# Indoles Rather than Triazoles from the Ruthenium Porphyrin-Catalyzed Reaction of Alkynes with Aryl Azides

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**S** *Supporting Information*

**ABSTRACT:** An unprecedented reactivity of aryl azides toward alkynes is presented herein. The reaction performed well in the presence of 2 mol % of ruthenium porphyrin catalysts and afforded substituted indoles instead of triazoles. The procedure is particularly appealing for the synthesis of C3-functionalized indoles which bear EWG on the fragment coming from the azide. The method allowed the synthesis of 15 derivatives with yields up to 95%, high regioselectivity, and without requiring the time-consuming prefunctionalization of reagents and the addition of oxidants and/or additives.

**KEYWORDS:** *indole, azide, alkyne, ruthenium, porphyrin*
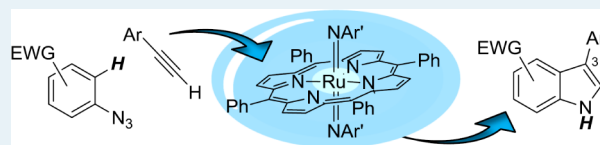
Indole-containing molecules represent one of the most important classes of heterocycles due to their chemical reactivity and pharmaceutical properties.[1] As a logical consequence, there is an increasing interest in the scientific community to develop convenient synthetic strategies to obtain this class of molecules, and several reviews have been published on this subject over the years.[2] The most important strategies to synthesize indoles employ either *ortho*-disubstituted or monofunctionalized arenes as the starting material (Scheme 1).

**Scheme 1. General Strategies Achieving Indoles**
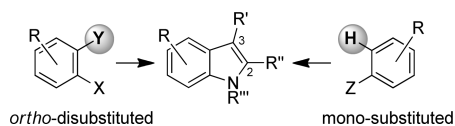


Even if *ortho*-disubstituted[2b,d,3] arenes are reagents in many classic synthetic routes such as Larock, Castro, Hegedus, Mori-Ban, Ma, and Cacchi syntheses, monosubstituted derivatives[2e] offer several advantages in terms of synthetic accessibility and structural versatility. Fischer[4] was the first to use *N*-arylhydrazines in his pioneering work, and later these molecules were applied by others in several Fischer related methodologies.[2d] Nowadays other monofunctionalised arenes, such as *N*-aryl enamines,[5] *N*-aryl imines,[6] nitroalkenes,[7] nitroarenes,[8] nitrosoarenes,[9] anilines,[10] acetanilides,[11] and azides,[12] are extensively used as substrates in indole syntheses.

Among the available aromatic substrates, azides display a favorable activity/sustainability relationship due to the formation of the ecofriendly $N_2$ as the only byproduct of the C−H bond amination. In these reactions the indole formation is due to *intra*molecular annulations in which the nitrene functionality is involved.

In the past decade we have largely employed aryl azides ($ArN_3$) as aminating agents,[13] and this paper reports for the first time the reactivity of $ArN_3$ toward alkynes in the presence of ruthenium complexes forming indoles through the activation of a $sp^2$ C−H bond of the azide itself. The following data assume a particular importance considering that transition metal-catalyzed *inter*molecular reactions of $ArN_3$ with alkynes usually afford triazoles.[14] To the extent of our knowledge, only one example has been reported of *intra*molecular annulations of *ortho*-azidoarylalkynes yielding indoles,[15] but the presence of a gold catalyst was crucial to activate the alkyne C≡C bond toward the azide.

The model reaction between 3,5-*bis*(trifluoromethyl) phenyl azide (**1a**) and phenylacetylene (**2a**) was performed by using different experimental conditions illustrated in Table 1. The reaction optimization enabled the synthesis of the C3-substituted indole **3a** obtained in a high yield and short reaction time.
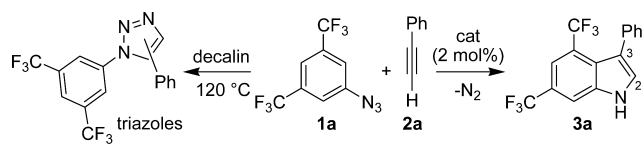
As reported in entry 1 of Table 1, the catalyst-free reaction of **1a** with **2a** in refluxing benzene occurred without a significant azide conversion and with the formation of 1-(3,5-*bis*(trifluoromethyl)phenyl)-5-phenyl-1*H*-1,2,3-triazole and 1-(3,5-*bis*(trifluoromethyl)phenyl)-4-phenyl-1*H*-1,2,3-triazole in a ratio 4:1 (12% total yield). The triazoles yield was quantitative when the reaction was executed in decalin at 120 °C; in both cases the formation of indole **3a** was not observed. No reaction occurred when the mixture of so-formed triazoles was treated with any of the ruthenium catalysts reported in Table 1, thus excluding that **3a** was obtained by a metal-catalyzed rearrangement of triazole formed by the [3 + 2]-cycloaddition of azide with alkyne.[16]

**Table 1. Synthesis of 3a**[a]



| entry | catalyst | conv.[b] | t (h) | 3a yield[c] |
|---|---|---|---|---|
| 1 | none | 15% | 6 | |
| 2 | Ru$^{II}$(TPP)CO (4) | 100% | 6 | 65% |
| 3 | [Ru$^{IV}$(TPP)(OMe)$_2$]$_2$O (5) | 90% | 14.5 | 60% |
| 4 | Ru$^{VI}$(TPP)(NAr)$_2$ (6) | 100% | 1 | 86% |
| 5 | Ru$^{VI}$(TPP)(NAr)$_2$ (6) | 100%[d] | 2.5 | 73% |
| 6 | Ru$^{VI}$(TPP)(NAr)$_2$ (6) | 29%[e] | 12.5 | 19% |
| 7 | Ru$^{VI}$(TPP)(NAr)$_2$ (6) | 96%[f] | 12 | 36% |

[a]Catalyst (0.01 mmol) in 10.0 mL of refluxing benzene under $N_2$ with the mol ratio cat./1a/2a = 1:50:250. [b]The ArN$_3$ conversion (Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$) was monitored by IR spectroscopy (N$_3$ absorbance at 2116 cm$^{-1}$). [c]Isolated yield. [d]Refluxing 1,2-dichloroethane. [e]Refluxing n-hexane. [f]Decalin at 80 °C.

Complexes Ru$^{II}$(TPP)CO (TPP = dianion of tetraphenyl porphyrin) (4), [Ru$^{IV}$(TPP)(OMe)$_2$]$_2$O (5),[17] and Ru(TPP)-(NAr)$_2$ (Ar = 3,5-(CF$_3$)$_2$C$_6$H$_3$) (6)[18] were tested to study the effect of the Ru oxidation state on the catalytic efficiency. All catalysts promoted the synthesis of 3a in good yields but with different rates. The best catalytic performance was observed in refluxing benzene in the presence of 6 (entry 4, Table 1) which can be easily prepared in high yields through the reaction of the commercially available Ru(TPP)CO with 1a.[18] Complexes Co$^{II}$(TPP) and Fe$^{III}$(TPP)Cl were ineffective in catalyzing the reaction between 1a and 2a, and in both cases only traces of indole were formed.

The *inter*molecular reaction of acyl azides with alkynes to afford oxazoles instead of triazoles was already reported;[19] however, this is the first account which describes the reaction of aryl azides and alkynes affording indoles. Consequently, our first concern was to propose a reaction mechanism to highlight the synthetic potentiality of the present procedure. Considering that the catalytic activity of Ru(TPP)(NAr)$_2$ (6) was higher than Ru(TPP)CO (4) and previous studies of our[18,20] and other research groups[21] on the role of *bis*-imido ruthenium(VI) porphyrin complexes as catalytic intermediates in amination reactions promoted by ruthenium(II) derivatives, we can suggest an active role of 6 in the formation of indole 3a. The catalytic role of 6 was supported by the stoichiometric reaction transfer of a "NAr" moiety from Ru(TPP)(NAr)$_2$ (6) to phenylacetylene (2a), yielding the corresponding indole 3a in 50% yield (see the SI). On the basis of the proposed reactivity of nitrenes toward acetylenes to form highly unstable antiaromatic 1H-azirines[22] and taking into account a recent paper on the formation of a Ru(IV) aziro intermediate by the reaction of a Ru(VI) nitrido complex with an alkyne,[23] we propose the mechanism reported in Scheme 2. We suggest that the first step of the cycle could be the formation of the "elusive" N-substituted-1H-azirine intermediate A that cannot rearrange itself to become a more stable 2H-azirine and can easily be involved in a ring opening reaction. Then, the polarization of a sp$^2$ C−H aromatic bond, placed in *ortho* positions with respect to a EWG, favors a hydrogen-transfer reaction (HAT) which is responsible for the indole formation. The regioselective formation of the C3-functionalized indole can be explained by the stabilization of the partial positive charge, formed during

**Scheme 2. Proposed Mechanism of the 3a Formation**
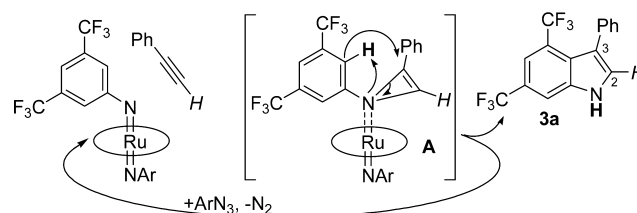


the ring opening reaction, on the more substituted carbon atom of the alkyne. It is important to remember that even if thermal[22c,24] or metal-mediated[12d,25] rearrangements of 2H-azirines to indoles have already been reported, no one example of stable 1H-azirines is present in the literature due to their high energetic nature.[22a]

The formation of the unstable 1H-azirine A was supported by the following experiments. (i) The phenylacetylene C−H bond is not involved in the HAT reaction as established by the reaction of PhC≡CD with 1a. The indole bearing the deuterium atom on the C2 position of the ring was exclusively formed indicating that the phenylacetylene C−D bond does not break during the catalytic reaction. (ii) The very low kinetic isotopic effect ($k_H/k_D$ = 1.1), which was achieved by reacting 2a with an equimolar amount of 1a and its deuterated derivative 3,5-(CF$_3$)$_2$C$_6$D$_3$N$_3$, suggested that the activation of the sp$^2$ aromatic C−H bond is not the rate-determining step of the cycle. (iii) Any attempt to detect the 1H-azirine intermediate A by NMR spectroscopy during the catalytic reaction failed in accord to a rapid rearrangement of A to indole which prevented the accumulation of A during the reaction. Furthermore, the synthesis of 3a was not influenced by the addition of the radical trap TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxy) to exclude the formation of long-lived radical intermediates in this reaction.

The mechanism shown in Scheme 2 points out that good catalytic activity should be obtained by introducing EWG on the ArN$_3$ to polarize the aromatic C−H bond. Bearing in mind the above information we studied the scope of the reaction by using 2 mol % of the catalyst Ru(TPP)(NAr)$_2$ (6) and an alkyne excess with respect to the azide (Table 2). When a very high excess of alkyne was required to produce good indole yields (synthesis of 3k−3n and 8m), alkyne was quantitatively recovered at the end of the catalytic reaction by distillation under reduced pressure and reused to reduce costs of the procedure (see the SI). In all the cases reported in Table 2 the missing mass balance was an aniline and diazene mixture derived from a partial decomposition of the employed azide. It should be underlined that we employed complex 6 as catalytic species instead of using the *bis*-imido corresponding to the employed azide for each reaction due to the difficulty obtaining stable imido complexes from azides 1k−1n. Only *bis*-imido Ru(TPP)(NAr')2 (Ar' = 3,5-(NO$_2$)$_2$C$_6$H$_3$) (7) was stable enough to be prepared in high yields (see the SI) and employed as the catalyst for the synthesis of 3j. A similar 3j yield of 80% was obtained by using 7 instead of 6 as the catalytic species. For the synthesis of 3k−3n and 8m we tried to synthesize the opportune *bis*-imido *in situ* before adding alkyne, but indoles were formed in lower yields than aforementioned as well as when Ru(TPP)CO (4) was used as the catalyst. It is worth noting that the use of 6 as the catalyst implied a sacrificial role of nitrene "ArN" moieties of the *bis*-imido catalyst which were transferred to alkyne forming the corresponding undesired

**Table 2. Complex 6-Catalyzed Synthesis of Indoles[a,b]**
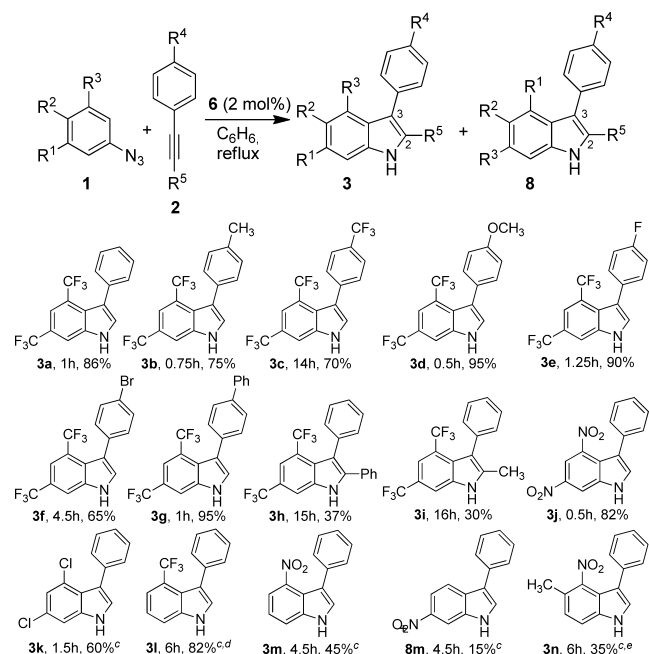


$^a$Catalyst **6** (0.01 mmol) in 10.0 mL of refluxing benzene under $N_2$, mol ratio **6**/azide/alkyne = 1:50:250. $^b$Isolated yield. $^c$Mol ratio **6**/azide/alkyne = 1:50:1000. $^d$NMR yield calculated in the **3l/8l** mixture. $^e$Isomer **8n** was formed in traces (see SI)

indole **3a**. This collateral reaction can be tolerated since the small quantity of **3a** can be separated from the desired indole during purification.

Initially the reactivity of 3,5-*bis*(trifluoromethyl)phenyl azide (**1a**) toward differently substituted alkynes was tested. The reaction of **1a** with aromatic terminal alkynes **2a**–**2g** afforded the desired C3-functionalized indoles in high yields and with complete regioselectivities; the formation of C2-substituted indoles was never observed. The catalytic efficiency of the reaction depends on the electronic characteristic of $R^4$, and best yields and shortest reaction times were achieved when $R^4$ was an electron-donating group (compare **3c** and **3d**, Table 2). The use of an alkyne excess prevented the functionalization of the C2 position of the indole by the aryl azide as recently reported in the presence of **6** by C. M. Che and co-workers.[26]

Despite aromatic internal alkynes **2h**–**2i** being converted into the corresponding indoles, the steric hindrance of the alkyne was responsible for incomplete azide conversion, long reaction times, and modest indole yields. Nevertheless, it is important to underline that compound **3i** was the only isolated indole, and the formation of the isomer which bears the methyl and phenyl groups on the C3 and C2 positions, respectively, was not observed. Unfortunately, the reported procedure was not effective using aliphatic alkynes, such as trimethylsilyl acetylene or 1-heptyne, as reaction substrates.

The synthetic versatility of the reported methodology was then investigated by reacting phenyl acetylene (**2a**) with aryl azides **1j**–**1n**. When $R^1 = R^3 = NO_2$, indole **3j** was precipitated from the reaction mixture as a pure compound and obtained in a good yield without any further purification. Lower yields were achieved by replacing the two nitro groups with two chlorine atoms (compound **3k**, Table 2). As reported in Table 2, compounds of type **3** were formed as sole reaction products by employing 3,5-disubstituted ($R^1 = R^3$) aryl azides as the

substrates. In this case two equivalent C–H bonds on the *ortho* position of the azide group were present, and therefore the activation of one or the other afforded the same indole as the reaction product. Conversely, if $R^1 = H$ and $R^3 = CF_3$ or $NO_2$ the chemoselectivity of the reaction decreased, as a result of the formation of both isomers **3** and **8** (see general scheme of Table 2) due to the presence of two chemically different $sp^2$ C–H bonds in the *ortho* position with respect to the $N_3$ substituent. An electron-withdrawing $R^3$ group can activate both of these two C–H bonds because it is located either in an *ortho* or a *para* position with respect to the C–H bond involved in the reaction. When $R^3$ was a $CF_3$ group, the isomer **3l** was the strongly favored reaction product indicating that a trifluoromethyl group activated the cleavage of a C–H bond placed in an *ortho* position better than in a *para* position, always referring to $R^3$. The isomer **8l** was formed in 5% yield as revealed by GC-MS and $^{19}F$ NMR analyses. The replacement of $CF_3$ by a $NO_2$ group provoked a decrease in the reaction selectivity, isomer **8m** was formed in higher yields (15%) than **8l** probably due to the mesomeric effect of the nitro group. The indole formation was not observed when 3,4,5-trimethoxy-phenyl azide was reacted with phenylacetylene (**2a**) to support the importance of the electronic withdrawing properties of azide aromatic substituents for the catalytic efficiency. Only traces of indole were formed by using 4-nitrophenyl azide or 4-(trifluoromethyl)phenyl azide confirming the directing role of the EWG on the aryl moiety of the azide. Finally, it should be noted that indoles **3b**, **3i**, and **3n** were obtained without the contemporary amination of the benzylic methyl group, although there was good catalytic activity of the ruthenium(VI) *bis*-imido **6** in benzylic aminations by $ArN_3$.[18]

In conclusion, we have reported a novel synthesis of indoles by an intermolecular reaction of aryl azides with alkynes. The catalytic reaction occurred in the presence of 2 mol % of a Ru porphyrin catalyst, and the presence of oxidant species and/or additives was not required. The scope of the reaction was studied employing reagents that are either commercially available (alkynes) or can easily be obtained in a single step (azides); 15 indole derivatives were isolated with yields up to 95% and, except for two cases, with complete regioselectivity. The reaction works for the synthesis of indole bearing substituents such as Cl, $NO_2$, and Br suitable for further chemical modification. In addition, the employment of terminal alkynes allowed the regioselective synthesis of C3-substituted indoles where the C2 position is available for ensuing functionalization.[2g,27] A preliminary mechanistic proposal was provided, and a more in-depth investigation is in progress to furnish a more detailed picture of this novel reaction.

## ■ ASSOCIATED CONTENT

### ⓢ Supporting Information

Experimental procedures, characterization data, and $^1H$ and $^{13}C$ NMR spectra for all products are 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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