

Homogeneous Catalysis

Palladium-Catalyzed Dearomative Methoxyallylation of 3-Nitroindoles with Allyl Carbonates

Jia-Hao Xie, Chao Zheng, and Shu-Li You*

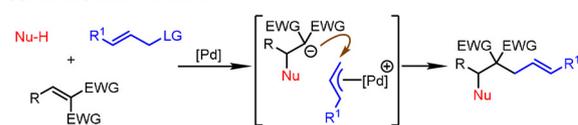
Abstract: Herein we report a Pd-catalyzed dearomative methoxyallylation of 3-nitroindoles with readily available allyl carbonates. Good yields (up to 86 %) and diastereoselectivity (up to >20:1 dr) are obtained for a wide range of substrates. The compatibility of gram-scale synthesis and the relatively low catalyst loading (down to 1 mol% of [Pd]) enhance the practicality of this method. The kinetic experiments indicate that the rate-determining step of this reaction is the nucleophilic attack of the alkoxide anion.

Palladium-catalyzed allylic substitution reaction has become one of the most important methods for constructing C–C or C–X (X = O, N, S, etc.) bonds in modern organic chemistry.^[1] However, most examples of this type of reactions can basically construct only one bond. In this regard, nucleophilic-addition-induced allylic alkylation (NAAA) reaction, in which an external nucleophile initially attacks a Michael acceptor, and the newly formed nucleophile reacts with the electrophilic π -allyl-Pd species, becomes quite attractive (Scheme 1 a).^[2] Two distinct chemical bonds are formed sequentially in a well-controlled fashion, and versatile dual functionalization of a polarized C=C double bond can be achieved by using this method.^[3] To be noted, this reaction design largely relies on the utilization of benzylidenemalononitrile or its analogs as the Michael acceptors, thus impeding further synthetic applications of this method.

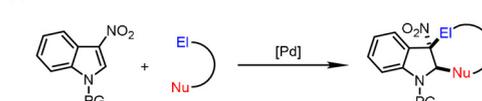
Catalytic dearomatization reactions have proved themselves as a powerful method for converting simple planar aromatics into diverse three-dimensional, cyclic products.^[4] In this regard, the dearomatization of indoles triggered by nucleophilic addition to an intra- or intermolecular electrophile has been extensively studied.^[5] On the other hand, the dearomatization of electron-deficient indoles has also been recognized as a complementary method to access densely functionalized indolines.^[6] Particularly, the dearomative cyclization of 3-nitroindoles with a series of amphiphilic reagents leads to the installation of a nucleophile and an electrophile at the C2 and C3 positions of the indole ring, respectively (Scheme 1 b).^[7]

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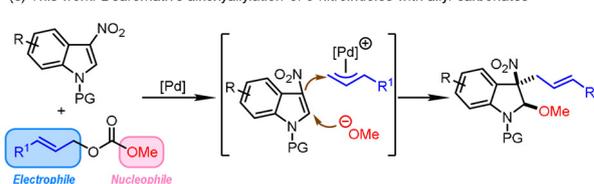
(a) Pd-catalyzed NAAA reaction



(b) Dearomative cyclization of 3-nitroindoles



(c) This work: Dearomative alkoxyallylation of 3-nitroindoles with allyl carbonates



Scheme 1. Palladium-catalyzed NAAA reactions and dearomatization of 3-nitroindoles.

Encouraged by these literature precedents, we recently applied the NAAA strategy to the Pd-catalyzed dearomatization of 3-nitroindoles with allyl methyl carbonates (Scheme 1 c). Herein, both nucleophilic methoxy anion and electrophilic π -allyl-Pd species are generated from the allyl methyl carbonates, and react at the C2 and C3 positions of 3-nitroindoles, respectively, affording the desired dearomatized products.^[2b] Compared with the known dearomative cyclization of 3-nitroindoles, the major challenge of this reaction design is how to regulate the reactivity of the three components towards the expected reaction sequence. We envisioned that this particular sequence can be achieved since methoxy anion, a hard nucleophile, preferentially attacks 3-nitroindole, a hard Michael acceptor. On the contrary, the in situ generated carbanion, a soft nucleophile, is more prone to attack the soft electrophilic π -allyl-Pd species. Herein, we report the results of this study.

We initiated our studies by optimizing the conditions for the model reaction of *N-tert*-butyloxycarbonyl-3-nitroindole (**1a**) with allyl methyl carbonate (**2a**, 2 equiv) (Table 1, see the Supporting Information for more details). First, the performance of various ligands was evaluated in the presence of Pd₂dba₃ (5 mol %) as the Pd precatalyst in MeCN at room temperature. Among tested, dppf (**L5**) and Xantphos (**L6**) were able to promote the desired reaction, delivering the target molecule **3aa** in moderate NMR yields and diastereomeric ratio (33–45 % yields, 4.1–6.4:1 dr) (entries 5 and 6), while phosphinoxazoline (PHOX) ligand **L9** showed increased efficiency in terms of the NMR yield (77 %) and diastereomeric ratio (7:1) of **3aa** (entry 9). Further screening

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Table 1: Optimization of the reaction conditions.^[a]


Reaction scheme: **1a** + **2a** $\xrightarrow[\text{MeCN, T, 72 h}]{\text{Pd}_2\text{dba}_3 (5 \text{ mol}\%), \text{L} (11 \text{ mol}\%)}$ **3aa**

Structures of ligands L1-L9 are shown below the reaction scheme.

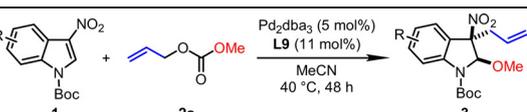
Entry ^[a]	L	T [°C]	Yield [%] ^[b]	dr ^[b]
1	L1	rt	—	—
2	L2	rt	5	—
3	L3	rt	—	—
4	L4	rt	messy	—
5	L5	rt	33	4.1:1
6	L6	rt	45	6.4:1
7	L7	rt	2	—
8	L8	rt	—	—
9	L9	rt	77	7.0:1
10 ^[d]	L9	40	84 (69 ^[e])	7.0:1
11 ^[d]	L9	50	81	6.8:1
12 ^[d,f]	L9	40	74	5.7:1
13 ^[d,g]	L9	40	63	6.3:1
14 ^[d,h]	L9	40	41	8.2:1

Ar = 3,5-(CF₃)₂-C₆H₃

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), Pd₂dba₃ (5 mol%), **L** (11 mol%) in solvent (0.5 mL) at specific temperature (T [°C]) for 72 h under argon. [b] Determined by ¹H NMR of the crude reaction mixture using CH₂Br₂ as an internal standard. [c] (*rac*)-**L1** (22 mol%) was used a mixture of two diastereoisomers (1.1:1 dr). [d] For 48 h. [e] Isolated yield of 0.2 mmol scale reaction. [f] **2a** (0.15 mmol) [g] Pd₂dba₃ (2.5 mol%), **L9** (5.5 mol%). [h] With MeCN (1 mL).

of solvents and Pd precatalyst did not lead to better results. Subsequent investigations indicated that a full conversion of **1a** was observed, along with an increased yield of **3aa**, when reactions were conducted at elevated temperatures (40 or 50 °C) (entries 10 and 11). At 40 °C, product **3aa** was isolated in 69% yield with 7.0:1 dr. Furthermore, reducing the number of equivalents of **2a**, catalyst loading or solvent concentration was detrimental to reaction yield (entries 12–14).

With the optimized reaction conditions in hand (entry 10, Table 1), we next investigated the scope of indoles (Table 2). In general, 3-nitroindoles bearing an electron-withdrawing group (CO₂Me, F, Cl, Br, NO₂, CN) attached at the C4, C5, or C6 position of the indole ring provided their desired products (**3ba**, **3ca**, **3ea–3ka**) in moderate to good yields (52–85%) and diastereoselectivity (3.8:1–8.7:1 dr). The lower yield of **3da** (34%) with an electron-donating methyl group attached at the C5-position of the indole ring was likely attributed to

Table 2: Substrate scope of 3-nitroindoles.^[a]


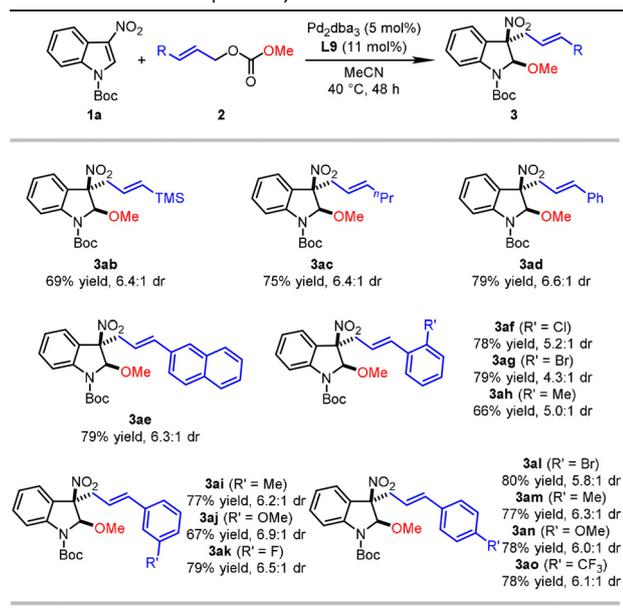
Reaction scheme: **1** + **2a** $\xrightarrow[\text{MeCN, 40 °C, 48 h}]{\text{Pd}_2\text{dba}_3 (5 \text{ mol}\%), \text{L}_9 (11 \text{ mol}\%)}$ **3**

3aa	3ba	3ca	3da
69% yield, 7.0:1 dr	52% yield, 3.8:1 dr	69% yield, 8.7:1 dr	34% yield, 7.0:1 dr
3ea ^[b]	3fa	3ga	3ha
70% yield, 7.3:1 dr	71% yield, 6.8:1 dr	74% yield, 5.1:1 dr	59% yield, 5.5:1 dr
3ia ^[c]	3ja ^[c]	3ka	3la
74% yield, 6.5:1 dr	85% yield, 7.1:1 dr	73% yield, 6.9:1 dr	84% yield, >20:1 dr
3ma ^[b]	3na ^[b]	3oa	3pa
80% yield, >20:1 dr	71% yield, >20:1 dr	72% yield, >20:1 dr	75% yield, >20:1 dr
3qa ^[b]	3ra ^[b]	3sa ^[b]	3ta
86% yield, >20:1 dr	81% yield, >20:1 dr	70% yield, 6.9:1 dr	28% yield, 5.7:1 dr
			3ta'
			61% yield

[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol), Pd₂dba₃ (5 mol%), **L9** (11 mol%) in MeCN (1.0 mL) at 40 °C for 48 h under argon. Dr values were determined by ¹H NMR of the crude reaction mixture. Isolated yields of the major diastereoisomers were reported. [b] For 24 h. [c] For 36 h.

the poor electrophilicity of the substrate. To our delight, the reactions of 7-substituted 3-nitroindoles provided their desired products (**3la–3ra**, 71–86% yields) with excellent diastereoselectivity (>20:1 dr), and the substituents with varied electronic properties were well tolerated at this position. The structure and relative configurations of **3ca** and **3na** were unambiguously established by X-ray crystallographic analyses.^[8] Notably, the bromine substituents on the indole ring were tolerated under Pd⁰-catalysis (**3ba**, **3ea**, **3ka** and **3qa**). Besides, 7-azaindole could be also applied in this reaction, leading to **3sa** in 70% yield with 6.9:1 dr. Finally, the *N*-Boc protecting group was found crucial for this reaction. When *N*-CO₂Me protected substrate was subjected to the standard conditions, the yield of the desired product was significantly decreased (**3ta**, 28%). A byproduct 1-allyl-3-nitro-1*H*-indole (**3ta'**) was obtained in 61% yield.^[9] The incorporation of other *N*-protecting groups such as Ts and Bn led to no desired products.

Next, the scope of allyl carbonates was also tested (Table 3). Substrates with trimethylsilyl or propenyl group gave products (**3ab** and **3ac**) in moderate yields (69% and 75% respectively) and diastereoselectivity (6.4:1 dr). Various

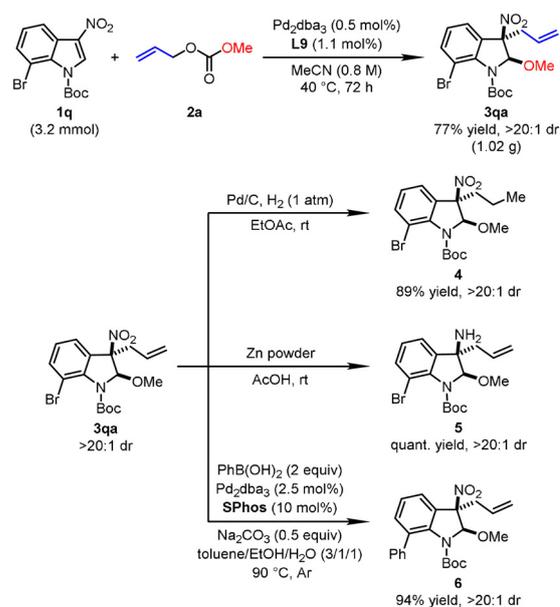
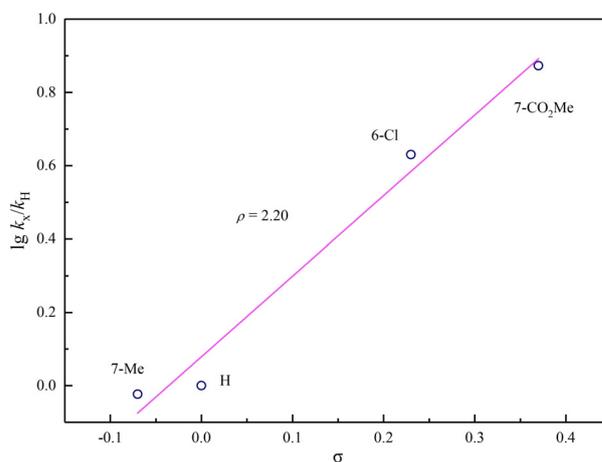
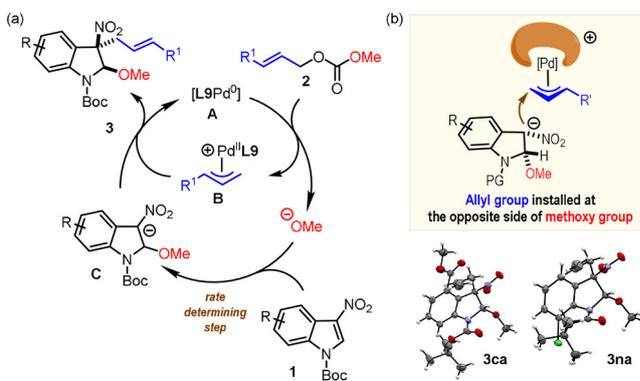
Table 3: Substrate scope of allyl carbonates.^[a]

[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol), Pd₂dba₃ (5 mol%), **L9** (11 mol%) in MeCN (1.0 mL) at 40 °C for 48 h under argon. Dr values were determined by ¹H NMR of the crude reaction mixture. Isolated yields of the major diastereoisomers were reported.

aryl allyl carbonates bearing either an electron-donating or an electron-withdrawing group were well tolerated regardless of the substitution patterns, providing the desired dearomatized products (**3ad–3ao**) with moderate yields (66–79%) and diastereoselectivity (4.3:1–6.3:1 dr). Notably, the diastereoselectivity of the reactions with *ortho*-substituted aryl allyl carbonates was slightly reduced (**3ag** and **3ah** vs. **3ai**, **3al** and **3am**), probably due to the steric hindrance in the transition state for the nucleophilic attack to the π -allyl-Pd species.

A successful gram-scale synthesis of **3qa** demonstrated the practicality of this reaction (Scheme 2). Product **3qa** was obtained in 77% yield (1.02 g) with >20:1 dr at a lower catalyst loading (1 mol% based on [Pd]), albeit that a longer reaction time (72 h) was required. Diverse transformations of the dearomatized product **3qa** were also carried out. First, the hydrogenation of the terminal C=C double bond was executed in the presence of 10% Pd/C, affording product **4** in 89% yield. In addition, the nitro group in **3qa** could be easily reduced to amine with Zn in CH₃CO₂H, affording **5** in quantitative yield. Furthermore, the bromine substituent in **3qa** could be readily transformed into a phenyl group to afford **6** in 94% yield via Suzuki–Miyaura cross-coupling reaction.

To shed light on the reaction mechanism, we have performed Hammett analysis for a series of 3-nitroindoles by ¹H NMR (Figure 1, see SI for details). A positive ρ value (2.20) was observed, indicating the accumulation of negative charge during the rate-determining step. Based on these results, a plausible catalytic cycle was proposed for the Pd-catalyzed dearomative methoxyallylation of 3-nitroindoles (Figure 2a). The reaction is initiated with the coordination of Pd⁰ catalyst **A** to the allylic carbonate. The subsequent

**Scheme 2.** Gram-scale synthesis and transformations of **3qa**.**Figure 1.** Hammett plot of the reaction.**Figure 2.** a) A proposed catalytic cycle. b) A working model for the diastereoselective control and X-ray crystallographic structures of **3ca** and **3na**.

oxidative addition leads to the π -allyl-Pd^{II} intermediate **B** with the concomitant release of methoxy anion. The nucleophilic attack of this methoxy anion to the C2 position of the 3-nitroindole generates the key intermediate **C** with a formal negative charge developed at the C3 position of the indole ring. This step is likely the rate-determining step according to the results of Hammett plot analysis. Finally, the nucleophilic attack of **C** to **B** furnishes the desired dearomatized product with the regeneration of Pd⁰ catalyst. According to the relative configuration of **3ca** and **3na**, the allyl group is preferably installed at the opposite side of the indoline ring with respect to the methoxy group due to the minimized steric hindrance in the transition state for the nucleophilic attack to π -allyl-Pd species (Figure 2b).

In summary, Pd-catalyzed nucleophile-addition-induced allylic alkylation strategy was successfully employed in the dearomatization of electron-deficient indoles. Intermolecular dearomative methoxyallylation reaction of 3-nitroindoles with allyl carbonates proceeded smoothly under mild conditions. The target multi-functionalized indoline products were obtained in good yields with good to excellent diastereoselectivity. The practicality of this method was exemplified by its wide substrate scope, compatibility of gram-scale synthesis at low catalyst loading, and expedient transformations of the product. The Hammett analysis revealed the nucleophilic attack of methoxy anion to 3-nitroindoles as the rate-determining step in the proposed catalytic cycle.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: 3-nitroindole · allylic substitution · dearomatization · diastereoselectivity · palladium

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