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# Palladium-Catalyzed Annulation of Aryltriazoles and Arylisoxazoles with Alkynes

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**Abstract.** We developed herein a palladium-catalyzed annulation of aryltriazoles and arylisoxazoles with internal alkynes via C-H bond activation process. 4,5-disubstituted-3*H*-naphtho[1,2-*d*][1,2,3]triazoles and 4,5-disubstituted-naphtho[2,1-*d*]isoxazoles could be afforded in good yields, respectively. The starting materials are readily available and the scope and applications of this transformation were explored. The reaction offers a practical approach to naphthalene fused heterocycles.

**Keywords:** Triazole; Polycylces; Isoxazole; Palladium; Annulation

As the rapid development and application of click reaction in many areas, especially, copper(I)-catalyzed cycloaddition of azides with alkynes (CuAAC), triazole chemistry has gained considerable attentions in the past few dacades.[1] The 1,2,3-triazole moiety is not only connecting linkers, but also privileged scaffolds used as important pharmacophores in medicinal chemsitry.[2] A large number of triazole derivatives show interesting therapeutic acitivites and have been used as potential drug candidates for the treatment of cancer, HIV, etc.[2] 1,2,3-triazoles fused polycycles, a subclass of triazoles, possess a wide range of biological activities (Figure 1). For instance, triazole fused polycycles I, II and III showed important anticancer activity.[3] The sugar derived fused triazoles IV possed an significant glycosidase, galactosidase and SGLT2 inhibitory activities.[4] Morpholine fused triazoles V has been found to have potential against Alzheimer disease activities.[5] Consequently, the development of efficient synthetic methodology to access these triazole fused polycycles is of great importance.

Various synthetic methods of polycyclic triazole fused derivatives have been developed in the past few decades. Traditionally, building the azide and alkyne group in one molecular, followed by an

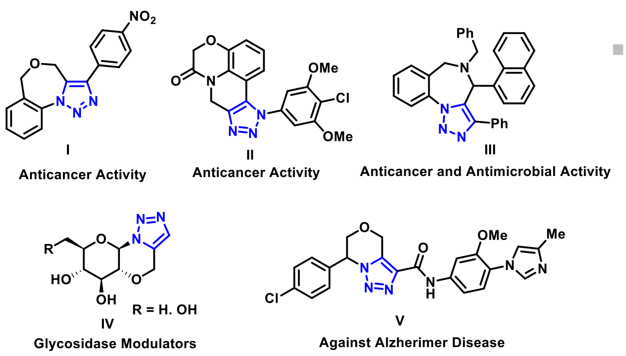
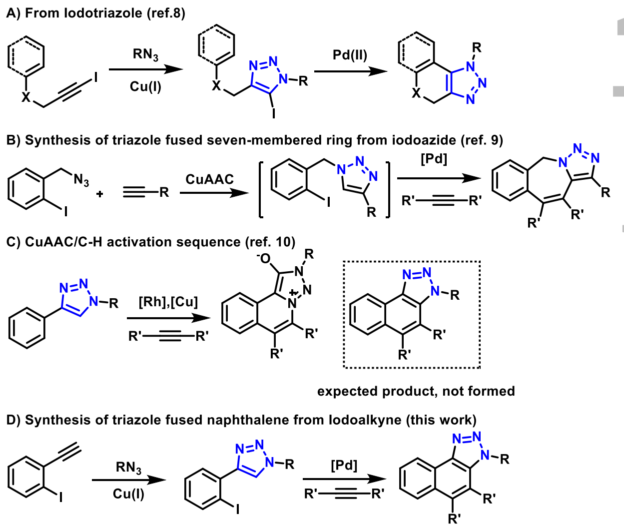



**Figure 1.** Selected biologically active 1,2,3-triazole fused polycycles.




**Scheme 1.** Synthesis of triazoles fused polycycles by CuAAC/C-H activation sequence.

intramolecular azide alkyne cycloaddition could generate polycyclic triazoles, however relative complicated cycloaddition precursors need to be prepared.[6] Other methods such as organo-catalyzed cycloaddition of cyclic ketone with azides have also been reported.[7] Direct C-H activation/annulation of simple triazoles, which are relatively easily obtained via the well-established CuAAC reaction, would be

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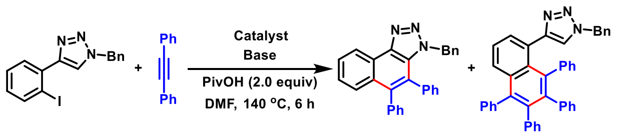
one of the most efficient strategies to make more complex polycyclic triazoles (Scheme 1). However, to realize the selective cleavage of the undirected C-H bond of triazole in the presence of other aromatic C-H bonds is extremely challenging. [8] An alternative strategy is the application of triazole iodide intermediate in an intramolecular arylation reaction (Scheme 1A). [8a] In 2016, Lautens group reported a Cu/Pd-catalyzed alkyne insertion/C-H functionalization strategy to achieve seven-membered pocyclic triazoles (Scheme 1B). [9] Naphthalene-fused triazoles are an important type of polyaromatics and their synthesis haven't been reported. Recently, Chen and Wu tried to use a rhodium-catalyzed oxidative annulation between triazole and internal alkynes to construct naphthalene-fused triazoles via double C-H activation, however due to the difficulty in cleaving the inert triazole C-H bond, another mesoionic triazolo[5,1-*a*] isoquinolium derivatives were obtained rather than expected naphthalene-fused triazoles (Scheme 1C).[10] Transition-metal catalyzed direct C-H activation and subsequent annulations has been widely exploited for the synthesis of various heterocyclic aromatic compounds due to its atom- and step-economic features.[11] In particular, palladium-catalyzed inter- or intramolecular annulation of aryliodides with alkynes and alkenes. [12] Inspired by these above mentioned studies and following our recent interests in construction of multisubstituted triazoles,[13] we envisioned that a palladium-catalyzed annulation of 1,2,3-triazole substituted aryliodides with internal alkynes may occur to give naphthalene-fused polycyclic triazoles (Scheme 1D).

We initiated our investigation by employing 1-benzyl-4-(2-iodophenyl)-1*H*-1,2,3-triazole **1a** and 1,2-diphenylethyne **2a** as model substrates in the presence of 20 mol% of $Pd(OAc)_2$ as catalyst, 2.0 equivalents of PivOH as additive, under $N_2$ in DMF at 140 °C for 6 h and 2.0 equivalents of various bases were firstly screened (Table 1, entries 1-5). As a result, $Cs_2CO_3$ and $Ag_2CO_3$ were not effective to the designed reaction (Table 1, entries 1-2). Using NaOAc or $Li_2CO_3$ as base, only the product **3a´**, which is confirmed by X-ray (See Supporting Information), can be detected as product (Table 1, entries 3-4). To our delight, the reaction proceeded smoothly to afford the desired product **3a** in good yield when DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) was employed as base (Table 1, entry 5). Various palladium catalysts including $Pd(CF_3CO_2)_2$, $Pd(PPh_3)_4$, $Pd_2(dba)_3$ and $Pd(PPh_3)_2Cl_2$ were then tested, we found that only $Pd(CF_3CO_2)_2$ led to the formation of the desired product **3a** (Table 1, entries 6-9). A higher NMR yield of product **3a** was obtained when the reaction was proceeded at 160 °C (Table 1, entry 10). We were pleased to find that DBN (1,5-Diazabicyclo[4.3.0]non-5-ene) was found to be a more effective base to furnish **3a** in 62% isolated yield (Table 1, entry 11). The yields decreased when the reaction was run at lower temperature or reduced the amount of alkyne **2a** and catalyst (Table 1, entries 12-14).

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




1a 2a 3a 3a'

| Entry | Catalyst (mol %) | Base (equiv) | Yield[b](%)**3a/3a'** |
|---|---|---|---|
| 1 | $Pd(OAc)_2$ (20) | $Cs_2CO_3$ (2.0) | N.R. |
| 2 | $Pd(OAc)_2$ (20) | $Ag_2CO_3$ (2.0) | N.R. |
| 3 | $Pd(OAc)_2$ (20) | NaOAc (2.0) | 0/34 |
| 4 | $Pd(OAc)_2$ (20) | $Li_2CO_3$ (2.0) | 0/60 |
| 5 | $Pd(OAc)_2$ (20) | DBU (2.0) | 52/0 |
| 6 | $Pd(CF_3CO_2)_2$ (20) | DBU (2.0) | 51/0 |
| 7 | $Pd(PPh_3)_4$ (20) | DBU (2.0) | N.R. |
| 8 | $Pd_2(dba)_3$ (20) | DBU (2.0) | N.R. |
| 9 | $Pd(PPh_3)_2Cl_2$ (20) | DBU (2.0) | N.R. |
| 10[c] | $Pd(OAc)_2$ (20) | DBU (2.0) | 56/16 |
| 11[c] | $Pd(OAc)_2$ (20) | DBN (2.0) | 65(62)[d]/9 |
| 12 | $Pd(OAc)_2$ (20) | DBN (2.0) | 50/9 |
| 13[c] | $Pd(OAc)_2$ (10) | DBN (2.0) | 45/9 |
| 14[c,e] | $Pd(OAc)_2$ (20) | DBN (2.0) | 55/22 |

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.4 mmol), catalyst (20 mol%), base (2.0 equiv), PivOH (2.0 equiv) in DMF (1 mL) under $N_2$ at 140 °C for 6 h, unless otherwise noted. [b]NMR yield using trimethoxybenzene as the internal standard. [c]The reaction was run at 160 °C. [d]The number in the parentheses is the isolated yield. [e]0.2 mmol **2a** was employed.

With optimal conditions established, we next investigated the substrate scope of the synthesis of naphthalene-fused triazoles. The results were summarized in Table 2. Various substituents on the phenyl ring of aryltriazoles were found to be well tolerated. For instance, various benzyl azide-derived aryltriazoles, including electron-rich and electron-deficient groups substituted benzyl aryltriazoles, can be employed in this reaction to give the corresponding naphthalene-fused triazoles in good yields under standard conditions. (Table 2. entries 1-5). Naphthyl, cinnamyl groups, phthalimide-protected amines skeletons and long chain alkyl group onto the nitrogen of the triazole were all well tolerated under the standard conditions (Table 2, entries 6-10). The variety of aryliodide was also explored, the results revealed that *o*-iodophenylacetylene with different substituents derived aryltriazoles were also amenable to this reaction (Table 2, entries 11-12). We next investigated the substrate scope of this reaction with regard to alkynes. To our delight, diphenylacetylenes

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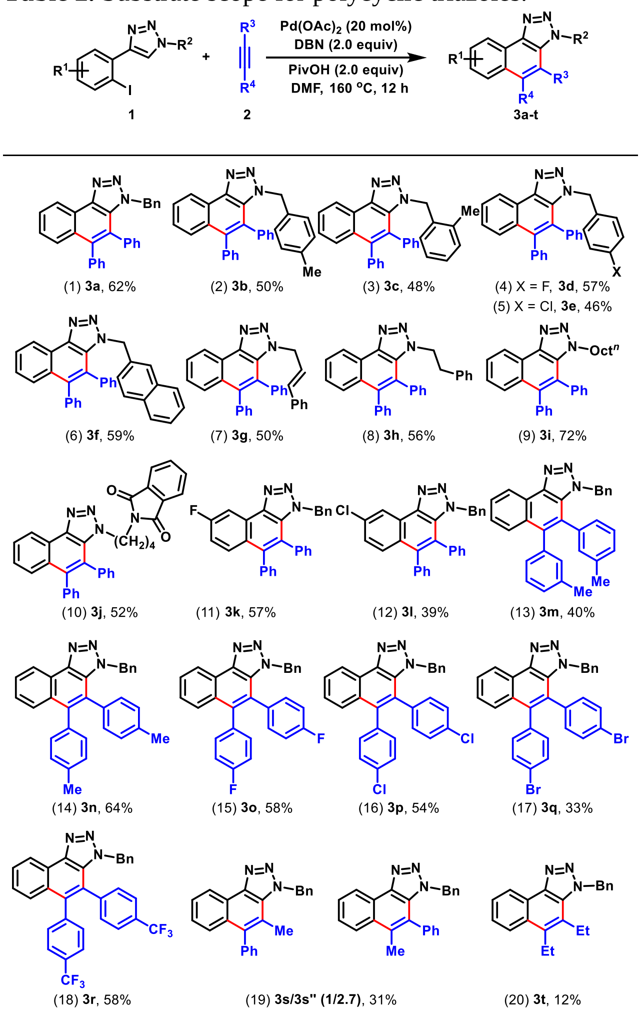
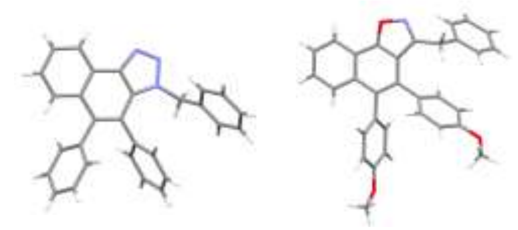
bearing either an electron-donating group (3-Me, 4-Me) or an electron-withdrawing group (4-F, 4-Cl, 4-Br, 4-$CF_3$) onto the phenyl ring, could also be applied to this reaction to furnish the corresponding naphthalene-fused triazoles products, albeit with lower yields in some cases (Table 2, entries 13-18). In addition, non-symmetrical alkyne **2i** was investigated under standard conditions and the corresponding annulation products **3s** and **3s″** were afforded with moderate regioselectivity and yields (Table 2, entry 19). The aliphatic alkyne **2j** was also applicable to the current catalytic system albeit with low yield of the annulation product **3t** (Table 2, entry 20). The structures of the products were unambiguously confirmed by the single crystal X-ray diffraction of compounds **3a** and **3s** (Figure 2). [14]

**Table 2.** Substrate scope for polycyclic triazoles.[a,b]




[a]Reaction conditions: **1** (0.2 mmol), **2** (0.8 mmol), $Pd(OAc)_2$ (20 mol%), DBN (2.0 equiv), PivOH (2.0 equiv) in DMF (2 mL) under $N_2$ at 160 ºC for 6-12 h, unless otherwise noted. [b]Isolated yields.

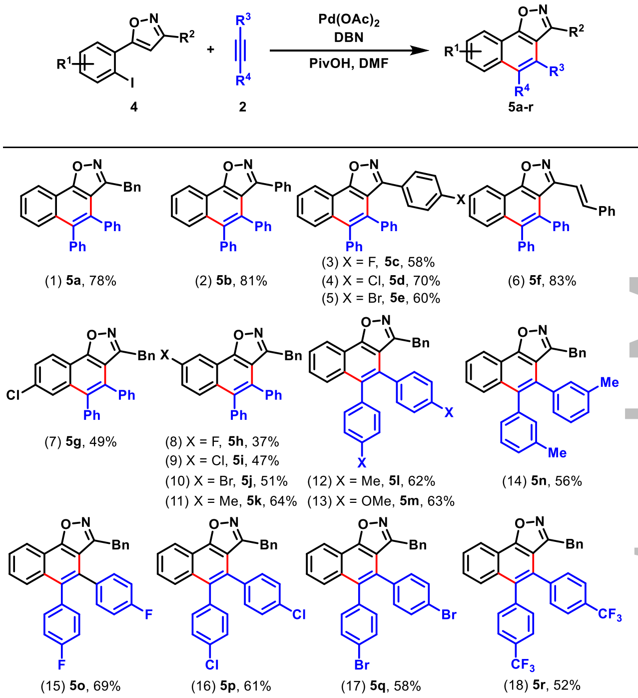
Encouraged by these aforementioned results, we then attempt to expand the generality of this palladium-catalyzed annulation protocol to other heterocycle systems rather than triazoles. We gratefully found that 5-(2-iodophenyl)isoxazoles, which were readily synthesized from 1-ethynyl-2-iodobenzene and oxime chloride through [3+2] cycloaddition,[15] can react with internal alkynes to afford naphthalene-fused isoxazoles in good yields under the similar reaction conditions (Table 3).



**3a** CCDC: 1889110 **5m** CCDC: 1888871

**Figure 2.**X-ray structure of **3a** and **5m**

**Table 3.** Substrate scope for polycyclic isoxazoles.[a,b]




[a]Reaction conditions: **4** (0.2 mmol), **2** (0.4 mmol), $Pd(OAc)_2$ (20 mol%), DBN (2.0 equiv), PivOH (2.0 equiv) in DMF (2 mL) under $N_2$ at 140 ºC for 6-12 h, unless otherwise noted. [b]Isolated yields.

Further substrate scope investigation revealed that 5-(2-iodophenyl)isoxazoles with various substituents onto the isoxazole and iodobenzene as well as diverse alkynes with different functional groups were well tolerated. It was noteworthy that this naphthalene-fused isoxazoles synthesis protocol was relatively more efficient than the triazoles system and resulted in higher yields of the corresponding annulation products (Table 3, entries 1, 6, 14 and 17 VS Table 2, entries 1, 7, 13 and 17). The structure of the naphthalene-fused isoxazole product was also

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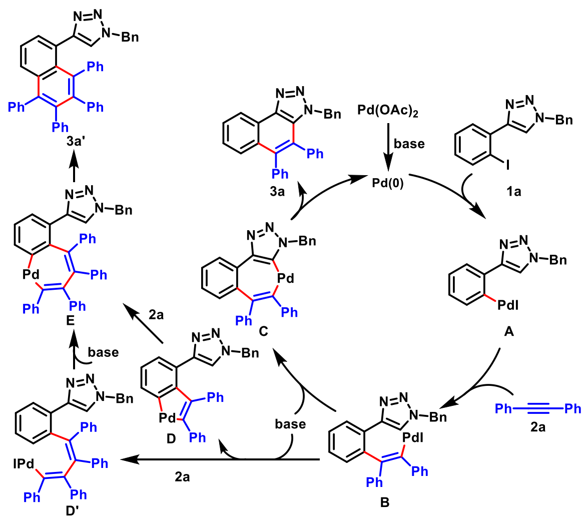
confirmed by the single crystal X-ray diffraction of compound **5m** (Figure 2).[16]

Based on these observations and the previous studies related to the palladium-catalyzed annulation reactions,[17] a plausible mechanism for the reaction of aryltriazole with alkyne was proposed in Scheme 2. The reaction starts with the oxidative addition of **1a** with Pd(0) to generate arylpalladium(II) intermediate **A**, which subsequently react with alkyne **2a** to furnish the vinylpalladium species **B**. An electrophilic attack of this vinylic palladium intermediate **B** to the C-5 position of triazole affords a seven-membered palladacycle **C**, and the subsequent reductive elimination to furnish the adduct **3a** with the generation of the active Pd(0) catalyst. With regard to the formation of the adduct **3a'**, participation of another route, which involves a successive insertion of two molecules of alkyne **2a** and the subsequent cyclopalladation to generate a different seven-membered palladacycle intermediate **E**. The corresponding adduct **3a'** was formed through the subsequent reductive elimination of intermediate **E**. It is noteworthy that the selection of base is critical to selectively generate the adducts **3a** or **3a'**. Probably, the better solubility in organic solvent[18] and the relatively steric hindrance of DBN resulted in the favorable transformation from **B** to **C** and prevented the successive insertion of the second molecular of alkyne.




**Scheme 2.** Proposed reaction mechanism.

In conclusion, we have demonstrated that naphthalene-fused triazoles and isoxazoles frameworks can be readily constructed by the palladium-catalyzed annulation of 2-iodoaryltriazole and 2-iodoarylisoxazoles with alkynes, respectively. This method exhibits a broad scope with respect to aryltriazoles, arylisoxazoles and alkynes. The employment of appropriate base such as DBN has found to be critical to conduct the reaction regioselectively. This protocol provides a straightforward ring extension method for the construction of polycyclic aromatic compounds. Further study to evaluate the utilities of the products and extend the scope of related heterocyclic substrates are now in progress.

## Experimental Section

**General procedure:** To a mixture of $Pd(OAc)_2$ (0.04 mmol, 0.2 eq.), PivOH (0.4 mmol, 2.0 eq.), 1-benzyl-4-(2-iodophenyl)-1*H*-1,2,3-triazole **1a** or 3-benzyl-5-(2-iodophenyl)isoxazole **4a** (0.2 mmol, 1.0 eq.) and 1,2-diphenylethyne **2a** (0.8 mmol, 4.0 eq.) in DMF (2 mL) under $N_2$ atmosphere, DBN (0.2 mmol, 2.0 eq.) was added. The system was stirred at 160 °C or 140 °C until the complete consumption of 1-benzyl-4-(2-iodophenyl)-1*H*-1,2,3-triazole **1a** or 3-benzyl-5-(2-iodophenyl)-isoxazole **4a** detected by TLC analysis. The resulting mixture was washed with water and extracted with ethyl acetate. The organic layer was filtered on celite and evaporated under reduced pressure. Purification by flash column chromatography (PE:EA = 10:1) afforded the desired product **3a** or **5a**.

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