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Pd/C-Catalyzed Carbonylative Synthesis of 2-Aminobenzoxazinones from 2-Iodoaryl Azides and Amines

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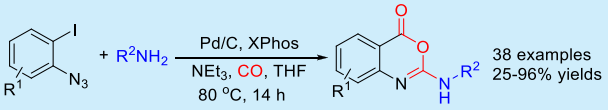
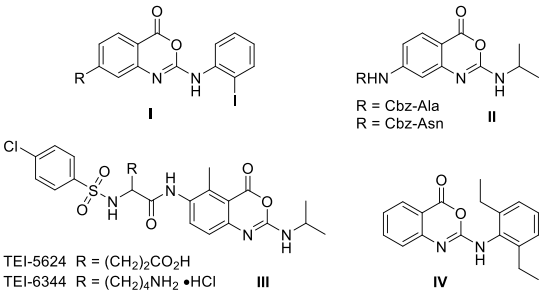
Supporting Information

ABSTRACT: A palladium-catalyzed carbonylative procedure for the synthesis of 2-aminobenzoxazinones from 1-azido-2-iodobenzenes and amines has been developed. A broad range of 2-aminobenzoxazinone derivatives were prepared in moderate to excellent yields by using Pd/C as the catalyst under CO atmosphere. Notably, by using organic azides as the substrates, external oxidant usage can be successfully avoided and only forms N_2 as the byproduct.



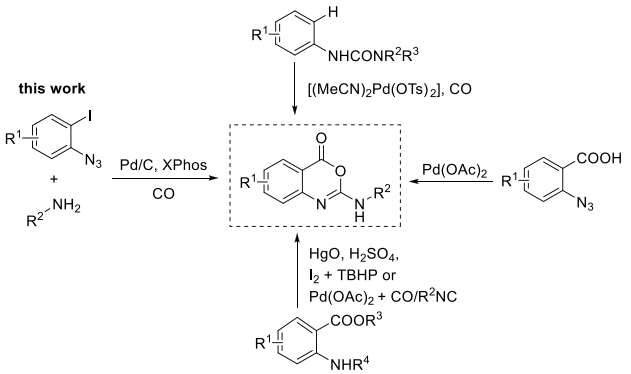
Benzoxazinones are an important class of heterocyclic scaffolds, which present widely in bioactive compounds and natural products.[1] These valuable heterocycles have been commonly applied as precursors for the synthesis of pharmaceutically active compounds as well.[2] Among them, 2-amino-substituted benzoxazinones have been frequently applied for treating diseases in the past few decades.[3] Some representative examples are selected and shown in Scheme 1.

Scheme 1. Selected Bioactive 2-Aminobenzoxazines



Compounds I as effective inhibitors of the complementary enzyme C1r have been reported.[4] Compounds II are good inhibitors of HSV-1 protease.[5] Derivatives of III showed strong and highly specific inhibition of human sputum elastase (HSE).[6] Compound IV is a chemically stable PSA-specific inhibitor, which shows potent PSA-inhibitory activity.[7] Hence, the development of new procedures for the synthesis of 2-amino-substituted benzoxazinones has attracted a lot of attention over the past decades. Ordinary methods for constructing these heterocyclic compounds are based on 2-aminobenzoic acid derivatives; however, some procedures need to be performed in the presence of concentrated acid or toxic catalyst or under oxidative conditions[8] (Scheme 2). An alternative procedure using palladium-catalyzed carbonylation of 1,1-disubstituted 3-phenylureas[9] or palladium-catalyzed cross-coupling/cyclization of 2-azidobenzoic acids with isocyanides has been developed as well.[10]

Scheme 2. Procedures for the Synthesis of 2-Aminobenzoxazines



On the other hand, transition-metal-catalyzed carbonylation reactions using low cost and accessible carbon monoxide as the C1 building block have been widely applied in organic synthesis,[11] and such types of reaction have been used for constructing various biologically active heterocycles as well.[12] Moreover, azides are interesting compounds and have been broadly utilized in the synthesis of functionalized 1,2,3-triazoles through click reaction.[13] Compared with traditional methods for generating 2-amino-substituted benzoxazinones, using azides as the substrates to construct N-containing heterocycles could avoid the use of external oxidants and only forms N_2 as the byproduct.[10,14] Combining the recent work of our group with the continued exploration of palladium-catalyzed carbonylation reactions,[15] herein we describe the application of 2-iodoaryl azides and amines as substrates in palladium-catalyzed carbonylative transformation. A variety of 2-amino-substituted benzoxazinones were isolated in moderate to excellent yields with good functional group tolerance.

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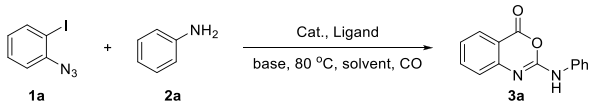
Initially, we selected 1-azido-2-iodobenzene **1a** and aniline **2a** as the model substrates to optimize the reaction conditions, using $Pd(OAc)_2$ (5 mol %) and XPhos (10 mol %) as the catalytic system and Et_3N (1.5 equiv) as the base in toluene (1 mL) under CO (5 bar) atmosphere at 80 °C. To our delight, the desired product was obtained in 67% yield (Table 1, entry 1). The yields of the desired product can be further improved when other catalysts such as $Pd(PPh_3)_4$ (85% yield was obtained with $Pd_2(dba)_3$) or Pd/C were used (Table 1, entries 2 and 3). In the case of using Pd/C as the catalyst, the desired product **3a** was formed in 91% yield. Different ligands were tested subsequently; however, regardless of monodentate ligands such as PPh_3 and $^tBu_3P{\cdot}HBF_4$ or bidentate ligands such as dppp and dppf, all showed ineffectiveness for the generation of the desired product (Table 1, entries 4−7). The bases had a crucial effect on this transformation, and when K_2CO_3 and DBU were used as the bases, the yield of **3a** decreased to 40% and 0%, respectively (Table 1, entries 8 and 9). Solvent screening revealed that THF is the best medium for this transformation and gave the target product **3a** in 99% yield (Table 1, entries 10−14). Control experiments indicated that no target product could be detected in the absence of Pd/C, XPhos, or Et_3N (Table 1, entries 15−17). Undesirably, when we changed the temperature to 60 °C or the pressure of CO to 1 bar, the reaction yields were reduced to 58% and 75%, respectively (Table 1, entries 18 and 19). Satisfactorily, the catalyst loading can be decreased to 1 mol % Pd/C and is still able to provide the desired product **3a** in 95% isolated yield (Table 1, entry 20).

Table 1. Optimization of Reaction Conditions[a]

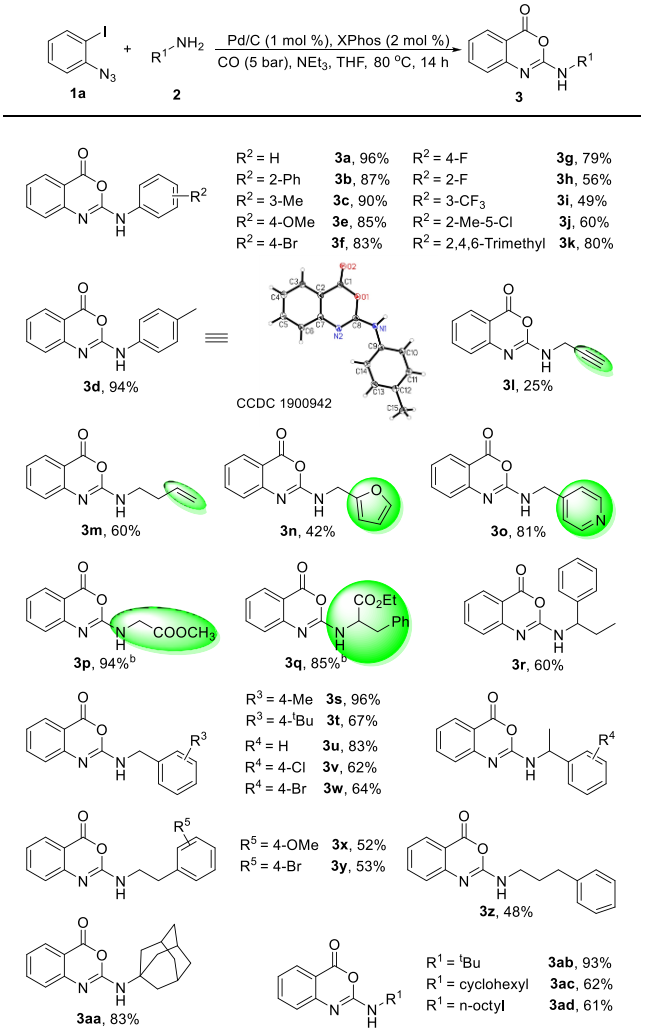


entry	catalysts	ligands	solvents	yield[b] (%)
1	$Pd(OAc)_2$	XPhos	toluene	67
2	$Pd(PPh_3)_4$	XPhos	toluene	74
3	Pd/C	XPhos	toluene	91
4	Pd/C	PPh_3	toluene	trace
5	Pd/C	dppp	toluene	0
6	Pd/C	dppf	toluene	0
7	Pd/C	$^tBu_3P{\cdot}HBF_4$	toluene	12
8[c]	Pd/C	XPhos	toluene	44
9[d]	Pd/C	XPhos	toluene	0
10	Pd/C	XPhos	DMF	60
11	Pd/C	XPhos	1,4-dioxane	92
12	Pd/C	XPhos	DCE	33
13	Pd/C	XPhos	CH_3CN	72
14	Pd/C	XPhos	THF	99
15	-	XPhos	THF	0
16	Pd/C	-	THF	0
17[e]	Pd/C	XPhos	THF	0
18[f]	Pd/C	XPhos	THF	58
19[g]	Pd/C	XPhos	THF	75
20[h]	Pd/C	XPhos	THF	98 (95)[i]

[a]Reaction conditions: **1a** (0.15 mmol), **2a** (0.18 mmol), catalysts (5 mol %), ligands (10 mol %), and Et_3N (1.5 equiv) in solvent (1 mL) at 80 °C for 14 h under CO (5 bar). [b]Yields were determined by GC-FID analysis using *n*-hexadecane as an internal standard. [c]K_2CO_3 (1.5 equiv). [d]DBU(1.5 equiv). [e]No base. [f]60 °C. [g]CO (1 bar). [h]Pd/C (1 mol %), XPhos (2 mol %) [i]Isolated yield. XPhos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl. $BuPAd_2$ = di(1-adamantyl)-*n*-butylphosphine. dppp = 1,3-bis(diphenylphosphino)-propane. dppf = 1,1′-bis(diphenylphosphino)ferrocene. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene. DMF = *N*,*N*-dimethylformamide. DCE = 1,2-dichloroethane.

With the optimized reaction conditions in hand (Table 1, entry 20), we next set out to explore the substrate scope of this reaction with a range of amines. As shown in Scheme 3, anilines with a series of different functional groups including electron-donating (Ph, MeO), electron-neutral (Me), and electron-withdrawing (F, Br, CF_3) all showed good reaction activities, forming the corresponding products in 49−96% yields (Scheme 3, **3a**−**3i**), and even sterically hindered 2-phenylaniline could transform into the desired product **3b** in an excellent yield of 94%. These results of reactions indicated that the aromatic ring with electron-donating functional groups had a positive effect on the efficiency of this transformation. Notably, there are disubstituted and trisubstituted functional groups on the aromatic ring of aniline, and the reaction can be

Scheme 3. Synthesis of 2-Aminobenzoxazinones from Amines[a]



[a]Reaction conditions: **1a** (0.3 mmol, 1.0 equiv), **2** (0.36 mmol, 1.2 equiv), Pd/C (3.2 mg, 1 mol %), XPhos (2 mol %), and Et_3N (1.5 equiv) in solvent (2 mL) at 80 °C for 14 h under CO (5 bar), isolated yield. [b]Used 3.0 equiv of Et_3N.

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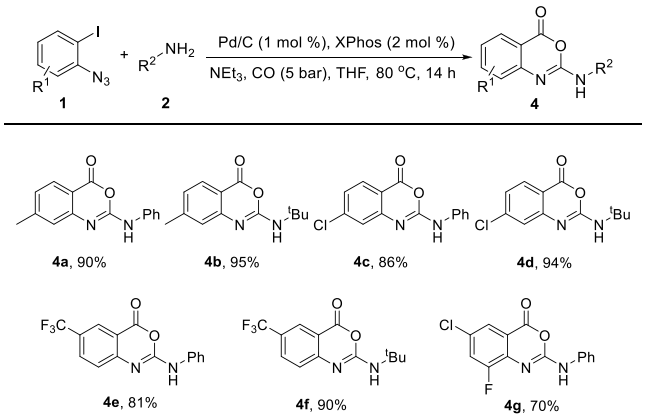
performed smoothly, leading to the desired products in 60% and 80% yields, respectively (Scheme 3, **3j**, **3k**). Next, different aliphatic amines were investigated. Interestingly, the aliphatic amine bearing group of terminal alkyne **1l**, terminal olefin **1m**, furan **1n**, and pyridine were well-tolerated, giving the desired products **3l**−**3o** in 25−81% yields.

Furthermore, amino acid ester hydrochlorides **2p** and **2q** could react with **1a** to give the desired **3p** and **3q** in 94% and 85% yields, respectively. Satisfactorily, aliphatic amines with alkyl chains of different lengths all engaged in this reaction smoothly to deliver the corresponding 2-amino-substituted benzoxazinones **3r**−**3ad** in moderate to good yields (48−93%). Particularly, for sterically hindered alkylamines such as 1-adamantanamine **1aa**, *tert*-butylamine **1ab**, and cyclohexaneamine **1ac**, all could be converted into the corresponding products in good yields. In addition, octylamine **1ad** containing eight carbons could give **3ad** in 61% yield. The relative configuration of the desired product was certificated by X-ray diffraction analysis of **3d**.

Subsequently, various 1-azido-2-iodobenzenes were prepared and reacted with aniline and *tert*-butylamine under the standard conditions. As shown in Scheme 4, the corresponding

Scheme 4. Synthesis of 2-Aminobenzoxazinones from 1-Azido-2-iodobenzenes[a]



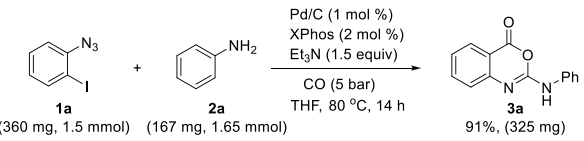
[a]Reaction conditions: **1** (0.3 mmol, 1.0 equiv), **2** (0.36 mmol, 1.2 equiv), Pd/C (3.2 mg, 1 mol %), XPhos (2 mol %), and Et_3N (1.5 equiv) in solvent (2 mL) at 80 °C for 14 h under CO (5 bar), isolated yield.

products **4a**−**4d** were formed in good to excellent yields with the tested substrates. Furthermore, 1-azido-2-iodobenzene **1d** bearing a stronger electron-withdrawing (CF_3) group can be well transformed into the reaction and provide the corresponding products **4e** and **4f** in 81% and 90% isolated yields, respectively. Disubstituted 1-azido-2-iodobenzene **1e** engaged in the reaction well, affording the desired product **4g** in 70% yield.

Based on the optimal reaction conditions, we scaled up the reaction to a 1.5 mmol level (Scheme 5). To our delight, the reaction of **1a** (1.5 mmol) and **2a** (1.65 mmol) was performed in 5 mL of THF under the standard conditions, giving the desired product **3a** in 91% isolated yield.

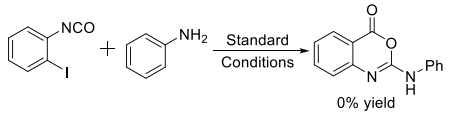
In order to get some insight into the reaction pathway, 1-iodo-2-isocyanatobenzene was prepared and tested with aniline under our standard conditions (Scheme 6). However, to our surprise, no desired product could be detected. On the other hand, 2-nitro-*N*-phenylbenzamide can be excluded as an

Scheme 5. Synthesis of 2-Aminobenzoxazinone in the 1.5 mmol Level[a]



[a]Reaction conditions: **1a** (1.5 mmol), **2a** (1.65 mmol), Pd/C (1 mol %), XPhos (2 mol %), and Et_3N (1.5 equiv) in THF (5 mL) at 80 °C for 14 h under CO (5 bar).

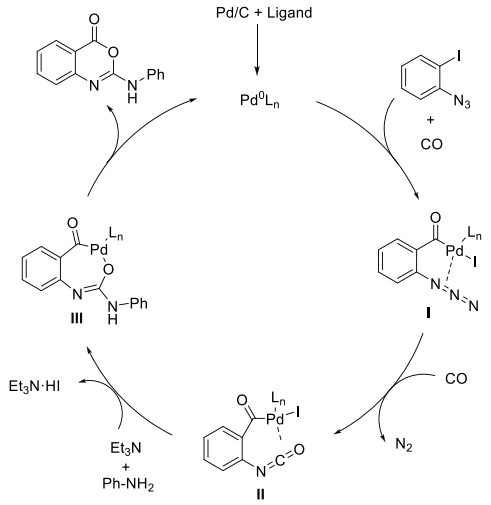
Scheme 6. Reaction with 1-Iodo-2-isocyanatobenzene



intermediate as well, as it will produce 1*H*-quinazoline-2,4-dione in the presence of CO via 2-isocyanato-*N*-phenylbenzamide.[16] Hence, we believe azide and then isocyanate coordinated to the benzoyl palladium complex should be the intermediate.

On the basis of these results and previous literature,[10,14b,17] we proposed a simplified possible reaction mechanism (Scheme 7). Initially, 1-azido-2-iodobenzene undergoes

Scheme 7. Proposed Reaction Mechanism



oxidative addition with ligand-coordinated Pd(0) and insertion of CO to afford intermediate **I**. Subsequently, a Pd-coordinated intermediate **II** was formed after the release of N_2 and another CO insertion. Then complex **III** is formed by nucleophilic attack of amine at isocyanate C in the presence of Et_3N. Finally, the terminal benzoxazinone products were eliminated from complex **III** after reductive elimination and meanwhile regenerate the active Pd(0) species which is ready for the next catalytic cycle.

Finally, in order to further prove the usefulness of this procedure, the synthesis of bioactive 2-aminobenzoxazine was carried out (Scheme 8). By using 2,6-diethylaniline as the substrate, the desired 2-((2,6-diethylphenyl)amino)-4*H*-benzo[*d*][1,3]oxazin-4-one, which is a PSA-specific inhibitor, was isolated in 88% yield.

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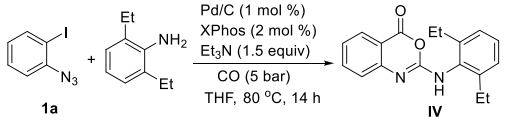
Scheme 8. Synthesis of Bioactive 2-Aminobenzoxazine



[a]Reaction conditions: **1a** (0.3 mmol, 1.0 equiv), 2,6-diethylaniline (0.36 mmol, 1.2 equiv), Pd/C (1 mol %), XPhos (2 mol %), and Et_3N (1.5 equiv) in solvent (2 mL) at 80 °C for 14 h under CO (5 bar). [b]**1a** (1 mmol, 1.0 equiv), 2,6-diethylaniline (1.2 mmol, 1.2 equiv), Pd/C (1 mol %), XPhos (2 mol %), and Et_3N (1.5 equiv) in solvent (2 mL) at 80 °C for 18 h under CO (5 bar). Isolated yields.

In conclusion, an efficient palladium-catalyzed carbonylation of 1-azido-2-iodobenzenes with amines for the synthesis of 2-aminobenzoxazinones has been developed. In the presence of Pd/C as the catalyst, various amines with different functional groups were all transformed into the corresponding products under mild conditions in good to excellent yields. Additionally, amino acid ester hydrochloride can be successfully applied to this reaction as well.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00966.

General comments, general procedure, optimization details, analytical data, and NMR spectra (PDF)

Accession Codes

CCDC 1900942 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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