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Cobalt(II) Phthalocyanine-Catalyzed Highly Chemoselective Reductive Amination of Carbonyl Compounds in a Green Solvent

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Abstract: Cobalt phthalocyanine has been employed for the highly chemoselective reductive amination of aldehydes and ketones in ethanol as a green solvent. A large range of functional groups such as nitro, acid, amide, ester, nitrile, halogen, lactone, methoxy, hydroxy, alkene, *N*-benzyl, *O*-benzyl and heterocyclic rings were well tolerated under the present reaction conditions.

Keywords: chemoselectivity; cobalt phthalocyanine; diphenylsilane; green chemistry; reductive amination

Introduction

Amines and their derivatives are highly versatile building blocks for various bioactive organic substrates such as pharmaceuticals[1] and agrochemicals.[2] Amines are widespread among natural products and the pharmaceutical industries abound with drugs based on amine moieties.[3] Consequently, the synthesis of amines is a very active field in medicinal chemistry and modern organic synthesis. The direct reductive amination of carbonyl compounds is the most attractive method for the preparation of amine derivatives in organic synthesis.[4] Several reagents including catalytic hydrogenation,[5] gum acacia-Pd nanoparticles,[6] H_2-Fe_2O_3/Au nanoparticles,[7] Pd/C/HCOO-NH_4,[8] triazole-derived iridium(I) carbine complexes,[9] $[Ir(cod)_2]$,[10] Rh(I) catalysts,[11] $Pd(PhCN)_2Cl_2$-BQC-H_2,[12] $NaBH_3CN$,[13a] $NaBH(OAc)_3$,[13b] and $NaBH_4$-$H_3PW_{12}O_{40}$[13c] have been developed for reductive amination. However, most of these reagents have one or more drawbacks in terms of functional group tolerance, side reactions and harsh reaction conditions. Reductive amination with $NaBH_4$ and Lewis acids requires an excess of the amine (up to five-fold) in order to suppress the reduction of carbonyl compounds.[14] This limitation was overcome by employing organosilanes as mild and environmentally benign reducing agents, such as Et_3SiH-TFA,[15] Bu_3SnH-DMF,[16] $InCl_3$-Et_3SiH,[17] $InCl_3$-$Zn(ClO_4)_2 \cdot 6H_2O$-Et_3SiH,[18] $FeCl_3$-PMHS,[19] $PhSiH_3$-$ReIO_2(PPh_3)_2$.[20] The use of excess amounts of catalyst, hydrogen source and non eco-friendly solvents limit the scope of these methods.[17,18]

Recently, cobalt-based catalysts have been employed for the reduction of carbonyl[21] and nitro[22] compounds, hydroformylation,[23] amidocarbonylation[24] reactions, etc., but have not explored much for the reductive amination of carbonyl compounds.[25]

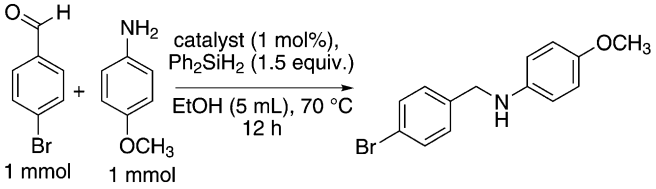
In continuation of our work on the development of efficient catalytic processes,[22,26,27] here, in the present work, we have successfully applied cobalt(II)phthalocyanine (CoPc) for the highly chemoselective and efficient reductive amination of carbonyl compounds using diphenylsilane as hydrogen source in ethanol. This is the first report on the use of CoPc/Ph_2SiH_2 for chemoselective reductive amination of carbonyl compounds in ethanol.

Results and Discussion

To optimize the best reaction conditions, the reductive amination of 4-bromobenzaldehyde with 4-methoxyaniline was carried out by using different catalysts, hydrogen sources and solvents under varying temperature conditions. The progress of the reaction was monitored by TLC and GC-MS. Among the different catalysts cobalt phthalocyanine was found to be the most active catalyst at 70 °C (Table 1, entry 9), however, no reaction was observed at room temperature. Furthermore, in order to confirm whether the corresponding metal salts from which the metal phthalocyanines were prepared could be able to catalyze the reaction, $FeSO_4 \cdot 7H_2O$, $CoCl_2 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$, $NiCl_2 \cdot 6H_2O$, $NiSO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$ were also used. No difference was observed in the catalytic activity of FePc and $FeSO_4 \cdot 7H_2O$ (Table 1, entries 2 and 8), and yield was slightly decreased with CuPc as compared to $CuSO_4 \cdot 5H_2O$ (Table 1, entries 7 and 11). Surprisingly, a significant increase in yield was observed in case of CoPc and NiPc as compared to corresponding metal salts (Table 1, entries 3–6, 9 and 10). In the absence of catalyst, the desired product was obtained in $<5\%$ yield (Table 1, entry 1), which showed the necessity of the catalyst.

Furthermore, an investigation of the role of different hydrogen sources revealed diphenylsilane as the best hydrogen source with 95% yield of the desired product (Table 2, entry 5). The use of other organosilanes as reducing agents did not provide comparable yields (Table 2, entries 6–9). Ammonium and potassium formate gave the desired product in very low yields of 15 and 17%, respectively (Table 2, entries 2 and 3). When $NaBH_4$ was used as hydrogen source the reductive amination product was obtained in only 46% yield along with alcohol as by-product (Table 2, entry 4). In hydrazine hydrate, no reductive amination product was observed and the corresponding hydrazone of the aldehyde was observed as the only prod-

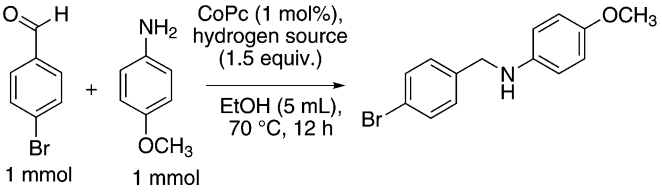
Table 1. Optimization of the reaction conditions for different catalytic systems.



Entry	Catalyst	Yield [%][a]
1	–	<5
2	$FeSO_4 \cdot 7H_2O$	19
3	$CoCl_2 \cdot 6H_2O$	<5
4	$CoSO_4 \cdot 7H_2O$	10
5	$NiCl_2 \cdot 6H_2O$	35
6	$NiSO_4 \cdot 7H_2O$	7
7	$CuSO_4 \cdot 5H_2O$	36
8	FePc	18
9	CoPc	95
10	NiPc	67
11	CuPc	18

[a] Yield was determined by GC-MS analysis of the reaction mixture.

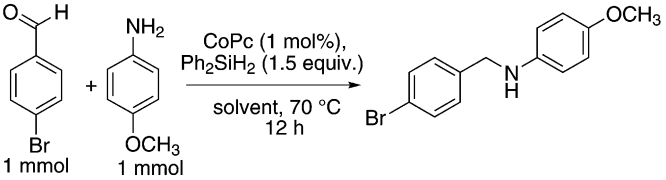
Table 2. Optimization of hydrogen source for the reaction.



Entry	Hydrogen source	Yield [%][a]
1	–	0
2	$HCOONH_4$	15
3	HCOOK	17
4	$NaBH_4$	46[b]
5	Ph_2SiH_2	95
6	$PhSiH_3$	34
7	PMHS	0
8	$(CH_3)_2ClSiH$	27
9	Et_2SiH_2	0
10	$NH_2NH_2 \cdot H_2O$	0[c]

[a] Yield was determined by GC-MS analysis.
[b] The alcohol was obtained in 29% yield.
[c] The hydrazone derivative was observed in 88% yield.

Table 3. Optimization of the solvent for the reaction.



Entry	Solvent	Yield [%][a]
1	–	<5
2	EtOH	95
3	MeOH	89
4	MeCN	92
5	H_2O	0
6	EtOH:H_2O (1:1)	42
7	DMSO	12
8	DMF	<5
9	1,4-dioxane	20
10	THF	5
11	toluene	0

[a] Yield was determined by GC-MS analysis of the reaction mixture.

Table 4. CoPc-catalyzed reductive amination of different aldehydes and amines.[a]

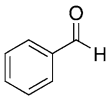
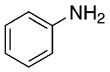
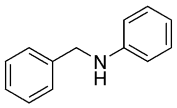
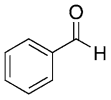
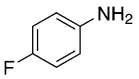
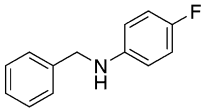
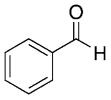
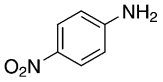
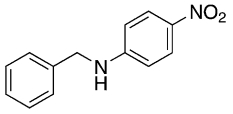
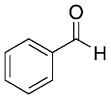
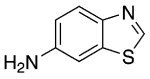
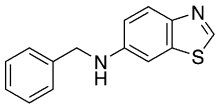
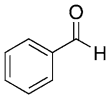
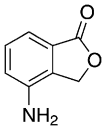
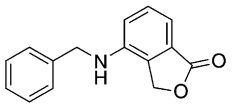
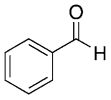
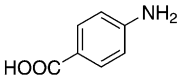
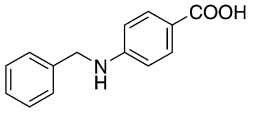
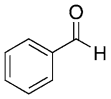
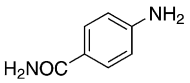
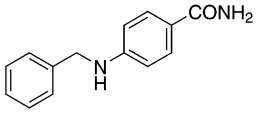
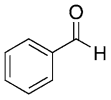
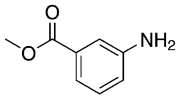
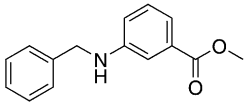
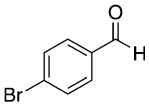
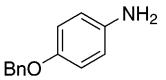
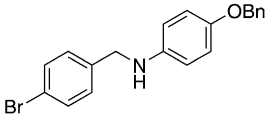
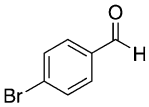
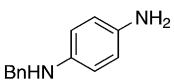
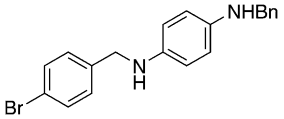
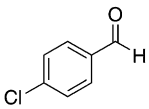
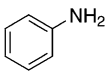
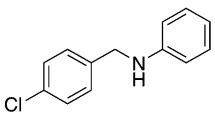
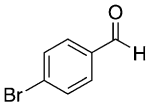
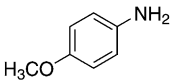
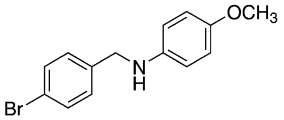
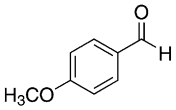
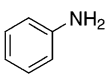
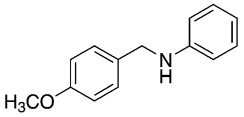
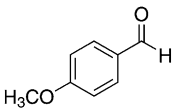
Entry	Aldehyde	Amine	Product	Yield [%][b]
1				87
2				90
3				79
4				92
5				95
6				88
7				85
8				80
9				70
10				71
11				93
12				95
13				86
14				77

Table 4. (Continued)

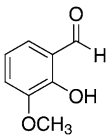
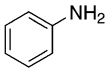
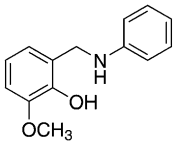
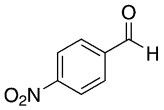
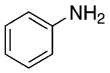
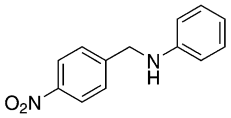
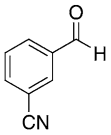
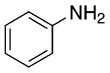
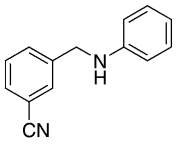
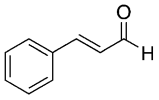
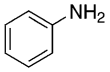
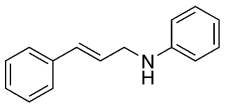
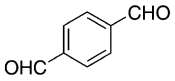
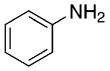
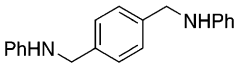
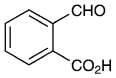
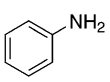
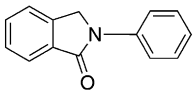
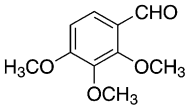
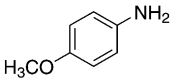
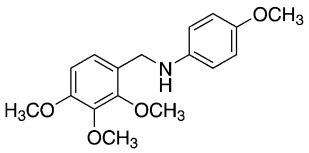
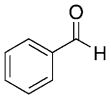
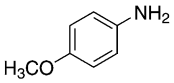
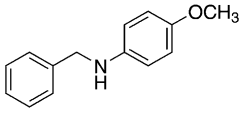
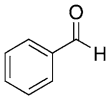
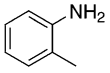
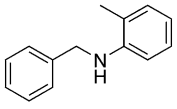
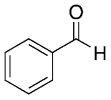
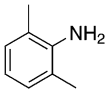
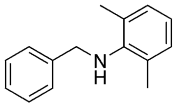
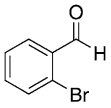
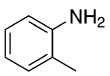
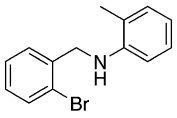
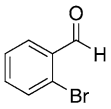
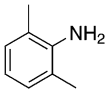
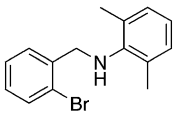
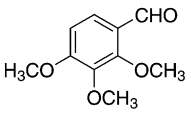
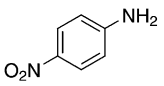
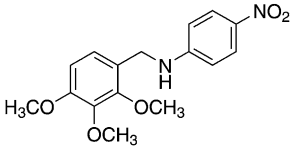
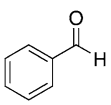
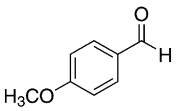
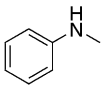
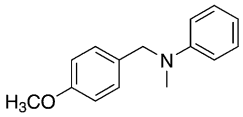
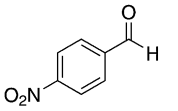
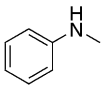
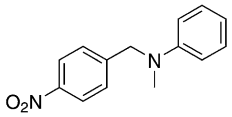
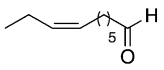
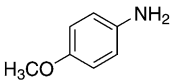
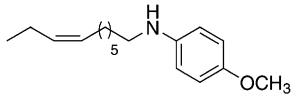
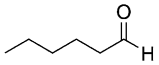
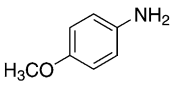
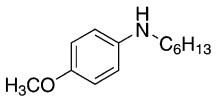
Entry	Aldehyde	Amine	Product	Yield [%][b]
15				93
16				91
17				89
18				96
19				82[c]
20				92
21				89
22				93
23				89
24				75[d]
25				90
26				13[d]
27				0[d]
28				95

Table 4. (Continued)

Entry	Aldehyde	Amine	Product	Yield [%][b]
29				88
30				32
31				91
32				79

[a] *Reaction conditions:* aldehyde (1 mmol), amine (1 mmol), CoPc (1 mol%), EtOH (5 mL) at 70 °C for 12 h.
[b] Yield of isolated product.
[c] Two equivalents of aniline were used.
[d] Yield based on GC-MS analysis of reaction mixture.

uct (Table 2, entry 10). Also, no product was obtained without a hydrogen source (Table 2, entry 1).

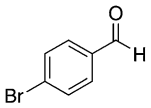
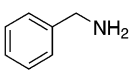
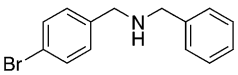
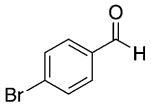
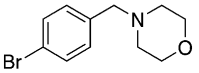
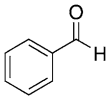
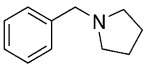
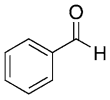
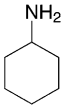
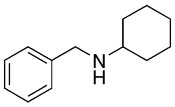
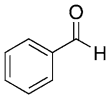
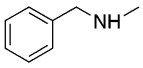
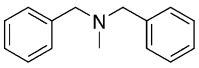
The change in solvent had a significant influence on the yield. Comparative yields were obtained in ethanol, methanol and acetonitrile (Table 3, entry 2–4). As ethanol is considered among the green solvents, it was considered as the solvent of choice. Very low yields (5–20%) of desired product were observed in DMSO, DMF, 1,4-dioxane and THF (Table 3, entries 7–10), whereas no product was observed in water and toluene (Table 3, entries 5 and 11).

With best reaction conditions in hand, the scope of the method was explored by the reactions of various substituted aldehydes and amines. The observation of high yields and chemoselectivity in most of the cases (Table 4) clearly demonstrated the generality of this method. Recently, Sousa and Farnandes have reported that $Re_2IO_2(PPh_3)_2$ catalyzed the highly chemoselective reductive amination of aldehydes.[20] The use of non eco-friendly solvent (THF) and release of toxic PPh_3 from catalyst limit the scope of the method.

The reductive amination of chloro- or bromo-substituted aldehydes proceeded smoothly and the desired products were obtained in good yields (Table 4, entries 9–12). Recently, we have reported the CoPc-catalyzed reduction of aromatic nitro compounds to proceed chemoselectively using hydrazine hydrate as reducing agent in ethylene glycol.[22] In the present case, using diphenylsilane in ethanol left the aromatic nitro group unaltered (Table 4, entries 3 and 16). Also, very good yields of products were obtained when hydroxy- and/or methoxy-substituted aldehydes were used as substrates (Table 4, entries 13–15, 21 and 29). One of the major problems associated with reductive amination is intolerance of C=C bonds,[5] however, in the present case high chemoselectivity was observed in the reductive amination of aldehydes containing conjugated as well as isolated C=C bonds (98 and >99%, respectively) with excellent yields (Table 4, entries 18 and 31). The reaction of 2-carboxybenzaldehyde and aniline afforded *N*-phenylisoindolone as the only product which is of biological importance (Table 4, entry 20).[28] The reaction of benzene-1,4-dicarboxaldehyde with two equivalents of aniline lead to reductive amination at both aldehyde groups (Table 4, entry 19). The nitrile group was also tolerated and a good yield of product was obtained (Table 4, entry 17). Poly-substituted derivatives of benzaldehyde were also well tolerated and the corresponding products were obtained in very good yields (Table 4, entries 15 and 21). A relatively low yield was recorded from 2,6-dimethylaniline in comparison to 2-methylaniline indicating the effect of steric hindrance (Table 4, entries 23–26). The most unfavorable combination such as 2,3,4-trimethoxybenzaldehyde and 4-nitroaniline was also considered, but no product was observed (Table 4, entry 27). Good to excellent yields were obtained in the reductive amination of aliphatic aldehydes (Table 4, entries 18, 31 and 32).

The scope of the method was further extended to other amines. Halogen-substituted amines such as 4-fluoro- and 4-iodoaniline were efficiently utilized for the reductive amination of benzaldehyde and 4-methoxybenzaldehyde, respectively (Table 4, entries 2 and 14). The reaction of 6-aminobenzothiazole and benzaldehyde was also very efficient (Table 4, entry 4). One of the major advantages of the present

Table 5. CoPc-catalyzed reductive amination of aldehydes and aliphatic amines.[a]

Entry	Aldehyde	Amine	Product	Yield [%][b]
1				85
2				88
3				53[c]
4				94
5				93

[a] *Reaction conditions:* aldehyde (1 mmol), amine (1 mmol), CoPc (1 mol%), EtOH (5 mL) at 70 °C for 12 h.
[b] Yield of isolated product.
[c] Yield based on GC-MS analysis of reaction mixture.

method is the tolerance of functional groups such as lactone, carboxylic acid, amide and ester on amines, which are generally not considered in reductive amination due to their lower reactivity towards aldehydes and incompatibility with reducing agents.[8–11] In the present case, these groups were well tolerated and the desired products were obtained in good yields (80–95%) with high chemoselectivity (Table 4, entries 5–8).

High chemoselectivity was recorded with *O*-benzyl- and *N*-benzyl-substituted amines (Table 4, entries 9 and 10). The reductive amination of benzaldehyde and 4-methoxybenzaldehyde with secondary anilines like *N*-methylaniline afforded high yields (Table 4, entries 28 and 29). However, a low yield was observed in the case of 4-nitrobenzaldehyde (Table 4, entry 30). Aliphatic primary as well as secondary amines also afforded good yields (Table 5, entries 1–5).

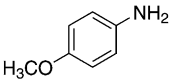
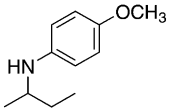
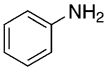
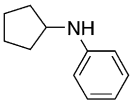
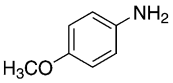
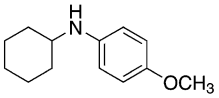
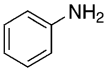
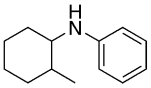
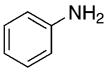
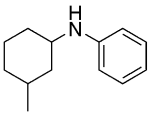
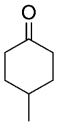
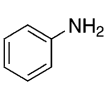
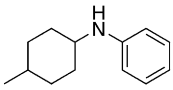
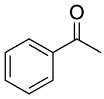
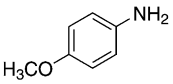
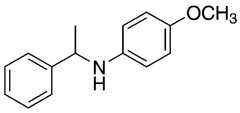
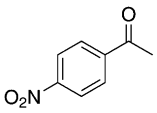
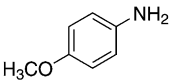
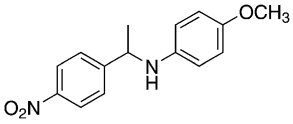
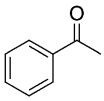
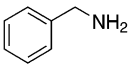
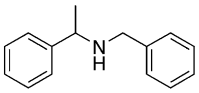
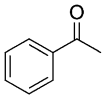
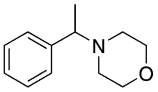
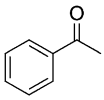
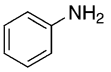
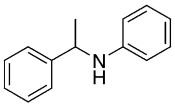
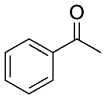
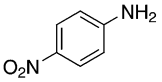
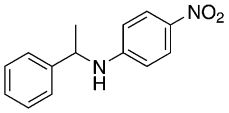
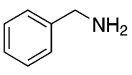
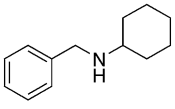
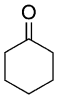
Various aromatic and aliphatic (cyclic as well as acyclic) ketones were also tested for the reductive amination and the desired products were obtained in good yields (Table 6). Aliphatic ketones showed good reactivity and the corresponding products were obtained in 75–95% yields (Table 6, entries 1–6, 13 and 14). Acetophenones are generally considered to be difficult substrates for reductive amination reactions, resulting in no or nerely low conversions depending on the reaction conditions,[13b,29a] or requiring enhanced quantities of catalytic activators like Bu_2SnCl_2.[29b] In our hands, using standard conditions allowed for the realization of low to moderate yields of the desired products (Table 6, entries 7–11). However, when acetophenone was treated with 4-nitroaniline, no reaction was observed (Table 6, entry 12).

To study the mechanism of the reaction, the model reaction was carried out using Ph_2SiD_2 in ethanol. The clear insertion of deuterium on the carbon of the double bond (as confirmed by ^{1}H NMR) indicated that hydrosilylation of the imine to give an intermediate *N*-silylamine occurred, followed by solvolysis with ethanol or a trace amount of water (Scheme 1).[20] The formation of diethoxydiphenylsilane as a by-product confirmed the solvolysis of *N*-silylamine with ethanol. No change in oxidation state (as monitored by UV-VIS spectrophotometry) and color of CoPc was observed during the reaction and thus ruled out the involvement of any hydridocobalt species as previously reported.[21,22]

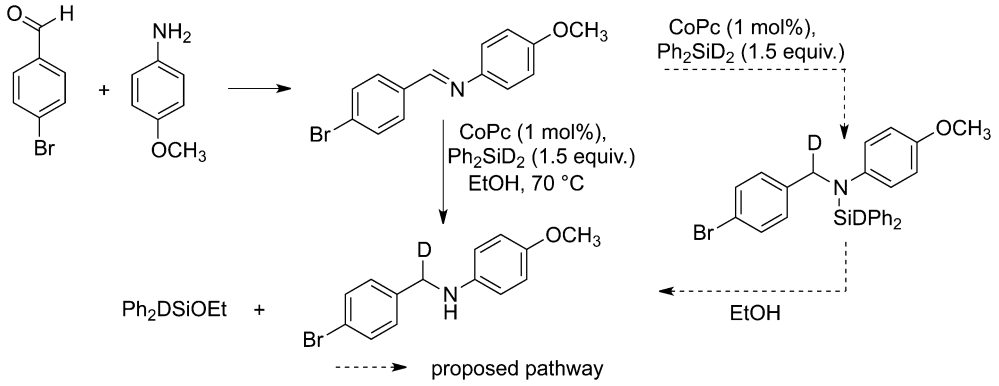
However, the exact role of CoPc is not clear, the Lewis acidic character of CoPc[30] might be responsible for imine activation *via* a Lewis acid-base interaction. In order to verify this, a competitive reaction of two imines having different electronic characters was carried out using our standard reaction condition (Scheme 2). The higher yield of product was observed from the more electron-rich imine due to its greater Lewis basic character. This indicated the possible role of a Lewis acid-base type interaction in catalyzing the reaction (Figure 1).

This observation was further supported by the fact that no reaction took place in the presence of a stronger Lewis base, triethylamine (1.0 equiv.) which may be due to a preferred interaction of CoPc with triethylamine as compared to imine. A similar Lewis

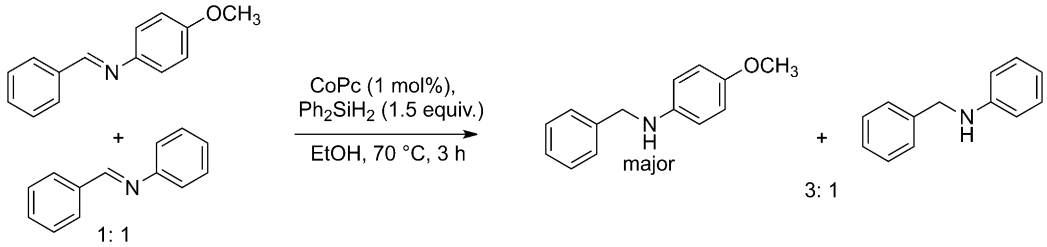
Table 6. CoPc-catalyzed reductive amination of different ketones and amines.[a]

Entry	Ketone	Amine	Product	Yield [%][b]
1				93
2				90
3				91
4				86
5				89
6				91
7				62
8				65
9				11[c]
10				14[c]
11				52[c]
12				0[c]
13				75
14				95[c]

[a] *Reaction conditions:* ketone (1 mmol), amine (1 mmol), CoPc (1 mol%), EtOH (5 mL) at 70 °C for 12 h.
[b] Yield of isolated product.
[c] Yield based on GC-MS analysis of reaction mixture.



Scheme 1. Hydrosilylation of imine using CoPc/Ph_2SiD_2 in ethanol.



Scheme 2. Competitive reaction of electronically different imines with Ph_2SiH_2 in ethanol.

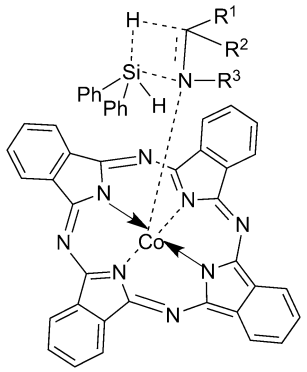


Figure 1. Activation of an imine by CoPc.

acid-base type mechanism was also proposed by Rajagopal et al. for the AlPc-catalyzed cyanosilylation of aldehydes.[31]

Conclusions

In conclusion, cobalt phthalocyanine has been established for the first time as a catalyst for the efficient and chemoselective reductive amination of carbonyl compounds to generate higher amines. Use of a green solvent with a low loading of catalyst under ambient reaction conditions makes the present method superior to earlier reported methods. Other remarkable advantages of this methodology include high isolated yields, clean reactions and easy work-up procedure.

Experimental Section

General Experimental Procedure for Reductive Amination of Carbonyl Compounds Catalyzed by the CoPc/Ph_2SiH_2 System

To a stirred suspension of CoPc (0.01 mmol) in ethanol (5 mL) were added carbonyl compound (1.0 mmol), amine (1.0 mmol) and diphenylsilane (1.5 mmol) at room temperature and then the temperature was raised to 70 °C. On completion of the reaction (as monitored by TLC), the reaction mixture was filtered and passed through anhydrous Na_2SO_4. The crude product was purified by column chromatography over silica-gel (60–120) mesh with an appropriate mixture of *n*-hexane and ethyl acetate.

Acknowledgements

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