Very Important Publication

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Synthesis of 3,3-Disubstituted Oxindoles Containing a 3-(4-Aminobut-2-ynyl) Unit *via* Domino Heck–Sonogashira Reaction in Water

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Abstract: In this study, palladium-catalyzed domino Heck–Sonogashira reactions have been developed in water. Using this strategy, a series of 3-(4-aminobut-2-ynyl)oxindole derivatives with an all-carbon quaternary center at the 3-position were easily synthesized. The reactions provided products in excellent yields with a broad substrate tolerance. The target product was readily converted into a pharmaceutically active molecule, which is used as a 5-HT_7 receptor antagonist.

Keywords: domino reaction; Heck reaction; oxindoles; Sonogashira reaction; terminal alkynes; water

The 3,3-disubstituted oxindole framework is a key structural unit found in various natural products and drugs.[1] As shown in Figure 1, amedalin[2a] (**1**) is an antidepressant drug, which was synthesized in the early 1970s, isapheninum[2b] (**2**) is a laxative used for several years as a non-prescription drug before it was taken off the market in 1972, and linopiridine[2c] (**3**) is in Phase III clinical trials for the treatment of Alzheimer's disease. Recently, a series of new oxindole compounds exhibiting pharmaceutical activity has been reported.[3] (Phenylpiperazinylbutyl)oxindoles (**4**, Figure 1) are selective 5-HT_7 receptor antagonists, and (phenylpiperidinylbutyl)oxindoles (**5**) can be used as neurokinin receptor antagonists. Thus, the 3,3-disubstituted oxindole framework is commercially important; hence, it is imperative for organic chemists to develop new synthetic procedures for obtaining these sub-units.[4]

As a powerful method for constructing complex organic molecules, domino reactions for the one-step formation of two or more bonds under identical reaction conditions have been extensively employed by synthetic chemists.[5] Domino Heck reactions using a Heck reaction as an initiation reaction have been explored in the literature and are becoming a focus for researchers.[6] Several domino Heck reactions, such as Heck–Suzuki,[6a,7] reductive Heck,[8] Heck-C–H activation,[9] Heck-carbohalogenation,[6b] and Heck-aza-Michael,[10] have been reported, and some of them[11] have been employed for the total synthesis of natural products and their analogs. Most recently, our

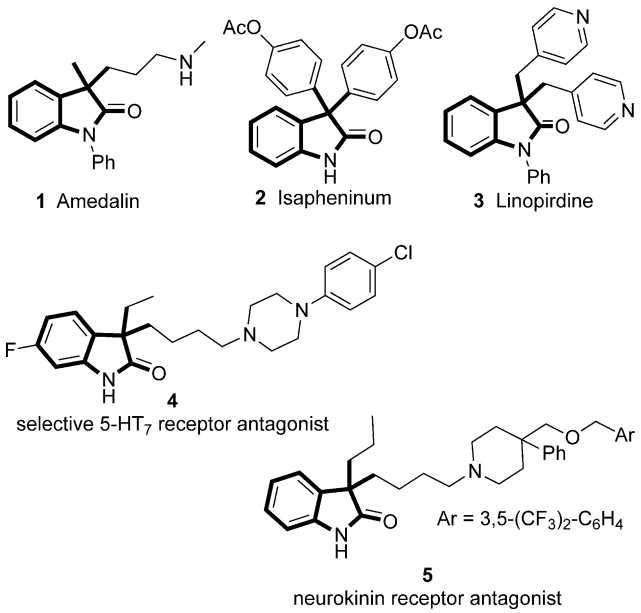


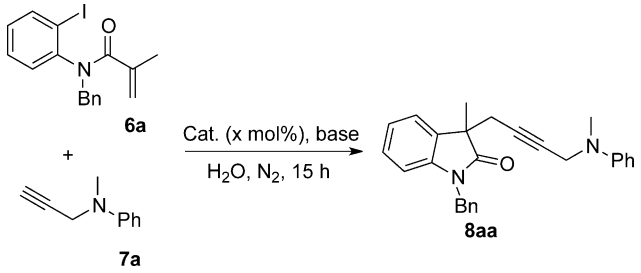
Figure 1. Pharmaceutically active compounds and drugs containing 3,3-disubstituted oxindole units.

group[12] has reported the first example of a three-component domino Heck–Negishi coupling reaction for synthesizing novel purine compounds. The domino Heck reaction of 2-haloaniline derivatives is a very direct, effective method for synthesizing oxindoles. Grigg[7a] and Somfai[6a] have employed domino Heck–Suzuki coupling reactions for synthesizing 3,3-disubstituted oxindoles. In 2007, Zhu and co-workers[13] have developed a domino Heck-cyanation process for obtaining 3,3-disubstituted oxindoles with the CN group. Balalaie[14a] has reported a domino carbopalladation-Sonogashira reaction of *N*-(2-halophenyl)propiolamide compounds for synthesizing 3-arylideneoxindoles. Li[14b] has developed a domino Heck–Sonogashira palladium-catalyzed process in the presence of a copper(I) co-catalyst. Recently, the development of new synthetic methods with a low environmental impact is one of the most important branches of modern synthetic chemistry.[15] Thus, the reactions using water as the medium have attracted significant attention, and many organic reactions in water have been reported by our group[16] and other[15,17] groups. Herein, we report an efficient synthesis of new 3-alkyl-3-(4-aminobut-2-ynyl)-substituted oxindole compounds by a domino Heck–Sonogashira sequence palladium-catalyzed process in water. The most important aspect of this sequence is to easily construct the structural framework of 3,3-disubstituted oxindoles **4** and **5**.

Initially, *N*-(2-iodophenyl)methacrylamide (**6a**) and *N*-methyl-*N*-propargylaniline (**7a**) were selected as model substrates for optimizing the reaction conditions (Table 1). When $PdCl_2$ was used as the catalyst, the reaction proceeded well in the presence of Et_3N, and the desired domino product **8aa** was isolated in 49% yield (entry 1). A different palladium source can affect the reaction outcome: higher yields were obtained when $Pd(PPh_3)_4$ was employed (entry 3). Subsequently, several bases were examined, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) provided the desired product in 95% yield (entry 6). The reaction was clearly affected by temperature. Poor yields were obtained at lower temperature (entry 13), yet similar yields were obtained above 60 °C, but the yield of the product decreased at 100 °C (entry 16). Finally, a series of experiments was conducted for determining the lowest effective amount of $Pd(PPh_3)_4$, which was determined to be 2 mol%; this reaction provided nearly the same yield as a reaction with 10 mol% $Pd(PPh_3)_4$ (entries 17–19). Thus, the optimized reaction conditions are as follows: 2 mol% of $Pd(PPh_3)_4$, 0.1 mmol of *N*-(2-iodophenyl)methacrylamide (**6a**), 2.0 equiv. of *N*-methyl-*N*-propargylaniline (**7a**), and 3.0 equiv. of DBU in 0.5 mL of water at 90 °C (entry 18).

Subsequently, a range of substituted aniline derivatives was employed in the domino Heck–Sonogashira process under the optimized conditions. Scheme 1 shows the effect of the haloaniline subunit on the reaction outcome. *N*-(2-Bromophenyl)methacrylamide (**6b**) afforded the target products **8aa** in 59% yield, while *N*-(2-chlorophenyl)methacrylamide (**6c**) failed to produce 3,3-disubstituted oxindoles. On the other hand, the iodine-substituted aniline provided the product in 95% yield; hence, iodine is selected as the best leaving group for the following investigation. As shown in Scheme 2, a comparison experiment was conducted to investigate the effect of the substitution of the amide nitrogen atom. *N*-Methylamide **6d** smoothly gave the 3,3-disubstituted oxindole **8da** in 94% yield. The unprotected amide **6e** afforded a result similar to that in a previous study[9b,14b] and failed to produce the target products **8ea**. However, the desired product **8fa** was not obtained when *N*-Boc-amide **6f** was used. 2-Iodoaniline derivatives **6g–j** with electron-donating or electron-withdrawing groups were well tolerated and afforded the desired

Table 1. Optimization of the domino Heck–Sonogashira reaction conditions.[a]

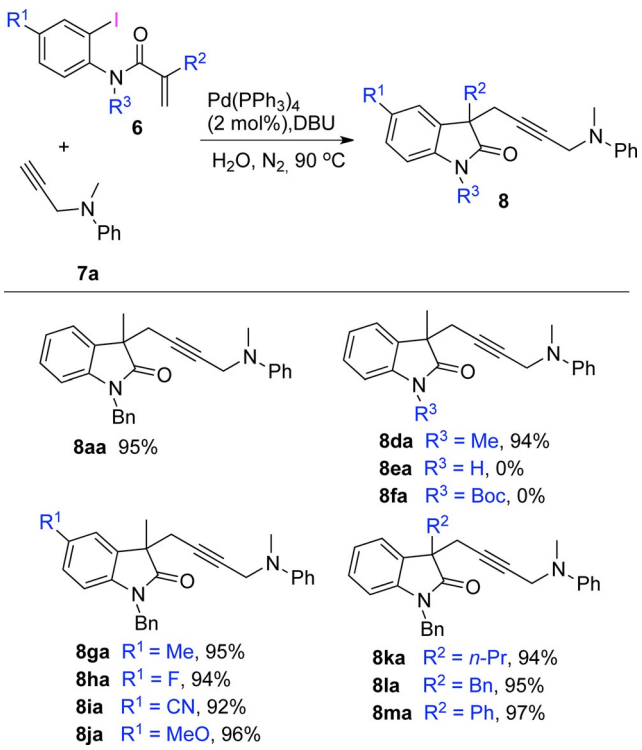


Entry	Cat.	x	Base	Temp. [°C]	Yield [%][b]
1	$PdCl_2$	10	Et_3N	60	49
2	$Pd(OAc)_2$	10	Et_3N	60	57
3	$Pd(PPh_3)_4$	10	Et_3N	60	80
4	$PdCl_2$·dppf	10	Et_3N	60	32
5	$PdCl_2$·$(PPh_3)_2$	10	Et_3N	60	75
6	$Pd(PPh_3)_4$	10	DBU	60	95
7	$Pd(PPh_3)_4$	10	pyridine	60	40
8	$Pd(PPh_3)_4$	10	pyrrolidine	60	88
9	$Pd(PPh_3)_4$	10	piperidine	60	88
10	$Pd(PPh_3)_4$	10	DABCO	60	65
11	$Pd(PPh_3)_4$	10	K_2CO_3	60	50
12	$Pd(PPh_3)_4$	10	DBU	40	65
13	$Pd(PPh_3)_4$	10	DBU	r.t.	39
14	$Pd(PPh_3)_4$	10	DBU	70	96
15	$Pd(PPh_3)_4$	10	DBU	90	96
16	$Pd(PPh_3)_4$	10	DBU	100	94
17	$Pd(PPh_3)_4$	5	DBU	90	96
18	$Pd(PPh_3)_4$	2	DBU	90	95
19	$Pd(PPh_3)_4$	1	DBU	90	90

[a] *Reaction conditions:* **6a** (0.1 mmol), **7a** (0.2 mmol), base (0.3 mmol), N_2, stirring for 15 h at the corresponding temperature shown in the table.

[b] Isolated yields of products are given based on **6a**.

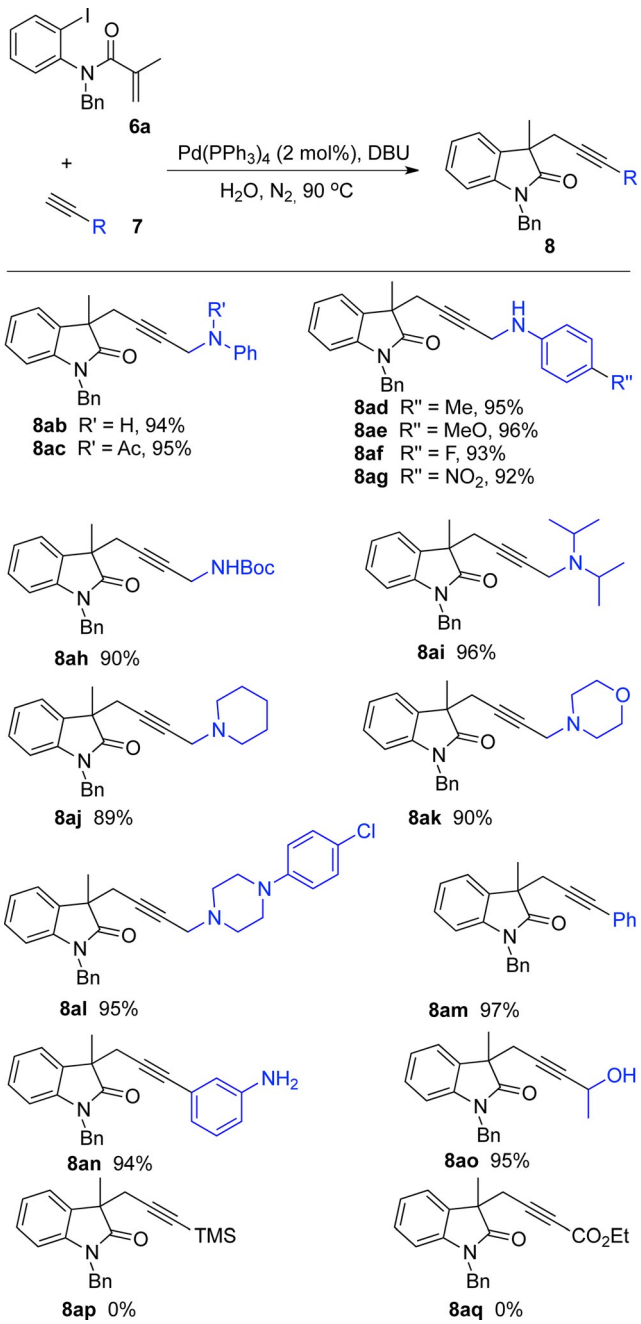
Scheme 1. Effect of the haloaniline subunit on the reaction outcome. *Reaction conditions:* **6** (0.1 mmol), **7a** (2.0 equiv.), DBU (3.0 equiv.), $Pd(PPh_3)_4$ (2 mol%), H_2O (0.5 mL), 90 °C, N_2, stirring overnight. Isolated yields of products are given based on **6**.



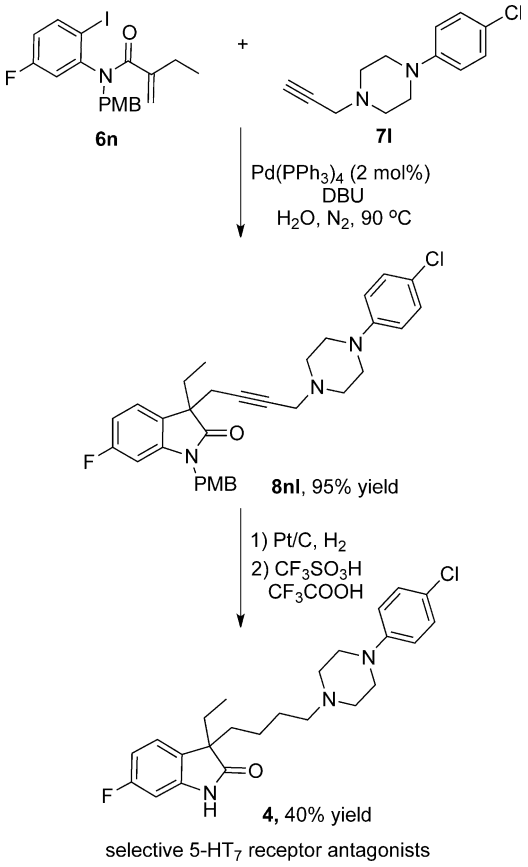
Scheme 2. Reaction of various substituted aniline derivatives. *Reaction conditions:* **6** (0.1 mmol), **7a** (2.0 equiv.), DBU (3.0 equiv.), $Pd(PPh_3)_4$ (2 mol%), H_2O (0.5 mL), 90 °C, N_2, stirring overnight. Isolated yields of products are given based on **6**.

domino products in good yields (**8ga**–**8ja**). Subsequently, variation of the substituent on the acrylamide was evaluated; the desired domino reaction of 2-propyl-, 2-benzyl- and 2-phenylacrylamides (**6k**, **6l**, **6m**) smoothly proceeded and afforded the corresponding 3,3-disubstituted oxindole compounds in good yields (**8ka**–**8ma**).

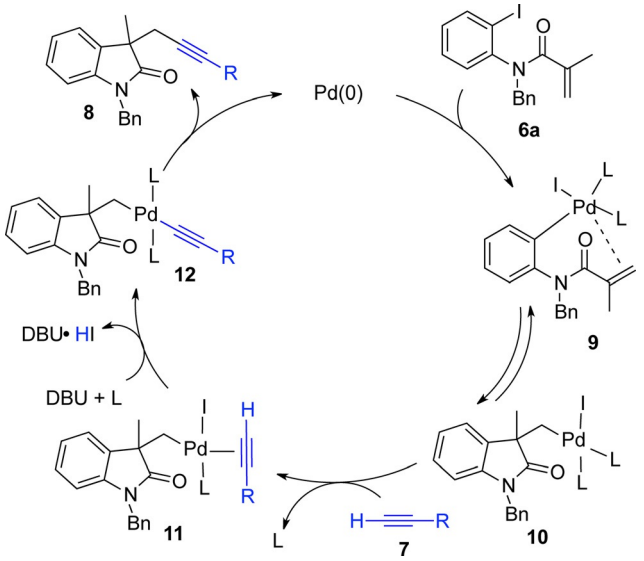
Next, various propargylamine-bearing compounds were examined for determining the scope of the domino reaction. From the experimental results shown in Scheme 3, the substituents of the propargylamine nitrogen atom marginally affect the domino Heck–Sonogashira process. Unprotected amine **7b** and the acetyl-protected amine **7c** afforded the desired products in 94% and 95% yield, respectively (**8ab** and **8ac**). Propargylamine derivatives (**7d–g**)



Scheme 3. Reaction of various alkyne derivatives. *Reaction conditions:* **6a** (0.1 mmol), **7** (2.0 equiv.), DBU (3.0 equiv.), $Pd(PPh_3)_4$ (2 mol%), H_2O (0.5 mL), 90 °C, N_2, stirring overnight. Isolated yields of products are given based on **6a**.



Scheme 4. Synthesis of 5-HT_7 receptor antagonists.



Scheme 5. Proposed mechanism of the domino Heck–Sonogashira reaction.

with electron-donating or electron-withdrawing groups on the phenyl rings were well tolerated, affording the desired domino products in good yields (**8ad–8ag**). Following this, the propargylamine-containing chain or cyclic groups were also evaluated. The results show that all propargylamine-containing chain or cyclic groups could readily afford the corresponding products in excellent yields (**8ah–8al**). For developing the scope of the optimized reaction conditions again, other types of alkynes were employed in the domino processes. Ethynylbenzene **7m** and **7n** as well as propargyl alcohol **7o** were smoothly transformed into the desired oxindoles **8am–8ao**. However, none of the desired products were obtained using ethynyltrimethylsilane **7p** and ethyl propiolate **7q** (**8ap** and **8aq**).

The new products of the domino Heck–Sonogashira reaction exhibit an all-carbon quaternary center at the 3-position with a propargyl group. This characteristic attracted our attention not only from a biological viewpoint, but also as a synthetically valuable adduct. Notably, the target products could be further converted to molecules which can be used as 5-HT_7 receptor antagonists and neurokinin receptor antagonists. As shown in Scheme 4, product **8nl** prepared from acrylamide **6n** and propargylpiperazine **7l** in 95% yield was transformed into known compound **4**, which is a selective 5-HT_7 receptor antagonist.

A possible mechanism for this domino Heck–Sonogashira process is shown in Scheme 5.[1b,18] In this mechanism, the first step involves the oxidative addition of Pd(0) to the carbon-iodine bond of acrylamide **6a** to form intermediate **9**. The intramolecular Heck insertion of intermediate **9** proceeds to form a primary alkylpalladium complex species **10**. Then, one of the ligands of the complex **10** is replaced by alkyne **7**, affording intermediate **11**. Ligated alkyne **11** is easily dehydroiodinated in the presence of base, forming the new intermediate **12**. Finally, the reductive elimination of intermediate **12** occurs to regenerate the active Pd(0) species and afford the desired product **8**.

In summary, a mild, general domino palladium-catalyzed Heck–Sonogashira reaction in water was developed for the synthesis of 3-(4-aminobut-2-ynyl)oxindole derivatives with an all-carbon quaternary center at the 3-position in excellent yields. This domino process can be applicable for various acrylamides and terminal alkynes. This reaction is attractive because the structures of the target products are similar to the molecules used as 5-HT_7 receptor antagonists and neurokinin receptor antagonists, which could be readily converted into the above antagonists.

Experimental Section

Typical Experimental Procedure for the Synthesis of Oxindole Derivatives in Water

To a Schlenk tube equipped with a magnetic stir bar, *N*-(2-iodophenyl)methacrylamide **6a** (0.1 mmol, 37.7 mg), *N*-

methyl-*N*-propargylaniline **7a** (0.2 mmol, 29 mg), and $Pd(PPh_3)_4$ (2.3 mg, 2 mol%) were added. The tube was sealed with threaded rubber stopper, evacuated and backfilled with N_2 (this process was repeated for 3 times). H_2O (0.5 mL) and DBU (0.3 mmol, 45 μL) were then added *via* syringe. The mixture was stirred at 90 °C until **6a** had disappeared (monitored by TLC). The reaction mixture was extracted with ethyl acetate (10.0 mL). The organic phase was dried over Na_2SO_4 and concentrated under vacuum. The resulting residue was purified by flash chromatography over silica gel (ethyl acetate/petroleum ether) to afford the desired product 1-benzyl-3-methyl-3-{4-[methyl(phenyl)amino]but-2-yn-1-yl}indolin-2-one (**8aa**) as a colorless oil; yield: 37.6 mg (95%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.26–7.30 (m, 7H), 7.12–7.16 (m, 2H), 6.93 (t, J = 7.6 Hz, 1H), 6.84 (t, J = 7.4 Hz, 1H), 6.77 (d, J = 8.0 Hz, 2H), 6.66 (d, J = 8.0 Hz, 1H), 4.83 (d, J = 15.6 Hz, 1H), 4.67 (d, J = 15.6 Hz, 1H), 3.87–3.97 (m, 2H), 2.75 (s, 3H), 2.72–2.76 (m, 1H), 2.57–2.62 (m, 1H), 1.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 179.6, 149.2, 142.1, 136.1, 133.1, 129.2, 128.8, 127.9, 127.6, 127.3, 123.3, 122.6, 118.0, 114.2, 109.1, 79.4, 77.8, 47.1, 43.5, 42.5, 38.3, 28.2, 22.3; HR-MS: m/z = 417.1942, calcd. for $C_{27}H_{26}N_2NaO$ $[M+Na]^+$: 417.1937.

Acknowledgements

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