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Pd-catalyzed 2,3-allenylation of Oxindoles with 2,3-Allenylic Carbonates

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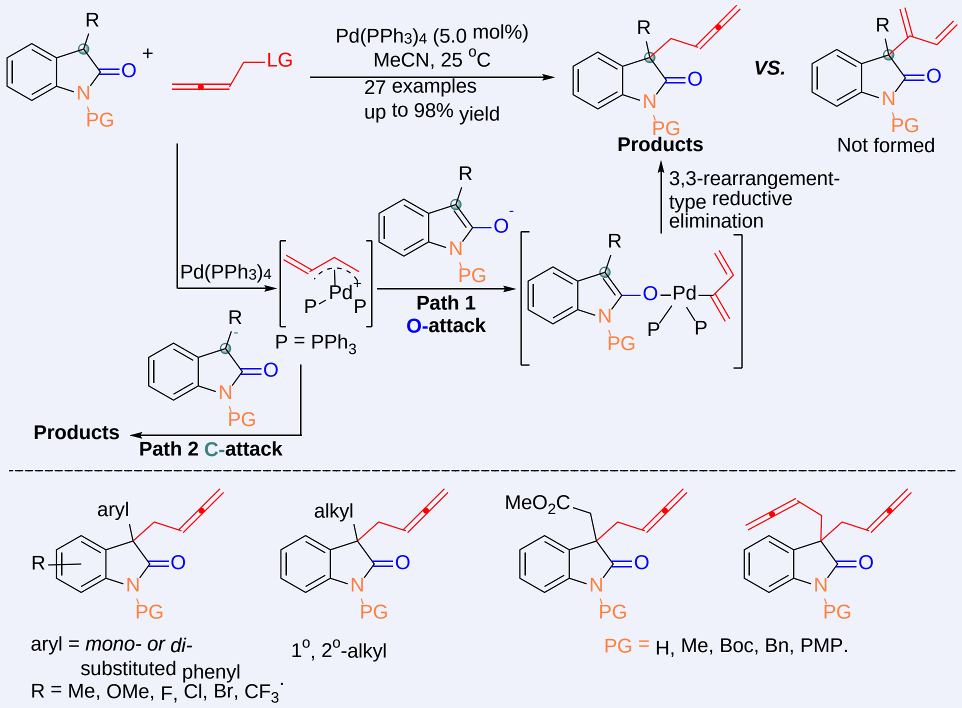
Keywords

palladium | allenes | chemoselectivity | allenylation | oxindoles

Main observation and conclusion

Allenes and oxindoles are two classes of very important compounds for medicinal chemistry and organic chemistry. Thus, it is of high interest to combine an allene and an oxindoles into one molecule. Here the first example of palladium-catalyzed exclusive 2,3-allenylation reaction of oxindoles with 2,3-allenylic carbonates has been successfully developed. A rationale for the selectivity of 2,3-allenylation over the expected 1,3-alkadienylation has been proposed.

Comprehensive Graphic Content



- Room temperature reaction
- Versatile allene and amide functionalities
- High chemoselectivity
- Wide substrate scope
- High yields

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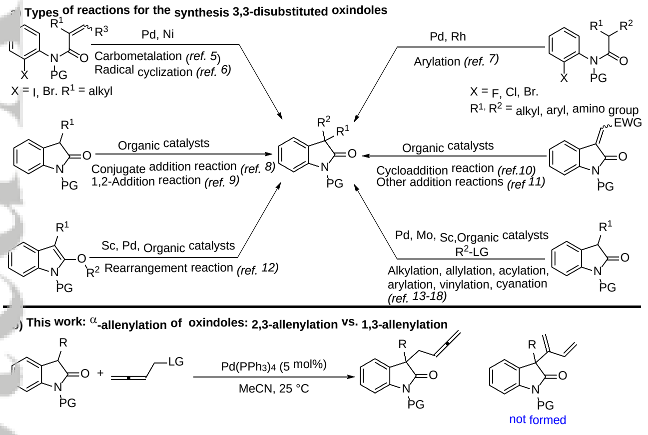
Background and Originality Content

Oxindoles are a very important class of compounds[1] exist in many natural products such as Horsfiline[2a] and Coerulescine[2b] and various bioactive compounds.[2c-2g] In addition, they are also important building blocks in organic synthesis.[1b,3] Thus, much attention has been paid to the synthesis of this type of compounds[4-18] (Scheme 1a). On the other hand, allenes[19-20] have become more and more important in medicinal chemistry and organic chemistry due to their unique pharmacological, biological,[21] and chemical properties,[22-23] we reasoned that the 2,3-allenylation of oxindoles would not only be an excellent combination for medicinal chemistry but also dramatically increase the diversity of the oxindole derivatives. The challenge is the possible formation of the 1,3-dienylation products due to the nature of oxindole anion (pK_a ~ 23.5; ~ 16 for malonate)[24] since nucleophiles with a pK_a value of approximately 20 to 25 is in the border between "hard" and "soft".[25,26] Herein we wish to report the Pd-catalyzed 2,3-allenylation reaction of oxindoles with 2,3-allenylic carbonates providing oxindoles bearing an allene unit (Scheme 1b).[27]

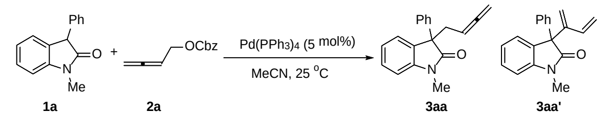
Scheme 1 Types of reactions for the synthesis 3,3-disubstituted oxindoles, pK_a value of some compounds, and 2,3-allenylation of oxindoles.



Results and Discussion

Oxindole **1a** and 2,3-allenylic benzyl carbonate **2a** were selected as the model substrates for optimizing reaction conditions. After some screening, the standard reaction conditions have been defined as using $Pd(PPh_3)_4$ (5 mol%) in MeCN at 25 °C, affording the 2,3-allenylation product **3aa** in 91% NMR yield, exclusively. $Pd(PPh_3)_2Cl_2$ or $Pd(OAc)_2$-PPh_3 failed to catalyze the reaction (Table 1, entries 2 & 3). Other palladium (0) sources, such as $Pd(dba)_2$, $Pd_2(dba)_3$, $Pd_2(dba)_3{\bullet}CHCl_3$, and $Pd(dmdba)_2$, were also screened and $Pd(PPh_3)_4$ was still the optimal (Table 1, entries 4-7). With $Pd(PPh_3)_4$ as the catalyst, the reaction in toluene at 25 °C afforded the product **3aa** in 88% yield (Table 1, entry 8). When using etheric solvents such as THF and dioxane, the yield was lower (Table 1, entries 9 & 10). DCM, DCE, acetone, ethyl acetate, and ethanol were also inspected with no better results (Table 1, entries 11-15). It is worth noting that **3aa** was selectively generated in this reaction, and 1,3-dienylation product **3aa'** was NOT observed in all the cases during our optimization of the reaction conditions.

Table 1 Optimization of reaction conditions for Pd-catalyzed 2,3-allenylation reaction of oxindole **1a** with **2a**.[a]



1a **2a** **3aa** **3aa'**

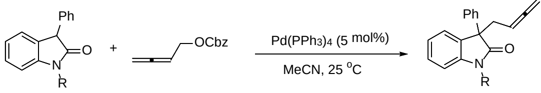
NOT observed

Entry	Deviation from standard conditions	NMR yields (**3aa**/**1a**, %)[b]
1	Standard conditions	91/0
2[c, d]	$Pd(OAc)_2$ (5 mol%) as catalyst	0/72
3[d]	$Pd(PPh_3)_2Cl_2$ as catalyst	0/98
4[c]	$Pd(dba)_2$ (5 mol%) as catalyst	84/0
5[c]	$Pd_2(dba)_3$ (2.5 mol%) as catalyst	83/0
6[c]	$Pd_2(dba)_3{\bullet}CHCl_3$ (2.5 mol%) as catalyst	79/0
7[c]	$Pd(dmdba)_2$ (5 mol%) as catalyst	83/0
8	Toluene as solvent	88/0
9	THF as solvent	76/0
10	Dioxane as solvent	88/0
11	DCM as solvent	90/0
12	DCE as solvent	88/0
13	Acetone as solvent	68/0
14	Ethyl acetate as solvent	70/0
15	Ethanol as solvent	77/0

[a] Standard reaction conditions: The reaction of **1a** (0.24 mmol), **2a** (0.20 mmol) and $Pd(PPh_3)_4$ (5 mol%) in MeCN (1.0 mL) was conducted at 25 °C. [b] NMR yield with CH_2Br_2 as the internal standard. [c] PPh_3 (10 mol%) was added. [d] DCE as solvent.

With the optimized reaction conditions (Table 1, entry 1), the scope of the N-substituent was investigated. Methyl or *tert*-butoxycarbonyl groups provided the products **3aa** and **3ba** in 90% yield and 88% yield, respectively (Table 2, entries 1 & 2). The reaction also worked with easily removable benzyl group-substituted oxindole **1c**, *p*-methoxyphenyl group-substituted oxindole **1c'** (with the reported pKa of 23.5),[24] and even the N-non-substituted oxindole **1d**, leaving further opportunities for elaboration of the N-substituent (Table 2, entries 3-5). Again, the corresponding **3aa'**-type 1,3-diene products were NOT formed (see Scheme 1c).

Table 2 Survey on *N*-substituents.[a]



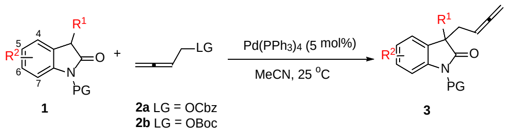
1 **2a** **3**

Entry	R	Yield (**3**, %)[b]
1	Me (**1a**)	90% (**3aa**)
2	Boc (**1b**)	88% (**3ba**)
3	Bn (**1c**)	80% (**3ca**)
4	PMP (**1c'**)	84% (**3c'a**)
5	H (**1d**)	81% (**3da**)

[a] Standard reaction conditions: The reaction of **1** (1.2 mmol), **2a** (1.0 mmol) and $Pd(PPh_3)_4$ (5 mol%) in MeCN (5.0 mL) was conducted at 25 °C. [b] Isolated yield.

A series of 3-mono-substituted oxindoles smoothly underwent this transformation, producing a variety of 3-(2,3-butadien- yl) oxindoles in moderate to good yields. 3-Aryl-substituted oxindoles bearing different substituents on the 3-phenyl were tested. As shown in Table 3, the variation of electronic and steric effects was tolerated: the substrates with methoxy, fluoro, chloro, methyl, ethyl, isopropyl at the para- or ortho-position of the phenyl ring could react with 2,3-allenylic carbonate **2** afforde the corresponding products in 74%-99% yields (Table 3, entries 3-9). 2,4-Dimethyl, 2,5-dimethyl, 4-methoxy-2-methyl, and 4-chloro-2-methyl substituted aryl groups were also tolerated (66%-96%, Table 3, entries 10-13). Further exploration of the substrate scope was focused on the left hand phenyl ring on the oxindoles. Various 3-(*o*-tolyl)-oxindoles substituted with electron-donating groups (methyl and methoxy) and electron-withdrawing groups (fluoro, chloro, bromo and trifluoromethyl) also reacted to afford the 2,3-allenylation products (44%-96%, Table 3, entries 14-23). In addition, this reaction also worked with 3-alkyl-substituted oxindoles affording the corresponding products in 60%-70% (Table 3, entries 24-27).

Table 3 Substrate scope of $Pd(PPh_3)_4$-catalyzed 2,3-allenylation of oxindoles.[a]



1

2a LG = OCbz
2b LG = OBoc

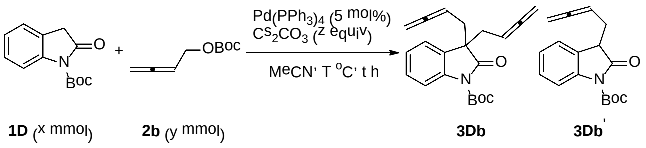
3

Entry	R^1	R^2	PG	Yield (**3**, %)[b]
1[c]	C_6H_5 (**1a**)	H	Me	90% (**3aa**)
2[c]	C_6H_5 (**1b**)	H	Boc	88% (**3ba**)
3[c]	4-$MeOC_6H_4$ (**1e**)	H	Me	89% (**3eb**)
4[c]	4-FC_6H_4 (**1f**)	H	Me	87% (**3fa**)
5[c]	4-ClC_6H_4 (**1g**)	H	Me	99% (**3ga**)
6[c]	2-MeC_6H_4 (**1h**)	H	Boc	98% (**3hb**)
7	2-EtC_6H_4 (**1i**)	H	Boc	84% (**3ib**)
8	2-$MeOC_6H_4$ (**1j**)	H	Boc	78% (**3jb**)
9	2-*i*-PrC_6H_4 (**1k**)	H	Boc	74% (**3kb**)
10	2-Me-4-MeC_6H_3 (**1l**)	H	Boc	66% (**3lb**)
11	2-Me-5-MeC_6H_3 (**1m**)	H	Boc	77% (**3mb**)
12	4-MeO-2-MeC_6H_3 (**1n**)	H	Boc	80% (**3nb**)
13	4-Cl-2-MeC_6H_3 (**1o**)	H	Boc	96% (**3ob**)
14[c]	2-MeC_6H_4 (**1p**)	5-Me	Boc	80% (**3pb**)
15	2-MeC_6H_4 (**1q**)	5-MeO	Boc	58% (**3qb**)
16[d]	2-MeC_6H_4 (**1r**)	5-F	Boc	95% (**3rb**)
17[c]	2-MeC_6H_4 (**1s**)	5-Cl	Boc	94% (**3sb**)
18[c]	2-MeC_6H_4 (**1t**)	5-Br	Boc	95% (**3tb**)
19[c]	C_6H_5 (**1u**)	6-Cl	Me	96% (**3ua**)
20[c]	2-MeC_6H_4 (**1v**)	6-Cl	Boc	89% (**3vb**)
21	2-MeC_6H_4 (**1w**)	6-Br	Boc	44% (**3wb**)
22	2-MeC_6H_4 (**1x**)	7-Cl	Boc	92% (**3xb**)
23	2-MeC_6H_4 (**1y**)	7-CF_3	Boc	85% (**3yb**)
24	*n*-C_7H_{15} (**1z**)	H	Boc	65% (**3zb**)
25	CH_2CO_2Me (**1A**)	H	Me	60% (**3Ab**)
26	*i*-Pr (**1B**)	H	Boc	70% (**3Bb**)
27	Cy (**1C**)	H	Boc	69% (**3Cb**)

[a] Standard reaction conditions: The reaction of **1** (0.6 mmol), **2b** (0.5 mmol) and $Pd(PPh_3)_4$ (5 mol%) in MeCN (2.5 mL) was conducted at 25 °C. [b] Isolated yield. [c] The reaction of **1** (1.2 mmol), **2** (1.0 mmol) and $Pd(PPh_3)_4$ (5 mol%) in MeCN (5.0 mL) was conducted at 25 °C. [d] The reaction of **1r** (0.5 mmol), **2b** (0.6 mmol) and $Pd(PPh_3)_4$ (5 mol%) in MeCN (2.5 mL) was conducted at 25 °C.

Besides, 3-non-substituted oxindole **1D** and 2,3-allenylic *tert*-butyl carbonate **2b** also worked well in this reaction, and only double-substituted product **3Db** was formed and no single-substituted product **3Db'** was observed (Table 4, entry 1). Even if the amount of **1D** was 2.3 equiv, the reaction at 25°C in the absence of a base still afforded double 2,3-allenylation product **3Db** albeit in a low yield (Table 4, entry 3).

Table 4. $Pd(PPh_3)_4$-catalyzed 2,3-allenylation of 3-non-substituted oxindole **1D**.



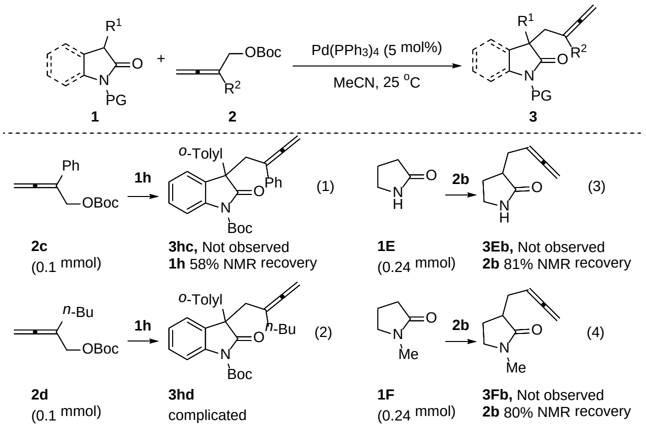
1D (x mmol) **2b** (y mmol) **3Db** **3Db'**

Entry	**1D** (x mmol)	**2b** (y mmol)	Cs_2CO_3 (z equiv)	T °C	t h	NMR yield (**3Db**/ **3Db'** %)	NMR recovery (**1D** %)
1	0.5	1.2	1.2	50	18	78 (76)/0	0
2	0.23	0.1	1.2	25	12	37/0	43
3	0.23	0.1	0	25	12	21/0	73
4	0.24	0.1	1.2	50	18	16/0	33
5	0.24	0.1	0	50	18	30/0	42

[a] Reaction conditions: The reaction of **1D**, **2b**, Cs_2CO_3, and $Pd(PPh_3)_4$ (5 mol%) in MeCN was conducted. NMR yield with CH_2Br_2 as the internal standard. Isolated yield is given in the parentheses.

However, the reaction of 1,1-disubstituted allenylic carbonate as the substrates failed (**2c** & **2d**) (Scheme 2, eqs (1) & (2)). No reaction occurred to pyrrolidin-2-one (**1E**) and 1-methylpyrrolidin-2-one (**1F**) (Scheme 2, eqs (3) & (4)).

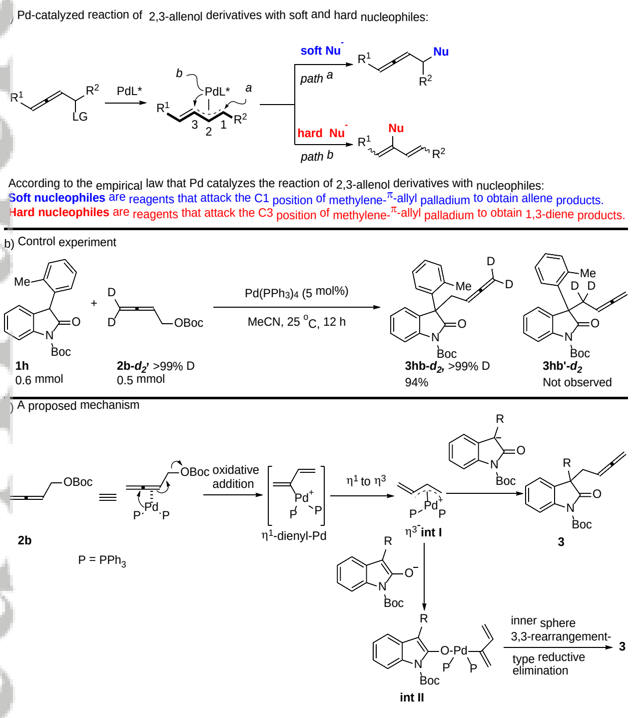
Scheme 2 Some failed substrates of $Pd(PPh_3)_4$-catalyzed 2,3-allenylation reaction.



[a] Reaction conditions: The reaction of **1** (1.2 equiv), **2**, and $Pd(PPh_3)_4$ (5 mol%) in MeCN was conducted. NMR yield or recovery with CH_2Br_2 as the internal standard.

As mentioned in the introduction, the regioselectivity of the Pd-catalyzed allenol derivatives with nucleophiles depended on the nature of the nucleophiles: Gore[28a] pioneered the Pd-catalyzed 2,3-allenylation reaction of 2,3-allenol derivatives with soft nucleophile forming allene products, exclusively[28-29] (Scheme 3a, path a). On the other hand, Vermeer[30a] reported the Pd-catalyzed coupling reaction of 2,3-allenol derivatives with hard nucleophile, affording 1,3-diene product (Scheme 3a, path b). Due to the nucleophile nature of oxindole anion, 1,3-dienes should be the expected products,[30] however, 2,3-allenylation products were formed exclusively here. We further performed a deuterium-labeling experiment to gain some insight into the reaction mechanism. The reaction of oxindole **1h** with terminal deuterium 2,3-allenylic *tert*-butyl carbonate **2b-*d*$_2$** gave product **3hb-*d*$_2$** (Scheme 3b). Thus, we proposed a possible mechanism as shown in Scheme 4b. Firstly, oxidative addition of **2b** with Pd(0) would form η^1-dienyl-Pd, which would immediately isomerize to the delocalized methylene-π-allyl palladium η^3-**int I**[21] via the σ-π rearrangement involving the coordination of the terminal C=C bond with Pd (Scheme 3c). The oxindole enol anion may approach the methylene-π-allyl palladium intermediate by the direct oxygen attack of the enolate at the Pd atom to form **int II**, which may most probably proceed via the inner-sphere 3,3-rearrangement- type reductive elimination[32] to afford **3**. It is also difficult to exclude the possibility of having η^3-**int I** reacted directly with the oxindole anion to form the final product **3**.

Scheme 3 Pd-catalyzed reaction of 2,3-allenol derivatives with soft and hard nucleophiles, control experiment, and a proposed mechanism.



Conclusions

In conclusion, we have developed the first example of Pd-catalyzed 2,3-allenylation reaction of oxindoles with allenylic carbonates for the efficient construction of allene derivatives bearing an oxindole unit. The reaction enjoys a wide substrate range and good yields with a different mechanism. Further studies are being pursued in our laboratory.

Experimental

Typical procedure for the synthesis of 3-(2,3-butadienyl)-1-methyl-3-phenylindolin-2-one (3aa): To a flame-dried Schlenk tube were added $Pd(PPh_3)_4$ (57.5 mg, 0.05 mmol), **1a** (266.5 mg, 1.2 mmol), and **2a** (203.8 mg, 1.0 mmol)/MeCN (5.0 mL) sequentially under Ar atmosphere at room temperature. The resulting mixture was stirred at 25 °C for 5.5 h as monitored by TLC and filtrated through a short column of silica gel (height: 3 cm, *Φ*: 3.5 cm) eluted with diethyl ether (60 mL). After evaporation, the residue was purified by column chromatography on silica gel to afford **3aa** (246.7 mg, 90%) as an oil [eluent: petroleum ether/ ethyl acetate = 15/1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, *J* = 7.6 Hz, 2 H, ArH), 7.36-7.18 (m, 5 H, ArH), 7.10 (t, *J* = 7.4 Hz, 1 H, ArH), 6.87 (d, *J* = 7.6 Hz, 1 H, ArH), 4.80-4.70 (quintet, *J* = 7.0 Hz, 1 H, =CH), 4.56-4.48 (m, 1 H, one proton of $=CH_2$), 4.44-4.36 (m, 1 H, one proton of $=CH_2$), 3.18 (s, 3 H, CH_3), 3.03-2.90 (m, 2 H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 210.0, 177.7, 143.9, 139.2, 131.4, 128.4, 128.3, 127.3, 127.0, 125.2, 122.4, 108.2, 84.3, 74.4, 56.3, 37.0, 26.3; IR (neat, cm^{-1}): 3056, 2930, 1954, 1707, 1608, 1491, 1468, 1369, 1344, 1252, 1182, 1158, 1128, 1086, 1019; MS (70 eV, EI) *m/z* (%): 275 [M$^+$, 46.27], 222 (100); HRMS Calcd for $C_{19}H_{17}NO$ [M$^+$]: 275.1310; Found: 275.1308.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2021xxxxx.

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Pd-catalyzed 2,3-allenylation of Oxindoles with 2,3-Allenylic Carbonates

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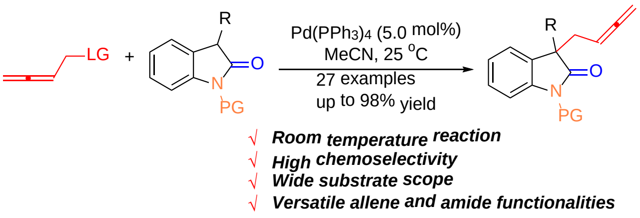

A palladium-catalyzed reaction of oxindoles with 2,3-allenylic carbonates afforded 3-allenyloxindoles efficiently under mild reaction conditions with an excellent chemoselectivity.

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