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One-Pot Synthesis of 2-Aminobenzophenones from 2-Alkynyl Arylazides Catalyzed by Pd and Cu Precursors

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Abstract: We describe a novel one-pot three-step reaction of 2-alkynyl arylazides through palladium-catalyzed formation of 3-hydroxy-3-phenylindolin-2-ones followed by hydrolysis of amide bonds and copper-catalyzed decarboxylation to give 2-aminobenzophenones. This synthetic method woks well with various 2-alkynyl arylazides and affords the products in moderate to good yields under mild reaction conditions.

Introduction

The 2-aminobenzophenone skeleton was considered as one of the most important organic structures, which could be found in many bioactive compounds, natural products and pharmaceuticals. [1] As shown in Figure 1, molecules with 2-aminobenzophenone moiety such as Nepafenac, [1a] Amfenac, [1a] Bromfenacum, [1a] Bromodomain inhibitor, [1a] CKD516 [1b] and Bradykinin B1 receptor antagonist [1c] have shown excellent bioactivities. Moreover, this prevalent core structure is widely used as highly versatile synthetic building blocks for the preparation of quinolines, [2] indoles [3] and benzodiazepines [4] as well as advanced organic materials. [5] Therefore, a variety of synthetic strategies for the construction of 2-aminobenzophenones have been established. [6-10] Among those reported methods, 2-aminobenzophenones could be generally accessed from various starting materials such as anilines, [6] 2-aminobenzonitriles, [7] 2-iodoanilines [8] and anthranilic acids. [9] Besides, several novel substrates were also employed for the preparation of 2-aminobenzophenones. [10] For example, Zhu and co-workers reported an efficient transformation of 2-arylindoles to 2-aminobenzophenones *via* a dearomatic C-C and C-N bond cleavage in the presence of oxygen (Scheme1, a). [10a] In 2019, Zhu's group disclosed a photoredox deoxygenative arylation of 2-(phenylsulfonamido)benzoic acids generated *in situ* from nthranilic acids and arylsulfonyl chlorides (Scheme1, b). [10b] In the same year, Wu's group described the formation of 2-aminobenzophenones by the *ortho*-C-H bond aroylation of anilines containing a 4-methoxy-2-pyridinyl directing group, which could be removed after two simple steps (Scheme1, c). [10c] Although much progress has been achieved, the development of efficient methods for the synthesis of 2-aminobenzophenones from novel starting materials is still highly desired.

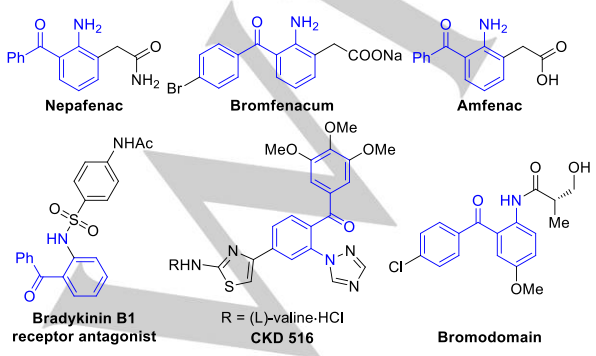
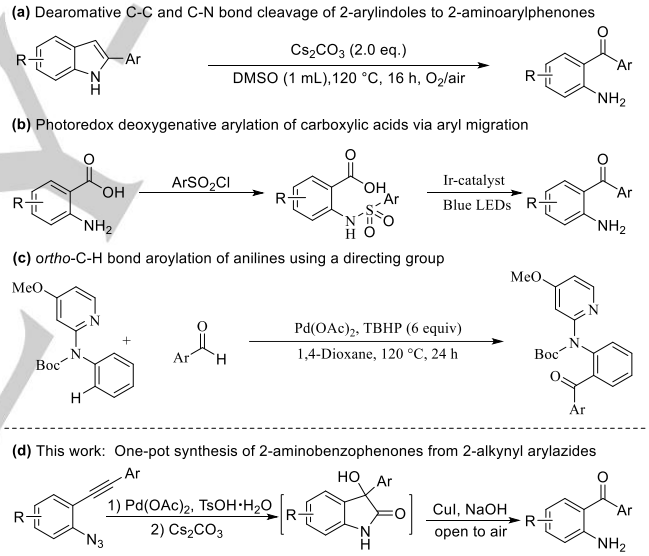


Figure 1. Bioactive molecules with 2-aminobenzophenone moiety.



Scheme 1. Synthetic methods to 2-aminobenzophenones.

Recently, various transformations of α-imino metal carbenes generated *in situ* from 2-alkynyl arylazides have been studied by us [11] and other groups. [12] In 2020, we reported the synthesis of imidazoloindolines by palladium-catalyzed one-pot cycloaddition reactions of thioureas with 3*H*-indol-3-ones generated *in situ* from 2-alkynyl arylazides. [11a] Later, 3-hydroxy-2-oxindoles were obtained by our group *via* acyloin rearrangements of 2-hydroxy-indolin-3-ones generated *in situ* from 2-alkynyl arylazides in the absence of thioureas. [11b] As a part of our ongoing interest on transformation of 2-alkynyl arylazides, we envisaged that 2-aminobenzophenones could be formed through one-pot hydrolysis / decarboxylation of 3-hydroxy-2-oxindoles generated *in situ* from 2-alkynyl arylazides (Scheme 1, d).

Results and Discussion

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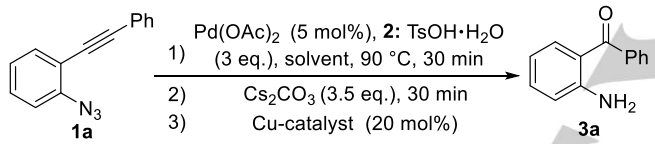
At the outset of this study, 1-azido-2-(phenylethynyl)benzene **1a** (1 eq.) and TsOH·H_2O **2** (3 eq.) were selected as the model substrates (Table 1). The reaction containing **1a** (0.1 mmol), **2** (3 eq.) and $Pd(OAc)_2$ (5 mol%) was conducted in 1,4-dioxane (1 mL) at 90℃ for 30 min followed by the addition of Cs_2CO_3 (3.5 eq.) for another 30 minutes. Then, CuI (20 mol%) was added to the above reaction solution and stirred for 18 hours. The desired product (2-aminophenyl)(phenyl)methanone **3a** was obtained in 52% yield (entry 1). The structure of **3a** was then confirmed by the analysis of ^1H and ^{13}C NMR. Later, other copper catalysts were investigated under the same reaction conditions. It was noted that $CuCl_2$, $Cu(OAc)_2$, $Cu(OTf)_2$, Cu_2O and $CuBr_2$ could afford the product **3a** in either lower yields or trace amounts (entries 2-6). Considering the solubility of starting materials, DMSO and DMF instead of 1,4-dioxane were employed as more polar solvents in this reaction, which gave the corresponding product **3a** in yields of 8% or 9%, respectively (entries 7-8). To our surprise, the product yield and reaction time were obviously improved when NaOH (2.0 eq.) was added as an additive, which gave the best results. The corresponding product **3a** was obtained in 70% yield after 4 hours (entry 9). In this reaction, the addition of NaOH could accelerate the hydrolysis of 3-hydroxy-2-oxindoles generated *in situ* from 1-azido-2-(phenylethynyl)benzene **1a.**

Table 1. Optimization of the reaction conditions. [a]

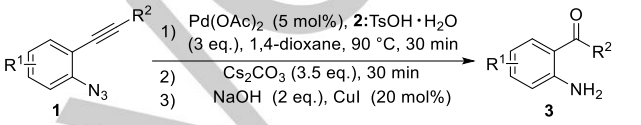


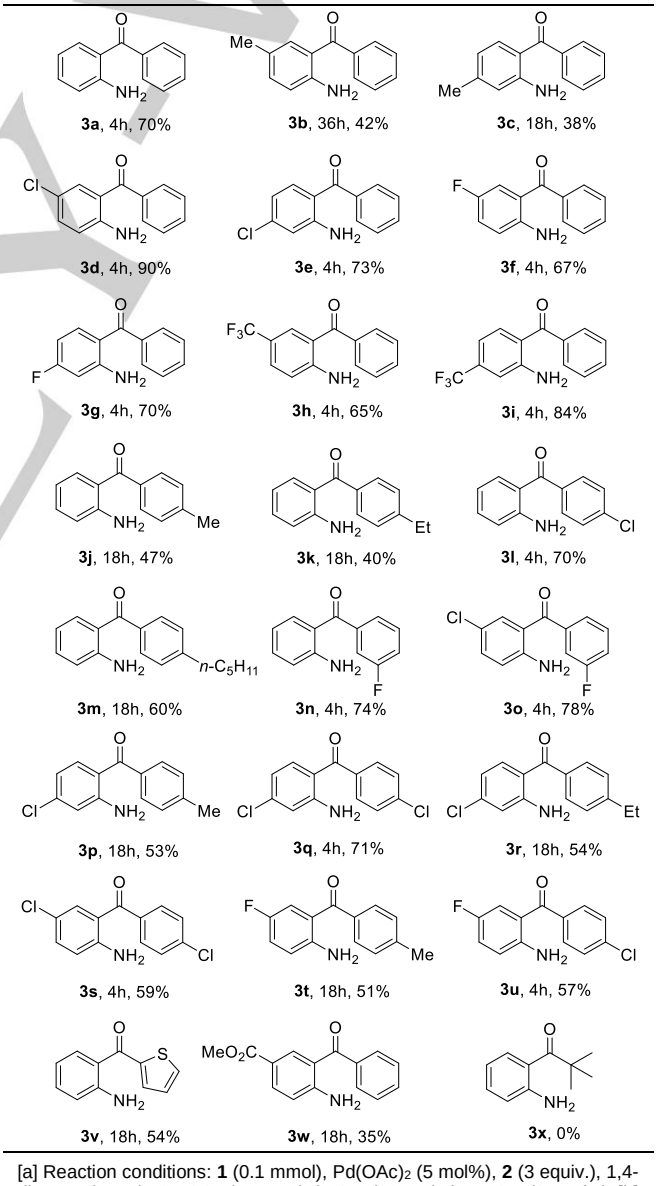
Entry	Catalyst	Time [h]	Solvent	Yield/%[b]
1	CuI	18	1,4-dioxane	52
2	$CuCl_2$	18	1,4-dioxane	38
3	$Cu(OAc)_2$	18	1,4-dioxane	trace
4	$Cu(OTf)_2$	18	1,4-dioxane	37
5	Cu_2O	18	1,4-dioxane	50
6	$CuBr_2$	18	1,4-dioxane	30
7	CuI	18	DMSO	8
8	CuI	18	DMF	9
9[c]	CuI	4	1,4-dioxane	70

[a] Reaction conditions: **1a** (0.1 mmol), $Pd(OAc)_2$ (5 mol%), **2** (3 equiv.), solvent (1 mL), Cs_2CO_3 (3.5 equiv.), catalyst (20 mol%). [b] Isolated yield. [c] NaOH (2 equiv.).

When the best optimized reaction conditions obtained in hand, we next explored the generality of the one-pot reactions of 2-alkynyl arylazides **1** for the preparation of 2-aminobenzophenones **3**. As shown in Table 2, various aryl or alkyl substituted 2-alkynyl arylazides **1a**-**1x** were checked under the standard reaction conditions. First, reactions of 2-alkynyl arylazides bearing electron-withdrawing or electron-donating groups on the aromatic ring (R^1) **1a**-**1w** were examined. It was found that the substrates with an electron-donating group (R^1 = 4-Me or 5-Me) gave the desired products **3b**-**3c** in lower yields of 42% and 38%, respectively. However, the starting materials with an electron-withdrawing group on the aromatic ring such as F, Cl, and CF_3 were all tolerable and provided the corresponding product **3d**-**3i** in moderate to excellent yields. Next, reactions of -alkynyl arylazides with substituted groups on the alkyne carbon (R^2 = 4-MePh, 4-EtPh, 4-ClPh, 4-(*n*-C_5H_{11}) Ph and 3-FPh) were also checked under the standard reaction conditions. The desired products **3j**-**3n** were obtained in 47-74% yields. The substrates with substituted groups R^1 and R^2 were also efficient to give the corresponding products **3o**-**3u** in yields of 51-71%. The substrate with a hetero-aromatic group (R^2 = 2-thiophen) was also tested, which led to the formation of **3v** in 54% yield. In addition, that reaction of substrate with an ester functional group resulted in the generation of **3w** in a lower yield of 35%, which might be the

Table 2. Substrates scope of the 2-alkynyl arylazides **1**. [a] [b]

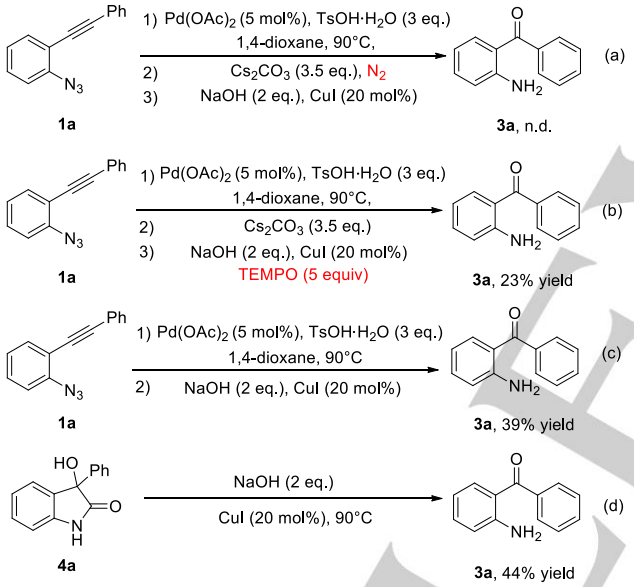




[a] Reaction conditions: **1** (0.1 mmol), $Pd(OAc)_2$ (5 mol%), **2** (3 equiv.), 1,4-dioxane (1 mL), Cs_2CO_3 (3.5 equiv.), CuI (20 mol%), NaOH (2 equiv.). [b] Isolated yield.

reason of partial hydrolysis of ester group under the basic reaction conditions. Unfortunately, repeating this reaction with a steric hindered group installed to the substrate (R^2 = *t*-Bu), did not give the desired product **3x**. And only the acyloin rearrangement product 3-(*tert*-butyl)-3-hydroxyindolin-2-one was obtained in 76% yield.

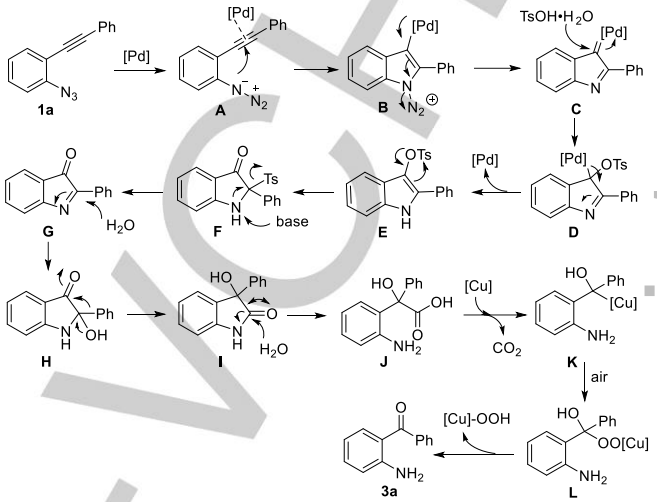
In order to understand the reaction mechanism, several control experiments were then examined as depicted in Scheme 2. First, the reaction of 1-azido-2-(phenylethynyl)benzene **1a** was tested under a nitrogen atmosphere, which did not afford the corresponding product **3a** (Scheme 2a). Next, a radical scavenger such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) was used to repeat the reaction. It was found that the product **3a** could be still obtained in 23% yield, which was dramatically affected by the radical scavenger (Scheme 2b). Therefore, a radical process might be involved in the reaction. Replacing the weak base Cs_2CO_3 with NaOH led to the formation of product **3a** in quite low yield of 39% (Scheme 2c). When the reaction of 3-hydroxy-3-phenylindolin-2-one **4a** was proceeded in the presence of NaOH (2 eq.) and CuI (20 mol%), the product **3a** was also obtained in 44% yield (Scheme 2d).



Scheme 2. Control Experiments.

Based on the above experimental results and our previous work,[11] we tentatively propose a possible mechanism in Scheme 3 for the transformation of **1a** to (2-aminophenyl)(phenyl)methanone **3a**, although it is highly speculative. The 1-azido-2-(phenylethynyl)benzene **1a** was initially activated by palladium catalyst to generate α-imino Pd carbene **C**,[13] which could be attacked by TsOH·H_2O to give complex **D**. Next, a rearrangement of **D** led to intemediate **E** [11d] and the palladium catalyst was regenerated. In the presence of Cs_2CO_3, **E** was converted to **F** after a 1,3-Ts shift process.[15] Although **F** was unstable, it was still detected by TLC and LC-MS in our previous work.[11f] Subsequently, a reductive desulfonation of **F** [16] afforded 2-phenyl-3*H*-indol-3-one **G**.[11f,14] Then, a hydrolysis of C=N double bond of **G** led to the formation of 2-hydroxy-2-phenylindolin-3-one **H**, which was followed by an acyloin rearrangement[17] to give **I**.[11e]

The amide bond of **I** was then hydrolysed to generate **J**. After a copper-catalyzed decarboxylation of **J** , the active copper species **K** was formed, which was then oxidized to product **3a** and regenerated the copper catalyst.[18] In this proposed mecahnism, the water involved in the hydrolysis process might come from the crystal water of TsOH·H_2O and/or neutralization reaction.



Scheme 3. Proposed mechanism.

Conclusion

In conclusion, we have disclosed a novel one-pot, three steps reaction from 2-alkynyl arylazides for the preparation of 2-aminobenzophenones. The corresponding products were obtained in moderate to good yields under mild reaction conditions. In this reaction, 2-alkynyl arylazides are used as simple starting materials, which can be easily accessed. Further applications of this strategy are currently underway and will be reported in future.

Acknowledgements

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Keywords: Azides • 2-Aminobenzophenones • Decarboxylation • Hydrolysis • One-pot

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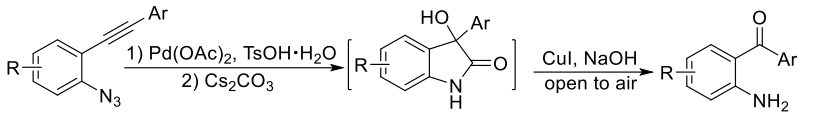

3a-3w

35-90% yield

A novel one-pot three-step synthetic method to 2-aminobenzophenones from 2-alkynyl arylazides has been disclosed. This reaction is catalyzed by palladium to form 3-hydroxy-3-phenylindolin-2-ones, which is followed by hydrolysis of amide bonds and copper-catalyzed decarboxylation to generate 2-aminobenzophenones. The desired products are afforded in moderate to good yields under mild reaction conditions.