

# Nickel Phthalocyanine Assisted Highly Efficient and Selective Carbonyl Reduction in Polyethylene Glycol-400

Praveen Kumar Verma · Upendra Sharma ·  
Neeraj Kumar · Manju Bala · Vishal Kumar ·  
Bikram Singh

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**Abstract** Nickel phthalocyanine with polyethylene glycol-400 is described as a reusable green catalytic system for highly chemo- and regioselective reduction of carbonyl compounds to corresponding alcohols at room temperature. The catalytic system showed wide substrate scope covering aromatic, hetero aromatic and aliphatic carbonyl compounds with high turnover number and frequency. In the present study, 1,3- and 1,4-benzenedicarbaldehydes have been regioselectively reduced to corresponding alcohols for the first time. The catalyst was reused up to seven times without any significance loss in activity.

**Keywords** Nickel phthalocyanine · Carbonyl reduction · Chemoselectivity · Regioselectivity · Reductive amination

## 1 Introduction

The selective reduction of carbonyl functionalities is one of the most important and basic chemical transformation in organic chemistry. It is an important step in the synthesis of natural products [1, 2], bulk and fine chemicals [3, 4].

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P. K. Verma · U. Sharma · N. Kumar (✉) · M. Bala ·  
V. Kumar · B. Singh (✉)  
Natural Plant Products Division, Council of Scientific and  
Industrial Research (CSIR), Institute of Himalayan Bioresource  
Technology, Palampur 176 061, HP, India  
e-mail: neerajnp@rediffmail.com

B. Singh  
e-mail: bikram\_nnp@rediffmail.com

Numerous methods have been developed to accomplish this transformation selectively in the presence of other reducible functionalities [5, 6] using trialkyl boranes with ionic liquid [7], and metal such as Au [8–11], Mn [12], Ir [13–16], Pt [17], Ru [18–31], Rh [32–34], Os [35, 36]. Use of costly metal, stoichiometric amount of additives and poor selectivity limits their scope.

Iron and nickel are abundantly available and found to be effective for carbonyl reduction due to their cost effectiveness over other frequently used transition metals [37–49]. In this view, Casey et al. have described the bifunctional iron complex for chemoselective hydrogenation of ketones under mild reaction conditions albeit with low TON/TOF [37–45]. Morris et al. have applied diamine based iron complex for hydrogenation of acetophenones with high conversion (TON = 225) but high pressure and excess of base were used [37–45]. Recently, Milstein et al. have efficiently catalyzed the hydrogenation of ketones by iron pincer complex with high TON (1880). However, less substrate scope, use of base and low TOF limits the scope of these reactions [37–45]. Earlier reported nickel based catalytic systems were less efficient, require additives and showed low turnover number/turnover frequency (TON/TOF) [46–49].

Sodium borohydride (NaBH<sub>4</sub>) has also been reported for carbonyl reduction without using any metal under solvent free conditions [50, 51]. However, use of excess NaBH<sub>4</sub> long reaction time and lack of chemoselectivity limits their scope [50]. Solid acids in combination with NaBH<sub>4</sub> have been shown to affect the reaction time and chemoselectivity [51]. In this case equivalent amount of the solid acids was required which can be avoided. In these reports the presence of NaBH<sub>4</sub> was not able to reduce carbonyl compounds with –OH group in aromatic ring as they formed sodium phenolates [50]. Moreover, regioselective reduction of dicarbaldehydes, which is important, has never been

reported. While working on the development of metal phthalocyanine-catalyzed reduction methodologies [52–54], here, we disclose nickel phthalocyanine (NiPc) catalyzed highly chemo- and regioselective method for reduction of carbonyl compounds to corresponding alcohols with high TON/TOF.

## 2 Experimental

### 2.1 Materials and Instrumentation

High grade solvents were used for all reactions. Column chromatography was carried out with 60–120 mesh silica gel. Silica (60–120 mesh) and TLC silica gel 60 F<sub>254</sub> plates were purchased from Merck India Ltd. Carbonyl compounds, amines, NMR solvents were purchased from sigma Aldrich and spectrochem. <sup>1</sup>H NMR and <sup>13</sup>C NMR experiments were performed on Bruker Avance-300 spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from an internal standard. The GC–MS analysis was carried out on a Shimadzu (QP 2010) series GC–MS (Tokyo, Japan) equipped with a FID, AOC-20i auto-sampler coupled, and a DB-5 capillary column, (30 × 0.25 mm i.d., 0.25 μm).

### 2.2 General Procedure for the Reduction of Carbonyl Compounds

To a mixture of carbonyl compound (250 or 500 or 1,000 mg) and catalyst ( $1.7 \times 10^{-3}$  mmol) in PEG-400 (2 or 3 or 4 mL), sodium borohydride (0.5 equiv.) was added. The reaction solution was stirred at room temperature and the progress of the reaction was monitored by TLC (silica gel; hexane/ethyl acetate) and GC–MS. After completion, the reaction mixture was extracted with diethyl ether (3 × 15 mL). The combined diethyl ether fractions were dried under reduced pressure. The crude product was analyzed directly by GC–MS. To obtain the isolated yield product mixture was subjected to column chromatography (silica 60–120; *n*-hexane/ethyl acetate mixture).

### 2.3 General Procedure for the Reductive Amination

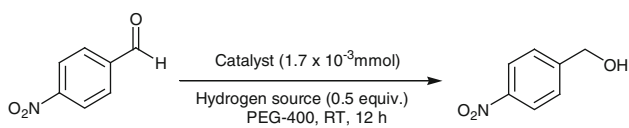
To a mixture of carbonyl compound (250 mg), amine (1 equiv.) and catalyst ( $1.7 \times 10^{-3}$  mmol) in PEG-400 (2 mL), was added. Sodium borohydride (0.5 equiv.) was added after the complete consumption of both reactants to the imine as monitored by TLC and stirring was continued. The reaction solution was stirred at room temperature and the progress of the reaction was monitored by TLC (silica gel; hexane/ethyl acetate) and GC–MS. After completion, the reaction mixture was extracted with diethyl ether

(3 × 15 mL). The combined diethyl ether fractions were dried under reduced pressure. The crude product was analyzed directly by GC–MS.

## 3 Results and Discussion

Initially, to access the best reaction conditions various hydrogen sources were tested in different solvents for the reduction of 4-nitrobenzaldehyde with nickel based catalysts. As expected, no reaction was observed without hydrogen source (Table 1, entries 1, 2, 5). Up to 50 % yield was observed with NaBH<sub>4</sub> in the absence of catalyst after 12 h (Table 1, entry 3). In the presence of NiCl<sub>2</sub> with NaBH<sub>4</sub> moderate yield (65 %) was observed after 12 h (Table 1, entry 4). Surprisingly, NiPc enhanced the rate of reaction and full conversion was observed in just 20 min (Table 1, entry 6). Borohydrides are the most conventional reducing agents in organic synthesis due to their stability, high selectivity and ease of handling. Desired product was

**Table 1** Optimization of reaction conditions for reduction of 4-nitrobenzaldehyde<sup>a</sup>



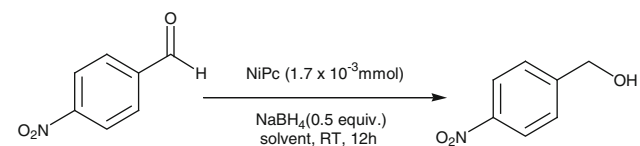
Entry	Catalyst	Hydrogen source	Yield <sup>b</sup> (%)
1	–	–	NR
2	NiCl <sub>2</sub>	–	NR
3	–	NaBH <sub>4</sub>	50
4	NiCl <sub>2</sub>	NaBH <sub>4</sub>	65
5	NiPc	–	NR
6	NiPc	NaBH <sub>4</sub>	>99 <sup>c</sup>
7	NiPc	NH <sub>2</sub> NH <sub>2</sub> ·H <sub>2</sub> O	NR
8	NiPc	HCOONH <sub>4</sub>	NR
9	NiPc	HCOOK	NR
10	NiPc	DPS	NR
11	NiPc	PMHS	NR
12	NiPc	HMDS	NR
13	NiPc	H <sub>2</sub> O	NR
14	NiPc	HCOOH	NR
15	NiPc	TES	NR
16	NiPc	CDMS	NR

NR no reaction, *DPS* diphenyl silane, *PMHS* poly(methylhydrosiloxane), *HMDS* hexamethyl disilane, *TES* triethyl silane, *CDMS* chlorodimethyl silane

<sup>a</sup> Reactions were carried out by using 250 mg of substrate, [substrate]/[catalyst] ratio = 250:1 (w/w)

<sup>b</sup> Yield was calculated on the basis of GC–MS analysis, yield = con. × sel./100

<sup>c</sup> Reaction time, 20 min

**Table 2** Optimization of solvent for reduction of 4-nitrobenzaldehyde<sup>a</sup>


Entry	Catalyst	Hydrogen source	Solvent	Yield <sup>b,c</sup> (%)
1	NiPc	NaBH <sub>4</sub>	H <sub>2</sub> O	48
2	NiPc	NaBH <sub>4</sub>	Ethanol	75
3	NiPc	NaBH <sub>4</sub>	i-PrOH	86
4	NiPc	NaBH <sub>4</sub>	Methanol	44
5	NiPc	NaBH <sub>4</sub>	PEG-400	>99 <sup>d</sup>
6	NiPc	NaBH <sub>4</sub>	Ethylene glycol	23
7	NiPc	NaBH <sub>4</sub>	THF	7
8	NiPc	NaBH <sub>4</sub>	Toluene	NR
9	NiPc	NaBH <sub>4</sub>	1,4-Dioxane	NR

<sup>a</sup> Reactions were carried out by using 250 mg of substrate, [substrate]/[catalyst] ratio = 250:1 (w/w)

<sup>b</sup> GC yield, yield = conv. × sel./100

<sup>c</sup> Reaction time, 12 h

<sup>d</sup> Reaction time, 20 min

not observed with other tested hydrogen sources (Table 1, entries 7–16). The change of solvents (Table 2) showed that the hydrogenation of carbonyl group was facilitated in protic solvents (Table 2, entries 1–6) and full conversion was observed in PEG-400 within 20 min (Table 2, entry 5). PEG is a widely available, non-toxic, biodegradable, thermally stable, non-volatile, low price and recyclable green solvent. In the recent years, it has been used effectively as green solvent for number of organic transformations.

With best reaction conditions in hand, the reduction of various carbonyl compounds was carried to check the scope of the present catalytic system. A variety of aromatic aldehydes efficiently hydrogenated to the corresponding alcohols. The hydrogenation of benzaldehyde was (TON = 5,105; TOF = 20,423 h<sup>-1</sup>) and yield (Table 3, entry 1). To the best of our knowledge such a high TON and TOF with full conversion was not observed earlier [37–49].

Halogen substituted aldehydes were efficiently reduced to the corresponding alcohols in good to excellent yields without any dehalogenation (Table 3, entries 2, 3). The hydroxy, methyl, methoxy, nitrile and acid functionalities present in the aromatic ring remained unaffected during the reduction of the corresponding aldehydes (Table 3, entries 4–8). High selectivity was observed for the hydrogenation of *o*-, *m*- and *p*-nitro benzaldehydes to corresponding alcohols (Table 3, entries 9–11) [55, 56]. Also, high selectivity with good yield was observed in case of complex benzaldehydes (Table 3, entries 15, 16).

**Table 3** Reduction of aromatic aldehydes to corresponding alcohols<sup>a</sup>

Entry	Substrate	<i>t</i> (min)	Yield <sup>b</sup> (%)	TON/TOF (h <sup>-1</sup> )
1		15	92	5,105/20,423 <sup>c</sup>
2		20	83	1,443/4,333 <sup>d</sup>
3		20	89	711/2,137 <sup>d</sup>
4		20	90 <sup>e</sup>	1,092/3,280 <sup>d</sup>
5		30	91	2,246/4,492 <sup>d</sup>
6		25	94	1,019/2,444
7		20	84	943/2,833
8		20	87 <sup>f</sup>	855/2,568
9		55	87	1,707/1,876 <sup>d</sup>
10		55	90	1,764/1,939 <sup>d</sup>
11		20	92	895/2,688
12		35	91 <sup>g</sup>	1,001/1,727
13		35	64	1,037/1,778
14		20	70	1,004/3,015
15		25	94	1,813/4,352 <sup>d</sup>
16		25	89	672/1,639

<sup>a</sup> Reactions were carried out by using 250 mg substrate unless specified, [substrate]/[catalyst] = 250:1 (w/w)

<sup>b</sup> Isolated yield

<sup>c</sup> Reactions were carried out by using 1 g of substrate, [substrate]/[catalyst] = 1,000:1 (w/w)

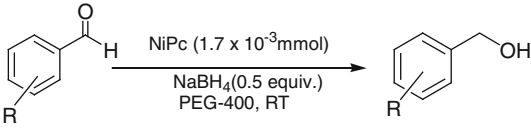
<sup>d</sup> Reactions were carried out by using 500 mg of substrate, [substrate]/[catalyst] = 500:1 (w/w)

<sup>e</sup> GC–MS yield

<sup>f</sup> Yield of phthalide

<sup>g</sup> Yield of 1,2-benzenedimethanol

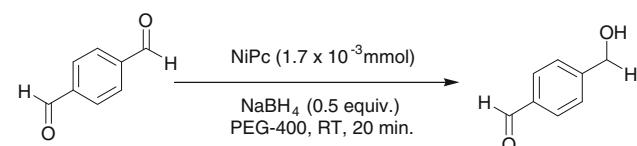
Regioselective reduction of aldehyde group in case of benzenedicarbaldehydes was not reported earlier. In the present study, high regioselectivity (>99%) was observed for 1,3- and 1,4-benzenedicarbaldehydes in 15 min with 41–67 % conversion (Table 4, entries 1, 3). However, regioselectivity was reduced to 68–77 % after full conversion (Table 3, entries 2, 4). Moderate isolated yield was

**Table 4** Regioselective reduction of dicarbaldehydes<sup>a</sup>


Entry	R	Time (min)	Conv. <sup>b</sup> (%)	Sel. <sup>b</sup> (%)
1	R = <i>m</i> -CHO	15	67	>99
2	R = <i>m</i> -CHO	35	100	68
3	R = <i>p</i> -CHO	15	41	>99
4	R = <i>p</i> -CHO	20	100	77

<sup>a</sup> Reactions were carried out by using 250 mg substrate, [substrate]/[catalyst] = 250:1 (w/w)

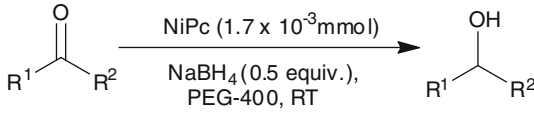
<sup>b</sup> On the basis of GC–MS analysis

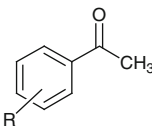
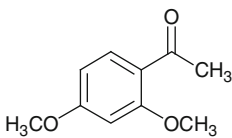
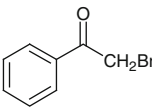
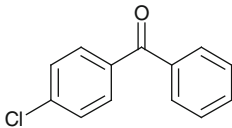
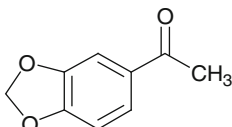
**Scheme 1** Regioselective reduction of dicarbaldehydes

obtained in both these cases (Scheme 1, Table 3, entries 13, 14). The reduction of both aldehyde groups was observed in case of 1,2-benzenedicarbaldehyde (Table 3, entry 12).

To further expand the scope of the method the reduction of various aromatic ketones was carried out. The excellent yield was observed under the same reaction conditions. Full conversion of acetophenone was observed within 15 min with good yield and high TOF (18,484 h<sup>−1</sup>), (Table 5, entry 1) which is more than the earlier reports [37–45]. Bromo, hydroxy, methoxy and nitro substituted acetophenones were efficiently converted into corresponding alcohols without affecting other functional groups (Table 5, entries 2–6). The present system selectively (78 %) catalyzed the hydrogenation of 2-bromoacetophenone with high yield (Table 5, entry 7). Also, 4-chloro benzophenone and 3,4-methylenedioxy acetophenone were selectively reduced to corresponding alcohols with good yield (Table 5, entries 8, 9).

In the present method high chemoselectivity was observed in case of cyclic as well as acyclic aliphatic carbonyl compounds with high TON/TOF (Table 6, entries 1–4). Chemoselective hydrogenation of unsaturated carbonyl compounds is a very challenging task in organic chemistry, and, generally, reduction of C=C bond also occurs [35, 36], however, in present method selective reduction of aldehyde group was observed without affecting conjugated or isolated C= bond (Table 6, entries 5, 6).

**Table 5** Reduction of aromatic ketones to corresponding alcohols<sup>a</sup>


Entry	Substrate	t (min)	Yield <sup>b</sup> (%)	TON/TOF (h <sup>−1</sup> )
1		15	94	4,621/18,484
2	R = <i>p</i> -Br	30	89	663/3,317
3	R = <i>m</i> -OH	25	86	1,899/4,632 <sup>c</sup>
4	R = <i>p</i> -OCH <sub>3</sub>	30	87	1,817/1,817 <sup>c</sup>
5	R = <i>p</i> -NO <sub>2</sub>	20	92	3,305/9,927 <sup>d</sup>
6		70	89	725/621
7		50	78 <sup>e</sup>	708/849
8		60	93	634/634
9		45	95	855/1,900

<sup>a</sup> Reactions were carried out by using 250 mg substrate unless specified, [substrate]/[catalyst] = 250:1 (w/w)

<sup>b</sup> Isolated yield

<sup>c</sup> Reactions were carried out by using 500 mg of substrate, [substrate]/[catalyst] = 500:1 (w/w)

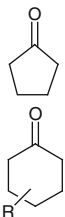
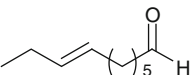
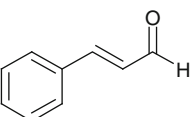
<sup>d</sup> Reactions were carried out by using 1 g of substrate, [substrate]/[catalyst] = 1,000:1 (w/w)

<sup>e</sup> GC–MS yield

The present catalytic system was also able to catalyze the hydrogenation of heteroaromatic aldehydes to corresponding alcohols with high TON and TOF. Furaldehyde and its derivative were efficiently reduced to corresponding alcohols (Table 7, entries 1, 2). Pyrrole-2-carboxaldehyde was reduced to corresponding alcohol in good yield (93 %) (Table 7, entry 3).

**Table 6** Reduction of aliphatic carbonyl compounds to corresponding alcohols<sup>a</sup>

$$\text{R}^1-\text{C}(=\text{O})-\text{R}^2 \xrightarrow[\text{NaBH}_4 (0.5 \text{ equiv.}), \text{ PEG-400, RT}]{\text{NiPc} (1.7 \times 10^{-3} \text{ mmol})} \text{R}^1-\text{CH}(\text{OH})-\text{R}^2$$

Entry	Substrate	<i>t</i> (min)	Yield <sup>b</sup> (%)	TON/TOF (h <sup>-1</sup> )
1		60	88 <sup>c</sup>	3,063/3,063
2	R = H	60	81 <sup>c</sup>	2,531/2,531
3	R = 3-CH <sub>3</sub>	30	87 <sup>c</sup>	2,292/4,585
4	R = 4-CH <sub>3</sub>	30	88 <sup>c</sup>	2,322/4,645
5		25	89	1,704/4,096
6		25	93	2,078/4,997

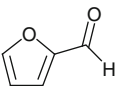
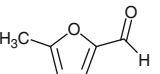
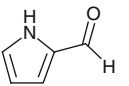
<sup>a</sup> Reactions were carried out by 500 mg substrate unless specified, [substrate]/[catalyst] = 500:1 (w/w)

<sup>b</sup> Isolated yield

<sup>c</sup> GC-MS yield

**Table 7** Reduction of heteroaromatic carbonyl compounds to corresponding alcohols<sup>a</sup>

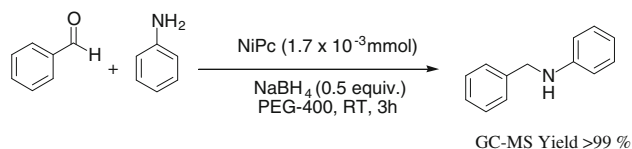
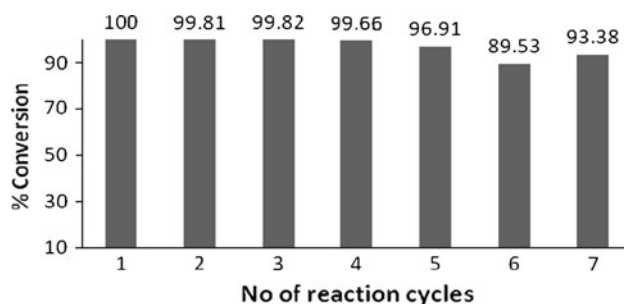
$$\text{R}^1-\text{C}(=\text{O})-\text{R}^2 \xrightarrow[\text{NaBH}_4 (0.5 \text{ equiv.}), \text{ PEG-400, RT}]{\text{NiPc} (1.7 \times 10^{-3} \text{ mmol})} \text{R}^1-\text{CH}(\text{OH})-\text{R}^2$$

Entry	Substrate	<i>t</i> (min)	Yield <sup>b</sup> (%)	TON/TOF (h <sup>-1</sup> )
1		30	92	2,838/5,676 <sup>c</sup>
2		40	87	1,166/1,749
3		45	93 <sup>d</sup>	1,444/1,926

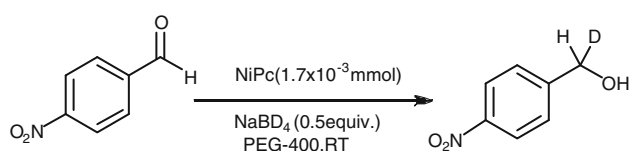
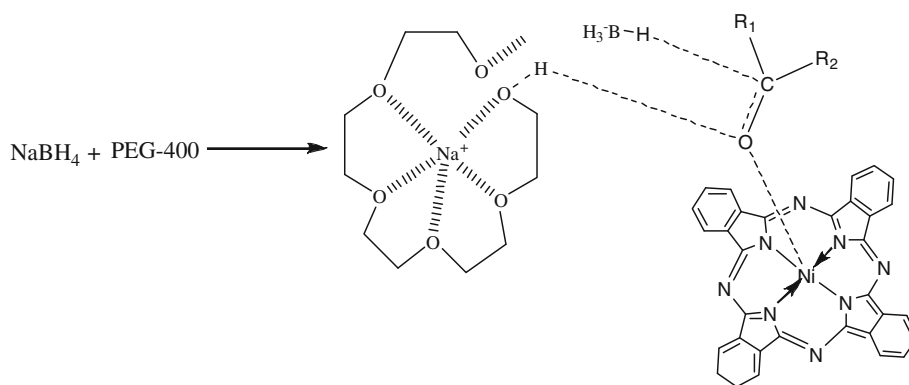
<sup>a</sup> Reactions were carried out by using 250 mg substrate unless specified, [substrate]/[catalyst] = 250:1 (w/w)

<sup>b</sup> Isolated yield

<sup>c</sup> Reactions were carried out by using 500 mg of substrate, [substrate]/[catalyst] = 500:1 (w/w)

<sup>d</sup> GC-MS yield

**Scheme 2** Reductive amination of benzaldehyde and aniline

**Fig. 1** Recyclability of catalytic system

**Fig. 2** Formation of crown ether-type complex and carbonyl group activation by NiPc



**Scheme 3** Reduction of benzaldehyde with NaBD<sub>4</sub>

In an extension of the hydrogenation of carbonyl compounds, the present catalytic system was successfully applied for the reductive amination of benzaldehyde with aniline in excellent yield (Scheme 2).

Further, the recyclability of the catalytic system was evaluated using 4-nitrobenzaldehyde as test substrate. After completion of reaction the product was extracted with diethyl ether. Successive reactions were carried out by sequential addition of fresh substrate and NaBH<sub>4</sub> to the crude remains after extracting the product. After fourth cycle PEG-400 was also added. The catalytic activity of the system was maintained up to five cycles and slight decrease in yield was observed after fifth cycle (Fig. 1). At the end of seven cycles the total turnover number of the reaction was calculated as 6,610.

To understand the mechanism, the model reaction was carried out under optimized conditions using NaBD<sub>4</sub>. The insertion of deuterium on the carbon of the carbonyl group (as confirmed by <sup>1</sup>H NMR) indicated the hydride attack followed by protonation with solvent to give the reduced product (Scheme 3). The hydride attack is thought to be facilitated by the formation of crown ether-type complex of PEG-400 with alkali metal of metal borohydrides [57]. No change in oxidation state (monitored by UV–vis spectrophotometer) and color of NiPc during the reaction ruled out the involvement of any Ni(I)Pc and hydridonickel species as previously reported [52–54, 58]. The exact role of NiPc in assisting the reaction is not clear, however, it is envisioned that Lewis acidic character of NiPc [59, 60] might be responsible for carbonyl group activation.

Therefore, we proposed that PEG-400, by making crown ether-type complex with sodium borohydride, is facilitating

the attack of hydride on carbonyl group which is activated by NiPc through Lewis acid–base interaction (Fig. 2).

## 4 Conclusions

In conclusion, a highly efficient, eco-friendly and green method has been developed for the high chemo- and regioselective reduction of carbonyl compounds to corresponding alcohols by using inexpensive NiPc with PEG-400 and NaBH<sub>4</sub> as hydrogen source at room temperature. The present method showed very wide substrate scope with high TON and TOF tolerating highly sensitive functional groups such as hydroxyl, carboxyl and olefin. Regioselective reduction of aldehyde group in case of benzenedicarbaldehydes was also reported first time. The catalyst can be reused up to seven times without any significance loss in activity. Rapid reaction, easy work up procedure and high efficiency make the present method most suitable for carbonyl group reduction. NiPc along with PEG-400 shows high impact for the replacement of precious transition metal based catalytic system generally used for the reduction of carbonyl compounds at pilot scale.

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