

# (NHC)Mn(I) complex catalyzed selective transfer hydrogenation of epoxides, azoarenes and nitroarenes utilizing ammonia borane

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**Abstract:** Herein, we have reported an effective protocol for the regioselective transfer hydrogenation (TH) of epoxides by utilizing a phosphine-free bis-NHC-Mn(I) complex and ammonia borane. By employing this strategy, aromatic epoxides were selectively converted to primary alcohols whereas secondary alcohols were obtained exclusively from aliphatic epoxides. The protocol was further extended for the TH of azoarenes and nitroarenes to hydrazoarenes and anilines respectively. Notably, a library of substrates with different functional groups were screened which resulted in the corresponding transfer hydrogenated product in good to excellent yields. A series of mechanistic investigations were carried out to understand the catalytic process.

## Introduction

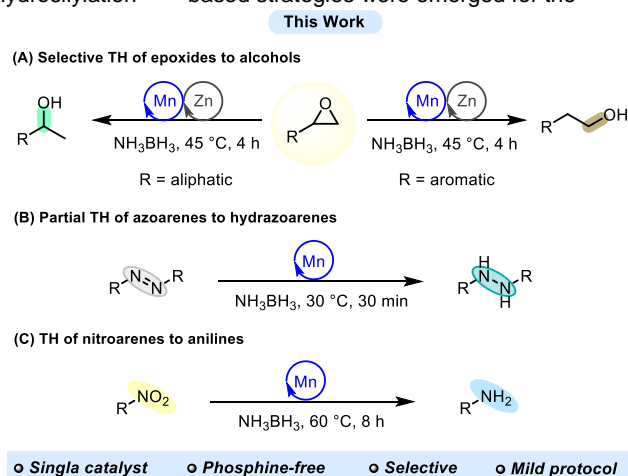
Transfer hydrogenation (TH) has gained significant importance in synthetic chemistry as it offers more selective hydrogenation of organic molecules and eliminates the use of highly flammable hydrogen gas, which is also difficult to store and handle.<sup>[1]</sup> Among the various sacrificial hydrogen donors such as alcohols, formic acid, hydrazines, etc., ammonia borane (AB) has emerged to be highly effective because of its low toxicity and high H<sub>2</sub> content (19.6 wt %).<sup>[2,3]</sup> Currently, there are numerous reports for the transition metal catalysed transfer hydrogenation of various organic molecules that use AB as a hydrogen source.<sup>[2]</sup>

One of the most exciting areas of contemporary chemical research is the creation of more environmentally friendly and sustainable catalytic systems using 3d metals.<sup>[4]</sup> Manganese being less toxic and the third most prevalent metal in the Earth's crust, has drawn a lot of attention of the scientific community. Although, Mn catalysed TH using different alcohols such as isopropanol, ethanol and methanol are known,<sup>[5]</sup> however, till date, only few protocols were established for the manganese catalysed transfer hydrogenation utilizing ammonia borane.<sup>[6–9]</sup> Notably, in most of these TH protocols, L<sub>n</sub>MnCO<sub>n</sub>X (X= Br/Cl; n = 2-4) complexes were employed as pre-catalysts and the corresponding L<sub>n</sub>MnCO<sub>n</sub>H complex is considered as the active catalyst.<sup>[5]</sup> These Mn(I) complexes were stabilized by ancillary CO ligand which on the other hand decreases the electron density on the metal center. Although, utilization of manganese-based

catalyst is exciting but less electron density on the metal center makes it less reactive towards such reaction.

N-heterocyclic carbene based metal complexes has gained increasing attention in the last decade for the transfer hydrogenation of various organic molecules.<sup>[10–15]</sup> The strong  $\sigma$ -donating and weak  $\pi$ -accepting properties of the NHC ligands, makes the metal center electron rich and enhances the complex stability.<sup>[16–18]</sup> More electron density on the metal center increases the hydricity of the hydride, hence facilitate the transfer hydrogenation reactions.<sup>[10,19]</sup> Thus, we hypothesized that compared to other Mn(I) complexes, (NHC)Mn(I) complexes will be more effective for the TH of organic molecules using ammonia borane which has not been explored.

Epoxides are promising intermediate that can be readily synthesised from olefins<sup>[20,21]</sup> and the reductive opening of epoxides is an important strategy for the synthesis of alcohols. Traditional protocols for the reduction of epoxides to alcohols, employed strong hydride donor reagents which suffered from poor regioselectivity and led to the generation of stoichiometric salt wastes.<sup>[22]</sup> During the past years, few transition metal mediated hydrogenation,<sup>[23–26]</sup> hydroborylation<sup>[27,28]</sup> and hydrosilylation<sup>[29,30]</sup> based strategies were emerged for the



**Scheme 1.** Bis(NHC)Mn(I) complex catalysed TH of epoxides, azoarenes and nitroarenes (This work)

selective ring opening of epoxides. Recently, Werner et. al reported the combination of Er(OTf)<sub>3</sub> and (PNP)Co(II) catalysed regioselective ring opening followed by TH of epoxides using ammonia borane.<sup>[31]</sup> Inspired by this, we hypothesized that phosphine-free, electron-rich (NHC)Mn(I) complex can have the potential for the TH of epoxide to selective alcohols.

Azoarenes are extensively utilized as dyes in textile industries which generates large amount of residual toxic wastes.<sup>[32,33]</sup> Hence, conversion of these azo compounds to useful chemicals is highly appreciated. One of the attractive approaches is the partial hydrogenation of azo compounds to hydrazo products which serves as the building blocks in various pharmaceutically relevant molecules. Recently, a few transition metal catalysed partial transfer hydrogenation of azo compounds to hydrazo product have been reported using ammonia borane.<sup>[34,35]</sup> However, this selective transformation has not been achieved using manganese-based catalyst. Although, TH of nitroarenes using different hydrogen donors is well established,

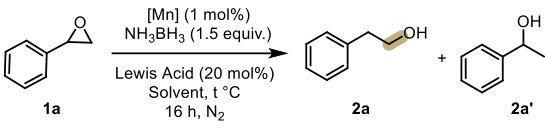
however similar transformation using ammonia borane employing homogeneous transition metal catalyst is rare.<sup>[36]</sup> Hence, we were also interested to explore the reactivity of (NHC)Mn(I) complex for the TH of nitroarenes using ammonia borane.

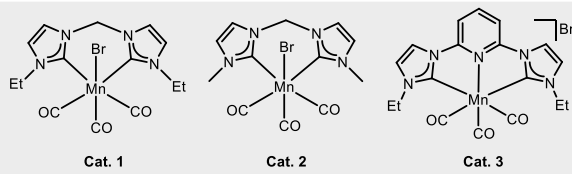
Herein, we report bis-NHC-Mn(I) catalysed transfer hydrogenation of epoxides, azoarenes and nitroarenes to alcohols, hydrazoarenes and anilines respectively using ammonia borane which to the best of our knowledge has not been reported using homogeneous manganese-based complex (Scheme 1).

## Results and Discussion

To acquire the optimal reaction condition for the regioselective ring opening of epoxide, styrene oxide (1a) was chosen as the benchmark substrate (Table 1). Initially, a series of NHC-based Mn(I) complexes were screened in the presence of 1.5 equiv. ammonia borane as the hydrogen source, 20 mol% Zn(OTf)<sub>2</sub> as

**Table 1.** Optimization of reaction parameters for the regioselective transfer hydrogenation of epoxides<sup>[a]</sup>





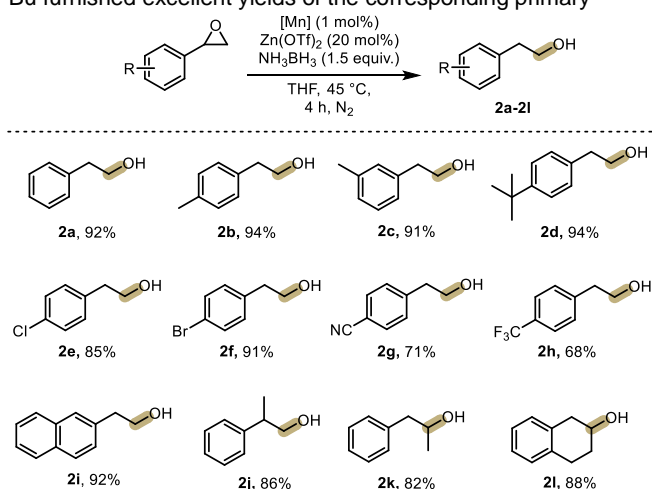
Entry	Catalyst	Lewis Acid	Solvent	Temp (°C)	Conversion (%)	Yield (%) <sup>[b]</sup> 2a:2a'
1	Cat. 1	Zn(OTf) <sub>2</sub>	THF	50	100	94:6
2	Cat. 2	Zn(OTf) <sub>2</sub>	THF	50	100	84:16
3	Cat. 3	Zn(OTf) <sub>2</sub>	THF	50	100	80:20
4	Cat. 1	Er(OTf) <sub>3</sub>	THF	50	92	70:22
5	Cat. 1	AlCl <sub>3</sub>	THF	50	0	0
6	Cat. 1	NaOTf	THF	50	0	0
7	Cat. 1	Yb(OTf) <sub>3</sub>	THF	50	86	62:24
8	Cat. 1	ZnCl <sub>2</sub>	THF	50	36	20:16
9	Cat. 1	-	THF	50	0	0
10 <sup>[c]</sup>	Cat. 1	Zn(OTf) <sub>2</sub>	THF	50	75	67:8
11 <sup>[d]</sup>	Cat. 1	Zn(OTf) <sub>2</sub>	THF	50	80	69:11
12	Cat. 1	Zn(OTf) <sub>2</sub>	THF	45	100	93:7
13	Cat. 1	Zn(OTf) <sub>2</sub>	THF	40	80	76:4
14	Cat. 1	Zn(OTf) <sub>2</sub>	ACN	45	100	81:19
15	Cat. 1	Zn(OTf) <sub>2</sub>	Dioxane	45	95	85:10

16	<b>Cat. 1</b>	Zn(OTf) <sub>2</sub>	Hexane	45	86	78:8
17 <sup>[e]</sup>	<b>Cat. 1</b>	Zn(OTf) <sub>2</sub>	THF	45	75	71:4
18 <sup>[f]</sup>	<b>Cat. 1</b>	Zn(OTf) <sub>2</sub>	THF	45	90	86:4
19 <sup>[g]</sup>	<b>Cat. 1</b>	Zn(OTf) <sub>2</sub>	THF	45	100	93:7

[a] Reaction Condition: 0.1 mmol of styrene oxide, 1 mol% Mn Cat., 1.5 equiv. NH<sub>3</sub>BH<sub>3</sub>, 20 mol% Lewis acid, t °C, solvent (0.2 M), 16 h. [b] Yield was determined from <sup>1</sup>H NMR by using 1,3,5-trimethoxybenzene as an internal standard. [c] 0.5 mol% Cat. 1. [d] 10 mol% Zn(OTf)<sub>2</sub>. [e] 1.0 equiv. NH<sub>3</sub>BH<sub>3</sub>. [f] 3 h. [g] 4 h.

Lewis acid at 50 °C in THF (Table 1, entries 1-3). Of these, **Cat. 1** showed the highest selectivity towards 2-phenylethanol (**2a**). Next, in the presence of **Cat. 1**, a range of Lewis acids (Er(OTf)<sub>3</sub>, AlCl<sub>3</sub>, NaOTf, Yb(OTf)<sub>3</sub> and ZnCl<sub>2</sub>) were screened and among them Zn(OTf)<sub>2</sub> was found to be the most effective and offered the highest conversion of **1a** as well as selectively towards the primary alcohol, **2a** (Table 1, entries 4-8). In the absence of Lewis acid, no conversion of **1a** was observed (Table 1, entry 9). By lowering the amount of catalyst to 0.5 mol% as well as Zn(OTf)<sub>2</sub> to 10 mol% separately, the conversion of styrene oxide was decreased to 75% and 80% respectively (Table 1, entries 10 and 11). Upon decreasing the reaction temperature to 45 °C, no reduction in yield of **2a** was observed, but on further decreasing the temperature to 40 °C, the yield of **2a** was dropped to 76% (Table 1, entries 12 and 13). Next, different solvents such as acetonitrile, dioxane and *n*-hexane were tested, however, none of them were found to be better than THF (Table 1, entries 14-16). On lowering the amount of ammonia borane to 1.0 equiv., the yield of **2a** was decreased (Table 1, entry 17). The reaction time was then decreased to 3 h which led to decrease in conversion of **1a** to 90% (Table 1, entry 18). Finally, the optimal reaction condition was identified as 1 mol% **Cat. 1**, 20 mol% Zn(OTf)<sub>2</sub> in THF at 45 °C for 4 h.

After determining the optimal reaction conditions, the generality of this methodology was tested by using various functionalized aromatic epoxides (Scheme 2). The model substrate styrene oxide provided 2-phenylethanol (**2a**) in 92% isolated yield. Epoxides with electron donating substituents like 4-Me, 3-Me, 4-<sup>t</sup>Bu furnished excellent yields of the corresponding primary

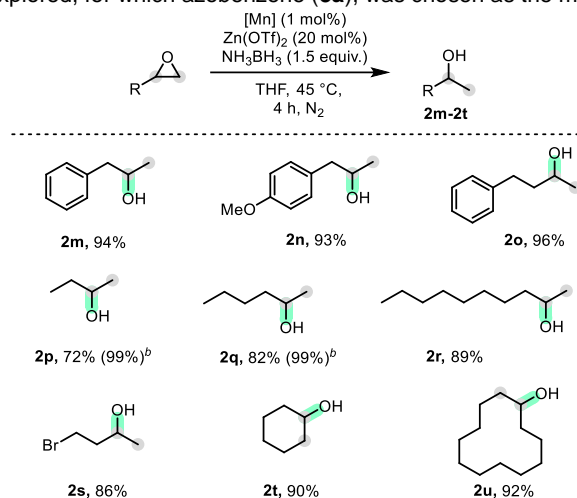


**Scheme 2.** Substrate scope for aromatic epoxides<sup>[a]</sup> [a] Reaction Condition: 0.2 mmol epoxide, 1 mol % **Cat. 1**, 1.5 equiv. NH<sub>3</sub>BH<sub>3</sub>, THF (0.5 mL), 45 °C, 4 h; isolated yields.

alcohols (**2b-2d**). Electron withdrawing groups such as 4-Cl, 4-Br, 4-CN, and 4-CF<sub>3</sub> provided the respective anti-Markovnikov alcohol in moderate to good yields (**2e-2h**). Moreover, 2-(naphthalen-2-yl)oxirane was also smoothly converted to the desired product (**2i**) in 92% isolated yield. Furthermore, 2-methyl-2-phenyloxirane and 2-methyl-3-phenyloxirane also resulted in the corresponding primary alcohol (**2j**) and secondary alcohol (**2k**) in 86% and 82% yields respectively. Under the standard conditions, 1,2-epoxytetralin was also smoothly converted to **2l**.

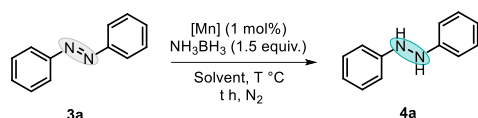
Next, the developed protocol was applied to 2-benzyloxirane which showed reverse regioselectivity and furnished secondary alcohol (**2m**) as sole product (Scheme 3). It is well documented in literature that nucleophilic ring opening of epoxide follow S<sub>N</sub>2 mechanism and led to the formation of ketone and not aldehyde.<sup>[37-39]</sup> Hence, we believed that our protocol also underwent similar mechanism followed by transfer hydrogenation to form secondary alcohol exclusively. Methoxy substituted 2-benzyloxirane, provided the expected secondary alcohol (**2n**) in good yield. 2-Phenethyloxirane also resulted in the desired alcohol (**2o**) in 96% isolated yield. Gratifyingly, various monoalkylated terminal epoxides such as ethyloxirane, butyloxirane, octyloxirane, and 2-bromoethyloxirane were converted smoothly to the respective secondary alcohols (**2p-2s**). Furthermore, 1,2-disubstituted cyclic aliphatic epoxides also resulted in the corresponding alcohols (**2t, 2u**) in excellent yields.

Then the catalytic activity of these Mn(I) complexes for the partial hydrogenation of azobenzene to hydrazobenzene was explored, for which azobenzene (**3a**), was chosen as the model



**Scheme 3.** Substrate scope for aliphatic epoxides<sup>[a]</sup> [a] Reaction Condition: 0.2 mmol epoxide, 1 mol % **Cat. 1**, 1.5 equiv. NH<sub>3</sub>BH<sub>3</sub>, THF (0.5 mL), 45 °C, 4 h; isolated yields. [b] GC yield using mesitylene as internal standard.

**Table 2.** Optimization of reaction parameters for TH of azobenzene to hydrazobenzene<sup>[a]</sup>

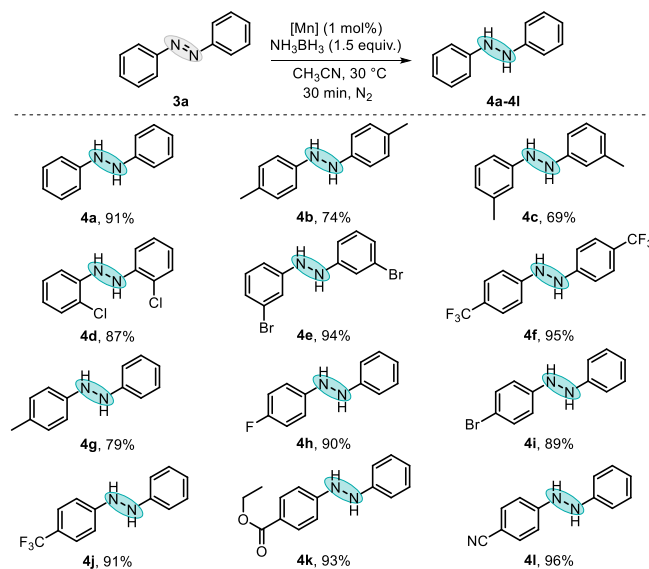


Entry	Catalyst	Time (h)	Temp (°C)	Solvent	Yield (%) <sup>[b]</sup>
1	Cat. 1	4	45	THF	71
2	Cat. 2	4	45	THF	66
3	Cat. 3	4	45	THF	59
4	-	4	45	THF	0
5	Cat. 1	4	45	Dioxane	51
6	Cat. 1	4	45	Hexane	7
7	Cat. 1	4	45	ACN	96
8 <sup>[c]</sup>	Cat. 1	4	45	ACN	79
9 <sup>[d]</sup>	Cat. 1	4	45	ACN	68
10	Cat. 1	4	40	ACN	97
11	Cat. 1	4	30	ACN	96
12	Cat. 1	4	25	ACN	82
13	Cat. 1	0.5	30	ACN	94
14	Cat. 1	0.25	30	ACN	65

[a] Reaction Condition: 0.1 mmol azobenzene, Mn cat. (1 mol%), NH<sub>3</sub>BH<sub>3</sub> (1.5 equiv.), solvent (0.2 M), 45°C, 4 h. [b] Yield was determined from <sup>1</sup>H NMR by using 1,3,5-trimethoxybenzene as an internal standard. [c] 0.5 mol% Cat. 1. [d] 1.0 equiv. NH<sub>3</sub>BH<sub>3</sub>.

substrate (Table 2). Initially, the reaction was carried out by varying different Mn(I) complexes (**Cat.1-3**) (1 mol%) in the presence of 1.5 equiv. of ammonia borane at 45 °C in THF, and among them **Cat. 1** was found to be the most effective and afforded **4a** in 71% yield within 4 h (Table 2, entries 1-3). In the absence of catalyst, no conversion of **3a** was observed (Table 2, entry 4). After that, different solvents such as dioxane, *n*-hexane and acetonitrile were screened and out of which acetonitrile afforded **5a** in 97% yield (Table 2, entries 5-7). Decreasing the catalyst loading to 0.5 mol% led to lower yield of the hydrazobenzene (Table 2, entry 8). Also, lowering the amount of ammonia borane to 1 equiv. resulted in 68% yield of **4a** (Table 2, entry 9). Gradually reducing the reaction temperature showed that 30 °C was optimal for maximum yield of hydrazobenzene (Table 2, entries 10-12). The reaction time was then reduced and using 1 mol% **Cat. 1** along with 1.5 equiv. ammonia borane in acetonitrile at 30 °C for 30 min was found to be the optimised reaction condition (Table 2 entry 13).

Subsequently, the substrate scope for the partial reduction of azoarenes under the optimised reaction parameters was evaluated (Scheme 4). Firstly, symmetrical azobenzenes were screened and the model substrate, azobenzene resulted in 91%



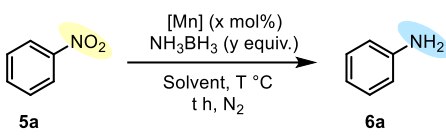
**Scheme 4.** Substrate scope<sup>[a]</sup> [a] Reaction Condition: 0.2 mmol azobenzene, 1 mol % **Cat. 1**, 1.5 equiv. NH<sub>3</sub>BH<sub>3</sub>, ACN (0.5 mL), 30 °C, 30 min; isolated yields.

yield of **4a**. In case of electron donating substituent (-Me) at *ortho* and *meta* position, the yield of corresponding hydrazobenzene (**4b**, **4c**) was found to be moderate. Azobenzene with electron withdrawing substituents like -Cl, -Br and -CF<sub>3</sub> at *ortho*, *meta* or *para* position, generated the respective hydrazobenzene (**4d-4f**) in excellent yields. After that, a series of unsymmetrical azobenzenes with electron donating as well as withdrawing groups were tested. A similar electronic effect was observed and in case of -Me substituent, the yield was found to be moderate (**4g**). The electron deficient groups such as -F, -Br, -CF<sub>3</sub>, -CO<sub>2</sub>Et and -CN containing azoarenes provided excellent yields of the products and exhibited good tolerance towards easily reducible groups such as -COOEt and -CN (**4h-4l**).

After observing the high reactivity of **Cat. 1**, its catalytic activity was further evaluated for the transfer hydrogenation of nitroarenes to anilines by using nitrobenzene (**5a**) as the model substrate. **Cat. 1** (1 mol%) in the presence of 3 equiv. of ammonia borane at 30 °C in acetonitrile afforded aniline (**6a**) in poor yield (Table 3, entry 1). The reaction temperature was then gradually increased to 50 °C which resulted only 21% yield of **6a** (Table 3, entries 2 and 3). Afterwards, other solvents such as dioxane and THF were tested and THF was found to be the best solvent for this reaction (Table 3, entries 4 and 5). The amount of ammonia borane was then increased to 4 equiv. which increased the yield of aniline (Table 3, entry 6). On further increasing the reaction temperature to 60 °C, the yield of aniline was slightly improved (Table 3, entry 7). The catalyst loading was then increased to 3 mol% which enhanced the yield of the product (Table 3, entry 8). At last, the reaction time was increased to 8 h which delivered aniline in 96% yield (Table 3, entry 9) and it was considered as the optimal reaction condition. The reaction was completely suppressed in the absence of catalyst (Table 3, entry 10).

With the optimal reaction conditions the generality for the transfer hydrogenation of nitroarenes to anilines was then explored. The model substrate **5a** provided a 91% isolated yield

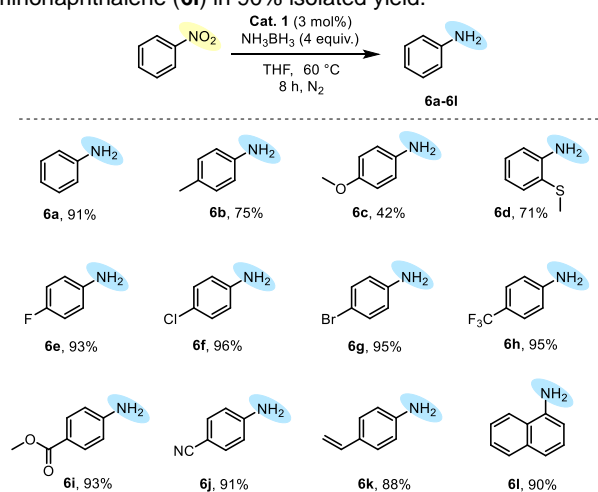
**Table 3.** Optimization of reaction parameters for transfer hydrogenation of nitroarenes<sup>[a]</sup>



Entry	Catalyst (x mol%)	NH <sub>3</sub> BH <sub>3</sub> (y equiv.)	Temp (°C)	Solvent	Time (h)	Yield (%) <sup>[b]</sup>
1	Cat. 1 (1)	3	30	ACN	0.5	3
2	Cat. 1 (1)	3	40	ACN	4	12
3	Cat. 1 (1)	3	50	ACN	4	21
4	Cat. 1 (1)	3	50	Dioxane	4	17
5	Cat. 1 (1)	3	50	THF	4	31
6	Cat. 1 (1)	4	50	THF	4	37
7	Cat. 1 (1)	4	60	THF	4	43
8	Cat. 1 (3)	4	60	THF	4	60
9	Cat. 1 (3)	4	60	THF	8	96
10	-	4	60	THF	8	0

[a] Reaction Condition: 0.1 mmol nitrobenzene, Mn cat. (x mol%), NH<sub>3</sub>BH<sub>3</sub> (y equiv.), solvent (0.2 M), T °C, 12 h. [b] Yield was determined <sup>1</sup>H NMR by using 1,3,5-trimethoxybenzene as an internal standard.

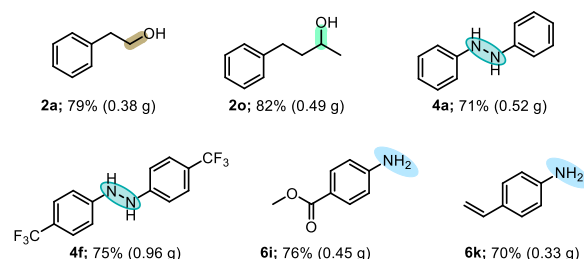
yield of aniline (**6a**). Nitroarenes with electron donating groups such as -Me, -OMe at *para* position and -SMe at *ortho* position furnished moderate to good yields of the corresponding anilines (**6b-6d**). Electron withdrawing substituents like -F, -Cl, -Br, -CF<sub>3</sub>, -COOMe, and -CN proceeded well and resulted in the respective anilines (**6e-6j**) in excellent isolated yields with good tolerance towards the reducible functional group like ester and nitrile. Moreover, substrate with vinyl group at the *para* position also converted smoothly to the expected product (**6k**). Under the standard condition, 2-nitronaphthalene produced 1-aminonaphthalene (**6l**) in 90% isolated yield.



**Scheme 5.** Substrate scope<sup>a</sup> [a] Reaction Condition: 0.2 mmol nitroarene, 3 mol % Cat. 1, 4 equiv. NH<sub>3</sub>BH<sub>3</sub>, THF (0.5 mL), 60 °C, 8h; isolated yields.

To further expand the synthetic utility of this approach, preparative-scale synthesis was carried out for the TH of epoxide, azoarene and nitroarene.

#### Preparative-scale synthesis



**Scheme 6.** Preparative-scale synthesis

#### Mechanistic Insight

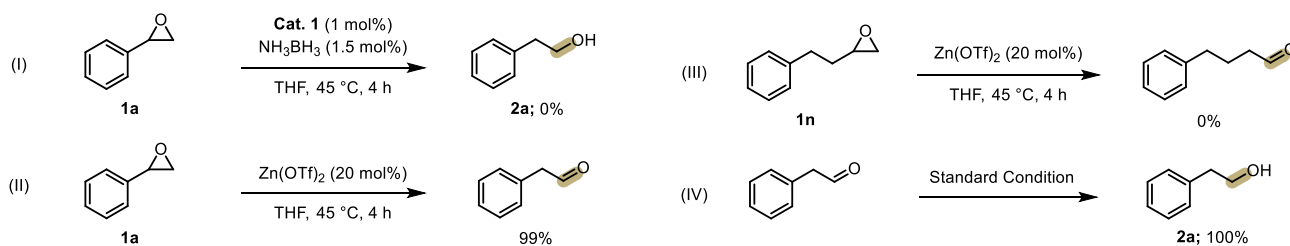
We then performed a few control experiments to understand the mechanism for the selective ring opening of epoxides. In the absence of Zn(OTf)<sub>2</sub>, no conversion of **1a** was observed, which suggested that Lewis acid was necessary for initiating the reaction (Scheme 7I). Reaction of styrene oxide with Zn(OTf)<sub>2</sub> resulted in complete conversion to phenylacetaldehyde whereas, in case of aliphatic oxirane (**1n**), no conversion was observed in the presence of only Lewis acid (Scheme 7AII and 7AIII). These two experiments suggested that the ring opening of aromatic epoxide to aldehyde was facilitated by Zn(OTf)<sub>2</sub> which was not in the case of aliphatic epoxide. Phenylacetaldehyde under the standard condition delivered **2a** in quantitative yield which specified that the former might be the intermediate in the reaction (Scheme 7AIV).

To determine the active catalyst, **Cat. 1** was reacted with 10 equiv. of ammonia borane at 45 °C and the reaction was analyzed *via* <sup>1</sup>H NMR after 10 min. The peak at -6.88 ppm suggested formation of Mn(I)-H which was well matched with the previously reported data (Scheme 7BI).<sup>[15]</sup> In the presence of **Cat. 1'**, under the reaction condition, 90% of **2a** was observed which indicated that Mn(I) hydride was the active catalyst (Scheme 7BII).

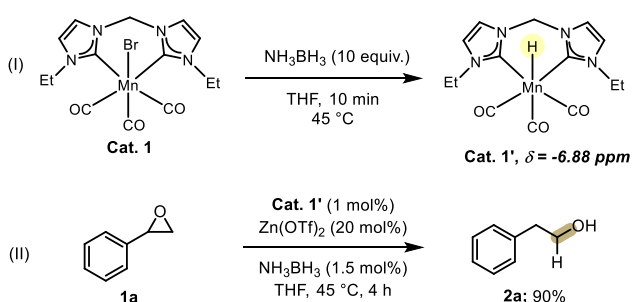
Next, the transfer hydrogenation of epoxide was investigated using deuterated ammonia borane as the hydrogen source. The reaction of **1a** in the presence of NH<sub>3</sub>BD<sub>3</sub> led to the formation of two products **2a-D1** and **2a-D1'** in 70% and 30% respectively (Scheme 7CI). This suggested that the reaction followed two pathways for the ring opening of epoxide i.e. Lewis acid assisted Meinwald rearrangement of epoxide to 2-phenylacetaldehyde followed by the transfer hydrogenation to give **2a-D1** and another by nucleophilic ring opening of **1a** by Mn-D catalyst to **2a-D1'**. With 2-phenethyloxirane, **2o-D1** was formed exclusively in the presence of NH<sub>3</sub>BD<sub>3</sub> which suggested that in the case of aliphatic epoxides the reaction proceeded *via* nucleophilic ring opening by Mn-D catalyst (Scheme 7CII). Additionally, both these experiments confirmed that BH<sub>3</sub> in ammonia borane was the source of hydride. <sup>11</sup>B NMR analysis of the reaction mixture revealed the formation of multitude of side products including polyborazine, cyclodiborazine and cyclotriborazine which was originated after dehydrogenation of ammonia borane (Fig. S4).

To understand the mechanism for the hydrogenation of nitroarenes to aniline, a reaction of azobenzene (**3a**) was carried

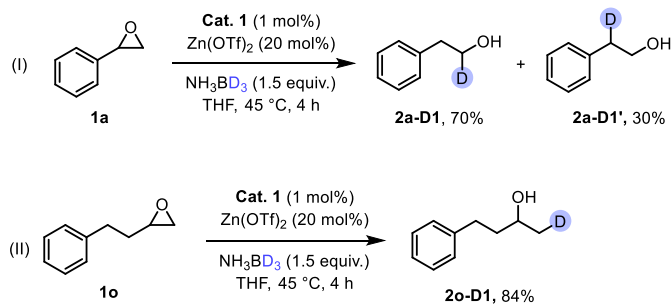
### A. Determination of intermediates



### B. Formation and reactivity of Mn-H

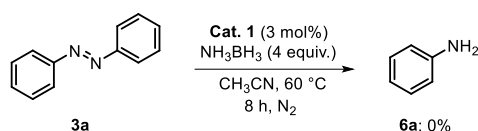


### C. Reaction using deuterated ammonia borane



Scheme 7. Control experiments

out under the optimized condition for the transfer hydrogenation of nitroarenes (Table 3, entry 9), which resulted in no aniline formation (**6a**). This suggested that the conversion of nitroarenes to anilines followed the direct route (Scheme 7).<sup>[40]</sup>

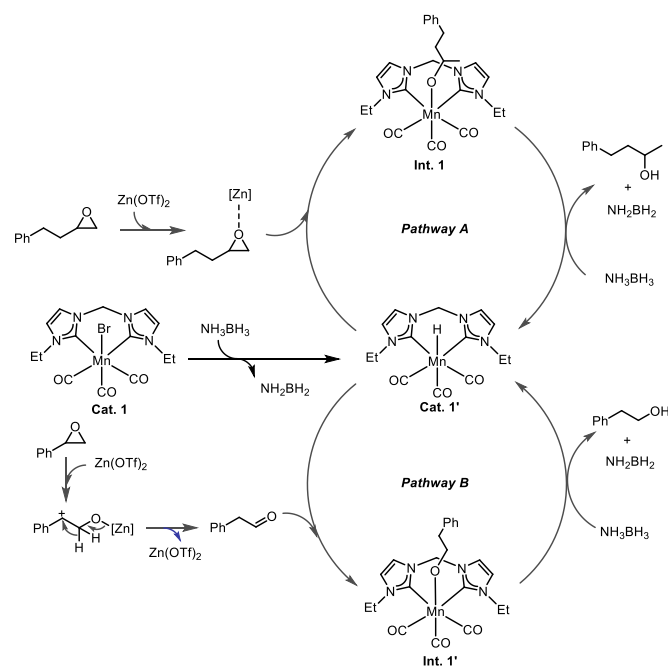


Scheme 7. Determination of mechanism for nitro reduction

Based on the mechanistic investigations and previous literature reports,<sup>[31,38]</sup> a plausible mechanism for the transfer hydrogenation of epoxide was proposed (Scheme 8). **Cat. 1** in the presence of ammonia borane led to the formation of Mn-H (**Cat. 1'**) followed by elimination of  $\text{NH}_2\text{BH}_2$ . Next, the reaction may follow two probable pathways based on the nature of the epoxides. Aliphatic epoxides followed pathway A where epoxide was first coordinated with  $\text{Zn}(\text{OTf})_2$  which then underwent nucleophilic ring opening by **Cat. 1'** at the most electrophilic and less hindered carbon centre which led to the formation of Mn-alkoxy intermediate (**Int. 1**). Subsequently, in the presence another molecule of ammonia borane, **Int. 1** resulted the desired secondary alcohol and regenerated **Cat. 1'**.

Aromatic epoxide followed pathway B where it underwent Meinwald rearrangement in the presence of  $\text{Zn}(\text{OTf})_2$  and afforded the corresponding aldehyde. Subsequently, the aldehyde was inserted to Mn-H which generated the alkoxy bound manganese species (**Int. 1'**). Thereafter, **Int. 1'** in the presence of  $\text{NH}_3\text{BH}_3$  furnished the desired product and regenerated the Mn-H (**Cat. 1'**). Additionally, formation of 30% **2a-D1'** during the reaction

of styrene oxide with  $\text{NH}_3\text{BD}_3$ , (Scheme 6C) specified that aromatic epoxide may also followed pathway A.



Scheme 8. Proposed mechanism for the TH of epoxides

## Conclusion

In summary, (NHC)Mn(I) complex catalyzed effective methodologies were developed for the selective transfer hydrogenation of epoxides, azoarenes and nitroarenes by

employing ammonia borane as the hydrogen source. Among the several NHC-based catalysts, Cat. 1 was found to be the most efficient. Employing the developed protocol, aromatic epoxides and aliphatic epoxides were selectively converted to primary alcohol and secondary alcohols respectively in good to excellent yields under mild conditions. Additionally, a variety of azoarenes were selectively converted to hydrazoarenes effectively. Cat. 1 also employed for the successful TH of nitroarenes to the corresponding anilines. Mechanistic study suggested involvement of (NHC)Mn(I)-H as the active catalyst during the reaction. A series of control experiments and reactions with deuterated ammonia borane were carried out to understand the mechanism. To the best of our knowledge, this is the first report for the Mn(I) catalysed transfer hydrogenation of epoxides, azoarenes as well as nitroarenes.

## Experimental Section

**Synthesis of Metal Complexes:** The metal complexes 1-3 were synthesized according to literature procedures.<sup>[11,15]</sup>

**Synthesis of alcohols from epoxides:** An oven-dried 5 mL screw-cap glass vial was charged with a magnetic stir-bar, epoxide (0.2 mmol), NH<sub>3</sub>BH<sub>3</sub> (0.3 mmol), Zn(OTf)<sub>2</sub> (0.04 mmol), Cat. 1 (1 mol%), and THF (0.2 M) under argon atmosphere. Then, the vial was sealed and placed in a preheated oil bath at 45°C for 4 h. After the completion of the reaction, the vial was allowed to cool at room temperature. The solvent was evaporated under reduced pressure, and the final product was purified by silica gel column chromatography using ethyl acetate/hexane as the eluent.

**Synthesis of hydrazoarenes from azoarenes:** An oven-dried 5 mL screw-cap glass vial was charged with a magnetic stir-bar, azoarene (0.2 mmol), NH<sub>3</sub>BH<sub>3</sub> (0.3 mmol), Cat. 1 (1 mol%), and ACN (0.2 M) under argon atmosphere. Then, the vial was sealed and placed in a preheated oil bath at 30°C for 30 min. After the completion of the reaction, the solvent was evaporated under reduced pressure, and the final product was purified by silica gel column chromatography using ethyl acetate/hexane as the eluent.

**Synthesis of anilines from nitroarenes:** An oven-dried 5 mL screw-cap glass vial was charged with a magnetic stir-bar, nitroarene (0.2 mmol), NH<sub>3</sub>BH<sub>3</sub> (0.8 mmol), Cat. 1 (3 mol%), and THF (0.2 M) under argon atmosphere. Then, the vial was sealed and placed in a preheated oil bath at 60°C for 8 h. After the completion of the reaction, the vial was allowed to cool at room temperature. The solvent was evaporated under reduced pressure, and the final product was purified by silica gel column chromatography using ethyl acetate/hexane as the eluent.

**Scale-up synthesis of alcohols from epoxides:** An oven-dried 15 mL screw-cap glass vial was charged with a magnetic stir-bar, epoxide (4 mmol), NH<sub>3</sub>BH<sub>3</sub> (6 mmol), Zn(OTf)<sub>2</sub> (0.8 mmol), Cat. 1 (1 mol%), and THF (0.2 M) under argon atmosphere. Then, the vial was sealed and placed in a preheated oil bath at 45°C for 4 h. After the completion of the reaction, the vial was allowed to cool at room temperature. The solvent was evaporated under reduced pressure, and the final product was purified by silica gel column chromatography using ethyl acetate/hexane as the eluent.

**Scale-up synthesis of hydrazoarenes from azoarenes:** An oven-dried 15 mL screw-cap glass vial was charged with a magnetic stir-bar, azoarene (4 mmol), NH<sub>3</sub>BH<sub>3</sub> (6 mmol), Cat. 1 (1 mol%), and ACN (0.2 M) under argon atmosphere. Then, the vial was sealed and placed in a preheated oil bath at 30°C for 30 min. After the completion of the reaction, the solvent was evaporated under reduced pressure, and the final product was purified by silica gel column chromatography using ethyl acetate/hexane as the eluent.

**Scale-up synthesis of anilines from nitroarenes:** An oven-dried 15 mL screw-cap glass vial was charged with a magnetic stir-bar, nitroarene (4 mmol), NH<sub>3</sub>BH<sub>3</sub> (16 mmol), Cat. 1 (3 mol%), and THF (0.2 M) under argon atmosphere. Then, the vial was sealed and placed in a preheated oil bath at 60°C for 8 h. After the completion of the reaction, the vial was allowed to cool at room temperature. The solvent was evaporated under reduced pressure, and the final product was purified by silica gel column chromatography using ethyl acetate/hexane as the eluent.

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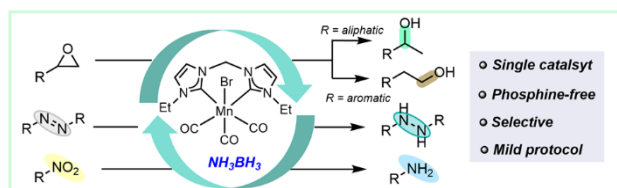
**Keywords:** Transfer hydrogenation • ammonia borane • bis(NHC)Mn(I) • epoxides • azoarenes • nitroarenes

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## Entry for the Table of Contents



Bis(NHC)Mn(I) catalysed effective transfer hydrogenation of epoxides, azoarenes and nitroarenes to alcohols, hydrazoarenes and anilines respectively under mild conditions using ammonia borane is demonstrated. A series of mechanistic investigations were carried out to understand the catalytic process.