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Cobalt-Catalyzed Sustainable Synthesis of Benzimidazoles by Redox-Economical Coupling of *o*-Nitroanilines and Alcohols

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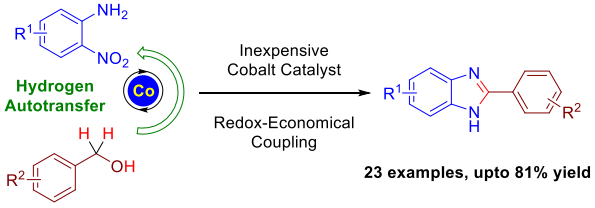


ABSTRACT: This study reveals cobalt catalyzed sustainable synthesis of benzimidazoles by redox-economical coupling of *o*-nitroanilines and alcohols. The major advantage of this report is the use of a commercially available cheap cobalt-catalyst to produce a wide variety of 2-substituted benzimidazoles by hydrogen autotransfer without using any additional external redox reagent and costly ligand system. A thorough mechanistic insight of the reaction is proposed by performing a series of control experiments.

INTRODUCTION

Aza-heterocycles are structurally important building blocks in pharmaceuticals, agrochemicals and materials chemistry.[1] Among them, benzimidazole and it's derivatives are the crucial structural motif for the pharmaceutical manufacturing, due to their potent bio-activities such as antiviral, antifungal, antiulcer, anticancer, antihelmintic activity etc.[2] Numerous essential medicines like omeprazole, astemizole telmisartan etc. and several important drugs that show prominent action against the treatment of viruses such as HIV, or influenza comprise the benzimidazole scaffold in the molecule (Figure 1).[2a] In addition, benzimidazoles show several other applications in bulk material industries for the preparation of optical brighteners, pigments, thermostable membranes, etc.[3]

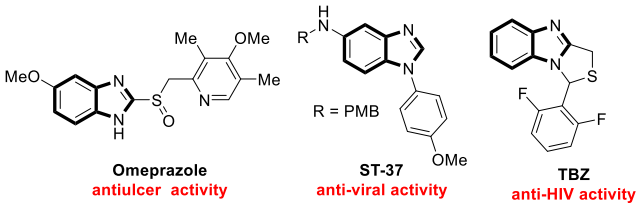
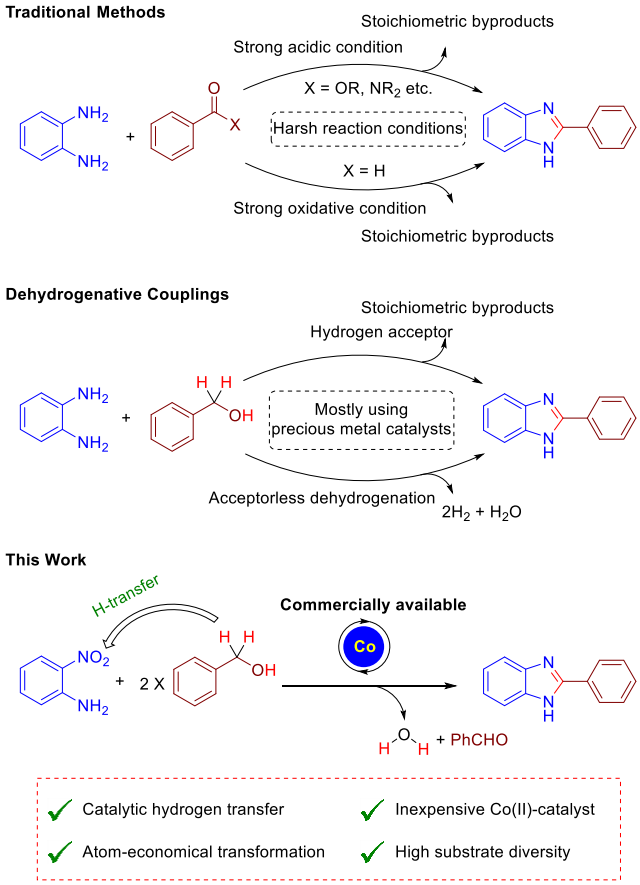


Figure 1. Therapeutically important benzimidazoles.

Due to the important pharmaceutical activities and other industrial applications, immense attention has been paid for the synthesis of substituted benzimidazole molecules.[4] Classically, two general methods are reported which comprise the reaction of substituted *o*-phenylenediamines with carboxylic acid derivatives at high temperature and under



Scheme 1. Methods for the synthesis of benzimidazoles.

strong acidic conditions (Scheme 1).[5] The second method involves the use of substituted aldehydes or alcohols and *o*-phenylenediamines under oxidative reaction conditions.[6] Both these approaches, although widely applied, suffer from the limited functional group tolerance and generation of stoichiometric quantities of waste, from the leaving groups, oxidants, additives etc.

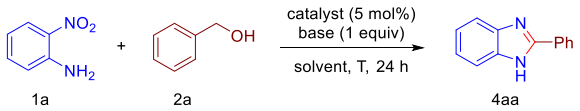
To circumvent the issues mentioned above, sustainable protocols for the synthesis of benzimidazoles from renewable materials are on high demand. Precious metal catalyzed activation of abundantly available alcohols by hydrogen transfer to a suitable hydrogen acceptor[7] or acceptorless dehydrogenation,[8] offers practical route for the synthesis of benzimidazoles (Scheme 1).[9] Even though major developments have been reported in this field using noble metals, the current trend has flitted towards the utilization of earth-abundant, non-precious base metals.[10] In this context, different catalysts based on first-row transition metals were also employed in the synthesis of benzimidazole by acceptorless dehydrogenation of alcohols.[11]

Apart from aromatic diamines which are prone to aerial oxidation, more stable *o*-nitroanilines has been studied as viable starting material for the synthesis of benzimidazole derivatives using different precious metal catalysts.[12] Iron catalysts have been used in the redox condensation of *o*-substituted nitrobenzenes with alkylamines or alcohols, to form 2-arylbenzimidazoles by using sulfur derivatives as an external reductant.[13] Cobalt bromide was used as a catalyst for the synthesis of benzimidazoles by reduction of nitrobenzenes, however less abundant benzylamines were used as the reductant cum coupling partner.[14] Recently, a cobalt nanoparticle based heterogenous catalytic system was reported for the synthesis of amines and imines including a single example of benzimidazole by reductive coupling of nitroarenes with alcohols.[15] It is evident that even though several protocols based on first-row transition metals are reported for the preparation of benzimidazoles, but in most of the cases decorative ligand framework is required, which makes the overall protocol expensive. Thus, an environmentally benign and economical route to the synthesis of benzimidazoles is still highly desirable. Herein, we report the aforesaid reaction, catalyzed by commercially available $Co(acac)_2$, to selectively produce 2-substituted benzimidazoles by transfer hydrogenation without using any external redox reagent and costly ligand system.

RESULTS AND DISCUSSION

We began the optimization study by treating 2-nitroaniline **1**a (1.0 equiv) and benzyl alcohol **2a** (2.0 equiv) in various solvents at 135 °C for 24 h in presence of different metal catalysts (5 mol%) and NaO^{t}Bu (1.0 equiv) under an argon atmosphere (Table 1). Reactions were performed in a closed vial which enforces the oxidation of alcohol and reduction of nitro by hydrogen transfer process without using any external redox reagent. The first reaction in toluene using $Co(acac)_2$ (**3**) as catalyst provided 60% isolated yield of the targeted benzimidazole **4aa** (entry 1). The metal catalyst was found to be necessary as only a trace amount of **4aa** was detected in the absence of **3**. More polar solvents like DMF was ineffective; however, 1,4-dioxane was found to be optimum for this reaction (entry 4).

Table 1. Optimization of the reaction conditions[a]



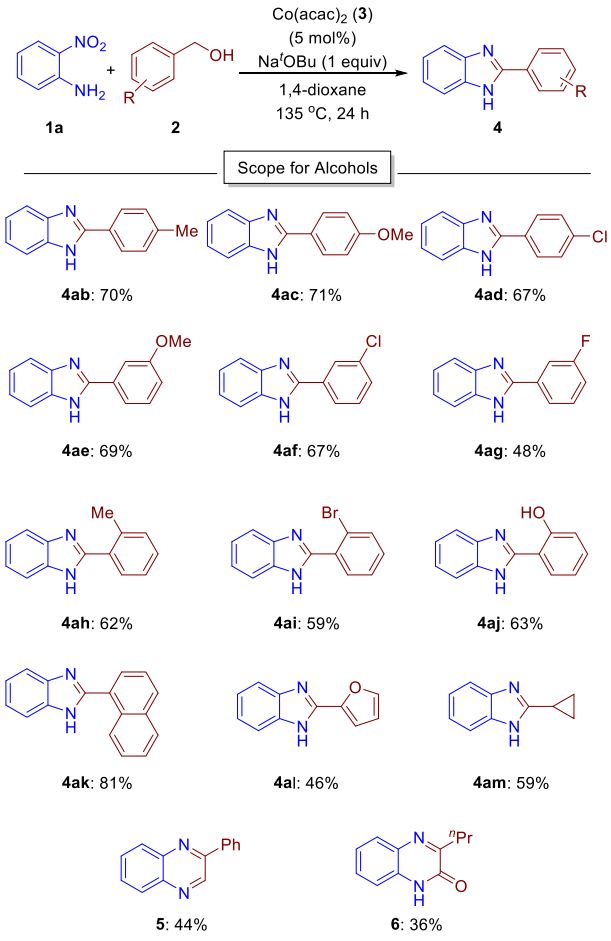
1a 2a 4aa

Sl No.	Catalyst	Base	T [^{o}C]	Solvent	Yield [%][b]
1	$Co(acac)_2$	NaO^{t}Bu	135	Toluene	60
2	-	NaO^{t}Bu	135	Toluene	Trace
3	$Co(acac)_2$	NaO^{t}Bu	135	DMF	NR
4	**$Co(acac)_2$**	**NaO^{t}Bu**	**135**	**1,4-Dioxane**	**73**
5	$Co(acac)_2$	KO^{t}Bu	135	1,4-Dioxane	52
6	$Co(acac)_2$	K_3PO_4	135	1,4-Dioxane	Trace
7	$CoCl_2 \cdot 4H_2O$	NaO^{t}Bu	135	1,4-Dioxane	55
8	$NiCl_2$	NaO^{t}Bu	135	1,4-Dioxane	Trace
9	$Co(acac)_2$	NaO^{t}Bu	110	1,4-Dioxane	47
10[c]	$Co(acac)_2$	NaO^{t}Bu	135	1,4-Dioxane	40
11[d]	$Co(acac)_2$	NaO^{t}Bu	135	1,4-Dioxane	28
12[e]	$Co(acac)_2$	NaO^{t}Bu	135	1,4-Dioxane	38
13[f]	$Co(acac)_2$	NaO^{t}Bu	135	1,4-Dioxane	24
14[g]	$Co(acac)_2$	NaO^{t}Bu	135	1,4-Dioxane	72

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), $Co(acac)_2$ (5 mol%), NaO^{t}Bu (0.5 mmol) in 1,4-dioxane (2 mL), under Ar for 24 h. [b]Isolated yield. [c]Reaction time 16 h. [d]1 equivalent **2a** was used. [e]Reaction performed under air. [f]0.5 equivalent NaO^{t}Bu was used. [g]1.5 equivalent NaO^{t}Bu was used.

Further study reveals that KO^{t}Bu as a base is less effective, while the weak phosphate base was inefficient (entries 5 and 6) using the same solvent, which implies that deprotonation of the alcohol is necessary for the hydrogen transfer process. Other cobalt salts like $CoCl_2.4H_2O$ also catalyzes the process with lesser yield, but $NiCl_2$ was found to be completely unproductive (entries 7 and 8). Lowering the temperature or reaction time had a negative impact on the reaction and lower yield of **4aa** was obtained. Second equivalent of alcohol was found to be necessary for the complete reduction of the nitro group (entry 11). Diminished yield was obtained when the reaction was performed under air (entry 12). This is most likely due to the interruption by the molecular oxygen in the hydrogen transfer from alcohol to nitro group. Finally, the amount of base was varied and equimolar quantity with respect to 2-nitroaniline was found to be optimum.

Table 2. Substrate scope using *o*-nitroaniline and various alcohols[a,b]

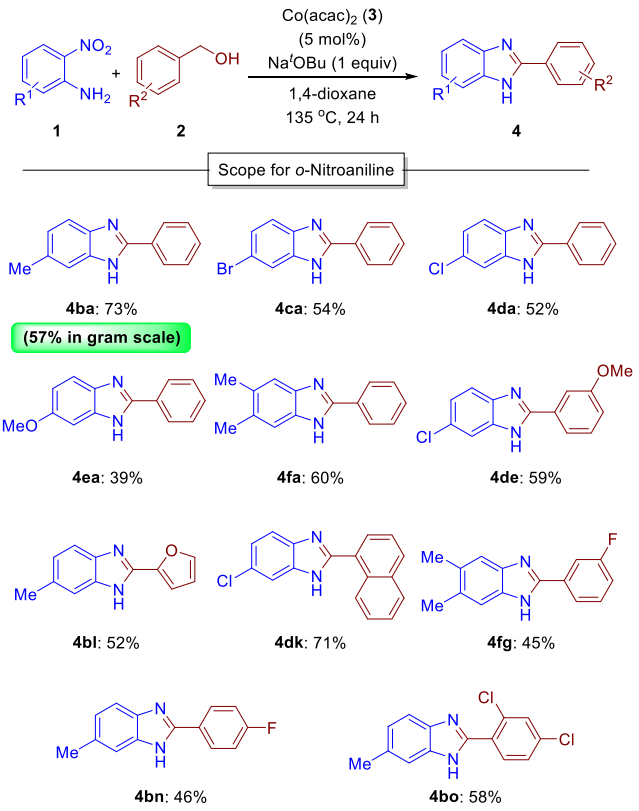


[a]Reaction conditions: **1a** (0.5 mmol), **2** (1.0 mmol), $Co(acac)_2$ (5 mol%), NaO^tBu (0.5 mmol) in 1,4-dioxane (2 mL), under Ar for 24 h. [b]Isolated yield.

The scope of different alcohols in the annulation reaction was investivated under optimized reaction condition (Table 2). Electron-rich 4-methyl or 4-methoxy substituted alcohols (**2b** and **2c**) underwent smooth conversion to the corresponding benzimidazole products in good yields. 4-Chlorobenzyl alcohol (**2d**) was also a competent substrate for the targeted heterocycle synthesis. Good yields were achieved for 3-methoxybenzyl alcohol (**2e**) and 3-chlorobenzyl alcohol (**2f**). However, comparatively lesser yield was obtained with 3-fluorobenzyl alcohol (**2g**). We were pleased to observe that sterically more demanding 2-substituted benzyl alcohols were also suitable substrates for the cyclization reaction. Both 2-methyl and 2-bromobenzyl alcohols offered decent yields of the benzimidazole products (**4ah** and **4ai**) without any detectable dehalogenation. Notably, free phenolic OH group in **2j** was also found to be compatible under the reaction condition. *α*-Naphthyl substituted benzimidazole **4ak** was synthesized in excellent yield. Biheteroaryl **4al** was synthesized from corresponding coupling partners in moderate yield. Lastly, the aliphatic alcohol **2m** underwent annulation with **1a** retaining of the strained cyclopropyl ring. Surprisingly, in case of other aliphatic alcohols, formation of six membered heterocycles were observed. 2-Phenyl ethanol provided 2-phenylquinoxaline **5**. Whereas, quinoxalinone derivative (**6**) was formed with *n*-pentanol in moderate yield.

Next, we studied the scope of several 2-nitroanilines in the redox-mediated annulation reaction (Table 3). Notably, because of the fast tautomerization in the benzimidazole **4**, both 4- and 5-substituted 2-nitroaniline derivatives yielded identical products. A good yield of the benzimidazole **4ba** was obtained with methyl substitution. In the case of halogen substituted nitroanilines moderate yield was observed (**4ca** and **4da**) without any dehalogenation. Comparatively lower productivity was noticed in the case of electron rich benzimidazole **4ea**. Disubstituted nitroaniline **1f** smoothly underwent coupling with benzyl alcohol. To verify the generality, different combinations of coupling partners were tested in the annulation reaction. The reaction between **1d** and *meta*-substituted **2e** delivered the targeted product in good yield. Similar efficiency was observed in the case of **4bl**, **4dk**, and **4fg**. Finally, 4-methyl-2-nitroaniline was tested in combination with two different alcohols and moderate to good yields (**4bn** and **4bo**) were obtained.

Table 3. Substrate scope using *o*-nitroaniline derivatives and various alcohols[a,b]

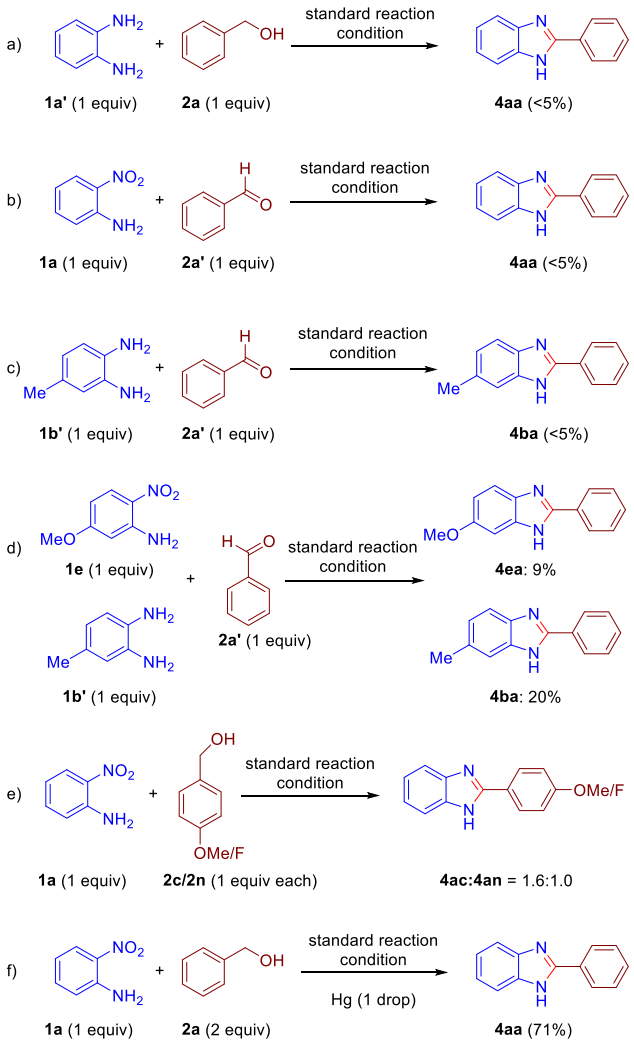


[a]Reaction conditions: **1** (0.5 mmol), **2** (1.0 mmol), $Co(acac)_2$ (5 mol%), NaO^tBu (0.5 mmol) in 1,4-dioxane (2 mL), under Ar for 24 h. [b]Isolated yield.

Several control experiments were performed to inspect the mechanism of the hydrogen transfer process. *o*-Phenylenediamine (**1a'**) was treated with benzyl alcohol under standard reaction condition (Scheme 2a), product formation was completely shut down in the absence of the hydrogen acceptor nitro functionality. Similarly, the nitro reduction didn't

occur in the absence of the hydrogen donor alcohol thus didn't lead to any detectable benzimidazole product when aldehyde **2a'** was used instead of the alcohol **2a** (Scheme 2b). Notably, only a trace amount of **4aa** was detected when pre-reduced **1b'** was reacted with pre-oxidized **2a'** under standard reaction condition (Scheme 2c). This result indicated the necessity of the hydrogen acceptor nitro group not only for the oxidation of the alcohol but also for the final oxidative aromatization of intermediate **4aa'** to form **4aa** (Scheme 3). Very interestingly, the same diamine **1b'** produced a significant amount of benzimidazole **4ba** in the presence of **1e** which acts as the hydrogen acceptor (Scheme 2d). After reduction, the corresponding diamine of **1e** also takes part in the annulation and generates **4ea**. Finally, the electronic effect in the alcohol partner was tested, and preference for the electron-rich **2c** was observed (Scheme 2e). This result indicates a faster oxidation rate by stabilization of the transition state during hydride transfer in the electron-rich system. Finally, smooth formation of benzimidazole (**4aa**) in presence of mercury drop discards the catalysis by the formation of heterogeneous cobalt nanoparticles (Scheme 2f).

Scheme 2. Mechanistic studies.



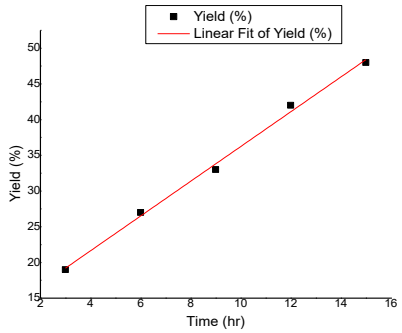
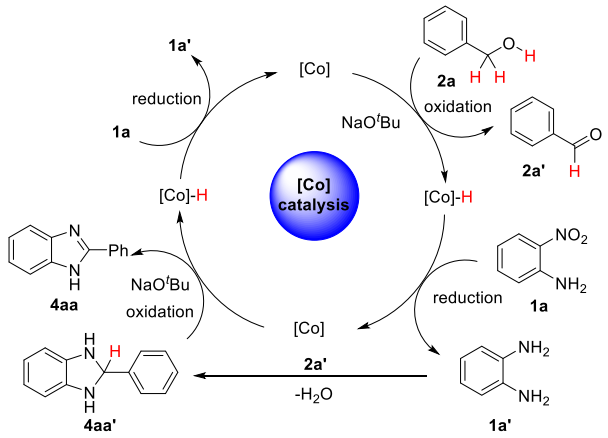


Figure 2. Kinetic plot for the cobalt catalyzed synthesis of benzimidazole **4ba**.

A quantitative analysis on the progress of the reaction was studied (Fig 2). The time dependent product formation exhibited a linear growth with increasing the reaction time. Careful analysis of the crude reaction mixture reveals that apart from the desired benzimidazole, the intermediate products like *o*-phenylenediamine **1a'**, aldehyde (**2a'**) and corresponding imine are present in the mixture. Based on these studies, the plausible mechanism of the hydrogen transfer and cyclization process is depicted in scheme 3. Base assisted oxidation of alcohol **2a** leads to aldehyde **2a'** and [Co]-H intermediate, which reduces the nitroaniline to diamine **1a'**. Condensation between **1a'** and **2a'** produces the dihydro-benzimidazole **4aa'** which upon oxidative aromatization delivered the product **4aa**. Notably, three equivalents of hydride are required to reduce the nitro functionality. Two of those are generating from the oxidation of excess alcohol, and the third equivalent is coming from the final dehydrogenation of **4aa'** to balance the stoichiometry.

Scheme 3. Proposed mechanism.



CONCLUSION

In summary, a cobalt catalyzed practical synthesis of benzimidazoles by the redox-economical coupling of *o*-nitroanilines and alcohols is reported. The developed hydrogen autotransfer process allows the reduction of nitro and oxidation of alcohol functionality, thus doesn't require any external redox reagent. The main highlight of this approach is the direct use of commercially available cheap $Co(acac)_2$ as catalyst without any additional ligand system. This procedure exhibits a sustainable and versatile synthetic method

which has the potential for further process developments using earth-abundant base metal catalysts.

EXPERIMENTAL SECTION

General Information. Catalytic reactions were performed under an argon atmosphere using pre-dried glassware and standard sealed tubes. 1,4-Dioxane was dried with calcium hydride and freshly distilled under argon. All substituted *o*-nitroanilines (**1a**–**1f**) and alcohols (**2a**–**2m**) were obtained from commercial sources and were used without further purification. Yields refer to isolated compounds, estimated to be >95% pure as determined by ^{1}H NMR. Thin-layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F254 aluminum sheets with detection under UV light at 254 nm. Chromatographic separations were carried out on chempure silica gel (100–200 mesh). Melting points (mp) were taken on a Labtronics LT-110 capillary melting point apparatus. Nuclear magnetic resonance (NMR) spectroscopy was performed using JEOL 400 MHz and Bruker 500 MHz spectrometers and HRMS was performed on Bruker Maxis Impact mass spectrometer (TOF). If not otherwise specified, chemical shifts (δ) are provided in ppm.

Procedure for Optimization Study (Table 1):

o-Nitroaniline (**1a**) (0.50 mmol, 1.0 equiv), phenylmethanol (**2a**) (1.0 mmol, 2 equiv), metal catalyst (5 mol%), and base (0.50 mmol, 1 equiv) were placed in a pre-dried 15 mL sealed tube. The tube was degassed and purged with argon three times. Then solvent (2.0 mL) was added, and the mixture was stirred at (110-135) °C in an oil bath for (16-24) h. At ambient temperature, EtOAc (8 mL) was added, and the reaction mixture was washed with brine (5 mL), dried over sodium sulfate, concentrated under a vacuum, and purified by silica gel column chromatography using 15% ethyl acetate in hexanes to get 2-phenyl-1*H*-benzo[*d*]imidazole (**4aa**) (40-73)% as an isolated product.

General Procedure for Cobalt catalyzed Synthesis of Benzimidazoles (GP):

o-Nitroaniline derivatives **1** (0.50 mmol, 1.0 equiv), substituted benzyl alcohols **2** (1.0 mmol, 2 equiv), $Co(acac)_2$ (**3**) (6.5 mg, 5 mol%), and NaO^{t}Bu (48 mg, 0.50 mmol, 1 equiv) were placed in a pre-dried 15 mL sealed tube. The tube was degassed and purged with argon three times. Then 1,4-dioxane (2.0 mL) was added, and the mixture was stirred at 135 °C in an oil bath for 24 h. At ambient temperature, EtOAc (8 mL) was added, and the reaction mixture was washed with brine (5 mL), dried over sodium sulfate, concentrated under a vacuum, and purified by silica gel column chromatography using 10–20% ethyl acetate in hexanes to deliver the benzimidazoles **4**.

2-Phenyl-1*H*-benzo[*d*]imidazole (4aa):[11a,16] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 2-nitroaniline (**1a**) (69 mg, 0.5 mmol), and phenylmethanol (**2a**) (108 mg, 1.0 mmol). After 24 h, purification by column chromatography using 15% ethyl acetate in hexanes yielded (**4aa**) (71 mg, 73%) as a white solid (mp 288-291 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.93 (br s, 1H), 8.19 (d, *J* = 7.2 Hz, 2H), 7.68 (d, *J* = 7.3 Hz, 1H), 7.59 – 7.41 (m, 4H), 7.32 – 7.12 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 151.6, 139.1, 130.7, 129.8, 129.5, 126.9, 123.0, 115.4.

2-(*p*-Tolyl)-1*H*-benzo[*d*]imidazole (4ab):[11a] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 2-nitroaniline (**1a**) (69 mg, 0.5 mmol), and *p*-tolylmethanol (**2b**) (122 mg, 1.0 mmol). After 24 h, purification by column chromatography using 14% ethyl acetate in hexanes yielded (**4ab**) (73 mg, 70%) as a white solid (mp 259-261°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 9.0 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.32 (m, 4H), 6.99 (d, *J* = 8.2 Hz, 1H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 151.3, 138.2, 130.5, 130.1, 128.8, 127.0, 123.6, 122.0, 21.1.

2-(4-Methoxyphenyl)-1*H*-benzo[*d*]imidazole (4ac):[11a] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 2-nitroaniline (**1a**) (69 mg, 0.5 mmol), and (4-methoxyphenyl)methanol (**2c**) (138 mg, 1.0 mmol). After 24 h, purification by column chromatography using 18% ethyl acetate in hexanes yielded (**4ac**) (79 mg, 71%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6) δ 8.08 (d, *J* = 7.9 Hz, 2H), 7.61 – 7.53 (m, 2H), 7.17 (m, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ + DMSO-d_6) δ 161.0, 152.1, 139.0, 128.4, 122.8, 122.2, 115.0, 114.3, 55.4.

2-(4-Chlorophenyl)-1*H*-benzo[*d*]imidazole (4ad):[11a] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 2-nitroaniline (**1a**) (69 mg, 0.5 mmol), and (4-chlorophenyl)methanol (**2d**) (143 mg, 1.0 mmol). After 24 h, purification by column chromatography using 18% ethyl acetate in hexanes yielded (**4ad**) (77 mg, 67%) as a white solid (mp. 290-292 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.94 (br s, 1H), 8.19 (d, *J* = 8.5 Hz, 2H), 7.75 – 7.46 (m, 4H), 7.22 (dd, *J* = 6.0, 3.1 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 150.7, 135.3, 129.7, 129.1, 128.7, 123.1, 119.3, 112.1.

2-(3-Methoxyphenyl)-1*H*-benzo[*d*]imidazole (4ae):[17] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 2-nitroaniline (**1a**) (69 mg, 0.5 mmol), and (3-methoxyphenyl)methanol (**2e**) (138 mg, 1.0 mmol). After 24 h, purification by column chromatography using 18% ethyl acetate in hexanes yielded (**4ae**) (77 mg, 69%) as a brown solid (mp. 200-202 °C). ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6) δ 7.76 – 7.68 (m, 2H), 7.64 – 7.55 (m, 2H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.18 (dd, *J* = 6.0, 3.1 Hz, 2H), 6.92 (dd, *J* = 8.3, 1.9 Hz, 1H), 3.78 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ + DMSO-d_6) δ 160.0, 151.9, 138.4, 131.6, 129.9, 122.5, 119.2, 116.4, 115.2, 111.6, 55.4.

2-(3-Methoxyphenyl)-1*H*-benzo[*d*]imidazole (4af):[18] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 2-nitroaniline (**1a**) (69 mg, 0.5 mmol), and (3-chlorophenyl)methanol (**2f**) (143 mg, 1.0 mmol). After 24 h, purification by column chromatography using 18% ethyl acetate in hexanes yielded (**4af**) (66 mg, 58%) as a white solid. (mp 233-235 °C). ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6) δ 8.16 (s, 1H), 8.04 (dd, *J* = 5.6, 2.5 Hz, 1H), 7.57 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.32 (d, *J* = 4.7 Hz, 2H), 7.18 (dd, *J* = 6.0, 3.1 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ + DMSO-d_6) δ 150.5, 134.7, 132.1, 130.1, 129.6, 126.8, 125.0, 122.7, 115.4.

2-(3-Fluorophenyl)-1*H*-benzo[*d*]imidazole (4ag):[19] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 2-nitroaniline (**1a**) (69 mg, 0.5 mmol), and (3-fluorophenyl)methanol (**2g**) (126 mg, 1.0 mmol). After 24 h, purification by column chromatography using 12% ethyl

acetate in hexanes yielded (**4ag**) (51 mg, 48%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.75 (m, 2H), 7.65 (dt, *J* = 6.5, 3.3 Hz, 2H), 7.44 (td, *J* = 8.2, 6.0 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.15 (td, *J* = 8.4, 2.0 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, DMSO- d_6) δ 162.5 (d, *J* = 243.5 Hz), 150.0, 149.9, 132.5, 132.42, 131.2 (d, *J* = 8.4 Hz), 122.6 (d, *J* = 2.5 Hz), 116.7 (d, *J* = 21.1 Hz), 113.1 (d, *J* = 23.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.6 (dd, *J* = 13.7, 9.0 Hz).

2-(*o*-Tolyl)-1*H*-benzo[*d*]imidazole (4ah):[20] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 2-nitroaniline (**1a**) (69 mg, 0.5 mmol), and *o*-tolylmethanol (**2h**) (122 mg, 1.0 mmol). After 24 h, purification by column chromatography using 12% ethyl acetate in hexanes yielded (**4ah**) (65 mg, 62%) as a white solid (mp 223-224 °C). ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6) δ 7.58 – 7.47 (m, 3H), 7.30 – 7.21 (m, 2H), 7.20 – 7.11 (m, 3H), 2.50 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ + DMSO-d_6) δ 152.4, 137.0, 130.7, 130.2, 129.6, 129.1, 125.5, 121.9, 114.9, 20.4.

2-(2-Bromophenyl)-1*H*-benzo[*d*]imidazole (4ai):[20] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 2-nitroaniline (**1a**) (69 mg, 0.5 mmol), and (2-bromophenyl)methanol (**2i**) (187 mg, 1.0 mmol). After 24 h, purification by column chromatography using 12% ethyl acetate in hexanes yielded (**4ai**) (81 mg, 59%) as a white solid (mp 241-244 °C). ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO- d_6) δ 7.98 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.65 – 7.59 (m, 3H), 7.35 (dd, *J* = 11.3, 3.8 Hz, 1H), 7.24 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ + DMSO-d_6) δ 150.3, 140.6, 133.8, 132.7, 131.5, 131.0, 127.8, 122.9, 121.1, 116.4.

2-(1*H*-Benzo[*d*]imidazol-2-yl)phenol (4aj):[21] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 2-nitroaniline (**1a**) (69 mg, 0.5 mmol), and 2-(hydroxymethyl)phenol (**2j**) (124 mg, 1.0 mmol). After 24 h, purification by column chromatography using 20% ethyl acetate in hexanes yielded (**4aj**) (66 mg, 63%) as a brown solid (mp 227-228 °C). ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6) δ 12.59 (br s, 2H), 7.87 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.54 (d, *J* = 3.0 Hz, 2H), 7.30 – 7.23 (m, 1H), 7.20 (ddd, *J* = 5.9, 2.9, 1.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.88 (dd, *J* = 11.3, 4.1 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ + DMSO-d_6) δ 158.8, 152.1, 131.4, 125.8, 122.7, 122.6, 118.8, 118.7, 117.6, 112.9.

2-(Naphthalen-1-yl)-1*H*-benzo[*d*]imidazole (4ak):[11a] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 2-nitroaniline (**1a**) (69 mg, 0.5 mmol), and naphthalen-1-ylmethanol (**2k**) (158 mg, 1.0 mmol). After 24 h, purification by column chromatography using 12% ethyl acetate in hexanes yielded (**4ak**) (99 mg, 81%) as a white solid (mp. 216-218 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.93 (br s, 1H), 9.11 (d, *J* = 8.1 Hz, 1H), 8.10 (d, *J* = 8.1 Hz, 1H), 8.07 – 8.00 (m, 2H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.73 – 7.56 (m, 4H), 7.32 – 7.21 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 151.4, 143.9, 134.5, 133.6, 130.5, 130.2, 128.4, 127.9, 127.5, 127.1, 126.4, 125.3, 122.7, 121.6, 119.1, 111.4.

2-(Furan-2-yl)-1*H*-benzo[*d*]imidazole (4al):[22] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 2-nitroaniline (**1a**) (69 mg, 0.5 mmol), and furan-2-ylmethanol (**2l**) (98 mg, 1.0 mmol). After 24 h, purification by column chromatography using 12% ethyl acetate in hexanes yielded (**4al**) (42 mg, 46%) as a pale yellow solid (mp. 284-286 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 5.9, 3.2 Hz, 2H), 7.54 (d, *J* = 1.3 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.23 (d, *J* = 3.5 Hz, 1H), 6.58 (dd, *J* = 3.6, 1.7 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 151.3, 143.8, 135.0, 130.2, 129.9, 129.0, 126.5, 122.6, 121.7, 118.9, 111.4.

2-Cyclopropyl-1*H*-benzo[*d*]imidazole (4am):[23] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 2-nitroaniline (**1a**) (69 mg, 0.5 mmol), and cyclopropylmethanol (**2m**) (72 mg, 1.0 mmol). After 24 h, purification by column chromatography using 10% ethyl acetate in hexanes yielded (**4am**) (47 mg, 59%) as a white solid (mp 227-229°C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.12 (br s, 1H), 7.44 – 7.35 (m, 2H), 7.12 – 7.02 (m, 2H), 2.09 (tt, *J* = 8.1, 5.2 Hz, 1H), 1.03 (ddd, *J* = 9.2, 5.4, 2.4 Hz, 4H). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ 156.9, 120.9, 120.8, 114.1, 9.37, 8.6.

2-Phenylquinoxaline (5):[24] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 2-nitroaniline (**1a)** (69 mg, 0.5 mmol), and 2-phenylethan-1-ol (122 mg, 1.0 mmol). After 24 h, purification by column chromatography using 5% ethyl acetate in hexanes yielded (**5)** (45 mg, 44%) as a yellow solid (mp 80-82 °C): ^{1}H NMR (400 MHz,$CDCl_3$) δ 9.34 (s, 1H), 8.22 – 8.08 (m, 4H), 7.85 – 7.73 (m, 2H), 7.65 – 7.48 (m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.0, 143.5, 142.5, 141.7, 136.9, 130.5, 130.4, 129.8, 129.7, 129.3, 127.7.

3-Propylquinoxalin-2(1H)-one (6):[25] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 2-nitroaniline (**1a)** (69 mg, 0.5 mmol), and butan-1-ol (75mg, 1.0 mmol). After 24 h, purification by column chromatography using 10% ethyl acetate in hexanes yielded (**6)** (34 mg, 36%) as a white solid (mp 183-185 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.56 (s, 1H), 7.85 – 7.81 (m, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.36 – 7.28 (m, 2H), 2.98 – 2.94 (m, 2H), 1.89 – 1.80 (m, 2H), 1.08 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 161.9, 156.4, 133.0, 131.0, 129.8, 128.9, 124.3, 115.6, 35.6, 20.4, 14.2.

6-Methyl-2-phenyl-1*H*-benzo[*d*]imidazole (4ba):[11a] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 4-methyl-2-nitroaniline (**1b**) (76 mg, 0.5 mmol), and phenylmethanol (**2a**) (108 mg, 1.0 mmol). After 24 h, purification by column chromatography using 12% ethyl acetate in hexanes yielded (**4ba**) (76 mg, 73%) as a pale yellow solid (mp 243-244 °C). ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6) δ 8.16 – 7.98 (m, 2H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.44 – 7.37 (m, 4H), 7.08 (dd, *J* = 8.3, 0.9 Hz, 1H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ + DMSO-d_6) δ 152.7, 138.8, 137.4, 131.0, 130.6, 130.0, 129.4, 125.8, 122.2, 115.2, 20.7.

Gram Scale Synthesis of 4ba: 4-methyl-2-nitroaniline (**1b)** (1 gm, 6.58 mmol), and phenylmethanol (**2a)** (1.42 gm, 13.16 mmol) $Co(acac)_2$ (**3**) (85 mg, 5 mol%), and base (632 mg, 6.58 mmol, 1 equiv) were placed in a pre-dried 150 mL sealed tube. The tube was degassed and purged with argon three times. Then solvent (27 mL) was added, and the mixture was stirred at 135 °C in an oil bath for 24 h. After completion of the reaction the solvent was evaporated and concentrated under a vacuum, and purified by silica gel column chromatography using 15% ethyl acetate in hexanes to obtain 6-methyl-2-phenyl-1*H*-benzo[*d*]imidazole (**4ba**) (780 mg, 57%) as an isolated product.

6-Bromo-2-phenyl-1*H*-benzo[*d*]imidazole (4ca):[22] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 4-bromo-2-nitroaniline (**1c**) (108 mg, 0.5 mmol), and phenylmethanol (**2a**) (108 mg, 1.0 mmol). After 24 h, purification by column chromatography using 10% ethyl acetate in hexanes yielded (**4ca**) (74 mg, 54%) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6) δ 8.11 (dd, *J* = 4.2, 2.6 Hz, 2H), 7.68 (s, 1H), 7.46 – 7.36 (m, 4H), 7.31 – 7.18 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ + DMSO-d_6) δ 153.2, 140.4, 138.5, 130.3, 129.7, 129.0, 127.0, 125.7, 117.9, 116.5, 115.5.

6-Chloro-2-phenyl-1*H*-benzo[*d*]imidazole (4da):[26] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 4-chloro-2-nitroaniline (**1d**) (86 mg, 0.5 mmol), and phenylmethanol (**2a**) (108 mg, 1.0 mmol). After 24 h, purification by as a solid (mp 212-214 °C). column chromatography using 10% ethyl acetate in hexanes yielded (**4da**) (60 mg, 52%).^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6) δ 8.10 (dd, *J* = 6.5, 2.5 Hz, 2H), 7.53 (d, *J* = 1.3 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.42 – 7.36 (m, 3H), 7.13 (dd, *J* = 8.5, 1.6 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ + DMSO-d_6) δ 153.2, 130.2, 129.8, 129.2, 128.9, 128.7, 127.9, 126.9, 123.0, 116.1, 114.8.

6-Methoxy-2-phenyl-1*H*-benzo[*d*]imidazole (4ea):[22] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 4-methoxy-2-nitroaniline (**1e**) (84 mg, 0.5 mmol), and phenylmethanol (**2a**) (108 mg, 1.0 mmol). After 24 h, purification by column chromatography using 20% ethyl acetate in hexanes yielded (**4ea**) (44 mg, 39%) as a white solid. (mp 146-147°C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 1H), 7.38 – 7.34 (m, 3H), 6.99 (d, *J* = 2.3 Hz, 1H), 6.85 (dd, *J* = 8.9, 2.4 Hz, 1H), 3.73 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 156.9, 151.8, 139.1, 134.1, 130.1, 129.8, 129.2, 126.7, 116.2, 112.8, 97.5, 55.9.

5,6-Dimethyl-2-phenyl-1*H*-benzo[*d*]imidazole (4fa):[22] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 4,5-dimethyl-2-nitroaniline (**1f**) (83 mg, 0.5 mmol), and phenylmethanol (**2a**) (108 mg, 1.0 mmol). After 24 h, purification by column chromatography using 20% ethyl acetate in hexanes yielded (**4fa**) (67 mg, 60%) as a white solid. (mp 249-252°C). ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6) δ 8.07 (d, *J* = 6.9 Hz, 2H), 7.42 – 7.26 (m, 5H), 2.28 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ + DMSO-d_6) δ 151.1, 145.9, 138.3, 131.3, 130.5, 129.4, 128.7, 126.6, 20.4.

6-Chloro-2-(3-methoxyphenyl)-1*H*-benzo[*d*]imidazole (4de):[27] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 4-chloro-2-nitroaniline (**1d**) (86 mg, 0.5 mmol), and (4-methoxyphenyl)methanol (**2e**) (138 mg, 1.0 mmol). After 24 h, purification by column chromatography using 20% ethyl acetate in hexanes yielded (**4de**) (76 mg, 59%) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.61 (m, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 1.9 Hz, 1H), 7.48 (d, *J* = 8.6 Hz, 1H), 7.30 (dd, *J* = 10.1, 5.8 Hz, 1H), 7.19 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.96 (dd, *J* = 8.3, 2.2 Hz, 1H), 3.68 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.3, 153.1, 139.6, 137.9, 130.6, 130.4, 128.8, 123.8, 119.0, 117.2, 116.2, 115.0, 111.7, 55.4.

2-(Furan-2-yl)-6-methyl-1*H*-benzo[*d*]imidazole (4bl):[28] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 4-methyl-2-nitroaniline (**1b**) (76 mg, 0.5 mmol), and furan-2-ylmethanol (**2l**) (98 mg, 1.0 mmol). After 24 h, purification by column chromatography using 12% ethyl acetate in hexanes yielded (**4bl**) (51 mg, 52%) as a white solid (mp 188- 192°C). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.42 (br s, 1H), 7.92 (d, *J* = 1.3 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.34 (s, 1H), 7.16 (d, *J* = 3.3 Hz, 1H), 7.02 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.71 (dd, *J* = 3.3, 1.8 Hz, 1H), 2.41 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 145.7, 144.4, 143.3, 138.4, 131.5, 131.4, 123.7, 115.0, 114.0, 112.3, 110.2, 21.3.

6-Chloro-2-(naphthalen-1-yl)-1*H*-benzo[*d*]imidazole (4dk):[29] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 4-chloro-2-nitroaniline (**1d**) (86 mg, 0.5 mmol), and naphthalen-1-ylmethanol (**2k**) (158 mg, 1.0 mmol) After 24 h, purification by column chromatography using 20% ethyl acetate in hexanes yielded (**4dk**) (99 mg, 71%) as a pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6) δ 8.51 (dd, *J* = 9.8, 6.6 Hz, 1H), 7.79 – 7.67 (m, 2H), 7.62 (t, *J* = 7.2 Hz, 1H), 7.44 – 7.23 (m, 5H), 7.02 (dt, *J* = 8.8, 4.2 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ + DMSO-d_6) δ 152.8, 139.7, 137.7, 133.4, 130.8, 130.1, 128.0, 127.9, 127.6, 127.3, 126.8, 126.0, 125.7, 124.6, 122.4, 115.8, 114.7.

2-(3-Fluorophenyl)-5,6-dimethyl-1*H*-benzo[*d*]imidazole (4fg): GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 4,5-dimethyl-2-nitroaniline (**1f**) (83 mg, 0.5 mmol), and (3-fluorophenyl)methanol (**2g**) (126 mg, 1.0 mmol). After 24 h, purification by column chromatography using 12% ethyl acetate in hexanes yielded (**4fg**) (54 mg, 45%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.70 (br s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 10.2 Hz, 1H), 7.53 (dd, *J* = 14.1, 8.0 Hz, 1H), 7.39 (s, 1H), 7.25 (td, *J* = 8.6, 2.4 Hz, 2H), 2.28 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 163.0 (d, *J* = 243.3 Hz), 149.6, 134.0, 133.3 (d, *J* = 8.4 Hz), 131.6 (d, *J* = 8.5 Hz), 122.8 (d, *J* = 2.3 Hz), 119.5, 116.7 (d, *J* = 21.2 Hz), 113.2 (d, *J* = 23.6 Hz), 112, 20.5. ^{19}F NMR (376 MHz, DMSO-d_6) δ -112.4 (td, *J* = 9.4, 6.6 Hz). HRMS (ESI) m/z calculated for $C_{15}H_{13}FN_2H$ $[M+H]^+$ 241.1136, found 241.1139.

2-(4-Fluorophenyl)-6-methyl-1*H*-benzo[*d*]imidazole (4bn):[30] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 4-methyl-2-nitroaniline (**1b**) (76 mg, 0.5 mmol), and (4-fluorophenyl)methanol (**2n**) (126 mg, 1.0 mmol)After 24 h, purification by column chromatography using 20% ethyl acetate in hexanes yielded (**4bn**) (52 mg, 46%) as a white solid (mp 180-182 °C). ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO-d_6) δ 8.08 (dd, *J* = 8.3, 5.5 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.31 (s, 1H), 7.13 – 6.84 (m, 3H), 2.39 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ + DMSO- d_6) δ 163.6 (d, *J* = 249.8 Hz), 151.0, 132.4, 128.6 (d, *J* = 8.4 Hz), 126.7, 126.6, 124.1, 115.8 (d, *J* = 21.8 Hz), 115.1, 114.4, 99.9, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.8 (m).

2-(2,4-Dichlorophenyl)-6-methyl-1*H*-benzo[*d*]imidazole (4bo):[31] GP was followed using cobalt catalyst (**3**) (6.5 mg, 5.0 mol%), 4-methyl-2-nitroaniline (**1b**) (76 mg, 0.5 mmol), and (2,4-dichlorophenyl)methanol (**2o**) (177 mg, 1.0 mmol). After 24 h, purification by column chromatography using 12% ethyl acetate in hexanes yielded (**4bo**) (80 mg, 58%) as a white solid (mp 103-105 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (br s, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.38 (s, 1H), 7.35 (s, 1H), 7.14 (d, *J* = 3.5 Hz, 1H), 7.03 (d, *J* = 8.6 Hz, 1H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 145.3, 143.9, 138.1, 137.0, 133.1, 130.4, 124.7, 122.7, 120.7, 115.1, 114.6, 112.4, 111.0, 21.8.

Procedure of Control Experiments (Scheme 2):

Procedure of Scheme 2a: *o*-Phenylenediamine (**1a'**) (0.50 mmol, 1.0 equiv), phenylmethanol (**2a**) (0.5 mmol, 1 equiv), cobalt catalyst (**3**) (6.5 mg, 5 mol%), and NaO^{t}Bu (48 mg, 0.50 mmol, 1 equiv) were placed in a pre-dried 15 mL sealed tube. The tube was degassed and purged with argon three times. Then 1,4-dioxane (2.0 mL) was added, and the mixture was stirred at 135 °C in an oil bath for 24 h. At ambient temperature, EtOAc (8 mL) was added, and the reaction mixture was washed with brine (5 mL), dried over sodium sulfate, concentrated under a vacuum, and the crude mixture was carefully analyzed by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard (**4aa** yield <5%).

Procedure of Scheme 2b: *o*-Nitroaniline (**1a**) (0.50 mmol, 1.0 equiv), benzaldehyde (**2a'**) (0.5 mmol, 1.0 equiv), cobalt catalyst (3) (6.5 mg, 5 mol%), and NaO^{t}Bu (48 mg, 0.50 mmol, 1 equiv) were placed in a pre-dried 15 mL sealed tube. The tube was degassed and purged with argon three times. Then 1,4-dioxane (2.0 mL) was added, and the mixture was stirred at 135 °C in an oil bath for 24 h. At ambient temperature, EtOAc (8 mL) was added, and the reaction mixture was washed with brine (5 mL), dried over sodium sulfate, concentrated under a vacuum, and the crude mixture was carefully analyzed by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard (**4aa** yield <5%).

Procedure of Scheme 2c: 4-methylbenzene-1,2-diamine (**1b'**) (0.50 mmol, 1.0 equiv), benzaldehyde (**2a'**) (0.5 mmol, 1.0 equiv), cobalt catalyst (3) (6.5 mg, 5 mol%), and NaO^{t}Bu (48 mg, 0.50 mmol, 1 equiv) were placed in a pre-dried 15 mL sealed tube. The tube was degassed and purged with argon three times. Then 1,4-dioxane (2.0 mL) was added, and the mixture was stirred at 135 °C in an oil bath for 24 h. At ambient temperature, EtOAc (8 mL) was added, and the reaction mixture was washed with brine (5 mL), dried over sodium sulfate, concentrated under a vacuum, and the crude mixture was carefully analyzed by ^{1}H NMR using 1,1,2,2-tetrachloroethane as an internal standard (**4ba** yield <5%).

Procedure of Scheme 2d: 4-methylbenzene-1,2-diamine (**1b'**) (0.50 mmol, 1.0 equiv), 5-methoxy-2-nitroaniline (**1e**) (0.50 mmol, 1.0 equiv) and benzaldehyde (**2a'**) (0.5 mmol, 1.0 equiv), cobalt catalyst (**3**) (6.5 mg, 5 mol%), and NaO^{t}Bu (48 mg, 0.50 mmol, 1 equiv) were placed in a pre-dried 15 mL sealed tube. The tube was degassed and purged with argon three times. Then 1,4-dioxane (2.0 mL) was added, and the mixture was stirred at 135 °C in an oil bath for 24 h. At ambient temperature, EtOAc (8 mL) was added, and the reaction mixture was washed with brine (5 mL), dried over sodium sulfate, concentrated under a vacuum, and careful analysis of the crude mixture by ^{1}H NMR (using 1,1,2,2-tetrachloroethane as an internal standard) revealed yield of **4ea** = 9% and **4ba** = 20%.

Procedure of Scheme 2e: *o*-Nitroaniline (**1a**) (0.50 mmol, 1.0 equiv), (4-methoxyphenyl)methanol (**2c**) (0.5 mmol, 1.0 equiv) and (4-fluorophenyl)methanol (**2n**) (0.5 mmol, 1.0 equiv), cobalt catalyst (**3**) (6.5 mg, 5 mol%), and NaO^{t}Bu (48 mg, 0.50 mmol, 1 equiv) were placed in a pre-dried 15 mL sealed tube. The tube was degassed and purged with argon three times. Then 1,4-dioxane (2.0 mL) was added, and the mixture was stirred at 135 °C in an oil bath for 24 h. At ambient temperature, EtOAc (8 mL) was added, and the reaction mixture was washed with brine (5 mL), dried over sodium sulfate, concentrated under a vacuum, and careful analysis of the crude mixture by ^{1}H NMR revealed the ratio of **4ac:4an** = 1.6:1.0.

Procedure of Scheme 2f (Mercury Drop Test): *o*-Nitroaniline (**1a**) (0.50 mmol, 1.0 equiv), phenylmethanol (**2a**) (1.0 mmol, 2 equiv), Co(acac)$_2$ (**3**) (6.5 mg, 5 mol%), and NaO^{t}Bu (48 mg, 0.50 mmol, 1 equiv) were placed in a pre-dried 15 mL sealed tube. The tube was degassed and purged with argon three times. Then a drop of mercury and 1,4-dioxane (2.0 mL) were added in the reaction medium under a gentle stream of argon and the mixture was stirred at 135 °C in an oil bath for 24 h. At ambient temperature, EtOAc (8 mL) was added, and the reaction mixture was filtered through a short celite pad and filtrate was washed with brine (5 mL), dried over sodium sulfate, concentrated under a vacuum, and purified by silica gel column chromatography using 20% ethyl acetate in hexanes to deliver the 2-phenyl-1H-benzo[*d*]imidazole (**4aa**) (69 mg, 71%).

Kinetic Study of Product Formation (yield vs time): To determine the time dependent progress of the reaction, 5 sets of reactions containing 4-methyl-2-nitroaniline (**1b**) (38 mg, 0.25 mmol), phenylmethanol (**2a**) (55 gm, 0.5 mmol), Co(acac)$_2$ (**3**) (3.3 mg, 5 mol%), and NaO^{t}Bu (24 mg, 0.25 mmol, 1 equiv) were placed in pre-dried 15 mL sealed tubes. The tubes were degassed and purged with argon three times. Then 1,4-dioxane (2 mL) was added in each tube, and stirred at 135 °C in an oil bath for (3-15 h). At regular interval of 3 hours, the reaction vessels were removed one by one and quenched with EtOAc (8 mL) and the solvent was evaporated and concentrated under a vacuum, and passed through a short pad silica using 20% ethyl acetate in hexanes and concentrated under a vacuum. Careful analysis of the crude mixture by ^{1}H NMR (using 1,1,2,2-tetrachloroethane as an internal standard) revealed the time dependent yield of 6-methyl-2-phenyl-1H-benzo[*d*]imidazole (**4ba**).

Sl No.	Time (hour)	Yield (%)
1	3	19
2	6	27
3	9	33
4	12	42
5	15	48

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: Copies of ^{1}H and ^{13}C{^{1}H} NMR spectra for all compounds (PDF).

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Notes

The authors declare no competing financial interest.

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