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Recent Advancements in Manganese Pincer Complexes for Catalytic N-Methylation of Amines Using Methanol as C1 Source

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ABSTRACT

N-Methylamines are an essential class of amines with growing uses in the material, agrochemical, essential fine and bulk chemicals and pharmaceutical sectors. Hence, N-methylations represent a significant class of chemical processes or reactions in the synthesis of organic compounds and drug discovery, providing access to sophisticated molecules, medications, biomolecules, and agricultural chemicals. For N-methylation processes, valuable late transition metal catalysts have been used in past few decades. The early transition metals are gaining a lot of interest lately because of their overall sustainability, reduced cast and reduced environmental impact. There are multiple applications in academia and industry for catalytic hydrogen methodology reactions in the synthesis of various molecular scaffolds. As an effective substitute in this context, manganese the third most common transition metal in crust of the earth - has developed. But the multifunctional ligand design of selection of suitable auxiliary ligands, which enable them to replicate the activities of noble metals, are crucial to the effectiveness of such manganese-based complexes. As methanol is utilized as a common solvent, cost effective reagents and sustainable feed stock for value added chemical, medicines and materials. Among its numerous uses, chemical synthesis of drug development still relies heavily on the use of methanol as a C1 source for the synthesis of carbon-carbon, carbon-nitrogen and carbon oxygen bonds. Additionally, methanol is less hazardous and in methylation processes yields only water as a by-product. The objective of the current investigation is to present the most recent development in the catalytic N-methylation of amines using methanol a major C1 source of CH3, from 2016 to 2023. In particular, the synthesis of N-methylamines via borrowing hydrogen methodology.

Keywords: N-methylamines, borrowing hydrogen methodology, homogeneous catalysis, methanol, manganese, pincer complexes, amines, aniline

I. INTRODUCTION

In organic chemistry, molecules that contain nitrogen are preferred and most abundant structures for instance, among the thousands of small molecules pharmaceuticals that have received FDA approval, over 80% compound have at least one nitrogen atom, with an average of 2.3 nitrogen's per drug.[1] Among different amines, *N*-methylamine including aniline functionalities are valuable class of amines, that are often

encountered in commercial pharmaceuticals, essential fine and bulk chemicals widely used in organic synthesis and often employed in drug discovery process (Fig.1).[2-8] Notably, *N*-methylamines are crucial precursors and intermediates that are widely employed in academic as well as industrial applications to create specialized chemicals, biomolecules, medication, agrochemicals and materials. Indeed, out of the 55 FDA approved medications in 2023 two that had *N*-methyl functionality [9] and more than 10 of the top 200 pharmaceuticals by retail sale between 2019 to 2023 contains an *N*-methyl moiety (Fig.2.).[10]

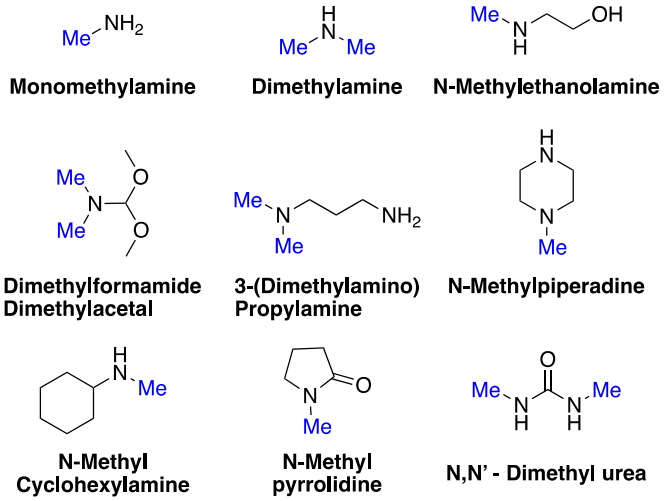


Fig. 1. Examples of *N*-methylated molecules as essential building blocks that are potentially valuable in the chemical industries.

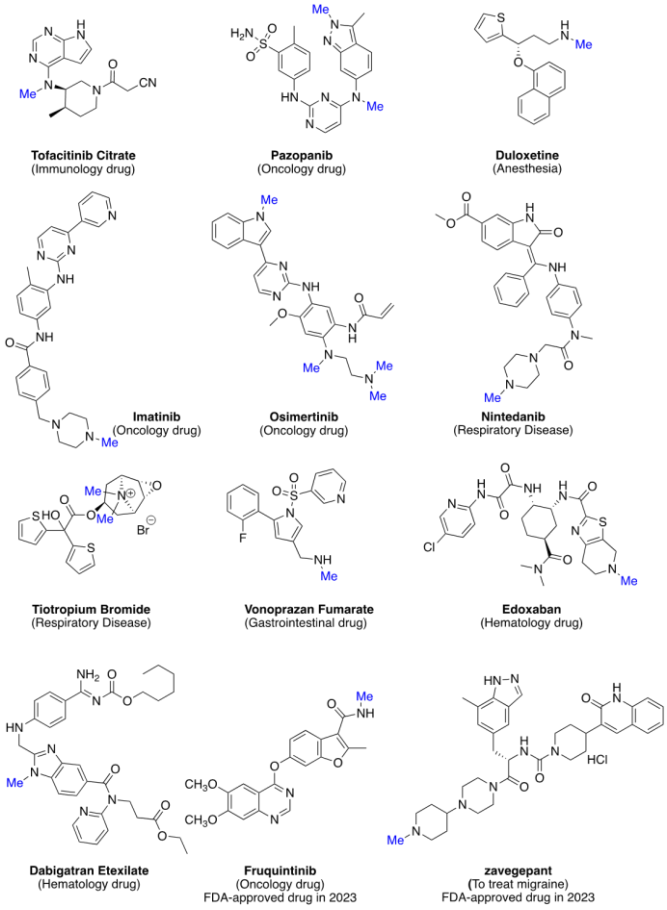


Fig. 2. Representative best-selling medications and newly FDA-approved medications with an *N*-methyl moiety.

In addition to these, *N*-methylamines functionality also present in pincer ligands complexes as tridented ligand as well as bidented ligand in organometallic chemistry and catalysis.[11] Despite being a straightforward chemical change, the *N*-methylation process is a potent toll for controlling the physicochemical characteristics and bioactivities of drug and biomolecules.[12] *N*-Methylation of peptides and DNA, for instance, increases these molecules hydrophobicity, bioavailability, and metabolic stability. It also plays crucial role in epigenetic modifications to gene expression and cellular phenotype.[13] Moreover, pharmacokinetics, the transport of drugs, enzyme activity and antibody activity are all regulated by *N*-methyl functionality. [13,14] Therefore, adding mono and dimethyl unit to peptides, DNA or amine-based compounds has proven to be a powerful method for adjusting their functions and researching the structure function relationship, which aids in the development of novel molecules for use in life science application. Considering the simplest and smallest methylation as a late-stage modification in bioactive compounds have the most profound impact on altering the biological properties of molecules.[15,16] This phenomenon is well-known as the "magic methyl effect".[17]

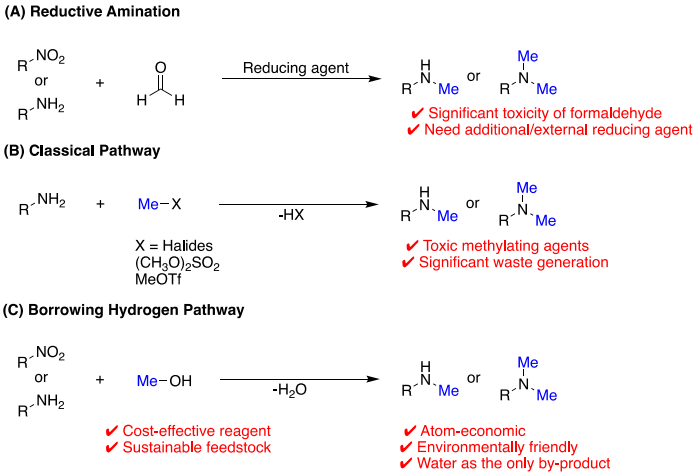


Fig. 3. Methodologies for the synthesis of *N*-methylamines.

Hence, new synthetic methodology for efficient, environmentally benign friendly and selective mono- and di-*N*-methylamines and their derivatives are of great interest. However, major challenges with these specific transformations need to considered first, A well-known traditional technique in the chemical and pharmaceutical industries for constructing *N*-methylamines is the Eschweiler-clarke reaction. this technique uses their formic acid or $NaBH_4$ as a reducing agent with formaldehyde.[18,19] Although formaldehyde is widely applicable affordable, abundant, its substantial toxicity and instability represent a risk and are recognized as carcinogens for humans. Conversely, methylating agents like methyl iodine (MeI), diazomethane (CH_2N_2), Methyl triflate (MeOTf) and dimethyl sulphate (DMS) are typically used in drug development to carry out *N*-methylation reaction.[13,20-22] However, some of these activated methylating agents are poisonous low atom-efficient and they should be used excessively and produced stoichiometric amount of inorganic wastes.[22-23] compared to these two approaches catalytic methylation reaction employing methanol as a possible C1 source of CH_3 are more environmentally benign, atom-economic and more sustainable because (a) methanol is an inexpensive, and bulk chemical that is globally produced in large quantities 171.84 million metric tonnes in 2022, The globally methanol production capacity expected to grow by more than 80% between 2021 and 2030.[24] (b) The only by product of this reaction is water, which is produced by the catalytic borrowing process. (c) Methanol act as both the source of C1 and H_2 and no extra reducing agents or pressurized apparatus is required for this reaction (Fig. 3).

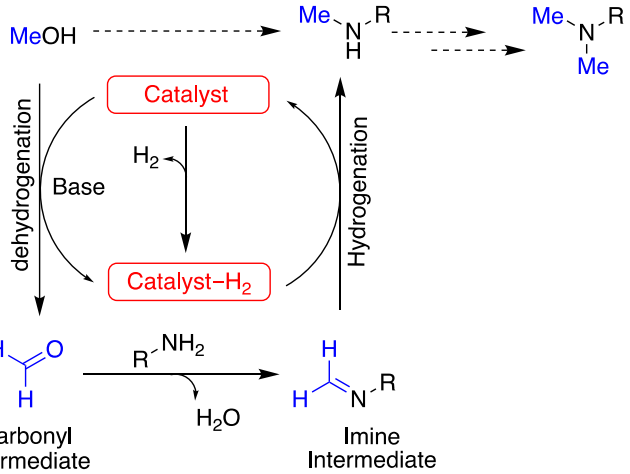
The synthesis of various *N*-methylamines is receiving a lot of attention due to the operational simplicity of MeOH and its prospective benefits in organic transformations [25] and energy technologies.[26] Using methanol as the methylating agents for selective mono-*N*-methylamines enabled by the borrowing hydrogen methodology.[27,28] The reaction of methanol with various amines have been performed to access divers mono- and di-*N*-methylamines product. Catalyst that are both homogeneous and heterogeneous were developed and utilized to accomplish these reactions. [25,27] Over the past few decades, noble-metal catalysts were employed for these reactions.[29] The early transition metals have recently gained much attention due to their lower cost, less toxicity, and overall sustainability. In this regards, manganese is the third most abundant base metal, cheep, non-toxic metal and environmentally benign and most suitable for given organic transformation.[30] Given the considered amount of research articles, few methodologies of *N*-methylation are reviewed in the past.[29,31-33]

Nonetheless, a more thorough evaluation of the recent advancement in manganese pincer complexes for catalytic *N*-methylation of amine using methanol as C1 source is missing in this systematic and in-depth analysis. Thus, we go into more comprehensively in this review of recent developments from (2016 to 2023) in the employing of MeOH as a methylation source to prepare *N*-methylamines that are simple, functionalized and structurally diverse. These amines can be synthesized by starting with amines and utilizing various manganese pincer complexes via borrowing hydrogen methodology.

II. REACTIVITIES, AND STRUCTURE OF MANGANESE PINCER COMPLEXES

N-Methylation of amines and/ or nitro compounds with methanol using Manganese based homogeneous catalysts

Based on the borrowing hydrogen approach, or hydrogen auto-transfer amines are catalytically *N*-methylated using methanol as methylating agents. [34,35] The following reaction stages are involved in this process. (1) Methanol is first dehydrogenated to formaldehyde in the presence of a catalyst with liberation of molecular hydrogen in the process. (2) The formaldehyde produced in situ then condenses with



Scheme-1: Reaction mechanism of *N*-methylation of amine via borrowing hydrogen methodology

amine to produces the equivalent imines as an intermediate. (3) Lastly, the desired mono-*N*-methylamine is produced by catalytic reduction of the imine with hydrogen that is liberated from methanol. Subsequently, the

already formed mono-*N*-methylamine is reduced to make *N,N*-dimethylated amine, and condensation with another formaldehyde molecules produces iminium ions (Scheme-1). [36]

III.CATALYSIS

N-Methylation of amines and/or Nitro Compounds with Methanol Using Homogeneous Manganese-Based Catalysts

Manganese catalyzed selective mono *N*-methylation of aniline with methanol

The selective mono methylation of amines with methanol is most challenging reaction as formation of side products such as *N,N*-dimethylated amines is in competition. Mono-*N*-methylated amine functionalities are valuable motifs, which play vital roles in the properties and activities of essential fine and bulk chemicals, molecule used in life science applications such as drug molecules and natural products. [31] In 2016, Beller and co-workers were described pioneering reports dealing with the mono-*N*-alkylation of amines using methanol in the presence of homogeneous catalyst (Fig. 4.).

Beller and coworkers performed the synthesis of mono-*N*-methylated derivatives in the presence of 3 mol% PNP manganese complex **Mn-1** As shown in **fig. 4.**, a series of aniline derivative. Efficient mono *N*-methylation of aniline by methanol occurred when toluene solution of reaction mixture containing *t*-BuOK (1 equiv., 1 mmol), anilines derivative (1 mmol) methanol (1 ml) and **PNP Mn-1** (3 mol%) was stirred at 100°C in closed condition for 24h. Reaction is highly selective as only mono-*N*-methylation of anilines has been observed.

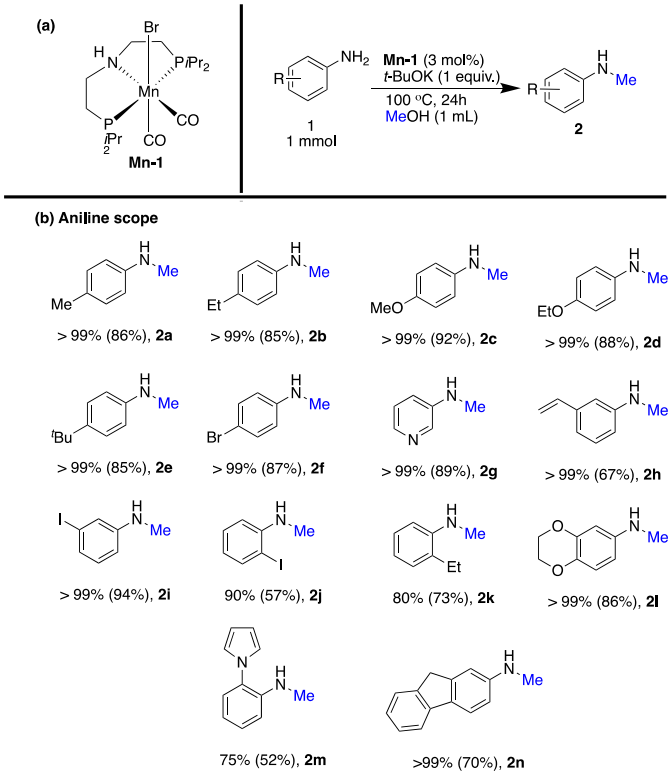


Fig. 4. *N*-methylation of primary anilines using methanol. (a) General reaction conditions: aniline derivative (1 mmol), Mn-1 (3 mol%), *t*-BuOK (1 equiv.), and toluene (2 ml) 100°C, 24h (b) Conversion was determined by GC (Isolated yield in parantheses) traces of reduction of double bond. 15% dehalogenation was observed.

Aniline **1a-1k** bearing alkyl substituent such as 4-Me (**1a**), 4-MeO (**1c**), 4-EtO (**1d**), 4tBu (**1e**), halogen substituent such as 4-Br (**1f**) and 3-I (**1i**) were reacted with methanol to gave the mono-*N*-methylated products in good to excellent isolated yields (**2a-2k**: 52% to 94%). In most cases the **PNP Mn-1** catalyst showed very good selectivity vide supra and even Br- and I- substituents were well tolerated (**2f**, **2i**), albeit in the case of sterically hindered 2-iodo *N*-methyl aniline **2j** some dehalogenation was observed. Again, aromatic (1n) and hetero aromatic substituted anilines (1m) were selectively monomethylated to the corresponding secondary *N*-methylaniline derivative (**2m**, **2n**) in good isolated yield (52-70%). In all the cases they didn't observed any traces of dialkylation products.

Mono-*N*-Methylation Of Anilines With Methanol Catalyzed By A Manganese Pincer Complex

In 2017, Sortais and co-workers described the PN3 P Mn(I)-2 catalysed *N*-methylation of anilines via the borrowing hydrogen approach. [37] Employing **PN³ P Mn (I)-2** pincer precatalyst (5 mol%), *t*-BuOK (20 mol%), MeOH (1 ml) and toluene (1 ml) as solvent a variety of electron rich arylamines undergo *N*-methylation at 120°C for 24h with methanol giving the corresponding mono-*N*-methylated arylamine product in high yield (Fig. 5.).

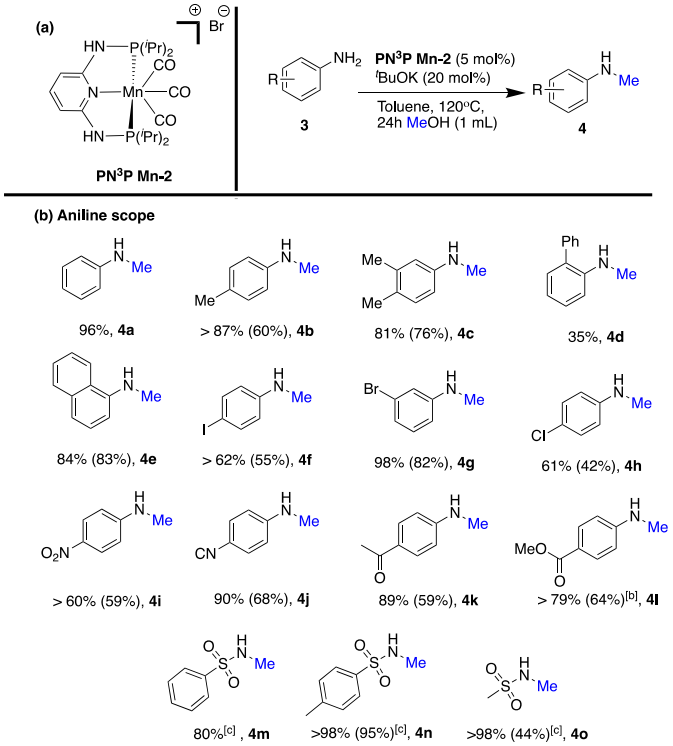


Fig. 5. *N*-methylation of primary anilines to give *N*-methyl-anilines under the catalysis of **PN³P Mn(I)-2**. Using methanol. (a) General reaction conditions: aniline (0.5 mmol), methanol (1 ml), toluene (1 ml), catalyst **PN³P Mn(I)-2** (5 mol %), and *t*-BuOK (20 mol %) were mixed in this order and heated in a closed Schlenk tube in an oil bath. Conversion determined by ^{1}H NMR (isolated yield in parantheses); [b] starting from ethyl 4-aminobenzoate **3l**, methyl 4-*N*-methylaminobenzoate **4l** was obtained; [c] 1.2 euiv. *t*-BuOK, 60h.

Aniline **3a-3h** bearing alkyl or halide substituent such as 4-Me (**3b**), 3,4 $(Me)_2$ (**3c**), naphthyl (**3e**) were reacted with methanol giving 81% to 96% conversion to the corresponding mono-*N*-methylaryl amines product in good isolated yield. (**4a-4e**; 62% to 96%). However, this catalytic system was sensitive to steric hindrance as 2-phenylaniline was methylated with only 35% conversion. The presence of halide substituents such as 4-I (**3f**),

3-Br (**3g**) and 4-Cl (**3h**) were methylated using methanol giving 61% to 98% conversion to the corresponding mono-*N*-methylarylamines product in moderate yield (4f-4h; 42% to 82%). Interestingly, this catalytic system was tolerant to several reducible or reactive functional group such as nitro (**4i**), cyno (**4j**), acetal (**4k**) and ester (**4l**) could be also be methylated in satisfactory yield. Furthermore, sulfonamides (**4m-4o**), which are common moieties in biologically active compounds, could be also be methylated under optimized reaction condition with excellent yields, although under harsher conditions for longer reaction time (1.2 equiv. of base for 60h).

Manganese- Catalyzed one-pot Conversion of Nitroarenes into *N*-Methylarylamine Using Methanol

In 2020, Morrill and coworkers reported bench stable **PN³P Mn(I)-3** pincer precatalyst for the *N*-methyl aryl amine from nitroarenes and methanol starting materials. [38] Using **PN³P Mn(I)-3** (5 mol%) as catalyst and KOH (2 equiv.) as base with methanol as a methylating agent as well as solvent, a variety of Nitroarenes react with methanol, accessing the corresponding *N*-methylated product in good yields (Fig. 6.). The reaction is highly selective as only monomethylation of Nitroarenes has been observed.

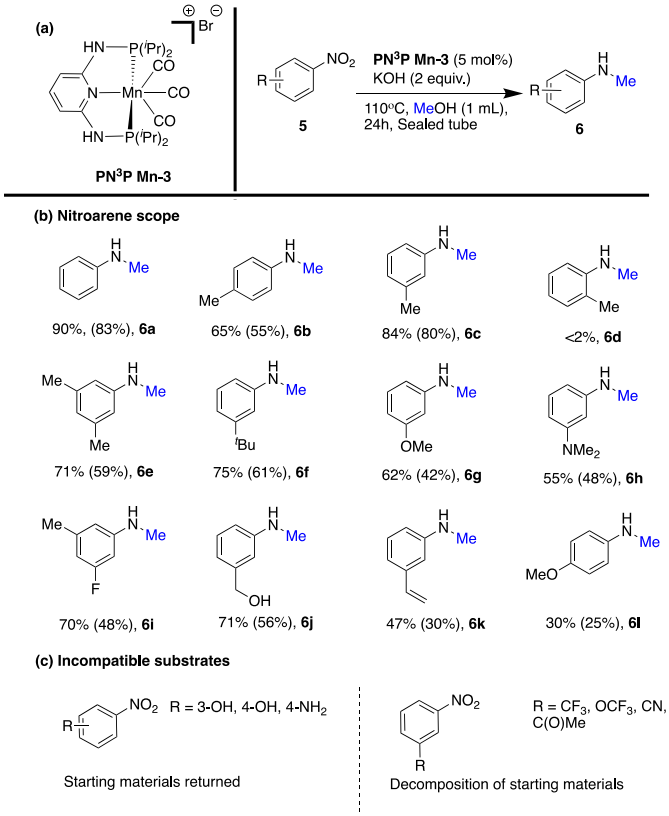
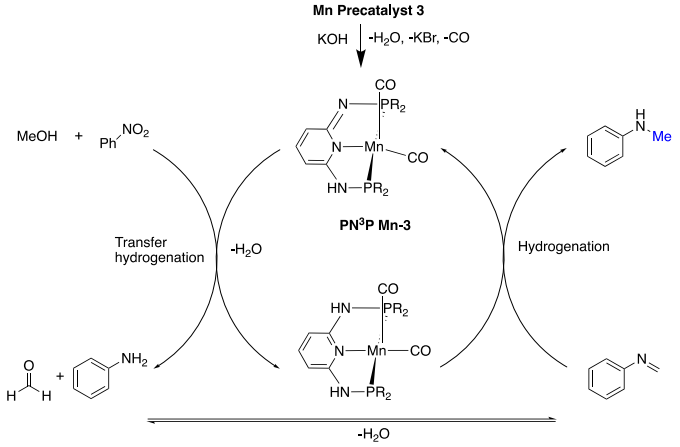


Fig. 6. *N*-methylation of nitroarenes to give *N*-methyl-anilines under the catalysis of **PN³P Mn(I)-3**. Using methanol. (a) General reaction conditions: nitroarenes (0.5 mmol), methanol (1 ml), toluene (1 ml), catalyst **PN³P Mn(I)-3** (5 mol %), and KOH (2 equiv.) were mixed in this order and heated in a closed Schlenk tube in an oil bath. Yields as determined by ^{1}H NMR analysis of the crude reaction mixture with 1,3,5-trimethylbenzene as the internal standard. (isolated yield in parentheses)

Nitroarenes (**5a-5i**) bearing alkyl substituent such as 4-Me (**5b**), 3-Me (**5c**), 3,5-Me (**5e**), 3-tBu (**5f**), 3-MeO (**5g**), 3-N(Me)$_2$ (**5h**), 3-F,5-Me (**5i**) were reacted with methanol giving 55% to 90% conversion to the corresponding product in moderate to good isolated yields (**6a-6i** ; 42% to 83%). Nevertheless, adding a 2-methyl substituent to the nitroarene caused the starting material to fully recover after a 16h reaction period. This could be related to the nitro functionalities increased steric shielding, which inhibited the transfer hydrogenation step.

Furthermore, more nitroarenes embedded functional groups that can undergo, dehydrogenation, including alcohols (**5i**) and alkenes (**5k**) can be present within the nitroarene and are preserved within *N*-methylarylamines (**6i** and **6k**) respectively. Under optimized reaction condition, 1-methoxy-4-nitrobenzene was reduced to 6% NMR yield; this climbed to 30% when the reaction temperature was raised to 130°C. A variety of nitroarenes containing hydroxyl or amino functionalities were unreactive with starting material returned. Moreover, Nitroarenes containing various electron with drawing groups at 3-position, such as CF_3, OCF_3, CN, and C(O)Me decomposition of starting materials was observed.



Scheme-2. Mechanistic studies of **PN³P Mn(I)-3** determined by ^1H NMR analysis of the crude reaction mixture with 1,3,5-trimethylbenzene as the internal standard.

A plausible reaction mechanism initiates with activation of **PN³P Mn(I)-3** (pre-catalyst) with KOH to form the active manganese complex Subsequent transfer hydrogenation converts nitrobenzene and methanol into aniline and formaldehyde, which can undergo a condensation reaction to form *N*-phenylmethanimine. Further, hydrogenation of *N*-phenylmethanimine with the manganese hydride provides access to the *N*-methylated product *N*-methylaniline with regeneration of the catalytically active species (Scheme-2).

IV. CONCLUSION AND OUTLOOK

Methanol's "ideal" characteristics such as cost-effective reagent, environmentally benign and sustainable feedstock for value-added chemicals make it crucial to valorize it in chemical synthesis to obtain the required chemicals. The borrowing hydrogen technique has been used to synthesis a variety of *N*-methylamines, with methanol used as $-CH_3$ source for the synthesis of medicines and biomolecules over the past few years. Due to the widespread applications of the resultant products in pharmaceuticals, and the materials sciences, the synthesis of *N*-methylated molecules using methanol via borrowing hydrogen methodology is remarkable. The use of homogeneous and heterogeneous catalysis based on noble and nonnoble metals is essential to the effectiveness of these *N*-methylation procedures. Although much progress has been made in catalytic *N*-methylamines reactions using MeOH, there are still certain obstacles to overcome. Most catalysts available today have a hard-working environment, have problems with selectivity, and need noble transition metal catalyst. Therefore, the creation of extremely active base metal catalysts that should function in extremely mild circumstances to selectively and highly efficiently synthesized *N*-methylamines is essential yet difficult. It is particularly desirable to generate mono- or di-*N*-methylation selectively under mild conditions with a high degree of functional group tolerance, as this is necessary to meet the needs of the pharmaceutical industry. The

application of MeOH assisted *N*-methylation processes for the selective insertion of -CH_3 moieties in peptides, DNA, and other biomolecules needs to be improved, and that is more crucial. Highlights of this synthesis include producing *N*-methylated products in an atom-efficient and sustainable way by using easily available anilines or nitroarenes and methanol. We think that scientists working in academic research labs and enterprises will find this review fascinating and helpful, given the growing significance of *N*-methylation reactions in organic synthesis, medicinal and biological chemistry.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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