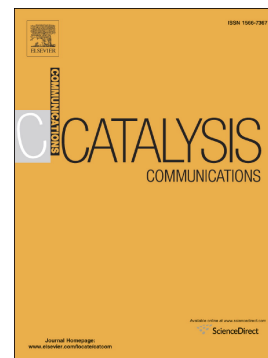# Journal Pre-proof

Application of a reusable co-based nanocatalyst in alcohol dehydrogenative coupling strategy: Synthesis of quinoxaline and imine scaffolds

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Application of a Reusable Co-Based Nanocatalyst in Alcohol Dehydrogenative Coupling Strategy: Synthesis of Quinoxaline and Imine Scaffolds

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Abstract:

A nitrogen doped carbon supported cobalt catalyzed efficient synthesis of imines and quinoxaline motifs is reported. $Co(OAc)_2$-Phen/Carbon-800 (Co-phen/C-800) showed the superior reactivity compared to other materials prepared at different temperature, in the synthesis of quinoxalines by the coupling between diamines and diols. Moreover, applying the transfer hydrogenation and acceptorless dehydrogenative coupling strategy, imines and quinoxaline derivatives were synthesized from the nitro compounds. The practical applicability of this protocol was demonstrated by the gram-scale synthesis and the reusability of the catalyst up to 8th cycle. Furthermore, several kinetic experiments were carried out to realize the probable mechanism.

Keywords: cobalt; heterogeneous catalysis; quinoxalines; imines; mechanistic investigations.

1. Introduction

In the atom economical and cost effective sustainable catalysis, one of the important aspect is separation and recyclability of the catalyst.[1] However, reusability of the catalyst is the prime challenge in the homogeneous catalysis.[2] Therefore, in the industry, mostly noble metal-based heterogeneous catalysts were employed for the synthesis of various pharmaceuticals, agrochemicals, bulk materials, etc.[3] Nevertheless, in the greener prospective, replacement of expensive noble metal-based systems with the non-precious and abundant transition metal catalysts received increasing interest in both academia and industry.[4, 5]

Replacement of the hazardous and waste generating chemicals with the biomass derived renewable feedstocks is one of the key target in the chemical research.[6] Although, approximately 75% of the carbohydrate biomass produced by nature, only 3-4% are utilized for the production of foods and chemicals.[7] Thus, for the synthesis of fine chemicals, employment of naturally available biomass carbohydrates as a raw material is one of the exciting areas of research.[8, 9] Importantly, catalytic conversion of carbohydrates to a variety of glycols such as ethanediol, propanediol, etc. were well explored.[10] Therefore, in the greener and sustainable perspective, use of these diols to synthesize the value added products remains an attractive strategy.

Quinoxaline scaffolds containing molecules have significant biological[11] and pharmacological properties.[12] However, in the traditional approach quinoxalines were synthesized by the reaction between reactive *di*-carbonyls with the *di*-amine molecules.[13] Recently, some other methods were also developed for their synthesis by employing 1,4-addition, oxidative coupling, cyclization-oxidation reaction strategies.[14] Nevertheless, the usage of expensive reactive reagents, poor yields, harsh reaction conditions are the major issues for most of these processes.[15] Notably, applying alcohol dehydrogenative coupling strategy[16, 17] there are several reports presented in the literature for the synthesis of

quinoxaline molecules.[18, 19] Inspired by these reports, we tried to synthesize these molecules through alcohol activation in presence of a heterogeneous cobalt catalysts.

In addition, imines are important class of nitrogen containing molecules used for the synthesis of materials, fragrances, fungicides, pharmaceuticals, etc.[20] Commonly, they are synthesized from expensive as well as reactive carbonyls and amines in the presence of Lewis acids.[21] Therefore, alternative greener approach to access these molecules is highly desirable. Following the alcohol dehydrogenative coupling strategy, several reports are known for the synthesis of imines by the reaction between alcohols and amines.[22] As nitro compounds are one of the surrogates for amines, hence direct synthesis of imines from nitro compounds and alcohols is more attractive.[23] Notably, only few reports [24], are known for the similar transformation under heterogeneous condition.

Herein, we report a practically useful and reusable cobalt catalyst for the direct synthesis of structurally diverse and biologically important quinoxaline and imine molecules. To the best of our knowledge, heterogeneous cobalt catalyzed the greener synthesis of quinoxalines by the reactions between nitroanilines and diols is not reported yet.

2. Experimental

2.1. Procedure for Synthesis of Co-phen/C-T Catalysts

Several nitrogen doped carbon supported cobalt nanoparticles were prepared by reacting cobalt precursor and phenanthroline (1:2 molar ratio) in ethanol, followed by the addition of carbon powder (Carbon Black) to the resultant reaction mixture at room temperature. Then, the solvent was evaporated under reduced pressure and the mixture was pyrolyzed under inert atmosphere (Scheme **S1**). In literature it is well known that the pyrolysis temperature has significant impact on the nature and activity of the materials.[25]

Hence, the pyrolysis of these materials was carried out at different temperature under N_2-atmosphere to get the diverse types of cobalt nanoparticles.

2.2. Quinoxaline Synthesis from Diamine

To an oven dried 9 mL screw cap tube, a magnetic stir-bar, diamine (0.5 mmol), vicinal diol (1.5 mmol), $CsOH.H_2O$ (0.375 mmol), Co-phen/C-800 (1.5 mol%) and toluene (2.5 mL) were added under argon atmosphere. Then, the tube was sealed and placed in a preheated oil bath at 150 °C for 24 h. After completion of the reaction, the tube was allowed to cool at room temperature. Then, the solvent was evaporated under reduced pressure. Finally, the product was purified by silica gel column chromatography using ethyl acetate/hexane as eluent.

2.3. Imine Synthesis from Nitroarene

An oven dried 9 mL screw cap tube was charged with a magnetic stir-bar, nitroarene (0.5 mmol), benzyl alcohol (2.0 mmol), Cs_2CO_3 (0.375 mmol), Co-phen/C-800 (1.5 mol%) and toluene (2.5 mL) under argon atmosphere. Next, the tube was sealed and placed in a preheated oil bath at 150 °C for 24 h. After completion of the reaction, the tube was allowed to cool at room temperature. The solvent was evaporated under reduced pressure. Then, the imine molecule was purified by deactivated silica gel column chromatography using ethyl acetate/hexane as eluent.

2.4. Direct Synthesis of Quinoxaline from Nitroamine

In an oven dried 9 mL screw cap tube a magnetic stir-bar, nitroamine (0.5 mmol), vicinal diol (2.5 mmol), $CsOH.H_2O$ (0.125 mmol), Co-phen/C-800 (1.5 mol%) and toluene (2.5 mL) were added under argon atmosphere. Then, the tube was sealed and placed in a preheated oil bath at 150 °C for 24 h. After completion of the reaction, the tube was allowed

to cool at room temperature. Next, the solvent was evaporated under reduced pressure. Finally, the quinoxalines was purified by silica gel column chromatography using ethyl acetate/hexane as eluent.

3. Results and discussion

We prepared a number of nitrogen doped carbon supported cobalt nanoparticles from various cobalt precursor and phenanthroline. To check the catalytic potentiality of these materials, initially we tested their activity for the synthesis of 2-methylquinoxaline. For this purpose, *o*-phenylenediamine and 1,2-propane diol were selected as model substrates.

At first, we screened several cobalt catalysts in this transformation, among them Co(OAc)$_2$-Phen/Carbon-800 (Co-phen/C-800) displayed the superior activity (Table **1**, entries 1-5). Few heterogeneous materials by using different support (e.g. alumina, silica) and different metals (Mn, Ni) doping were also screened for the synthesis of quinoxaline. However, all these materials were less efficient compare to Co-phen/C-800 (entries 6-9). Nevertheless, the material without N-doping or cobalt content showed the poor catalytic activity; signifies the importance of nitrogen and cobalt within the materials (entries 11-12). Afterwards, screening of bases (entries 13-15), solvents (entries 16-18) and optimization of other reaction parameters (entries 19-24 and SI) were performed. Finally, the yield of 2-methylquinoxaline was reached to 96% in toluene by using 1.5 mol% of Co(OAc)$_2$-phen/C-800 in presence of 3 equiv. of diol and 0.75 equiv. of CsOH.H$_2$O at 150 °C within 24 h (entry 24).

Table 1. Selected data for the optimization[a]
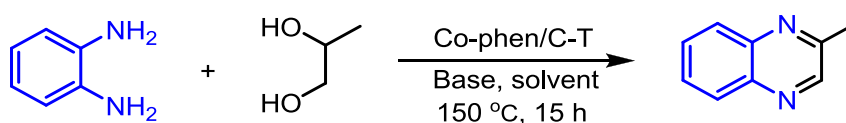
Entry	Catalyst (mol%)	Base (equiv.)	Yield (%)
1	$Co(OAc)_2$-phen/C-700 (6)	^tBuOK (0.5)	63
2	$Co(OAc)_2$-phen/C-800 (6)	^tBuOK (0.5)	84
3	$Co(OAc)_2$-phen/C-900 (6)	^tBuOK (0.5)	73
4	$Co(acac)_2$-phen/C-800 (6)	^tBuOK (0.5)	23
5	$CoCl_2$-phen/C-800 (6)	^tBuOK (0.5)	10
6	$Co(OAc)_2$-phen/Alumina-800 (6)	^tBuOK (0.5)	45
7	$Co(OAc)_2$-phen/Silica-800 (6)	^tBuOK (0.5)	67
8	$Ni(OAc)_2$-phen/C-800 (6)	^tBuOK (0.5)	55
9	$MnCl_2$-phen/C-800 (6)	^tBuOK (0.5)	30
10	$Co(OAc)_2$-phen/C-800 (6)	-	15
11	$Co(OAc)_2$-C-800 (6)	^tBuOK (0.5)	8
12	phen/C-800 (6)	^tBuOK (0.5)	2
13	$Co(OAc)_2$-phen/C-800 (6)	K_2CO_3(0.5)	29
14	$Co(OAc)_2$-phen/C-800 (6)	Cs_2CO_3(0.5)	83
15	$Co(OAc)_2$-phen/C-800 (6)	$CsOH.H_2O$ (0.5)	98
16[b]	$Co(OAc)_2$-phen/C-800 (6)	$CsOH.H_2O$ (0.5)	26
17[c]	$Co(OAc)_2$-phen/C-800 (6)	$CsOH.H_2O$ (0.5)	60
18[d]	$Co(OAc)_2$-phen/C-800 (6)	$CsOH.H_2O$ (0.5)	76
19[e]	$Co(OAc)_2$-phen/C-800 (3)	$CsOH.H_2O$ (0.5)	95
20[e]	$Co(OAc)_2$-phen/C-800 (1.5)	$CsOH.H_2O$ (0.5)	85
21[e]	$Co(OAc)_2$-phen/C-800 (0.75)	$CsOH.H_2O$ (0.5)	55
22[e,f]	$Co(OAc)_2$-phen/C-800 (1.5)	$CsOH.H_2O$ (0.75)	80
23[e,g]	$Co(OAc)_2$-phen/C-800 (1.5)	$CsOH.H_2O$ (0.75)	65

24[e]	Co(OAc)$_2$-phen/C-800 (1.5)	CsOH.H$_2$O (0.75)	96
25[e]	-	CsOH.H$_2$O (0.75)	6

[a]Reaction conditions: *o*-phenylenediamine (0.3 mmol), 1,2-propane-diol (0.9 mmol), toluene (1.5 mL) at 150 °C for 15 h; yields were determined by GC; [b]dioxan; [c]THF; [d]*p*-xylene; [e]24 h; [f]0.6 mmol diol; [g]0.45 mmol diol.

All the cobalt catalysts were characterized through various techniques such as X-Ray Diffraction Spectroscopy (XRD), X-Ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) etc. The powder pattern of the materials at different temperatures was shown in Figure **S4**. The characteristic 2θ values of 43.44°, 49.30° for these materials advocated the presence of metallic cobalt and 31.72°, 37.01°, 42.41°, 59.88° 62.84° indicated the existence of the oxide of cobalt.[26] To get insight into the surface of the materials, XPS measurement was carried out. The XPS analysis of the materials, formed at 700, 800 and 900 °C disclosed the nitrogen content of 6.2, 2.7 and 2.3 wt%, respectively. Notably, the N1s plots for these materials exposed mainly three characteristic peaks at i) 396.5 eV for pyridinic nitrogen, ii) 398.3 eV for pyrrolic nitrogen or nitrogen coordinated to cobalt, and iii) 402 eV for graphitic nitrogen (Figure **S6a**).[25] In addition, characteristic peaks of cobalt appear with binding energy of 778.5 eV and 793.8 eV, corresponds to Co2p$_{3/2}$ and Co2p$_{1/2,}$ respectively. Importantly, the satellite peaks at 786 eV and 802.4 eV also represent the oxidic nature of cobalt present in the surface (Figure **1a**). The TEM images of these materials disclosed the existence of CoO and Co$_3$O$_4$ which were uniformly dispersed over the N-doped carbon support. The average particle size of 17.53 nm and 18.2 nm was observed for the material at pyrolyzed at 700 °C and 800 °C, respectively. However, at 900 °C aggregation of the material lead to the larger particle size of 31.44 nm which indicate that growth of cobalt nanoparticle happened with increasing pyrolyzing temperature.[27] Importantly, presence of Co$_3$O$_4$ with well resolved lattice
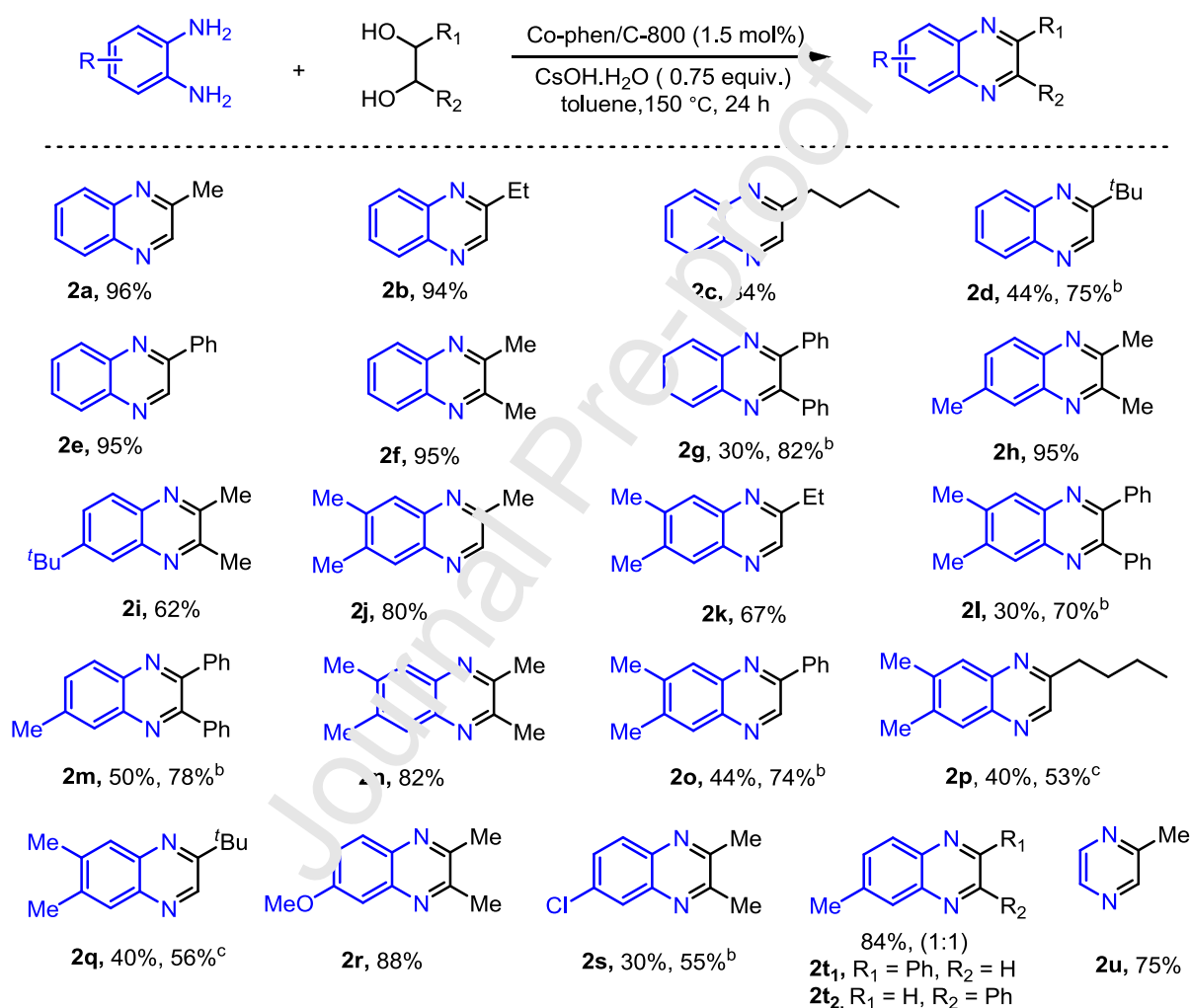
spacing of 0.24 nm for 311(Co_3O_4) plane was realized from the high resolution TEM images of the Co-phen/C-800 material (Figure **1b**).[25] Furthermore, the homogeneous distribution of the several elements such as Co, N, O and C in the material Co-phen/C-800 was recognized by the elemental mapping analysis using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) as shown in the Figure **S9**. Additionally, BET analysis of the Co-phen/C-800 material was carried out which displayed the BET surface area of 59 m^2/g and the average pore size of 1.4 nm.
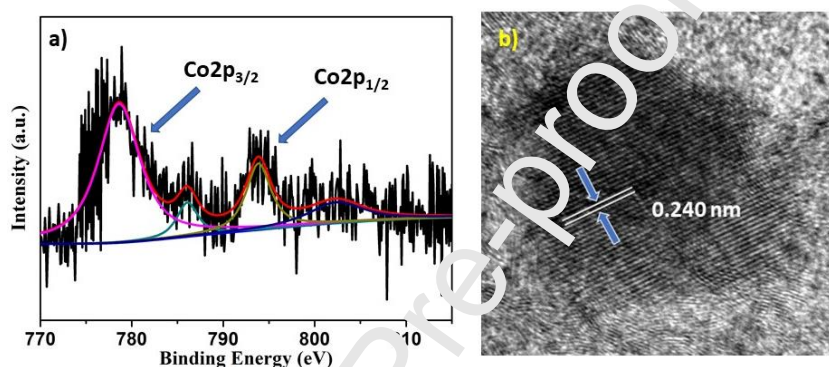
Figure 1. a) XPS Spectra of Co2p for Co-phen/C-800 material, b) TEM Images of Co-phen/C-800 material (scale bar 20 nm).

After achieving the optimum conditions (Table **1**, Entry 24) for 2-methylquinoxaline synthesis, next, we moved to explore the scope of the present catalytic process by employing variety of diamines and diols as mentioned in Table **2**. The reaction of 1,2-diaminobenzene with different diol molecules afforded the corresponding quinoxaline moieties up to 96% yield (**2a-g**). Additionally, quinoxaline scaffolds were synthesized efficiently, by altering both of diamine and diol molecules (**2h-q**). However, with diol having diphenyl or *tert*-butyl substitution lower yield of the desired product was observed (Table **2**). In addition to that, two regio-isomers (**2t₁** and **2t₂**) were obtained with an isomeric ratio of 1:1 (analyzed by ^{1}H-NMR spectroscopy) when unsymmetrical diamine and diol was used. 2-Methylpyrazine (**2u**) also synthesized using this protocol from ethylenediamine with good yield.
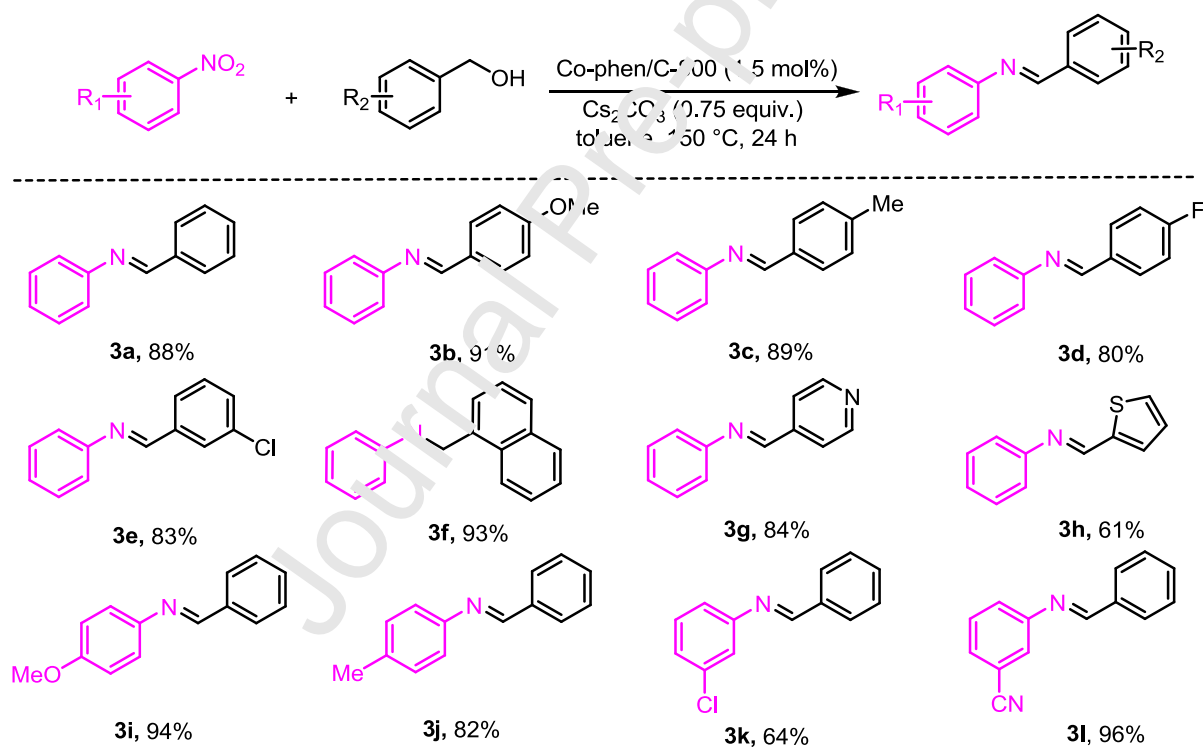
Table 2. Synthesis of quinoxalines from diamines*a*

2a, 96%   2b, 94%   2c, 94%   2d, 44%, 75%[b]

2e, 95%   2f, 95%   2g, 30%, 82%[b]   2h, 95%

2i, 62%   2j, 80%   2k, 67%   2l, 30%, 70%[b]

2m, 50%, 78%[b]   2n, 82%   2o, 44%, 74%[b]   2p, 40%, 53%[c]

2q, 40%, 56%[c]   2r, 88%   2s, 30%, 55%[b]   84%, (1:1)
2t₁, R₁ = Ph, R₂ = H
2t₂, R₁ = H, R₂ = Ph   2u, 75%

*a*Reaction conditions: diamine (0.5 mmol), diol (1.5 mmol), toluene (2.5 mL) at 150 °C for 24 h; isolated yield; *b*3 mol% catalyst for 28 h; *c*36 h.

Next, we tested the potential of this catalytic system towards the coupling between nitroarenes and benzyl alcohols for the synthesis of imines. However, during the optimization process, for the coupling between nitrobenzene and benzyl alcohol, CsOH.H₂O displayed

lower activity towards the imine formation (see SI). Hence, we again screened several bases and among them, Cs_2CO_3 presented superior activity in this transformation (SI, Table **S5**, 88% yield). Afterwards, to check the general applicability of this process, several substituted alcohols and nitro compounds were employed (Table **3**). Following this protocol, various imine molecules were synthesized in 61-96% yields (**3a-l**). In addition, alcohols containing naphthalene moiety or hetero nuclei also worked fine by employing this protocol (**3f-h**). Gratifyingly, the reducible -CN group was unaffected during this transformation; demonstrated the selectivity of this catalytic system (**3l**).

Table 3. Scope for the imines synthesis[a]

3a, 88% **3b,** 9% % **3c,** 89% **3d,** 80%

3e, 83% **3f,** 93% **3g,** 84% **3h,** 61%
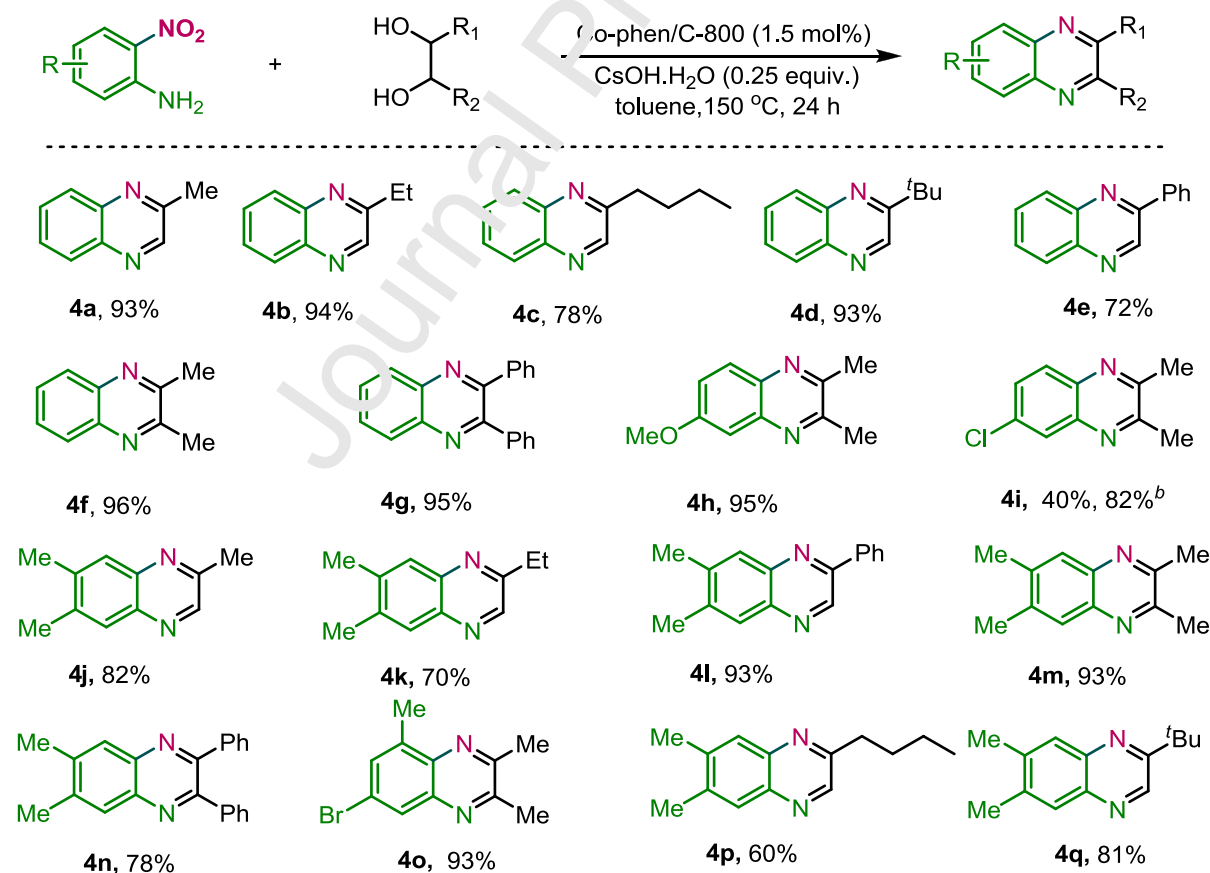
3i, 94% **3j,** 82% **3k,** 64% **3l,** 96%

[a]Reaction conditions: nitroarene (0.5 mmol), benzyl alcohol (2.0 mmol), toluene (2.5 mL) at 150 °C for 24 h; isolated yield.

After achieving the optimum conditions (Table **S6**), we explored the potential of this catalytic system towards the direct synthesis of a variety of quinoxaline scaffolds from 2-nitroanilines and diols (Table **4**). Several *mono-* and *di-*substituted diol derivatives furnished the desired products efficiently (**4a-g**). Additionally, a number of substituted 2-nitroanilines

smoothly furnished the desired quinoxaline scaffolds up to 95% yield (**4h-i**). Notably, substitution at the both of alcohols and nitroamines effectively transformed to the quinoxaline molecules in 60-93% yield (**4j-q**).

To demonstrate the practical applicability of this protocol, we carried out gram-scale synthesis of various quinoxalines and imines, where up to 87% yield was observed (Figure S**1**). Then, we evaluated the green chemistry metrics for the preparative scale synthesis of 2, 3, 6-trimethylquinoxaline (**2h**) from 4-methylbenzene-1, 2-diamine. The calculated E-factor of 4.23, 81% atom economy, 66.42% atom efficiency, 100% carbon efficiency and 66.58% of reaction mass efficiency in this transformation clearly exposed the novelty and sustainability of this protocol.

Table 4. Direct synthesis of quinoxalines from nitroamines[a]

4a, 93%   4b, 94%   4c, 78%   4d, 93%   4e, 72%

4f, 96%   4g, 95%   4h, 95%   4i, 40%, 82%[b]

4j, 82%   4k, 70%   4l, 93%   4m, 93%

4n, 78%   4o, 93%   4p, 60%   4q, 81%

[a]Reaction conditions: nitroaniline (0.5 mmol), diol (2.5 mmol), toluene (2.5 mL) at 150 °C for 24 h; isolated yield; [b]3 mol% catalyst.

The significant advantage of the heterogeneous system over the homogeneous catalytic condition is the separation and recyclability of the catalyst. To test the recyclability of this system, we carried out the synthesis of 2, 3-dimethylquinoxaline from 2-nitroaniline and isolated the heterogeneous cobalt catalyst after the reaction. Remarkably, this heterogeneous system did not lose its catalytic activity significantly even after 8th catalytic cycle (Figure **2**).
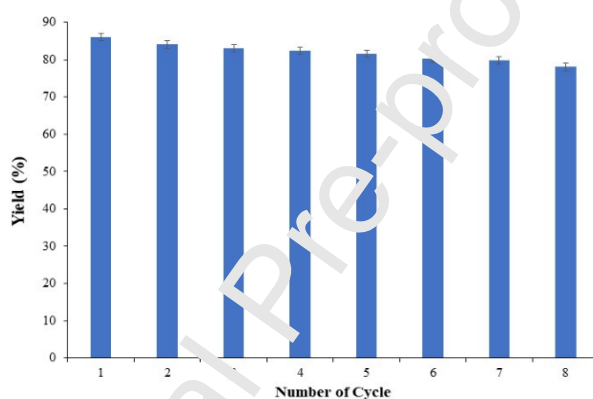
Figure 2. Recycling of Co-phen/C-800 catalyst.

The yield of 2-methylquinoxaline dropped considerably when the reaction was carried out with acid treated Co-phen/C-800 catalyst (Scheme **S2**). This experiment suggested that both Co-Nx and CoOx played vital role in this reaction.[28]

To understand these catalytic transformations using the heterogeneous cobalt system few kinetic experiments were carried out. The reduction of nitro compound follows either a direct route or condensation route depending upon the catalytic system.[29] Thus, in order to find which pathway was operating during the reduction of nitroarenes to anilines, a time dependent product distribution was carried out for the coupling of nitrobenzene and benzyl

alcohol (Figure **S2**). In this reaction formation of substantial amount of azobenzene indicated the preferential involvement of condensation route.

Afterwards, during the formation of quinoxaline from 2-nitroaniline a time dependent product distribution was carried out (Figure **S3**). Initially, considerable amount of diamine was observed and the amount of diamine decreased steadily with the progress of the reaction.

Subsequently, we performed a number of control experiments as mentioned in Scheme S**3**. During the reductive imination of nitrobenzene at the initial time (0.5 h) formation of a significant amount of the azobenzene and azoxybenzene was detected (Scheme **S3**). This study clearly specified the preferential involvement of condensation route in this transformation. To further support this, an experiment between azobenzene and benzyl alcohol was carried out which smoothly delivered the desired imine molecule (Scheme **S3B**). The conversion of nitrobenzene was quite low with only base which exposed the necessity of cobalt catalyst in this transformation (Scheme **S3C**).

Based on kinetic experiments, we proposed the schematic pathway for the formation of quinoxaline from the 2-nitroaniline molecule (Scheme **S4**). The time dependent product distribution study showed the formation of significant amount of diamine during the reaction which suggested that path **1** was more favourable. Nevertheless, the possibility of path **2** cannot be ruled out. Initially, 2-nitroaniline was transformed to the 1, 2-diamino benzene. After that, condensation between the *o*-phenylenediamine and the *in situ* generated dicarbonyl lead to form the species **R**. Finally, intra-molecular cyclization of the species **R** provided the quinoxaline product. In addition based on literature reports a interaction mechanism was proposed for this system (Scheme **S5**).[25]

4. Conclusion

In summary, we synthesized a number of N-doped carbon supported cobalt catalysts by varying pyrolysis temperature. Catalytic activity of these materials were tested towards the synthesis of 2-methylquinoxaline from *o*-phenelenediamine and among them, Co-phen/C-800 showed the superior results. PXRD analysis revealed the presence of metallic Co and oxidic cobalt in these materials. XPS study disclosed that minimum nitrogen content in Co-phen/C-900 compared to Co-phen/C-700 and Co-phen/C-800. The nanoparticle growth with higher pyrolyzing temperature and existence of Co_3O_4-species was suggested by TEM analysis. Additionally, employing transfer hydrogenation and alcohol dehydrogenative coupling approach, quinoxalines and imines were also synthesized from nitro compounds and alcohols. Moreover, the preferential involvement of diamine and condensation route during the formation of quinoxalines from 2-nitroamines was revealed by the kinetic studies and control experiments. Importantly, the recyclability of this system was tested up to 8th cycle and this heterogeneous system did not lose its catalytic activity significantly.

Author contribution statement:

Dibyajyoti Panja: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data Curation, Writing - Original Draft, Visualization
Bhaskar Paul: Data Curation, Formal analysis, Writing - Review & Editing
Bhuvaneshwari Balasubramaniam: Software, Formal analysis, Resources, Writing - Review & Editing
Raju K. Gupta: Resources, Writing - Review & Editing
Sabuj Kundu: Conceptualization, Validation, Writing - Review & Editing, Supervision, Project

administration, Funding acquisition

Conflicts of interest

There are no conflicts to declare

Acknowledgements

Supplementary data

Supplementary material

References

[1] R.M. Bullock, Catalysis without Precious Metals, Wiley-VCH Verlag, Weinheim, Germany, 2010.

[2] P. Munnik, P.E. de Jongh, K.P. de Jong, Recent developments in the synthesis of supported catalysts, Chem. Rev., 115 (2015) 6687-6718

[3] S. Nishimura, Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis, Wiley-VCH, New York, 2001.

[4] B. Su, Z.C. Cao, Z.J. Shi, Exploration of earth-abundant transition metals (Fe, Co, and Ni) as catalysts in unreactive chemical bond activation, Acc. Chem. Res., 48 (2015) 886-896.

[5] S.M. Coman, V.I. Parvulescu, Nonprecious Metals Catalyzing Hydroamination and C−N Coupling Reactions, Org. Process Res. Dev. 19 (2015) 1327-1355.

[6] I.T. Horvath, Introduction: Sustainable Chemistry, Chem. Rev., 118 (2018) 369-371.

[7] H. Röper, Renewable Raw Materials in Europe Industrial Utilisation of Starch and Sugar [1], Starch - Stärke, 54 (2002) 89-99.

[8] G.W. Huber, S. Iborra, A. Corma, Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering, Chem. Rev., 106 (2006) 4044-4098.

[9] C.H. Zhou, X. Xia, C.X. Lin, D.S. Tong, J. Beltramini, Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels, Chem. Soc. Rev., 40 (2011) 5588-5617.

[10] A. Corma, S. Iborra, A. Velty, Chemical Routes for the Transformation of Biomass into Chemicals, Chem. Rev., 107 (2007) 2411-2502.

[11] G. Cheeseman, E. Werstiuk, Quinoxaline chemistry: developments 1963-1975, in: Advances in heterocyclic chemistry, Elsevier, 1978, pp. 367-431.

[12] H.M. Refaat, A.A. Moneer, O.M. Khalil, Synthesis and antimicrobial activity of certain novel quinoxalines, Arch Pharm Res, 27 (2004) 1093-1098.

[13] M. Ayaz, Z. Xu, C. Hulme, Novel succinct routes to Quinoxalines and 2-Benzimidazolylquinoxalines via the Ugi reaction, Tetrahedron Lett, 55 (2014) 3406-3409.

[14] C. Deraedt, R. Ye, W.T. Ralston, F.D. Toste, G.A. Somorjai, Dendrimer-Stabilized Metal Nanoparticles as Efficient Catalysts for Reversible Dehydrogenation/Hydrogenation of N-Heterocycles, J. Am. Chem. Soc., 139 (2017) 18084-18092.

[15] M.J. Climent, A. Corma, J.C. Hernandez, A.B. Hungria, S. Iborra, S. Martinez-Silvestre, Biomass into chemicals: One-pot two- and three-step synthesis of quinoxalines from biomass-derived glycols and 1,2-dinitrobenzene derivatives using supported gold nanoparticles as catalysts, J. Catal., 292 (2012) 118-129.

[16] T. Irrgang, R. Kempe, 3d-Metal Catalyzed N- and C-Alkylation Reactions via Borrowing Hydrogen or Hydrogen Autotransfer, Chem. Rev., 119 (2019) 2524-2549.

[17] S.M.A. Hakim Siddiki, T. Toyao, K.-i. Shimizu, Acceptorless dehydrogenative coupling reactions with alcohols over heterogeneous catalysts, Green Chem., 20 (2018) 2933-2952.

[18] F. Xie, M. Zhang, H.F. Jiang, M.M. Chen, W. Lv, A.B. Zheng, X.J. Jian, Efficient synthesis of quinoxalines from 2-nitroanilines and vicinal diols via a ruthenium-catalyzed hydrogen transfer strategy, Green Chem., 17 (2015) 279-284.

[19] P. Daw, A. Kumar, N.A. Espinosa-Jalapa, Y. Diskin-Posner, Y. Ben-David, D. Milstein, Synthesis of Pyrazines and Quinoxalines via Acceptorless Dehydrogenative Coupling Routes Catalyzed by Manganese Pincer Complexes, ACS Catal., 8 (2018) 7734-7741.

[20] J. Gawronski, N. Wascinska, J. Gajewy, Recent Progress in Lewis Base Activation and Control of Stereoselectivity in the Additions of Trimethylsilyl Nucleophiles, Chem. Rev., 108 (2008) 5227-5252.

[21] G. Liu, D.A. Cogan, T.D. Owens, T.P. Tang, J.A. Ellman, Synthesis of Enantiomerically Pure N-tert-Butanesulfinyl Imines (tert-Butanesulfinimines) by the Direct Condensation of tert-Butanesulfinamide with Aldehydes and Ketones, J. Org. Chem., 64 (1999) 1278-1284.

[22] H.-A. Ho, K. Manna, A.D. Sadow, Acceptorless photocatalytic dehydrogenation for alcohol decarbonylation and imine synthesis, Angew. Chem. Int. Ed., 51 (2012) 8607-8610.

[23] C.C. Lee, S.T. Liu, Preparation of secondary and tertiary amines from nitroarenes and alcohols, Chem. Commun., 47 (2011) 6981-6983.

[24] D. Liu, P. Yang, H. Zhang, M. Liu, W. Zhang, D. Xu, J. Gao, Direct reductive coupling of nitroarenes and alcohols catalysed by Co-N-C/CNT@AC, Green Chem., 21 (2019) 2129-2137.

[25] T. Song, P. Ren, Y. Duan, Z. Wang, X. Chen, Y. Yang, Cobalt nanocomposites on N-doped hierarchical porous carbon for highly selective formation of anilines and imines from nitroarenes, Green Chem., 20 (2018) 4629-4637.

[26] R.V. Jagadeesh, D. Banerjee, P.B. Arockiam, H. Junge, K. Junge, M.M. Pohl, J. Radnik, A. Bruckner, M. Beller, Highly selective transfer hydrogenation of functionalised nitroarenes using cobalt-based nanocatalysts, Green Chem., 17 (2015) 898-902.

[27] Z. Yuan, B. Liu, P. Zhou, Z. Zhang, Q. Chi, Preparation of nitrogen-doped carbon supported cobalt catalysts and its application in the reductive amination, J. Catal., 370 (2019) 347-356.

[28] C. Tang, A.-E. Surkus, F. Chen, M.-M. Pohl, G. Agostini, M. Schneider, H. Junge, M. Beller, A Stable Nanocobalt Catalyst with Highly Dispersed CoNx Active Sites for the Selective Dehydrogenation of Formic Acid, Angew. Chem. Int. Ed., 56 (2017) 16616-16620.

[29] B. Paul, K. Chakrabarti, S. Shee, M. Maji, A. Mishra, S. Kundu, A simple and efficient in situ generated ruthenium catalyst for chemoselective transfer hydrogenation of nitroarenes: kinetic and mechanistic studies and comparison with iridium systems, RSc Adv., 6 (2016) 100532-100545.

Graphical abstract:

Highlights

- Quinoxalines were synthesized from nitroamines using a heterogeneous Co-catalyst.
- Various imines were also synthesized from nitroarenes and alcohols.
- This catalyst was recycled up to 8th cycle.
- Green chemistry metrics calculation showed the sustainability of this protocol.
- Several kinetic experiments were performed to understand the mechanisms.