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Regioselective Direct C-4 Functionalization of Indole: Total Syntheses of (−)-Agroclavine and (−)-Elymoclavine

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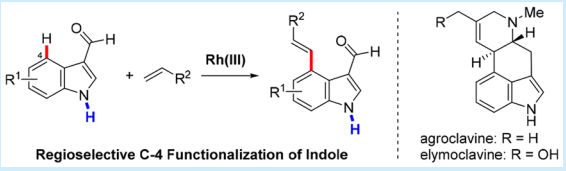
Supporting Information

ABSTRACT: An efficient rhodium-catalyzed method for direct C−H functionalization at the C4 position of unprotected indoles has been developed. The utility of this method is demonstrated by the concise total syntheses of agroclavine and elymoclavine in a divergent manner. These syntheses feature a Pd-catalyzed asymmetric allylic alkylation reaction to assemble the triyclic indole moiety, and a ring-closing metathesis reaction to form the D ring.



The 4-substituted indole frameworks are found in a wide variety of bioactive natural products and pharmaceuticals (Figure 1), which include the medicinally important ergot alkaloids (**1**−**4**),[1−3] ambiguine H,[4] and dragmacidin D.[5] As a result, there is continuing interest in the development of efficient methods for the synthesis of 4-substituted indoles,[6,7] and most of them are based on heteroannulation of substituted aromatic derivatives in a multistep scheme or utilize the expensive 4-haloindoles as starting materials.[2−7]

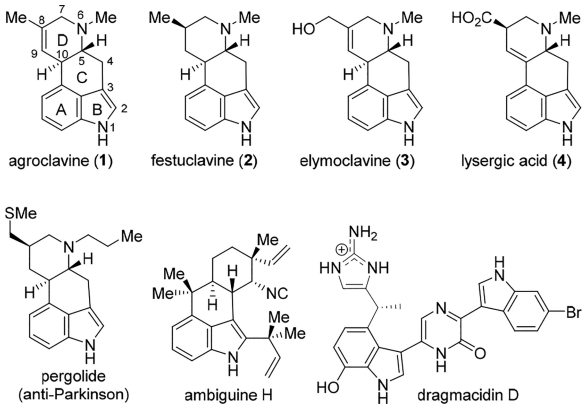
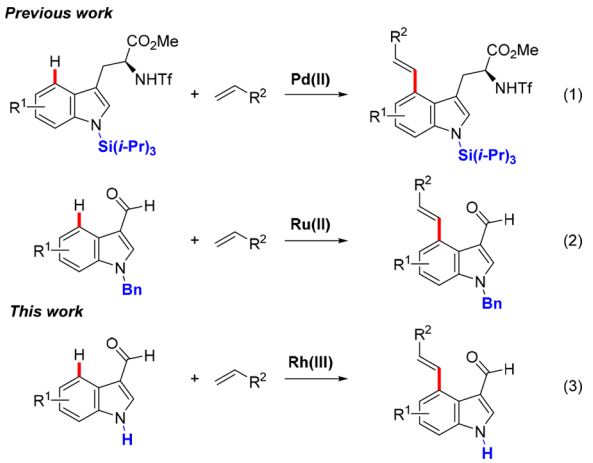


Figure 1. Natural products and drug derived from 4-substituted indoles.

The most desirable method undoubtedly is the direct C4 functionalization of simple indole derivatives. However, selective functionalization of C−H bonds at C4 positions of indoles is extremely difficult due to its inherently poor nucleophilic reactivity and high nucleophilic reactivity of the pyrrole moiety. Despite two successful approaches already reported, direct C4 functionalization is rarely used because of the toxic thallium reagent and harsh reaction conditions.[8,9] Transition-metal-catalyzed C−H bond functionalization can directly construct C−C and C−X bonds in a single step without prefunctionalization. It is a powerful strategy in organic synthesis,[10,11] and major breakthroughs have been achieved recently in transition-metal-catalyzed direct C−H functionalization at the C4 and C5−C7 positions of indoles.[12−15] In connection with our work on the total synthesis of 3,4-indole alkaloids,[16] we have reported the first site-selective Pd-catalyzed method for the direct olefination of tryptophans at the 4-position (Scheme 1, eq 1).[12a] Shortly after our work, Prabhu and co-workers described a Ru-catalyzed direct C4-functionalization of 1-benzyl-indole-3-carboxaldehydes by employing an aldehyde functional group as the directing group (Scheme 1, eq 2).[12b] However, the nitrogen of indole was protected in all reported methods. Until now, direct C−H functionalization at the C4 position, even at C5−C7 positions, of unprotected indoles has not been reported. We speculated that unprotected indoles could be employed as the starting material while an aldehyde is present at the C3 position as a directing

Scheme 1. Direct C-4 Functionalization of Indoles



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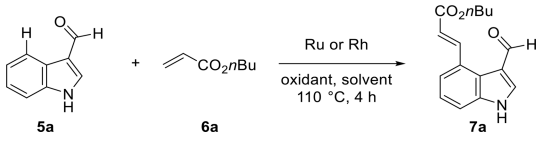
group.[12b,c,17] Herein, we report a method for direct C4-functionalization of unprotected indoles, which offer a strategically distinct approach to 4-substituted indoles in a straightforward manner (Scheme 1, eq 3). The utility of this method was demonstrated by the first catalytic asymmetric total syntheses of (−)-agroclavine (**1**) and (−)-elymoclavine (**3**).

Initially, 1-*H*-indole-3-carboxaldehyde (**5a**) and *n*-butyl acrylate (**6a**) were employed as model substrates and subjected to Prabhu's reaction conditions (Table 1, entry 1). The desired 4-

Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	mol %	solvent	yield (%)[b]
1	$[Ru(p\text{-cymene})Cl_2]_2$	5 mol %	DCE	32(55)
2	$[RhCp^*(MeCN)_3]SbF_6$	5 mol %	DCE	trace
3	$[RhCp^*Cl_2]_2$	5 mol %	DCE	61
4	$[RhCp^*Cl_2]_2$	5 mol %	toluene	18
5	$[RhCp^*Cl_2]_2$	5 mol %	THF	51
6	$[RhCp^*Cl_2]_2$	5 mol %	dioxane	53
7	$[RhCp^*Cl_2]_2$	5 mol %	*t*-AmOH	55
8	$\mathbf{[RhCp^*Cl_2]_2}$	**2.5 mol %**	**DCE**	**60**
9	$[RhCp^*Cl_2]_2$	1.25 mol %	DCE	45

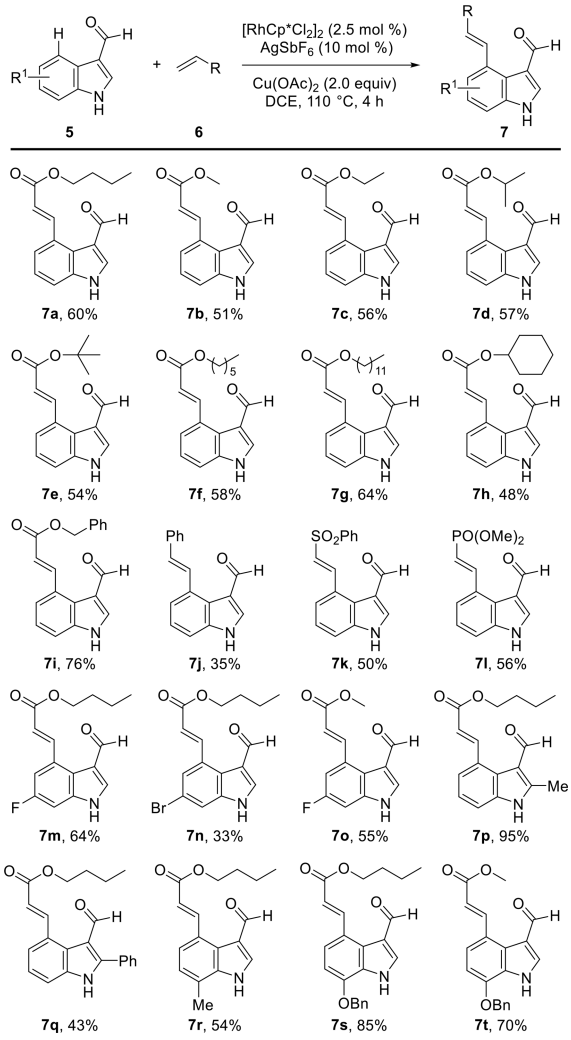
[a]Reaction conditions: **5a** (0.3 mmol), **6a** (1.2 mmol), $AgSbF_6$ (4 equiv of catalyst), $Cu(OAc)_2$ (0.6 mmol), solvent (1.0 mL). [b]Isolated yield, based on recovered starting materials in parentheses.

olefination product **7a** was obtained in 32% yield. Although the yield of **7a** was low, this result showed our proposal was correct. Encouraged by this initial result, we first attempted to improve the yield of **7a** using $[Ru(p\text{-cymene})Cl_2]_2$ as the catalyst. However, even after a variety of reaction conditions (various oxidants, solvents, and temperatures) were screened, no improvement was obtained. We then shifted to investigate the metal catalysts and found that they had remarkable influence on the reaction yield (Table 1, entries 1−3). $[RhCp^*(MeCN)_3]SbF_6$ provided **7a** in a trace amount (Table 1, entry 2). Gratefully, $[RhCp^*Cl_2]_2$ delivered **7a** in 61% yield (Table 1, entry 3). The effects of solvents were further examined, and DCE gave the best result (Table 1, entries 3−7). To our delight, we also found that the catalytic loading could be reduced to 2.5 mol % without a decrease of the yield (Table 1, entries 8 and 9). It is worthy to note that the reaction must be stopped when **5a** was close to completely consumed. Otherwise, a small amount of 2,4-diolefination product could be produced. The amount of 2,4-diolefination product increased with the prolonging of the reaction time.

Having optimized the reaction conditions, we next explored the scope of the reaction with respect to the alkene coupling partner and the indole-3-carboxaldehyde derivatives (Scheme 2). The substrate scope was quite general. A variety of acrylates and indole-3-carboxaldehyde derivatives could be used as reaction partners and gave the desired products in moderate to high yields. Particularly, **7p** was obtained in a remarkable yield of 95%. In addition, substrates with electron-rich groups on the phenyl moiety gave the desired products in higher yield (Scheme 2, **7s** and **7t**).

Having established the method for direct functionalization at the C4 position of 1-*H*-indole-3-carboxaldehyde derivatives, we

Scheme 2. Substrate Scope of 4-Substituted Indoles[a]



[a]Reaction conditions: **5** (0.3 mmol), **6** (1.2 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), and $Cu(OAc)_2$ (0.6 mmol) in DCE (1.0 mL) at 110 °C for 4 h.

turned our attention to the total synthesis of 3,4-substituted indole alkaloids. Agroclavine (**1**)[18] and elymoclavine (**3**)[19] were selected as the targets since **1** could be easily converted to festuclavine, costaclavine, setoclavine, and isosetoclavine,[20] and most importantly, **3** could be easily converted to lysergic acid (**4**) and drug pergolide.[21] In addition, the catalytic asymmetric total synthesis of **1** and the enantioselective synthesis of **3** have not yet been reported. Retrosynthetically, we envisioned **1** and **3** could be generated by late-stage manipulation of **8a** and **8b**, respectively (Scheme 3). The D-ring of both **8a** and **8b** could be formed via ring-closing metathesis (RCM) of **9a** and **9b**. The cyclization precursors **9a** and **9b** could be accessed from the common intermediate **10**. The key chiral **10** could be prepared from **11** by a Pd-catalyzed asymmetric allylic alkylation (AAA).[22] In turn, **11** could be readily obtained from **7b**.

Our synthesis commenced with **7b** (Scheme 4). During the preparation of **7b**, we found that the reaction can be scaled up to 20 g with only 0.5 mol % of catalyst to provide the product **7b** in higher yield (68%) than that run at small scale (see Table 1). Boc protection of the indole nitrogen gave aldehyde **12** in 85% yield. Condensation of aldehyde **12** with nitromethane provided the vinyl nitro compound **13**. Reduction of ester with DIBAL

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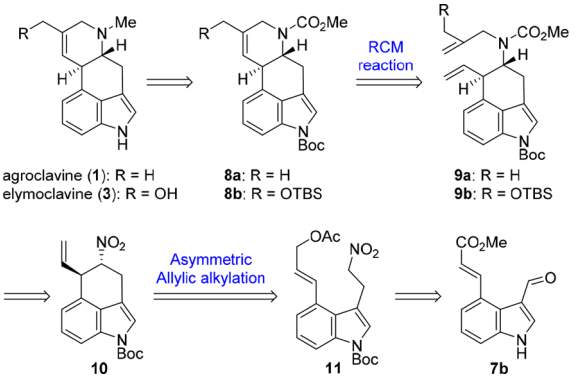
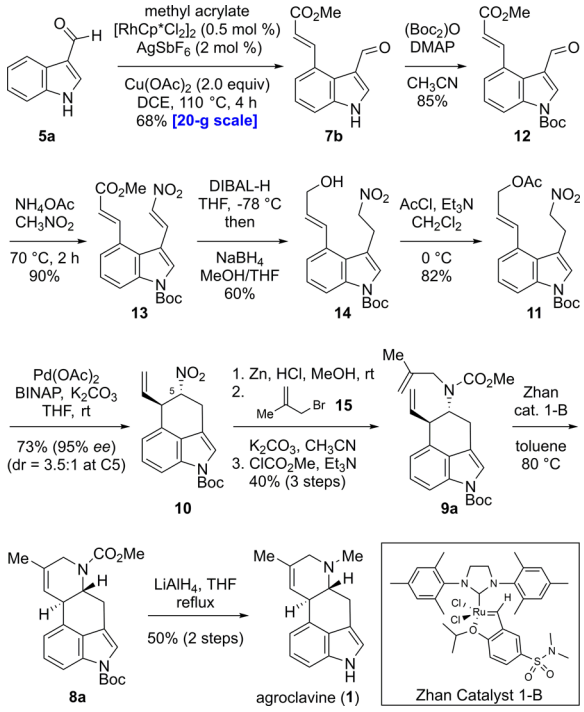
Scheme 3. Retrosynthetic Analysis for (−)-Agroclavine and (−)-Elymoclavine



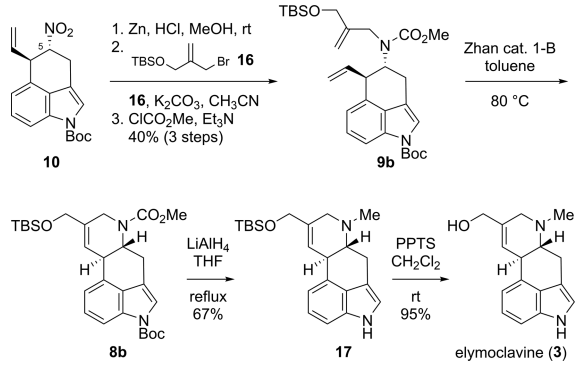
Scheme 4. Synthesis of (−)-Agroclavine



followed by reduction of olefin with $NaBH_4$ afforded allylic alcohol **14**. Acetylation of alcohol furnished the allylic acetate **11**. The intramolecular Pd-catalyzed AAA of the nitroacetate **11** employing (*S*)-(−)-BINAP as the ligand gave **10** and its C5 diastereoisomer in 73% yield (dr = 3.5:1), which could not be separated by flash column chromatography. The enantioselectivity of **10** was determined to be 95% by chiral HPLC analysis of the downstream product (see Supporting Information). Reduction of nitro with zinc provided the corresponding amine, which was alkylated with **15**. Subsequent protection of the resulting secondary amine with $ClCO_2Me$ gave carbamate **9a**. With diene **9a** available, the key RCM was examined. However, reaction of **9a** with Grubbs I and II catalysts as well as Hoveyda's catalyst at a variety of solvents and temperatures gave no desired cyclization product. To our delight, Zhan catalyst 1-B proved more powerful to promote the RCM reaction to deliver **8a** smoothly, which was not stable and immediately reduced with $LiAlH_4$ to give (−)-agroclavine (**1**). The physical data of our synthesized products **1** are identical to those reported in the literature.[18] Thus, we have achieved the first catalytic asymmetric total synthesis of **1**, which required only 11 steps from commercially available **5a**. Since agroclavine has already been converted to festuclavine, costaclavine, seto-clavine, and isosetoclavine, formal synthesis of these alkaloids was also achieved.[20]

Having successfully completed the total synthesis of **3** from intermediate **7b**, we then conducted the transformation of **10** into **3** following the same sequence as described for **1** (Scheme 5). Reduction of nitro **10** followed by alkylation of amine with

Scheme 5. Synthesis of (−)-Elymoclavine



allylic bromide **16** and protection of the resulting secondary amine with $ClCO_2Me$ gave diene **9b**. RCM of **9b** followed by reduction with $LiAlH_4$ gave **17**. Finally, removal of the TBS group with PPTS gave (−)-elymoclavine (**3**).[19]

In summary, we have developed a highly efficient method for the synthesis of 4-substituted indole via a rhodium-catalyzed direct functionalization of a wide range of unprotected indoles at the C4 position. This protocol featured mild reaction conditions, a low catalyst loading, and compatibility with diverse functional groups and provided a straightforward strategy for the preparation of 4-substituted indole derivatives. The utility of this method was further demonstrated by the first asymmetric total syntheses of (−)-agroclavine and (−)-elymoclavine. The total syntheses of agroclavine and elymoclavine were achieved in a divergent manner. We expect that this protocol will find broad use in chemical synthesis.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b01681.

Full experimental procedures, and ^1H and ^{13}C NMR spectra of compounds **1**, **3**, **7**−**14**, and **17** (PDF)

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Notes

The authors declare no competing financial interest.

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