Heterocycle Synthesis

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Platinum-Catalyzed Domino Reaction with Benziodoxole Reagents for Accessing Benzene-Alkynylated Indoles**

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Abstract: *Indoles are omnipresent in natural products, bioactive molecules, and organic materials. Consequently, their synthesis or functionalization are important fields of research in organic chemistry. Most works focus on installation or modification of the pyrrole ring. To access benzene-ring-functionalized indoles with an unsubstituted pyrrole ring remains more challenging. Reported herein is a platinum-catalyzed cyclization/alkynylation domino process to selectively obtain C5- or C6-functionalized indoles starting from easily available pyrroles. The work combines, for the first time, a platinum catalyst with ethynylbenziodoxole hypervalent iodine reagents in a domino process for the synthesis of polyfunctionalized arene rings and gives access to important building blocks for the synthesis of bioactive compounds and organic materials.*

Functionalized indoles occupy a privileged position in organic chemistry as they can be found in biomolecules, drugs, agrochemicals, and materials.[1] To access these important building blocks, a first approach consists in the introduction of functional groups onto simple, commercially available indoles. To have a more efficient alternative to well-established cross-coupling reactions, the transition-metal-catalyzed direct functionalization of a C–H bond on indoles has been intensively investigated in the last two decades. Nevertheless, this approach is mostly limited to the modification of the more reactive pyrrole ring (innate reactivity, Figure 1 a).[2] The functionalization of the benzene ring has been only rarely achieved and is limited to C2,C3-disubstituted indoles.[3] One notable exception is the selective iridium-catalyzed C7-borylation of indoles reported by Hartwig and co-workers.[4] We were particularly interested by the introduction of an alkyne onto the benzyl ring of indoles, as alkynes are key building blocks in medicinal, synthetic, and materials chemistry.[5] Direct alkynylation approaches can be used only to access 2- and 3-substituted indoles.[6] This is an important limitation, as either 5- or 6-alkynylated indoles can be found in bioactive compounds such as the 5-LOX (5-lipoxygenase) inhibitor **1**,[7a] and NMDA (*N*-methyl-D-aspartate receptor) antagonist **2** (Figure 1 b).[7b] Alkynylated carbazoles are especially important for organic materials, such as the macrocycle **3**, an organic sensor for the detection of TNT.[7c] If an efficient method for the synthesis of benzene-alkynylated indoles can be developed, more-complex compounds could then be easily obtained by using the well-established C–H functionalization at either the C2- and C3-positions, or transformations of the triple bond.

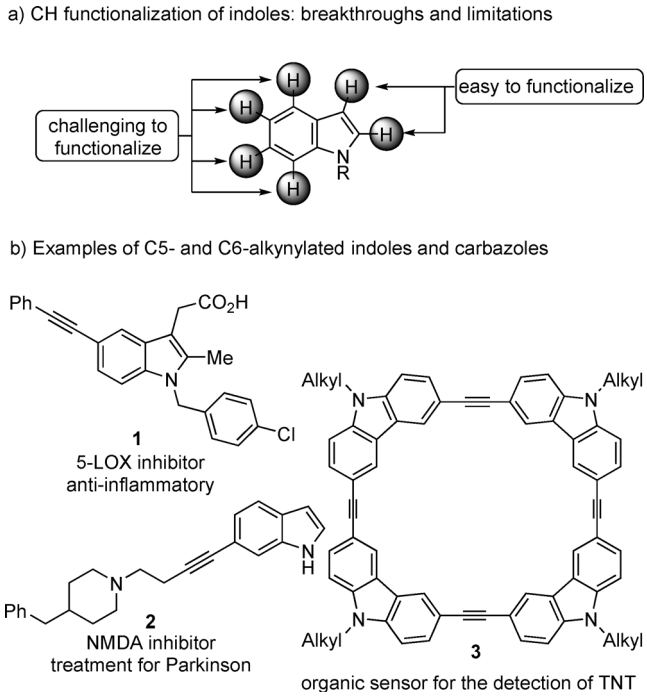

Figure 1. 5- and 6-Alkynylated indoles: Outside the scope of C–H functionalization.

As C–H metalation of the arene ring of indoles is extremely difficult in the presence of the more reactive C2 and C3 C–H bonds, we wondered if the desired reactive intermediate could be generated in situ during a metal-catalyzed cyclization step (Scheme 1). The use of such domino or cascade processes is one of the most efficient ways to increase molecular complexity in organic synthesis,[8] but it has not yet been applied to the synthesis of benzene alkynylated indoles. In fact, reported cascade approaches by the groups of Cacchi and Zhu for the synthesis of alkynylated indoles have focused on the construction of the pyrrole ring using palladium catalysis (Scheme 1 a).[9] To develop a domino process to access indoles functionalized on the benzene ring, another type of cyclization would be needed. In this respect, we were particularly attracted by the work of the groups of Alcaide, Hashmi, and Ma, among others, to form

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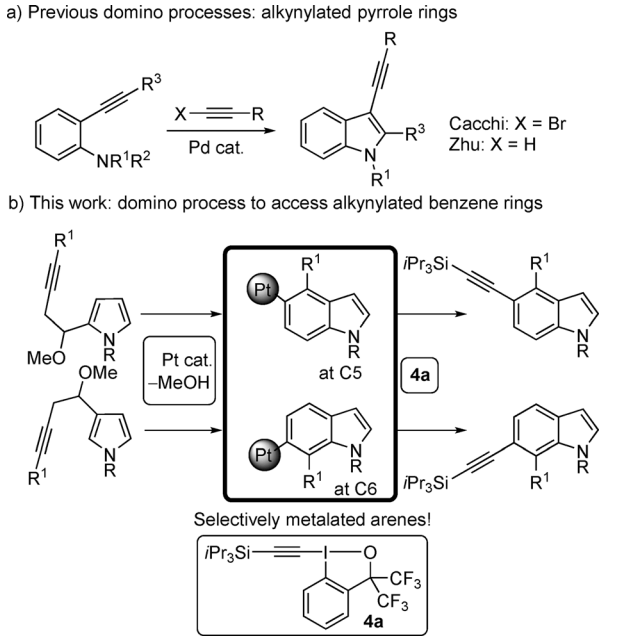


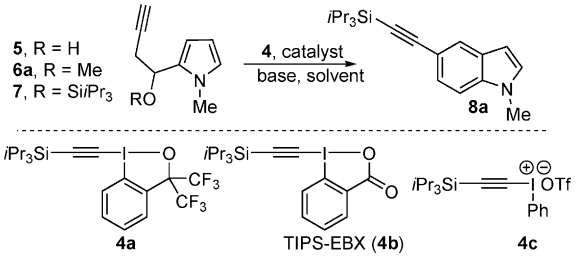
Scheme 1. Domino processes to access alkynylated indoles.

the benzene ring of heterocycles by the cyclization of alkynes[10] using well-established π-activation catalysts such as gold and platinum.[11] In fact, one single example of gold-catalyzed indole ring formation starting from easily available pyrrole ethers has been reported.[10b] This precedence provides a solid basis for the cyclization step of the domino process, but the envisaged alkynylation appeared highly challenging, as the generated intermediates are known to broadly favor protodemetalation over further C–C bond formation. The formation of a new C–C bond on a Csp^2 center of an indole arene ring after cyclization has to the best of our knowledge never been realized.

To solve the challenge associated with the low reactivity of gold intermediates in C–C bond-forming reactions, our group has turned to the exceptional reactivity of hypervalent iodine alkynylation reagents.[6b–d,12] We recently reported the first successful domino process in the synthesis of 3-alkynylated furans by the cyclization/alkynylation of allene ketones.[13] Although this work resulted in the synthesis of regioisomers difficult to access by C–H functionalization, it was still limited to the more reactive heteroarene class of substrates. Herein, we report that the change to a platinum catalyst in combination with the ethynylbenziodoxole (EBX) reagent **4a**[14] led to a successful cyclization/alkynylation domino process starting from pyrrole homopropargylic ethers to give either C5- or C6-alkynylated indoles in good yields and high regioselectivity (Scheme 1b). In addition to giving access to important building blocks and scaffolds, this new transformation also represents a breakthrough in the field of catalysis and hypervalent iodine chemistry, as it is the first example of a platinum-catalyzed process with EBX reagents.

We started our investigation with the pyrrole derivatives **5** and the hypervalent iodine reagent **4a**. The substrate **5** (see Table 1 for structure) is easily accessible in two steps from commercially available compounds and the generation of only one molecule of water is required for aromatization. The previous catalytic conditions developed in our group for the domino cyclization/alkynylation of allene ketones[13] were not suitable for the pyrrole system. After a broad screening of gold catalysts, the desired product could not be obtained. We then turned our attention to platinum catalysts (Table 1).[10c,11a] Preliminary results with $PtCl_2$ were promising, as 13% of the 5-ethynyl indole **8a** could be isolated with sodium carbonate as the base (entry 1). Attempts to modulate the reactivity of the catalyst by formation of a more electrophilic platinum salt (entry 2) or using nitrogen-based ligands (entries 3 and 4) both suppressed the formation of **8a**. In contrast, changing the base to sodium bicarbonate allowed increasing the yield to 40% (entry 5). Investigation of solvents showed that CH_3CN was best (entries 6–8). Neither the use of other hypervalent iodine reagents, such as TIPS-EBX (**4b**) or alkynyliodonium salt **4c** (entries 9,10), nor platinum(IV) or platinum(0) catalysts (entries 11 and 12) led to improved results. At this point, we decided to investigate the influence of the group eliminated in the aromatization step. Changing the leaving group from hydroxy to methoxy

Table 1: Optimization of the domino cyclization/alkynylation reaction.



Entry	Pyrrole	Catalyst	4	Base	Solvent	Yield [%][a]
1	**5**	$PtCl_2$	**4a**	Na_2CO_3	CH_3CN	13
2	**5**	$PtCl_2$/AgOTf	**4a**	Na_2CO_3	CH_3CN	<5
3	**5**	$PtCl_2$/bipy	**4a**	Na_2CO_3	CH_3CN	<5
4	**5**	$[Pt(NH_3)_2Cl_2]$	**4a**	Na_2CO_3	CH_3CN	<5
5	**5**	$PtCl_2$	**4a**	$NaHCO_3$	CH_3CN	40
6	**5**	$PtCl_2$	**4a**	$NaHCO_3$	toluene	30
7	**5**	$PtCl_2$	**4a**	$NaHCO_3$	THF	21
8	**5**	$PtCl_2$	**4a**	$NaHCO_3$	MeOH	14
9	**5**	$PtCl_2$	**4b**	$NaHCO_3$	CH_3CN	27
10	**5**	$PtCl_2$	**4c**	$NaHCO_3$	CH_3CN	<5
11	**5**	$PtCl_4$	**4a**	$NaHCO_3$	CH_3CN	<5
12	**5**	$[Pt(PPh_3)_4]$	**4a**	$NaHCO_3$	CH_3CN	<5
13	**6a**	$PtCl_2$	**4a**	$NaHCO_3$	CH_3CN	91
14	**7**	$PtCl_2$	**4a**	$NaHCO_3$	CH_3CN	80
15	**6a**	$PtBr_2$	**4a**	$NaHCO_3$	CH_3CN	98[b]
16	**6a**	PtI_2	**4a**	$NaHCO_3$	CH_3CN	<5
17	**6a**	$PtBr_2$	**4a**	$NaHCO_3$	CH_3CN/C_6H_5Cl (v/v = 1:5)	45
18	**6a**	$PtBr_2$	**4a**	$NaHCO_3$	CH_3CN/THF (v/v = 1:5)	96
19	**6a**	$PtBr_2$	**4a**	$NaHCO_3$	CH_3CN/THF (v/v = 1:10)	93

[a] Reaction conditions: **5**–**7** (0.10 mmol), catalyst (10 mol%), **4** (0.20 mmol), base (0.20 mmol), 0.1 M, RT, 72 h. Yield is that of the product isolated after column chromatography. [b] Not reproducible. bipy = bipyridine, Tf = trifluoromethanesulfonyl, THF = tetrahydrofuran.

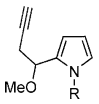
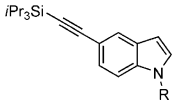
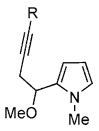
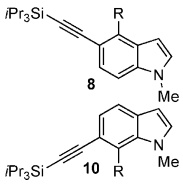
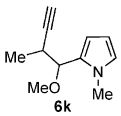
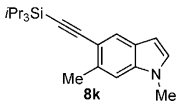
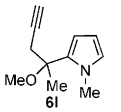
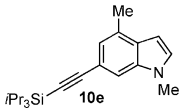
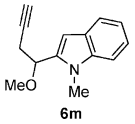
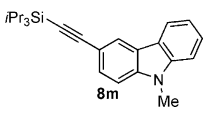
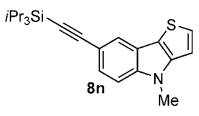
led to a major increase in yield to 91% (entry 13). A silyl ether could also be used,[10b] but led to a lower yield (80%, entry 14). A bromide counterion led to a slightly higher yield (entry 15) and iodide completely suppressed the reaction (entry 16). The results obtained with $PtCl_2$ and $PtBr_2$ were difficult to reproduce, probably because of the poor solubility of **4a** in CH_3CN. Using a cosolvent led to more reproducible results (entries 17–19), and THF was the best, thus giving the desired product **8a** in 96% yield (entry 18).

With optimized reaction conditions in hand, we then examined the scope of the cyclization/ethynylation domino reaction (Table 2). The indole **8a** was obtained in 84% yield upon isolation from a 0.3 mmol scale reaction (entry 1). Only C5-ethynylation was observed. Modification of the substituent on the nitrogen atom was investigated first. A tolyl and a benzyl group were well tolerated (entries 2 and 3), as well as different substituents on an alkyl chain such as methoxy and trifluoromethyl (entries 4 and 5). Substitution of the alkyne was examined next. The desired C5-alkynylated product **8f** was obtained in 70% yield with a methyl group (entry 6). With aromatic substituents, formation of the C6-alkynylated product **10** was observed for the first time. The C5-alkynylated product **8** was still the major product with either a phenyl, a tolyl, or a *para*-bromophenyl substituent (entries 7–9). The latter case also demonstrated that halogen substituents were tolerated under the reaction conditions, thus allowing further functionalization of the products by classical cross-coupling chemistry. With a naphthyl group, a 1:1 mixture of regioisomers was obtained (entry 10), and with a methyl substituent in the propargylic position, the C5-alkynylated product **8k** was obtained in 75% yield (entry 11). In contrast, when the tertiary ether **6l** was used, the C6-alkynylated product **10e** was formed (entry 12). The alkynylated carbazole **8m** was obtained in 76% yield (entry 13), and the domino process could also be applied to the synthesis of the thiophene-fused heterocycle **8n** in 78% yield (entry 14).

Having achieved the synthesis of C5-alkynylated indoles starting from C2-substituted pyrroles, we then turned to C3-substituted derivatives to achieve C6 functionalization. (Table 3). The pyrrole **9a**, bearing a terminal alkyne, gave the C6-alkynylated indole **10a** exclusively in 77% yield (entry 1). Substituted alkynes could also be used to access 6,7-disubstituted indoles in 47–53% yield (entries 2–4). Starting from tertiary ethers, 4,6-disubstituted products could be obtained (entries 5 and 6). In this case, the same products were obtained as when starting from C2-substituted pyrroles. We then wondered if more-complex trisubstituted indoles could be accessed. In fact, the 4,6,7- (**10g**) and 4,5,6-substituted (**10h**) indoles were obtained in 44 and 34% yield, respectively (entries 7 and 8). Although the yields are moderate, the synthesis of these polysubstituted compounds using another method would have been extremely difficult. Finally, the synthesis of the C6-alkynylated carbazoles **10i,j** was also possible (entries 9 and 10).

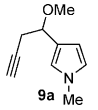
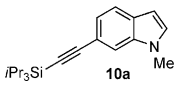
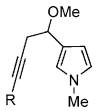
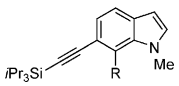
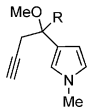
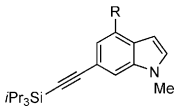
The developed domino process is highly complex. Consequently, any proposal about the reaction mechanism is highly speculative at this stage of development. Based on the well-established π-acidity of platinum,[11a] the first step of the catalytic cycle is most probably activation of the alkyne to give complex **A** (Scheme 2). At this point, cyclization could occur either at the C2- or C3-position of the pyrrole ring to give intermediates **B** or **D**, respectively. Attack on the more nucleophilic C2 position, thus leading to **B** is more probable. From **B**, two different pathways are possible: a 1,2 shift of the platinum-bearing vinyl group via the platinum carbene cyclopropane intermediate **C**[11a,15] to give the carbocation **D**, or 1,2-shift of the alkoxy substituent to give intermediate **G**.[10] C5- and C6-metalated intermediates **E** and **H**, respectively, will then be generated from the corresponding compounds **D** and **G** after deprotonation and aromatization by methanol elimination. The alkynylated products **8** and **10** can be formed by reaction of **4a** with organoplatinum intermediates. At this point, it is not clear if the alkynylation step proceeds through an oxidative addition/reductive elimination mechanism on

Table 2: Scope of 5-alkynylated indoles.

Entry	Substrate	Product	Yield [%][a]
			
1	R = Me (**6a**)	**8a**	84
2	R = tolyl (**6b**)	**8b**	81
3	R = benzyl (**6c**)	**8c**	83
4	R = 3-methoxy propyl (**6d**)	**8d**	80
5	R = 1,1,1-trifluorobutyl (**6e**)	**8e**	82
			
6	R = Me (**6f**)	**8f**	70
7	R = phenyl (**6g**)	**8g/10c** (4:1)	70 (56)[b]
8	R = tolyl (**6h**)	**8h/10k** (3:1)	69 (52)[b]
9	R = *p*-Br-phenyl (**6i**)	**8i/10l** (2.5:1)	62 (44)[b]
10	R = naphthyl (**6j**)	**8j/10d** (1:1)	31/31
11			75
12			54
13			76
14			78

[a] Reaction conditions: Substrate **6** (0.30 mmol), $PtBr_2$ (10 mol%), EBX reagent **4a** (0.60 mmol), $NaHCO_3$ (0.60 mmol), THF/CH_3CN (3 mL, v/v = 5:1), 72–120 h. Yield is that of the product isolated after column chromatography. [b] Yield determined by ^1H NMR spectroscopy. The yield of the isolated isomer **8** is given within parenthesis.

Table 3: Scope of 6-alkynylated indoles.

Entry	Substrate	Product	Yield [%][a]
1			77
			
2	R = Me (**9b**)	**10b**	49
3	R = phenyl (**9c**)	**10c**	53
4	R = naphthyl (**9d**)	**10d**	47
			
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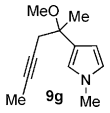
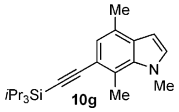
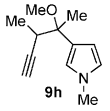
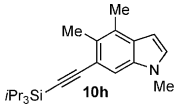
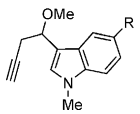
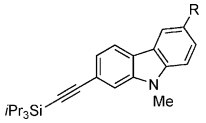
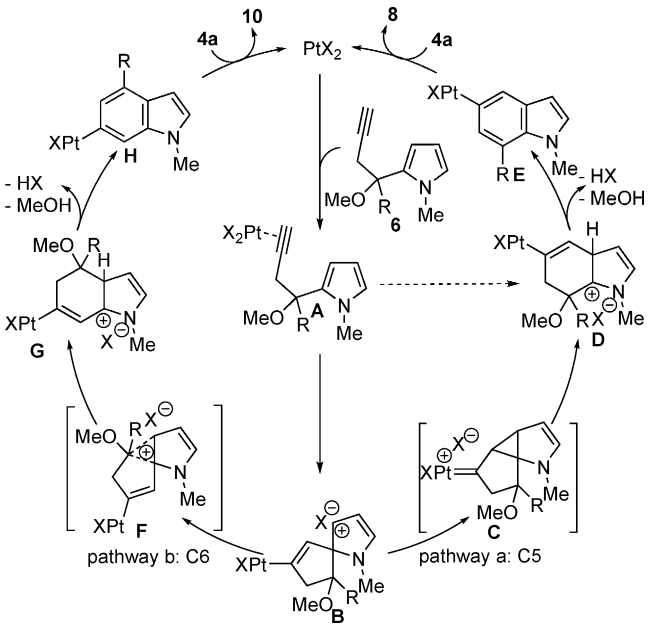
7			44
8			34
			
9	R = H (**9i**)	**10i**	58
10	R = OMe (**9j**)	**10j**	64

[a] Reaction conditions: Substrate **9** (0.30 mmol), $PtBr_2$ (10 mol%), EBX reagent **4a** (0.60 mmol), $NaHCO_3$ (0.60 mmol), THF/CH_3CN (3 mL, v/v = 5:1), 72–120 h. Yield is that of the product isolated after column chromatography.

platinum[16] or by direct nucleophilic attack of the organometallic intermediates onto reagent **4a**.

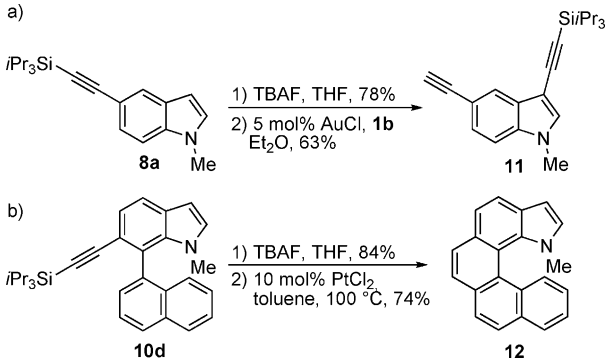
If the C3-substituted pyrrole is used as a starting material, the mechanism is simpler as C2-attack of the indole leads directly to a six-membered ring and therefore to exclusive formation of the C6-alkynylated product **10**. The observed regioselectivity for secondary ethers is in accordance with a shift of the vinyl group. In contrast, shift of the alkoxy group had been observed in the cyclization step when using gold catalysts.[10b] This shift may be due to an easier formation of platinum carbene intermediate **C** when compared to gold catalysts.[17] This result further emphasizes an advantage of the platinum catalyst, as with gold both C2- and C3-substituted pyrroles would have given C6-alkynylated products. With pyrroles substituted with tertiary ethers, C6-alkynylated products were observed independent of the structure of the starting material. In this case, the presence of the methyl group may further stabilize the transition-state **F** and favor the shift of the alkoxy group.



Scheme 2. Proposed mechanism for the domino cyclization/alkynylation.

The obtained alkynylated indoles are interesting building blocks, as the unsubstituted pyrrole ring can be easily further derivatized using established methods, and the terminal alkyne, obtained after silyl group removal, can serve as a platform for further functionalization. For example, deprotection of the alkyne **8a** followed by gold-catalyzed selective C3 alkynylation with TIPS-EBX (**4b**)[6b] gave the monoprotected diyne **11**, which was ready for further selective derivatization (Scheme 3a). Starting from naphthyl derivative **10d**, deprotection followed by platinum-catalyzed cycloisomerization[18] gave access to the helicene **12** (Scheme 3b). Helicenes are important molecules in asymmetric catalysis and material science, but have never been synthesized with a terminal pyrrole ring to the best of our knowledge.[19]

In conclusion, we have reported a new domino cyclization strategy for the efficient synthesis of C5- or C6-alkynylated indoles starting from easily available C2- or C3-substituted pyrroles. Our strategy is complementary to C–H functional-



Scheme 3. Further transformations of the alkynylated indole products. TBAF = tetra-*n*-butylammonium fluoride.

ization, as the benzene positions on indole are difficult to modify directly because of the higher reactivity of the pyrrole ring. Key for success was the unprecedented combination of a platinum catalyst with EBX reagents. The domino process realized in this work represents a new general strategy for the synthesis of alkynylated arenes. Further investigations will focus on the synthesis of other (hetero)arenes and on the introduction of different functional groups in the final bond-forming step.[20]

Keywords: alkynes · cyclization · heterocycles · hypervalent compounds · platinum

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