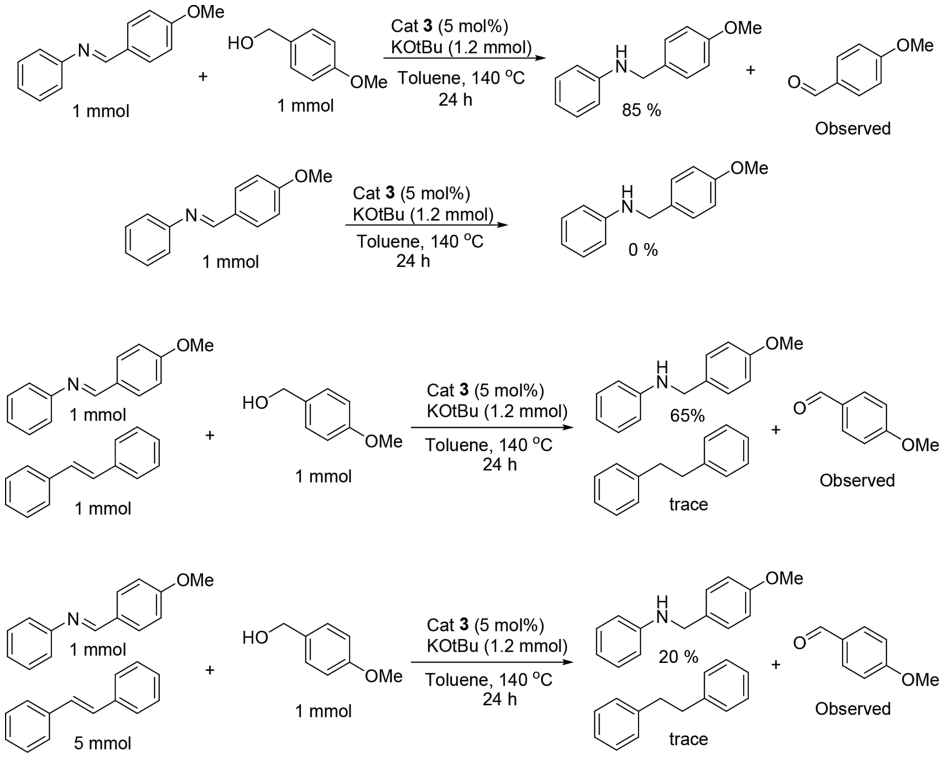
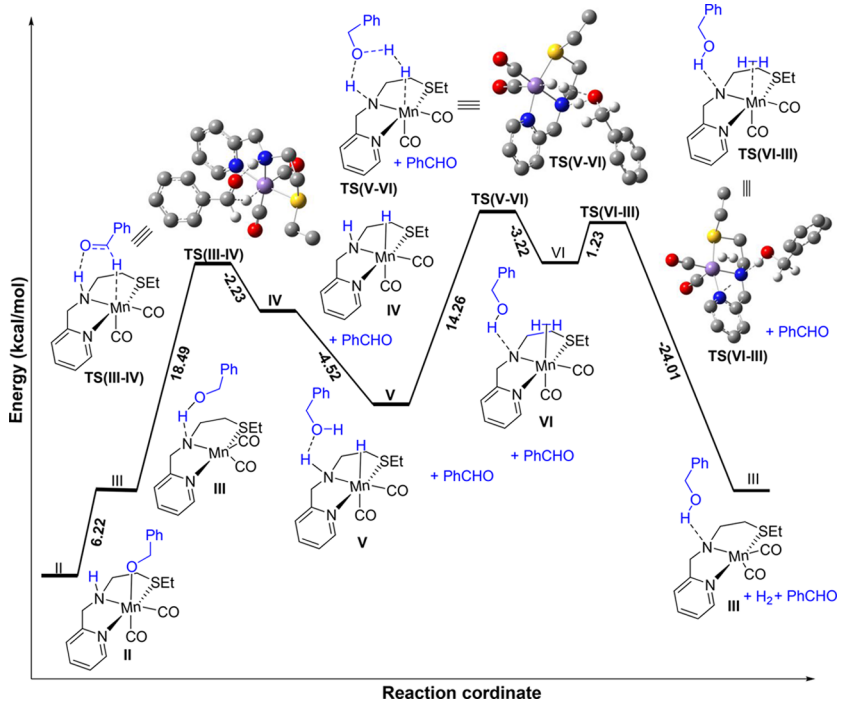
Scheme 3. Control Experiments



Scheme 4. Calculated Energy Profile of ADC Reaction of Benzyl Alcohol with Complex III[a]



[a]Energies are obtained at the B3PW91 DFT method (see Tables S2–S4 for details).

It is important to note that the quantity of the base used in our system is significantly lower compared to that in the triazine-based Mn-PNP system.[20c] Encouraged by the versatility of our current catalytic system, we tried to apply our protocol to synthesize 2,3-dihydro-1*H*-perimidines as they are an important class of compounds having useful biological activity.[28] Thus, when 1,8-diaminonaphthalene is reacted with different primary alcohol in the presence of catalyst **3**, corresponding 2,3-dihydro-1*H*-perimidine derivatives were isolated in good yields (Table 5). To the best of our knowledge, this is the first example of the dehydrogenative synthesis of 2,3-dihydro-1*H*-perimidines using the Mn complex under the phosphine-free condition.

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To gain a mechanistic insight, some control experiments were performed (Scheme 3). When an equimolar mixture of (*E*)-1-(4-methoxyphenyl)-*N*-phenylmethanimine and 4-methoxybenzyl alcohol was treated with catalyst **3** in the presence of KOtBu (1.2 mmol), *N*-(4-methoxybenzyl)aniline was obtained in an 84% yield, whereas when the reaction was done under the similar condition in the absence of the alcohol, no conversion of the imine to the corresponding amine was observed. Next, we studied the hydrogen autotransfer reaction in the presence of alkene. Thus, when an equimolar mixture of (*E*)-1-(4-methoxyphenyl)-*N*-phenylmethanimine, *trans*-stilbene, and 4-methoxybenzyl alcohol was treated under the optimized reaction condition of hydrogen autotransfer, 65% of corresponding amine was detected, and stilbene was not hydrogenated. Furthermore, when a mixture of (*E*)-1-(4-methoxyphenyl)-*N*-phenylmethanimine and *trans*-stilbene in a 1:5 ratio is treated with 4-methoxy benzyl alcohol (1 mmol) under the similar reaction condition, the yield of the desired amine dropped to 20%. Thus, the excess amount of alkene found to retard the hydrogen autotransfer reaction of imine.

On the basis of the previous reports,[19k,29] our observations and with the help of DFT calculations,[30] the plausible mechanism has been proposed and is presented in Scheme 4. Benzyl alcohol was taken as a model substrate to investigate the manganese (catalyst **3**)-catalyzed dehydrogenation reaction. First, the cationic complex in the presence of base and under heating condition gave the five-coordinated amide complex **I** $[PyCH_2NCH_2CH_2Mn(CO)_2]$. The catalysis commences with the adduct formation **III** through the hydrogen bonding between complex **I** and benzyl alcohol. We selected complex **II** as a reference point, which is more stable than complex **III** by 6.22 kcal/mol. Next, benzaldehyde was formed together with the manganese hydride complex **IV** via the hydride transfer of the α-methylene group of benzyl alcohol onto the metal center. This is going through the transition state **TS(III-IV)**, and the activation barrier for this reaction is 18.49 kcal/mol. This is the rate-determining step, and it is in accordance with the previous report.[29c] Next, the barrier was calculated for the release of H_2 from the complex **IV** with the involvement of benzyl alcohol. The first step is the generation of the adduct complex **V** via hydrogen bonding between N−H of the complex **IV** and O of benzyl alcohol. Then, it leads to the formation of the manganese-coordinated η^2-H_2 complex **VI** through **TS(V-VI)**. The activation barrier for this formation is 14.26 kcal/mol. The stabilization for complex **VI** is 3.22 kcal/mol compared to the **TS(V-VI)**. Finally, dissociation of the H_2 molecule has an activation barrier of only ∼1 kcal/mol to regenerate complex **III**, which shows a high stabilization of 24.01 kcal/mol from the TS as presented clearly in Scheme 4. The effect of various DFT methods, basis sets, dispersion corrections, etc. on the energy profile of the reaction was tested (Tables S2−S4, Supporting Information). The level of the calculation does not affect the overall trend of the results. Changes in geometry of these complexes along the path of the reaction are summarized in Table S5 (see Supporting Information).

CONCLUSIONS

In conclusion, we demonstrated the first phosphine-free Mn-based protocol to synthesize both amine and imine from the same set of alcohol and amine, only by tuning the reaction condition. We have observed a broad range of a substrate scope for both the reaction under the optimized reaction condition. The nature and stoichiometry of the applied base are crucial to obtain the maximum selectivity. This effective protocol has also been applied to synthesize the 2,3-dihydro-1*H*-perimidine derivatives. To the best of our knowledge, this is the first sustainable synthesis of 2,3-dihydro-1*H*-perimidines using the phosphine-free Mn complex. Furthermore, a mechanistic insight based on control experiments and DFT calculations is also presented. The versatility and the selectivity of the catalysts having a nontoxic earth-abundant manganese metal and a non-phosphine ligand system make this protocol sustainable and attractive.

EXPERIMENTAL SECTION

General Considerations. All chemicals were purchased from common commercial sources and used without any further purification. All solvents were dried by using standard procedure. The preparation of catalyst was carried out under an argon atmosphere with freshly distilled THF. All catalytic reactions were carried out under an argon atmosphere using dried glassware and standard syringe/septa techniques.

The DRX-400 Varian spectrometer and Bruker Avance III 600 and 400 spectrometers were used for recording NMR (^{1}H and ^{13}C) spectra using $CDCl_3$ as the solvent and TMS as an internal standard. Chemical shifts (δ) and spin−spin coupling constant (J) are reported in ppm and in Hz, respectively, and other data are reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, and br s = broad singlet. FTIR were collected on a PerkinElmer IR spectrometer. A Q-Tof ESI-MS instrument (model HAB 273) was used for recording mass spectra. X-ray crystallographic data were collected using an Agilent Super Nova (single source at offset, EOS) diffractometer. Data refinement and cell reduction were carried out by CrysAlisPro. Structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares on F^2 using SHELXL-97. All of the non-H atoms were refined anisotropically. SQUEEZE was used to reduce the contribution of dichloromethane to the overall electron density. The purity determination of the substrates and reaction monitoring was accomplished using TLC on silica gel 60 F254 plates (from Merck Company), and SRL silica gel (100−200 mesh) for column chromatography was used.

General Experimental Procedure for the N-Alkylation Reaction of Amine with Alcohol. A mixture of aniline derivatives (1.0 mmol), primary alcohol (1.2 mmol), tBuOK (1.2 mmol), and catalyst **3** (0.05 mmol) was refluxed with 2 mL of toluene at 140 °C for 24 h under an argon balloon. After cooling, chloroform was added to dilute the mixture and filtered through Celite. The filtrate was concentrated under reduced pressure, and the residue was purified using silica gel column chromatography with 2−20% ethyl acetate in hexane as an eluent.

General Experimental Procedure for the Synthesis of Imine Derivatives. A mixture of amine (1.0 mmol), primary alcohol (1.2 mmol), KOH (0.3 mmol), and catalyst **3** (0.05 mmol) was refluxed with 2 mL of toluene at 140 °C for 24 h in an open system under an argon balloon. After cooling, chloroform was added to dilute the mixture and filtered through Celite. The filtrate was concentrated under reduced pressure, and the residue was purified using silica gel column chromatography with 2−20% ethyl acetate in hexane as an eluent to get a pure compound.

General Experimental Procedure for the Synthesis of 2,3-Dihydro-1*H*-Perimidines Derivatives. A mixture of naphthalene-1,8-diamine (1.0 mmol), primary alcohol (1.2 mmol), KOH (0.3 mmol), and catalyst **3** (0.05 mmol) was refluxed with 2 mL of toluene at 140 °C for 24 h in an open system under an argon balloon. After cooling, chloroform was added to dilute the mixture and filtered through Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography with 2−20% ethyl acetate in hexane as an eluent to get a pure compound.

Computational Methodology. All the calculations were performed using the Gaussian-09 (revision D.01) program package.[31]

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Geometries of considered reactants, transition states, and intermediates were fully optimized using the B3PW91 method.[32] This method uses the same exchange functional as the B3LYP method but employs different and comparatively a newer correlation functional. The double-ζ quality SDD basis set with an effective core potential (ECP) was selected for a manganese atom, and the 6-31G(d,p) basis set was selected for all other atoms. Methods and basis sets were selected based on previous reports.[29b] Frequency calculations were performed at the same level of theory to distinguish the obtained stationary points as the minima or transition state on the potential energy surface. The effect of the toluene solvent was included in all the calculations with the help of the IEF-PCM method available in the Gaussian-09 program.[33] The reaction path was validated by following the reaction profile with the help of intrinsic reaction coordinate (IRC) calculations with mass-weighted coordinates.[34] The effect of higher basis set, different DFT methods, and dispersion corrections on the energy profile of the reaction was tested (Tables S2–S3). All four tested dispersion corrections show very similar energetics (Table S3). The overall energetics from dispersion corrected and uncorrected methods is also similar (Table S3), and the only difference is that the dispersion correction provides some extra stabilization to **TS(III-IV)**. The temperature variation has almost no effect on thermal corrections (Table S4).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00131.

Experimental procedures, characterization data, theoretical calculations, and copies of the ^{1}H NMR and ^{13}C NMR spectra of all the compounds (PDF)

X-ray crystallographic data (CCDC 1881759) for **1** (XYZ)

Accession Codes

CCDC 1881759 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

D.S. and K.D. designed the experiments. K.D., A.M., and D.P. carried out the experiments. H.K.S. performed the computational study. D.S. and K.D. performed the data analysis and wrote the manuscript with the input of all authors.

Notes

The authors declare no competing financial interest.

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