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Palladium Nanoparticles Supported on ZIF-8 As an Efficient Heterogeneous Catalyst for Aminocarbonylation

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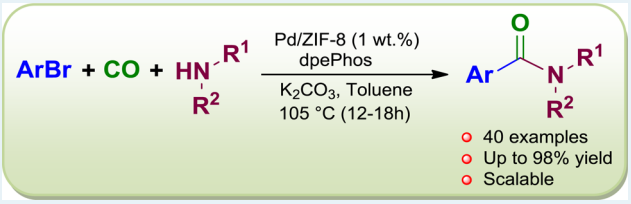
Supporting Information

ABSTRACT: Pd nanoparticles supported on ZIF-8 (PdNPs/ZIF-8) are described as an efficient heterogeneous catalyst for the aminocarbonylation of bromoarenes in the presence of phosphines and iodoarenes under phosphine-free conditions. The catalyst can be readily prepared and is air-stable. The palladium loading can be as low as 1 wt %, and the catalyst was recycled four times with negligible change in catalytic performance. A variety of pharmaceutically important amides was readily synthesized. A TON of 2540 was easily achieved in a batch reaction by scaling up to a gram scale. The catalyst reported can also be applied to the synthesis of cyclic and primary amides as well as an alkoxycarbonylation reaction to form an ester.



KEYWORDS: *aminocarbonylation, carbonylation, palladium nanoparticles, heterogeneous catalysis, ZIF-8, amide synthesis*

INTRODUCTION

Amide bond formation is one of the most important transformations in organic synthesis as well as in the chemical and pharmaceutical industries.[1] Its ever-demanding simple synthesis by the atom-efficient direct coupling of carboxylic acids with amines generally requires drastic conditions that are quite often not compatible with several functional groups or with less stable molecules.[2] To facilitate the coupling under mild conditions, high-molecular-weight coupling agents or derivatives of carboxylic acids are often used, which results in generating large amounts of waste that need to be addressed for large-scale industrial applications.[3] To address this problem, several atom-economical approaches for amide synthesis have been developed using alcohols and aldehydes as starting materials under oxidative conditions.[4] Another convenient method is aminocarbonylation, in which the required carbonyl functional group is generated catalytically in situ from readily available organic halides and carbon monoxide and are directly reacted with the amine to form the desired amide product.[5]

Aryl iodides are generally the substrate of choice in aminocarbonylation, and quantitative yields were reported in the presence of various homogeneous catalysts derived from palladium salts with or without phosphine ligands at temperatures in the range of 50−130 °C and 1−10 atm of carbon monoxide pressure.[5d−j] The corresponding less expensive aryl bromides are more attractive substrates, but the reaction often requires harsher conditions or tailor-made ligands.[6] For example, an atmospheric pressure aminocarbonylation was reported by Buchwald and co-workers using $Pd(OAc)_2$ in the presence of Xantphos ligand at 80−120 °C for the synthesis of a variety of Weinreb amides from aryl bromides.[6f] Another example was reported by Beller and co-workers using CataCXium A as the ligand for primary amide synthesis at 80−130 °C and 2 bar CO pressure from various substituted aryl bromides and heteroaryl bromides.[6e] Recently, palladium-based homogeneous catalysts were also reported for substrates such as benzyl chlorides and aryl chlorides.[7] Although these homogeneous palladium catalysts offer high selectivity and yields under relatively mild operating conditions, their industrial applicability is limited by the inherent problem of catalyst separation from the product and its recycle.[8] Moreover, the palladium residues in the product stream could be a serious issue in the pharmaceutical industry.[8]

In an attempt to address such limitations, Csajagi and co-workers reported a supported $Pd(PPh)_4$ catalyst that provided amide products up to 81% yield at 100 °C and 30 bar pressure under continuous flow mode using aryl iodides as the substrates.[9] In the case of aryl bromides, only 2-pyridyl bromides were reported with a moderate yield of 56%. Petricci and co-workers described microwave-assisted aminocarbonylation of aryl iodides in the presence of a Pd/C (palladium on charcoal) catalyst at 10 bar and 130 °C;[10] however, the less expensive aryl bromides are more challenging substrates for heterogeneous catalysts, and no efficient aminocarbonylation has been reported so far with it.

In our effort to develop promising catalysts for potential industrial applications, recently we reported Pd nanoparticles supported on MOF-5 (Pd/MOF-5) having low levels of

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palladium loading as a recyclable catalyst for the aminocarbonylation of aryl iodides under atmospheric pressure of carbon monoxide achieving quantitative yields of the corresponding amide products.[11] Although excellent yields were achieved for a variety of substrates, including heteroaryl compounds, this catalyst needs special handling because MOF-5 is moisture-sensitive, and structural changes occurred that negatively affect the catalytic performance.[11] Herein, we report air- and moisture-stable Pd nanoparticles supported on ZIF-8 (zeolitic imidazole framework)[12] as a robust and efficient catalyst for the aminocarbonylation of both aryl bromides and iodides under relatively mild operating conditions.

The advantage of using ZIF-8 as the support is due to its high surface area, easy preparation, stability in water, and its high temperature tolerance, even in the presence of methanol and acids/bases.[12] Its application as an efficient catalyst support has been demonstrated recently for various reactions, such as AuNPs-catalyzed oxidation of CO, NiNPs-catalyzed hydrolysis of ammonia borane, and IrNPs-catalyzed hydrogenation.[13,14]

RESULTS AND DISCUSSION

The Pd/ZIF-8 catalyst was easily prepared with PVA[15] as stabilizer and hydrazine as the reductant (see the Supporting Information (SI)). The morphology of ZIF-8 and Pd/ZIF-8 samples was characterized by XRD, BET and Langmuir surface area, SEM, TEM, and IR methods. The XRD patterns for ZIF-8 and Pd/ZIF-8 showed no difference between the samples. The sharp peaks showed good crystallinity of ZIF-8 (see the SI). The N_2 adsorption isotherm measurement indicated that the ZIF-8 material has a BET-specific surface area of 1303 $m^2\ g^{-1}$ and Langmuir surface area of 1789 $m^2\ g^{-1}$ and no significant change observed upon incorporation of Pd nanoparticles. SEM images also support the conclusion that no significant changes in the surface morphology occurred upon preparation of supported Pd on ZIF-8 (Figure 1A, B). The TEM images showed that Pd nanoparticles exist as dark-gray areas ranging from 4 to 9 nm, which are easily recognized from the surrounding light-gray background of ZIF-8 (Figure 1C, D). The Pd nanoparticles were well dispersed on the external surface of the ZIF-8 and no obvious aggregation was observed with samples having low palladium loadings of 1 wt %.

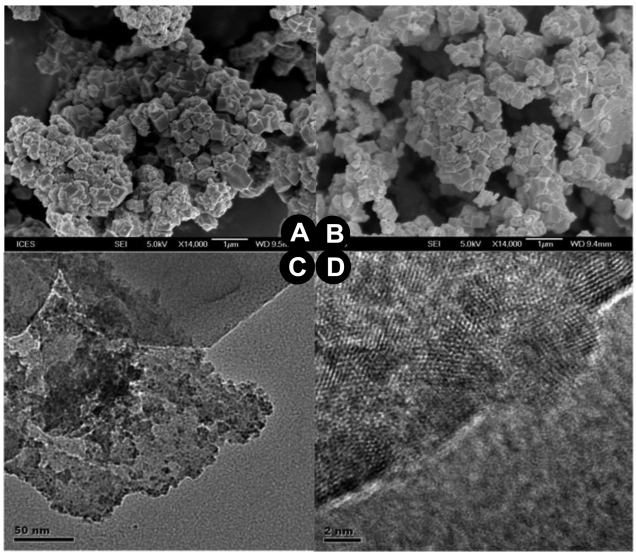
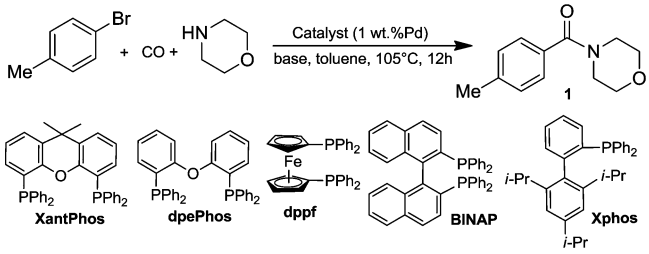


Figure 1. SEM images of (A) ZIF-8 and (B) Pd/ZIF-8 and (C, D) TEM images of Pd/ZIF-8.

Initial optimization studies were carried out using *p*-bromotoluene and morpholine as standard substrates at 105 °C and 4 bar of CO for 12 h as shown in Table 1. The presence of a phosphine ligand was found to be necessary because no appreciable amount of product was detected in its absence. Monodentate ligands, such as PPh_3 and XPhos, gave lower yields (32% and 58%, respectively). Bidendate ligands such as dppf, BINAP, and Xantphos, gave higher yields of 65%, 66%, and 76%, respectively, and near quantitative yield was achieved when dpePhos was used as the ligand. The employment of phosphine ligand is crucial for the success of the aminocarbonylation reaction. The adsorbed phosphine ligand could either alter the electronic properties to facilitate the oxidative addition step or promote the reductive elimination step by steric bulk around PdNPs, as suggested by Tagata and Nishida.[16] In addition, phosphine ligands could also stabilize PdNPs to prevent aggregation.

Other potential catalyst supports, such as Al_2O_3, MCM-41, and MOF-5, provided only 42%, 73%, and 84%, respectively. The amount of dpePhos can be reduced to 1 mol % without much change in the catalytic performance, and a TON > 400

Table 1. Optimization of Conditions for Aminocarbonylation of *p*-Bromotoluene with Morpholine



entry	catalyst	base	ligand (mol %)	ArBr (mmol)	yield (%)[a]
1	Pd/ZIF-8	K_2CO_3		0.3	n.d.
2	Pd/ZIF-8	K_2CO_3	PPh_3(5)	0.3	32
3	Pd/ZIF-8	K_2CO_3	XPhos(5)	0.3	58
4	Pd/ZIF-8	K_2CO_3	dppf(5)	0.3	65
5	Pd/ZIF-8	K_2CO_3	XantPhos(5)	0.3	76
6	Pd/ZIF-8	K_2CO_3	BINAP(5)	0.3	66
7	Pd/ZIF-8	K_2CO_3	dpePhos(5)	0.3	99
8	Pd/MOF-5[b]	K_2CO_3	dpePhos(5)	0.3	84
9	Pd/Al_2O_3	K_2CO_3	dpePhos(5)	0.3	42
10	Pd/MCM-41	K_2CO_3	dpePhos(5)	0.3	73
11	Pd/ZIF-8	K_2CO_3	dpePhos(1)	1.0	94[c]
12	Pd/ZIF-8[d]	K_2CO_3	dpePhos(1)	1.0	89
13	Pd/ZIF-8	K_3PO_4	dpePhos(1)	1.0	86
14	Pd/ZIF-8	DBU	dpePhos(1)	1.0	64
15	Pd/ZIF-8	$(i\text{-Pr})_2$NEt	dpePhos(1)	1.0	79
16	Pd/ZIF-8	Et_3N	dpePhos(1)	1.0	25
17	Pd/ZIF-8[e]	K_2CO_3	dpePhos(1)	1.0	78

[a]Bromotoluene (1 mmol, 1 equiv), CO (4 bar), morpholine (1.5 equiv), catalyst (24 mg), base (2 equiv), toluene (3 mL). Yields were calculated from GC analysis using a FFAP capillary column with *n*-dodecane as the internal standard. [b]The surface area of Pd/MOF-5 used was 718 $m^2\ g^{-1}$. [c]The corresponding homogeneous reaction with $Pd(OAc)_2$/dpePhos gave no product; a comparison with common homogeneous catalysts is given in the SI, Table S4. [d]Reaction was carried out under 1 bar of CO. [e]Pd/ZIF-8 (0.5 wt %).

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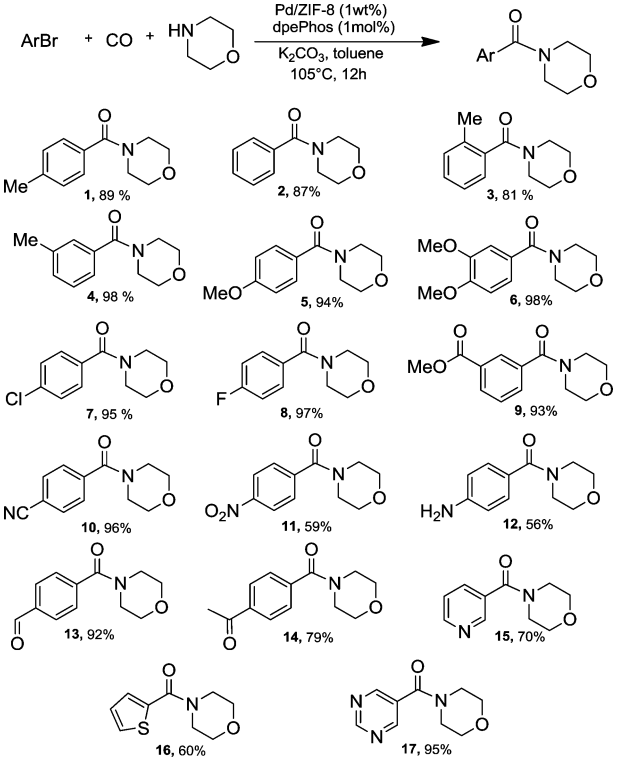
was achieved by using 1 mmol of substrate. Insoluble inorganic bases, such as K_2CO_3, and K_3PO_4, were found to be the best compared with the soluble organic bases, such as Hünig base, DBU, and Et_3N. The reaction can also be carried out at atmospheric pressures and only marginal decrease in yield (89%) was observed.

With the optimized condition in hand, first, we extended the scope of this aminocarbonylation reaction to a wide range of aryl bromides with morpholine as the amine (Table 2).

Table 2. Scope of the Aminocarbonylation of Aryl Bromides with Morpholine[a]

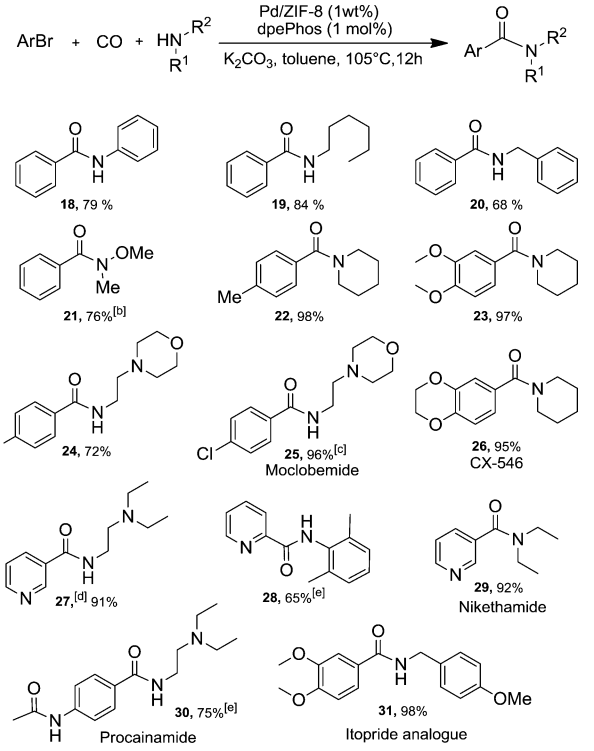


[a]ArBr (1 mmol, 1 equiv), CO (4 bar), NHR^1R^2 (1.5 equiv), Pd/ZIF-8 (24 mg, 0.21 mol % Pd), K_2CO_3 (1.5 equiv), toluene (3 mL); yields given are isolated yields.

Bromobenzene gave 87% isolated yield of **2** under the optimized conditions for 12 h. Sterically hindered ortho-substituted substrates, such as *o*-bromotoluene, showed slightly lower reactivity, as expected, and gave 81% yield to the amide **3**, as compared with the *m*-bromotoluene, which gave up to 98% yield of **4**. Excellent yields in the range of 93−98% were achieved for amides **5**−**10** with *p*-OMe-, *m*-COOMe-, *p*-Cl, *p*-F-, and *p*-CN-functionalized aryl bromides, and moderate yields of 56−59% were obtained for **11** and **12** with *p*-NH_2- and *p*-NO_2-substituted bromides. It is noteworthy that aldehyde- and ketone-substituted aryl bromides could be readily converted to the desired amides **13** and **14** in very good yields (92% and 79%, respectively) without any significant potential side reactions. Heterocyclic aryl bromides were also effective, and moderate to high yields were achieved for thiophenyl (**16**), pyridyl (**15**), and pyrimidyl (**17**) amides.

The effect of various amines in combination with suitable aryl bromides was also evaluated with the aim of application in the synthesis of pharmaceutically important amides. The results are presented in Table 3. Aromatic primary amines and benzyl

Table 3. Scope of the Aminocarbonylation of Aryl Bromides with Various Amines[a]



[a]ArBr (1 mmol, 1 equiv), CO (4 bar), NHR^1R^2 (1.5 equiv), Pd/ZIF-8 (24 mg, 0.21 mol % Pd), K_2CO_3 (1.5 equiv), toluene (3 mL); yields given are isolated yields. [b]The corresponding amine hydrochloride was used in presence of additional equiv of K_2CO_3. [c]Scaled up to six times and obtained 89% isolated yield with a TON of 2540. [d]Corresponding ^{11}C amide is a PET tracer for melenoma. [e]Reaction at 120 °C, 10 bar of CO, 18 h.

amines showed moderate yields compared with alkyl primary, secondary, and cyclic amines. Accordingly, aniline and benzylamine gave 79% and 68% yields of **18** and **20**, respectively, with bromobenzene, and 84% yield of **19** was observed with *n*-hexylamine. Weireb amide **21** was synthesized in 76% yield by using *N*,*O*-dimethylhydroxylamine hydrochloride. In this case, an additional equivalent of K_2CO_3 was used to generate the free amine from the hydrochloride salt. With cyclic secondary amines such as piperidine, the desired amides **22** and **23** were obtained in excellent yields, up to 98%.

Synthesis of several drug molecules and pharmacologically important compounds was attempted using this catalytic methodology. Aminocarbonylation of 1-chloro-4-bromobenzene with morpholinoethanamine gave 96% of Moclobemide **25**, a generic drug used in the treatment of depression.[19] The *p*-Cl substituent is tolerated under the reaction conditions. This synthesis was scaled up to six times using the same catalyst loading (24 mg) in a 24 h reaction, which gave up to 89% isolated yield with a TON of 2540. The corresponding fluoro derivative **24** was obtained in 72% yield. The CX-546 drug molecule **26** (developed by Cortex Pharmaceuticals for the treatment of schizophrenia)[18] was obtained in 95% yield. Aminocarbonylation of sterically bulky aniline, such as 2,6-dimethylaniline with 2-bromopyridine, gave a promising yield of 65% to the amide **28**, which is an important intermediate for the synthesis of Mepivacaine.[17] Nikethamide (**29**), a stimulant agent which mainly affects the respiratory cycle, could be

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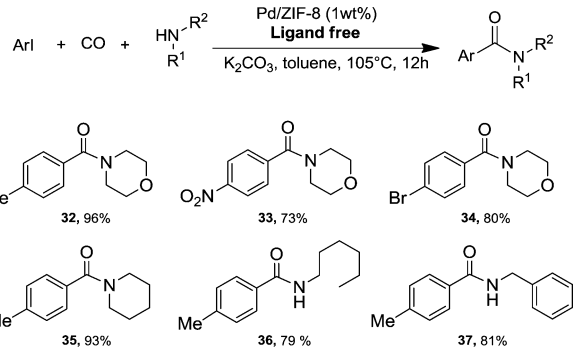
synthesized in 92% isolated yield. Procainamide (**30**),[20] another important antiarrhythmic drug, was also synthesized in 75% isolated yield under 10 bar of CO at 120 °C. The elevated conditions required may be due to the presence of an electron-withdrawing *p*-amide group present in the starting aryl bromide. An analogue of the Itopride drug molecule (**31**) was easily synthesized in 98% isolated yield.[6c]

Apart from the easy catalyst−product separation, the Pd/ZIF-8 catalyst showed promising recyclability and low levels of palladium leaching. The catalyst was efficiently recycled four times without any significant loss in catalytic activity for the standard aminocarbonylation of *p*-bromotoluene with morpholine under the optimized conditions. ICP−AES analysis was carried out using the filtrate after each run, and the palladium leaching was found to be less than 4 ppm in each run (see SI).

To understand if the leached catalyst is responsible for the observed catalytic activity, the filtrate of the standard aminocarbonylation of *p*-bromotoluene with morpholine was evaluated for further potential reaction. For this purpose, we chose the soluble Hünig base for easy filtration compared with the solid K_2CO_3 (see entries 11 and 15 in Table 1 for reactivity comparison). After 2 h of reaction, a yield of 28% of the amide was obtained. No appreciable further conversion was observed when the filtrate, after removing the solid catalyst, was subjected to aminocarbonylation for the next 8 h. This suggests that the heterogeneous PdNPs supported on ZIF-8 is the true active catalyst.[21]

The aminocarbonylation of more active aryl iodides could be easily carried out in the absence of ligands using the Pd/ZIF-8 catalyst, and various desired products **32**−**37** were obtained in very good yields, as presented in Table 4. This ligand-assisted

Table 4. Scope of the Aminocarbonylation of Aryl Iodides with Amines[a]

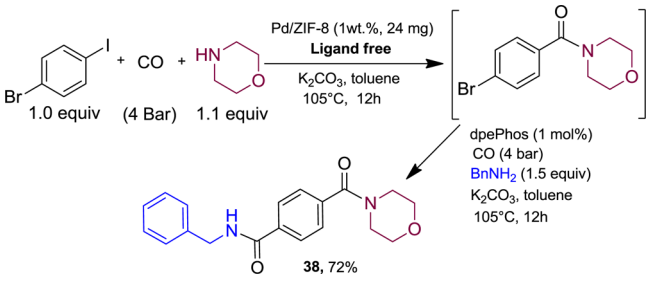


[a]ArI (1 mmol), CO (4 bar), NHR^1R^2 (1.5 equiv), Pd/ZIF-8 (24 mg, 0.21 mol % Pd), K_2CO_3 (1.5 equiv), toluene (3 mL); yields given are isolated yields.

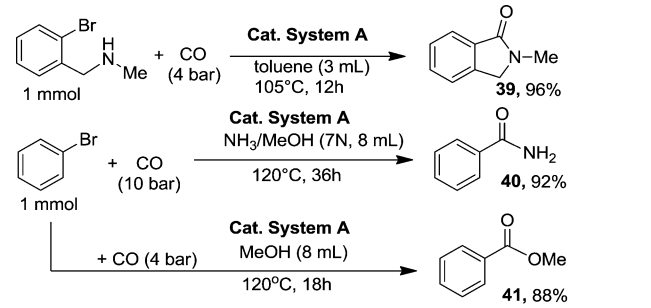
selective aminocarbonylation between aryl bromides and iodides was utilized for the sequential one-pot aminocarbonylation of *p*-iodobromobenzene to form the desired bisamide **38** in 72% isolated yield, as shown in Scheme 1.

The generality of this catalyst system was further investigated in the synthesis of cyclic amide, primary amide, and ester, as presented in Scheme 2. 2-Methylisoindolin-1-one **39** was obtained in 96% yield through an intramolecular aminocarbonylation of 1-(2-bromophenyl)-*N*-methylmethanamine. The aminocarbonylation of phenyl bromide with ammonia in methanol solution afforded the primary amide in 92% isolated yield of **40** in 36 h. Formation of the primary amide proceeds

Scheme 1. One-Pot Sequential Aminocarbonylation of *p*-Iodo Bromobenzene



Scheme 2. Synthesis of Cyclic Amide, Primary Amide and Ester from Phenyl Bromide Using Carbonylations



Cat. System A: Pd/ZIF-8 (1wt%, 24 mg), dpePhos (1 mol%), K_2CO_3 (2 equiv)

through the initial formation of the methyl ester, which was evident from the analysis of intermediate samples that showed its formation and disappearance over time. Accordingly, hydroesterification was investigated using methanol as the solvent, and methylbenzoate **41** was isolated in 88% yield in 18h of reaction.

In conclusion, we have reported an active and stable heterogeneous Pd nanoparticles catalyst supported on ZIF-8 for the aminocarbonylation of both bromoarenes and iodoarenes in the presence of various amines under relatively mild operating conditions. The catalyst can be easily prepared by a simple procedure without applying inert conditions. The catalyst is recyclable and offers low levels of palladium leaching. The synthesis of a variety of pharmaceutically important compounds was demonstrated, and a TON of 2540 was achieved in a single batch reaction. The broad applications of this catalyst system were demonstrated for the synthesis of various useful products, such as cyclic amide, primary amide, and carboxylic ester. Further studies on extending the application and scope of this catalyst is currently in progress in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, Characterization data for the catalysts and the products, NMR spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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