Direct Alkynylation

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Direct Alkynylation of Indole and Pyrrole Heterocycles**

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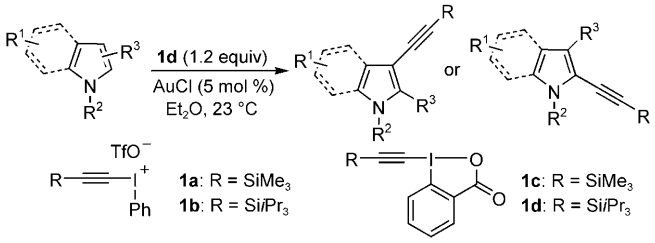
Indoles and pyrroles occupy a privileged position in pharmaceuticals, material sciences, and natural products.[1] Consequently, methods to synthesize and functionalize these heterocycles are of utmost importance in organic chemistry.[2] Metal-catalyzed cross-coupling is the method most often used for the introduction of (hetero)aryl, vinyl, or acetylene groups to indoles and pyrroles, but it requires premodification of the heterocycle.[3] Recently, the direct C–H functionalization of indoles and pyrroles has emerged as a more efficient alternative for the introduction of vinyl and aryl groups.[4] In contrast, examples of the direct alkynylation of aromatic compounds are scarce.[5] Recently reported methods include the gallium-catalyzed acetylenation of phenols and anilines;[5a,b] the palladium-catalyzed alkynylation of N-fused heterocycles,[5c] anilines,[5d] and indoles;[5e] the nickel-catalyzed alkynylation of azoles;[5f] the reaction of pyrroles with bromoacetylene ketone derivatives;[5g,h] and the oxidative N-alkynylation of indoles.[5i] The single example of alkynylation of indoles[5e] was limited to the use of aryl and alkenylbromoacetylenes in large excess (3 equiv). These substrates cannot be converted into free acetylenes and the large excess of reagent needed limited the practicability of the reaction. Furthermore, the reaction was limited to indoles with only methyl, methoxy, or ester functional groups. Indoles substituted at position 2 resulted in a low yield, and 3-substituted indoles could not be used. In view of the limited scope in the case of indoles and pyrroles, there is an urgent need for new alkynylation methods, especially when considering the importance of acetylenes in organic synthesis.[6] Herein, we report a functional group tolerant gold-catalyzed alkynylation of indoles and pyrroles. The reaction proceeds in high yield at room temperature in air by using benziodoxolone-derived hypervalent iodine reagent **1d**, and gives easily deprotected silylacetylene products (Scheme 1).

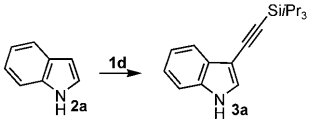
The limited results obtained with halogenated acetylene derivatives[5a–h] prompted us to consider using more-reactive hypervalent iodine reagents.[7,8] In particular, the use of alkynyliodonium salts as electrophilic/oxidative reagents for acetylene transfer are well-established.[8a–g] Surprisingly, their use for C–H functionalization has not yet been reported,



Scheme 1.

although other hypervalent iodine reagents have been highly successful in arylation and heteroatom-transfer reactions.[4g,h,9] However, no product could be isolated when the reaction conditions reported for the direct arylation of indole **2a** using copper[4g] and palladium[4h] catalysts were examined with alkynyliodonium salts **1a** and **1b**[8b,d–f] and neutral benziodoxolone-derived reagents **1c** and **1d** [8h,i] (Table 1, entries 1 and 2); the same result was also obtained with several other metal catalysts.[10] We then turned our attention to gold catalysts.[11] Their capacity to activate multiple π bonds[12] is well-established and they have also been used in the formation of C–C bonds with an accompanying change in the oxidation state of the gold center.[13] The functionalization of C–H bonds using gold catalysts has been realized in classical hydroarylation reactions.[14] Other reports remained limited to stoichiometric methods[15] or the introduction of heteroatoms.[16] Hydroarylation reactions were shown to be

Table 1: Optimization of alkynylation of indole (**2a**).



Entry	Catalyst	Solvent	Yield[a]
1	$Pd(OAc)_2$	AcOH	<5%
2	$Cu(OTf)_2$	CH_2Cl_2	<5%
3	AuCl	CH_2Cl_2	65%
4	$AuCl_3$	CH_2Cl_2	56%
5	[Au(NHC)Cl][b]	CH_2Cl_2	17%
6	AuCl	toluene	42%
7	AuCl	Et_2O	84%
8	AuCl	THF	85%
9	AuCl	CH_3CN	82%
10	AuCl	DMF	62%
11	AuCl	*i*PrOH	81%
12	AuCl	MeOH	51%

[a] Reaction conditions: 0.20 mmol **2a**, 5–10% mol catalyst, 1.2 equiv reagent, 4 mL solvent. Yield was determined by GC-MS. [b] NHC = 1,3-di(2,6-diisopropylphenyl)imidazol-2-ylidene.

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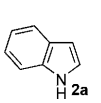
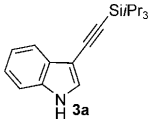
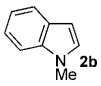
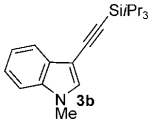
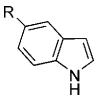
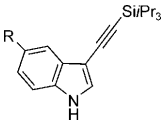
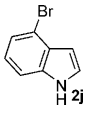
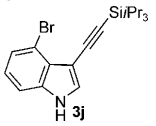
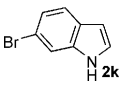
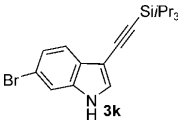
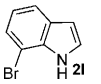
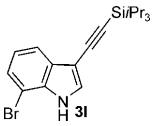
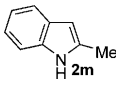
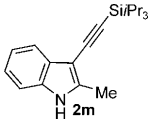
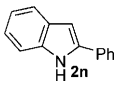
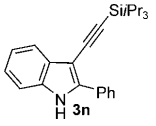
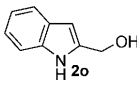
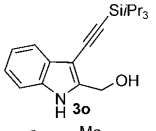
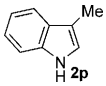
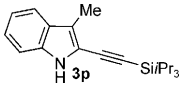
favored in the case of alkynes, and no alkynylation methods based on gold catalysts have so far been developed.[14a] The unique combination of 5 mol% AuCl and sterically hindered reagent **1d**[17] in CH_2Cl_2 led to the formation of the 3-alkynylation product **3a** exclusively in 65% yield (Table 1, entry 3). This constituted the first example of gold-catalyzed C–H alkynylation, as well as an unprecedented use of benziodoxolone-based hypervalent iodine reagents for acetylene transfer.

Examination of several gold catalysts (Table 1, entries 4 and 5)[18] confirmed that AuCl was the best catalyst. The reaction worked in a broad range of solvents (Table 1, entries 6–12), with the best reproducibility and scope obtained in Et_2O (Table 1, entry 7). Inert conditions or dry solvents were not needed for the reaction, and **3a** was isolated in 86% yield on a 0.40 mmol scale after column chromatography (Table 2, entry 1). Importantly, only a slight excess of reagent **1d** (20%) was needed to obtain good yields. This is a distinct advantage of the gold catalyst over the palladium catalysts, for which extensive dimerization of the acetylene group was observed.[5e] Compound **3a** was isolated in 84% yield when the reaction was performed on a 2.0 mmol scale with only 1 mol% of AuCl, which constitutes the lowest catalyst loading reported so far for C–H alkynylation reactions. Furthermore, 63% of 2-iodobenzoic acid (**4**) was recovered by a simple extraction procedure, thus demonstrating a further advantage of the benziodoxolone-based reagent. The obtained 2-iodobenzoic acid (**4**) can then be used for the synthesis of reagent **1d** in two steps and 76% overall yield, with one single recrystallization used for purification. The preparation of **1d** is straightforward, and 6 g of pure **1d** have been obtained from 2-iodobenzoic acid (**4**) in a single day. Deprotection using tetrabutylammonium fluoride (TBAF) allowed the isolation of the indole with a free acetylene substituent in 94% yield.

The scope of the reaction was then examined for several indole derivatives (Table 2). *N*-Methylindole (**2b**) gave the desired product in 83% yield (entry 2). Both electron-donating (entries 3 and 4) and electron-withdrawing (entries 5–9) groups were tolerated in the reaction, including OH (entry 4), CN (entry 5), CO_2H (entry 6), NO_2 (entry 7), Br (entry 8), and I (entry 9) groups, which have never been reported before. Importantly, yields higher than 90% were obtained for Br and I substituents (entries 8 and 9), thus making the method orthogonal to classical palladium(0) cross-coupling reactions, which is not the case for previously reported direct alkynylation methods based on palladium(0).[5c,e] The reaction was also successful for 4-, 6-, and 7-bromo-substituted indoles (entries 10–12). In contrast to previous reports,[5e] good yields were also obtained in the case of 2-substituted indoles (entries 13–15). Finally, 3-methylindole, a substrate for which no successful alkynylation has ever been reported,[5e] gave the 2-alkynylation product in 76% yield (entry 16).

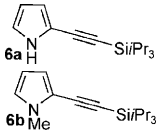
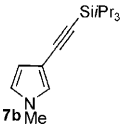
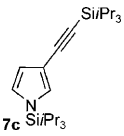
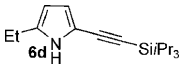
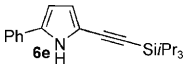
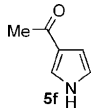
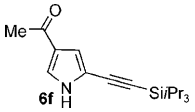
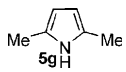
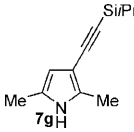
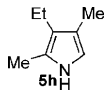
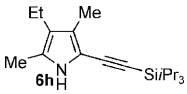
We then turned to the alkynylation of pyrroles (Table 3). Before this study, there was no report on metal-catalyzed direct alkynylation of these heterocycles. Pyrroles are sensitive compounds that usually require protection of the NH group.[19] In the context of an alkynylation reaction, bromopyrroles with unprotected NH groups are too unstable to be useful, and the use of classical Sonogashira reactions consequently involves multistep procedures to give the free acetylene derivatives. Gratifyingly, free pyrroles could be used in our protocol (Table 3, entries 1 and 4–8). For pyrrole

Table 2: Scope of the alkynylation reaction of indoles.

Entry	Substrate	Product	Yield[a]
1	 **2a**	 **3a**	86%
2	 **2b**	 **3b**	83%
			
3	R = OMe (**2c**)	**3c**	80%
4	R = OH (**2d**)	**3d**	76%
5	R = CN (**2e**)	**3e**	80%
6	R = CO_2H (**2f**)	**3f**	67%
7	R = NO_2 (**2g**)	**3g**	85%[b]
8	R = Br (**2h**)	**3h**	93%
9	R = I (**2i**)	**3i**	91%
10	 **2j**	 **3j**	80%[b]
11	 **2k**	 **3k**	77%
12	 **2l**	 **3l**	84%
13	 **2m**	 **2m**	90%
14	 **2n**	 **3n**	88%
15	 **2o**	 **3o**	82%
16	 **2p**	 **3p**	76%

[a] Reaction conditions: 0.40 mmol **2**, 0.48 mmol **1d**, and 0.02 mmol AuCl in 8 mL Et_2O at 23 °C under air for 12–15 h. Yields are reported for products isolated after column chromatography. [b] Purity > 95%; small amounts of **2** could not be separated from the desired product.

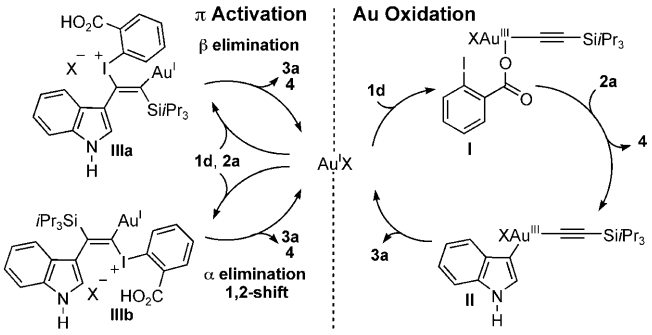
Table 3: Scope of the alkynylation reaction of pyrroles.

Entry	Substrate	Product	Yield[a]
1			62% (83%)[b]
2			48% (**6b**) 25% (**7b**)[b]
3			79%
4			58%
5			60%
6			58%
7			59%[b]
8			48%

[a] Reaction conditions: 0.40 mmol **5**, 0.48 mmol **1d**, and 0.02 mmol AuCl in 8 mL Et_2O at 23 °C under air for 12–15 h. [b] Yields based on **1d** with 3 equiv **5**.

itself, the 2-alkynylation product **6a** was obtained in 62% yield (entry 1). The yield could be increased to 83% by using three equivalents of pyrrole and one equivalent of **1d**. The reaction was sensitive to the steric bulk on the nitrogen atom: while 2-alkynylation product **6a** was obtained exclusively with pyrrole (**5a**; entry 1), a significant amount of 3-alkynylation product **7b** was isolated for *N*-methylpyrrole (**5b**; entry 2), and 3-alkynylation was observed exclusively for *N*-triisopropylsilyl-protected pyrrole (**5c**; entry 3). Consequently, the regioselectivity of the reaction can be controlled by the use of easily removable protecting groups. Monosubstituted (entries 4–6), disubstituted (entry 7), and trisubstituted (entry 8) pyrroles could also be used. An electron-withdrawing group was tolerated at the 3-position (entry 6), but not at the 2-position (result not shown). The use of monosubstituted pyrroles has rarely been reported in metal-catalyzed C–H functionalization reactions,[4f] and the use of di- and tri-substituted pyrroles is unprecedented.

Considering the numerous precedents for gold-mediated activation of π systems[12,14] and the few other examples of C–H functionalization,[15,16] at least two hypotheses could be considered for the mechanism: 1) Similar to the copper system,[4g] oxidation of gold(I) with **1d** to form a gold(III)–acetylene complex **I**, followed by indole metalation and reductive elimination[15b] (Scheme 2) or 2) gold-mediated addition of indole to the triple bond of **1d** to form vinyl–



Scheme 2. Working hypothesis for the mechanism of the alkynylation reaction.

gold complex **IIIa** or **IIIb**,[14] followed either by β-elimination or a α-elimination/1,2-shift sequence[8b] depending on the regioselectivity of the addition. No 1,2-migration of the silicon group was observed in the product when using **1d** with a ^{13}C label next to the silicon atom. Unfortunately, this result does not allow to distinguish between the proposed pathways, as an indole 1,2-shift could also account for this result. Clearly, further experiments are needed to fully understand the reaction mechanism.

In conclusion, we have reported the first gold-catalyzed direct alkynylation of indole and pyrrole heterocycles by using a benziodoxolone-based hypervalent iodine reagent. When compared with the only reported method for the direct alkynylation of indoles,[5e] functional-group tolerance was greatly increased and unprecedented substitution patterns could be obtained. The reaction efficiency was improved (1 mol% catalyst, 1.2 equiv alkyne, 23 °C compared with 10 mol% catalyst, 3 equiv alkyne, 50 °C) and easily deprotected silylacetylene derivatives were obtained. The catalytic, regioselective alkynylation of pyrroles was reported for the first time. The reaction further constitutes a departure from classical gold-catalyzed hydroarylation reactions and was efficient at an unprecedently low catalyst loading compared with other direct alkynylation methods. The unique properties of benziodoxolone-derived hypervalent reagents for acetylene transfer were discovered, which constitutes an important advance in the field of hypervalent iodine chemistry. The exceptional scope of the reaction, as well as the mild reaction conditions and simple experimental procedure (easily accessible reagent, no inert gas, no dry solvent) bode well for the application of the method in organic and medicinal chemistry.

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