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Palladium-Catalyzed Intramolecular Arylative Carboxylation of Allenes with CO_2 for the Construction of 3-Substituted Indole-2-carboxylic Acids

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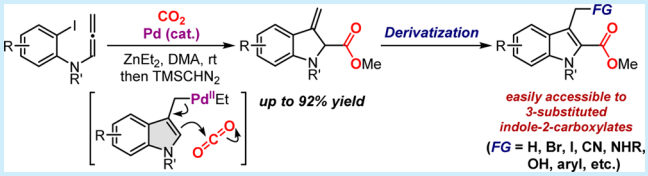
Supporting Information

ABSTRACT: Arylative carboxylation of allenes proceeded in an intramolecular manner to afford the corresponding β,γ-unsaturated carboxylic acids in high yields using $PdCl_2/PAr_3$ (Ar = C_6H_4-p-CF_3) and $ZnEt_2$ under 1 atm of CO_2. The intermediate of the cyclization/carboxylation sequence is thought to be a nucleophilic η^1-allylethylpalladium, which reacts with CO_2 at the γ-position of palladium. The products obtained could be efficiently converted into 3-substituted indole-2-carboxylate derivatives. One-pot synthesis of strychnocarpine, a β-carboline alkaloid, from the carboxylated product was also demonstrated.



Indole-2-carboxylic acids and their analogues (2-carboxyamides and amidines) are important structural motifs found in many natural products and biologically active compounds (Figure 1).[1−4] Among these, 3-substituted derivatives are especially important because the biological activities are mainly attributed to the chain structure of the 3-substituent[1] and because several naturally occurring substances have an additional six-membered heterocyclic ring attached at both of the 2,3-positions (e.g., strychnocarpine,[3] rutaecarpine,[4] etc.). Thus, development of concise and robust synthetic protocols to access 3-substituted indole-2-carboxylic acids using a readily available starting material is highly desirable.

Utilization of gaseous CO_2 for the construction of carboxylic acid derivatives via C−C bond formation has recently received considerable attention because CO_2 is an abundant, relatively nontoxic, and inexpensive C1 source.[5] These advanced technologies have expanded to carboxylation of indole nucleus with CO_2. Although indole-3-carboxylic acid derivatives can be synthesized in the presence of a Lewis acid or a Brønsted base with/without a catalyst under a CO_2 atmosphere,[6] fewer examples of the preparation of indole-2-carboxylic acids have been reported,[7] probably because electrophilic aromatic substitution of the indole nucleus usually occurs at the 3-position. Recently, the Iwasawa and Hou research groups

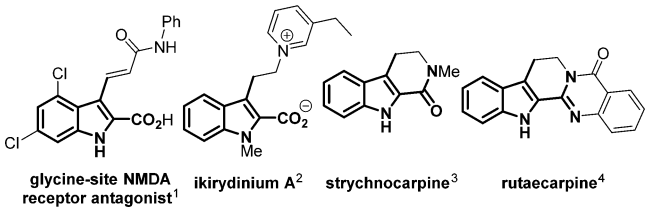


Figure 1. 3-Substituted indole-2-carboxylate skeletons.

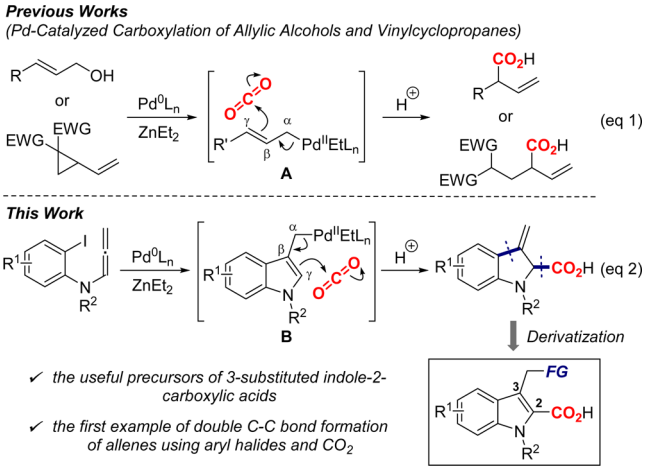


Figure 2. Our strategy for the construction of 3-substituted indole-2-carboxylic acids.

independently reported transition-metal-catalyzed carboxylations of 2-indole boronic acid derivatives as one of the substrates,[8] but the substrate scope did not cover any 3-substituted 2-borylindoles. We disclose herein a new catalytic method for the synthesis of 3-substituted indole-2-carboxylic acids using nucleophilic allylpalladium species.

We recently reported palladium-catalyzed carboxylation of allylic alcohols[9] and vinylcyclopropanes[10] in the presence of $ZnEt_2$ under 1 atm of CO_2 (Figure 2, eq 1). η^1-Allylethylpalladium **A** appears to be formed as an intermediate by reaction of the generated π-allylpalladium with $ZnEt_2$,[11,12] and the nucleophilic species **A** reacts with CO_2 at the γ-position. We

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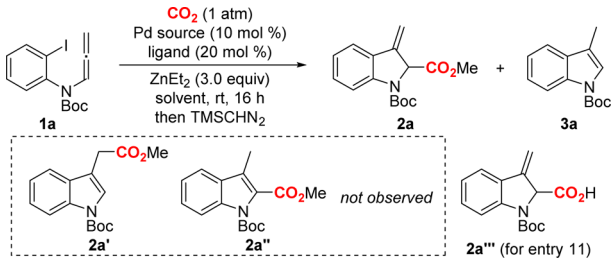
Table 1. Condition Screening



entry	Pd source	ligand	solvent	yield (%)[a] 2a	3a
1	$PdCl_2$	PPh_3	THF	44 (42)	53
2	$PdCl_2$	$P(C_6H_4\text{-}p\text{-}OMe)_3$	THF	42	41
3	$PdCl_2$	$P(C_6H_4\text{-}p\text{-}CF_3)_3$	THF	78	19
4	$PdCl_2$	$P(2\text{-furyl})_3$	THF	64	32
5	$Pd(OAc)_2$	$P(C_6H_4\text{-}p\text{-}CF_3)_3$	THF	54	34
6	$Pd(dba)_2$	$P(C_6H_4\text{-}p\text{-}CF_3)_3$	THF	26	27
7	$Pd(acac)_2$	$P(C_6H_4\text{-}p\text{-}CF_3)_3$	THF	50	27
8	$PdCl_2$	$P(C_6H_4\text{-}p\text{-}CF_3)_3$	dioxane	70	22
9	$PdCl_2$	$P(C_6H_4\text{-}p\text{-}CF_3)_3$	DMF	81	8
10	$PdCl_2$	$P(C_6H_4\text{-}p\text{-}CF_3)_3$	DMA	89 (86)	7
11[b]	$PdCl_2$	$P(C_6H_4\text{-}p\text{-}CF_3)_3$	DMA	(84)	ND[c]

[a]Yields determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. Isolated yields are given in parentheses. [b]With 6 mmol of **1a** in the presence of $PdCl_2$ (1 mol %) and $P(C_6H_4\text{-}p\text{-}CF_3)_3$ (2 mol %). Product was isolated as carboxylic acid **2a‴**. [c]Not determined.

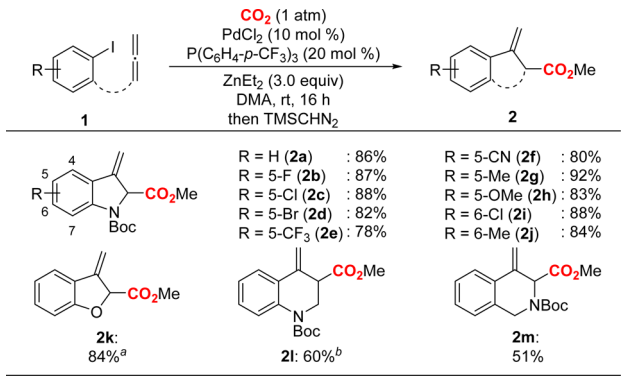


Figure 3. Substrate scope. Isolated yields are shown. [a]Product **2k** was partially isomerized into methyl 3-methylbenzofuran-2-carboxylate (**2k″**) (17% yield). These two products were separable by standard silica gel column chromatography. [b]$ZnEt_2$ was added using a syringe pump over 8 h, and the reaction mixture was stirred for an additional 8 h.

next focused on the use of *N*-allenyl-2-iodoanilines, which are known to undergo carbopalladation of the allene moiety intramolecularly, forming the corresponding π-allylpalladium species. This species has been reported to be trapped by a series of nucleophiles, including malonate and their derivatives, amines, acetate, and fluoride.[13] However, when $ZnEt_2$ is present, the polarity of the allylpalladium would be changed to nucleophilic (eq 2). If species **B** has sufficient nucleophilicity toward CO_2 at the γ-position (2-position of the indole ring), 3-methyleneindoline-2-carboxylates would be formed. We anticipated the capability of this dearomatization process because the resonance stabilization of the pyrrole part of the indole nucleus is relatively weak.[14,15] In another important aspect, this transformation would be the first example of a transition-metal-catalyzed C−C

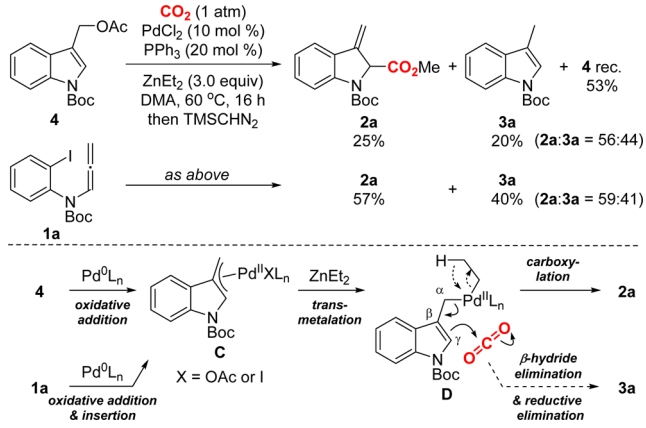


Figure 4. Carboxylation of 3-indolylmethyl acetate **4**.

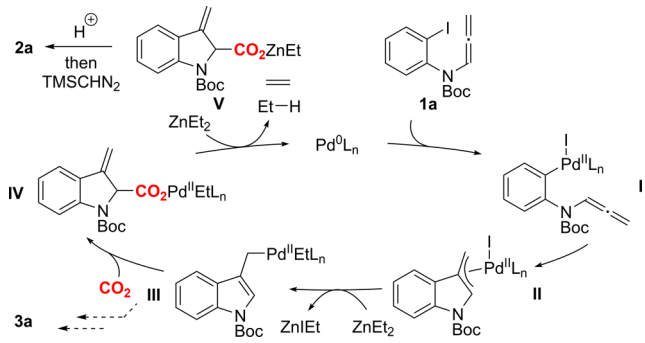


Figure 5. Plausible catalytic cycle.

bond-forming process between aryl halides and allenes followed by carboxylation with CO_2.[16] Furthermore, the *exo*-olefin at the 3-position of the product appears to be reactive, and it can be further functionalized by several methods along with aromatization, furnishing the desired 3-substituted indole-2-carboxylic acid derivatives.

First, we investigated the intramolecular arylative carboxylation of *N*-allenyl-2-iodoaniline **1a** using various palladium sources and ligands in the presence of $ZnEt_2$ at room temperature under a CO_2 atmosphere (1 atm). Substrate **1a** was readily prepared in three steps from 2-iodoaniline.[17] Yields were determined after methyl esterification with $TMSCHN_2$[9] (Table 1). According to previously established conditions,[9] $PdCl_2$ (10 mol %) with PPh_3 (20 mol %) was employed as a catalyst, and the expected carboxylated compound **2a** was obtained in 44% yield with 3-methylindole **3a** in 53% yield (entry 1). Regioselectivity was perfect, and regioisomer **2a′** was not observed at all. Aromatized product **2a″** was not detected even under basic conditions using $ZnEt_2$. Next, several phosphine ligands were screened using $PdCl_2$ as a palladium source. Although the use of $P(C_6H_4\text{-}p\text{-}OMe)_3$ resulted in a similar outcome (entry 2), the use of electron-deficient phosphines such as $P(C_6H_4\text{-}p\text{-}CF_3)_3$ and $P(2\text{-furyl})_3$ led to improvement of the product yield (entries 3 and 4). The trials for other Pd sources such as $Pd(OAc)_2$, $Pd(dba)_2$, and $Pd(acac)_2$ with $P(C_6H_4\text{-}p\text{-}CF_3)_3$ did not improve the yield of **2a** (entries 5−7). Among the potential polar solvents examined, use of DMA afforded product **2a** in 89% yield (86% isolated yield; entries 8−10). Carboxylation could be performed at gram scale (6.0 mmol, 2.14 g) without esterification with $TMSCHN_2$, affording carboxylic acid **2a‴** in high yield (84%, 1.39 g) using lower

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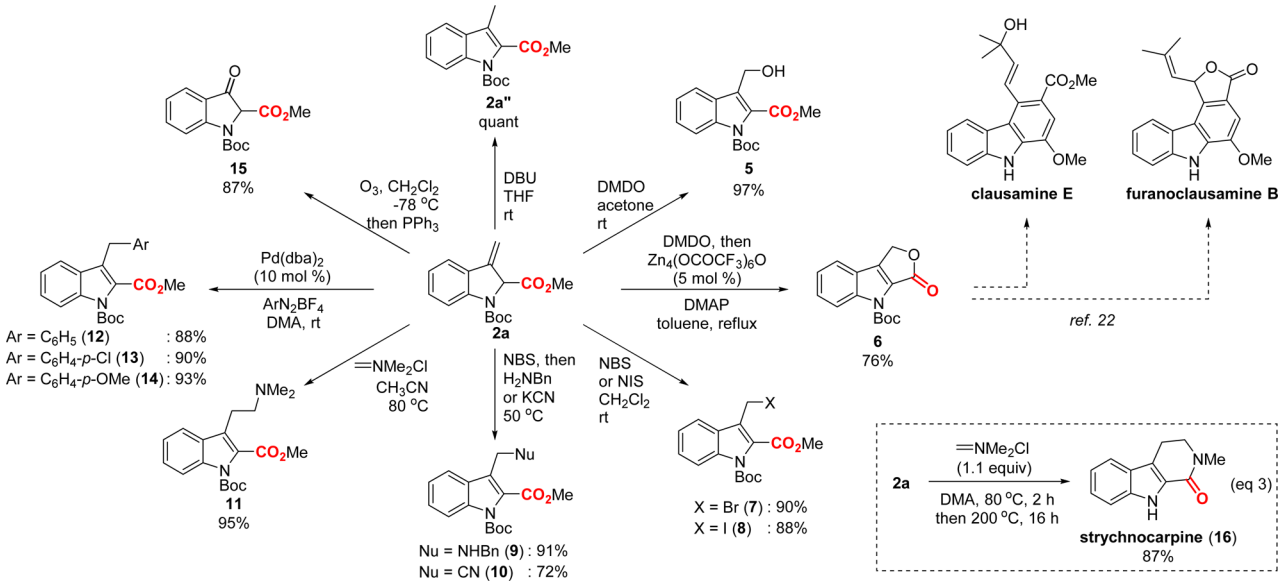

Figure 6. Derivatization of **2a** into 3-substituted indole-2-carboxylates and 3-oxindole-2-carboxylate.

loading of $PdCl_2$ (1 mol %) and $P(C_6H_4\text{-}p\text{-}CF_3)_3$ (2 mol %) (entry 11).[17]

With the optimized conditions in hand, substrate scope and limitations were investigated. As summarized in Figure 3, a variety of *N*-allenyl-2-iodoaniline derivatives bearing electron-withdrawing groups (F, Cl, Br, CF_3, and CN) and electron-donating groups (Me and OMe) on the aromatic ring (**1b**–**j**) could be converted into the corresponding 3-methyleneindoline-2-carboxylates **2b**–**j** in high yields. Notably, aryl bromide (**1d**), which potentially reacts with Pd(0) species,[18] was tolerated during the palladium-catalyzed process. Note that the cyano group (**1f**), which is incompatible in the strong base-mediated carboxylation,[7] remained intact. Moreover, the linker structure between the aromatic ring and the allene moiety was examined, showing that *O*-allenyl-2-iodophenol **1k** had high reactivity, and carboxylated products **2k** and **2k″** were obtained in 84% combined yield. The cyclization/carboxylation sequence could also provide access to 6-membered heterocyclic compounds, tetrahydroquinoline **2l** and tetrahydroisoquinoline **2m**, in good yields.

This arylative carboxylation of allenes is thought to proceed via the nucleophilic allylethylpalladium intermediate **B**, as depicted in eq 2 (Figure 2). To gain a mechanistic insight, we conducted carboxylation of 3-indolylmethyl acetate **4**, which is highly possible to be converted into η^3-allylpalladium intermediate **C** by oxidative addition to $Pd(0)L_n$ (Figure 4).[19] Although an electron-deficient phosphine, $P(C_6H_4\text{-}p\text{-}CF_3)_3$, did not promote the reaction, probably due to the retardation of oxidative addition, PPh_3 moderately promoted the carboxylation at 60 °C, affording 2-carboxylated compound **2a** in 25% yield with **3a** in 20% yield (**2a**/**3a** = 56:44) without generation of regioisomeric carboxylate **2a′**. When *N*-allenyl-2-iodoaniline **1a** was subjected to the same reaction conditions, **2a** and **3a** were obtained in 57 and 40% yields (**2a**/**3a** = 59:41), respectively. The same profiles between two reactions (similar ratio of **2a** and **3a** and no formation of **2a′**) strongly indicate that both carboxylations went through the same allylpalladium species: η^1-allylethylpalladium **D** was eventually produced via transmetalation of η^3-allylpalladium **C** (X = OAc or I) with $ZnEt_2$. The palladium atom should be located at the terminal carbon (the benzylic position) due to the avoidance of steric interaction between the ligands binding to the palladium atom and the indole nucleus. Intermediate **D** would then attack CO_2 at the γ-position to afford carboxylated product **2a**,[9,10,12] while β-hydride elimination of an ethyl ligand of **D** followed by reductive elimination led to the formation of **3a**.

On the basis on the above experimental data, a plausible catalytic cycle is proposed in Figure 5. First, oxidative addition of **1a** to $Pd(0)L_n$ followed by insertion of the allene moiety results in formation of η^3-allylpalladium **II**. Transmetalation between **II** and $ZnEt_2$ then proceeds to give the nucleophilic η^1-allylethylpalladium **III**, which reacts with CO_2 at the 2-position of the indole skeleton through dearomatization. The resulting palladium carboxylate **IV** could be reduced by $ZnEt_2$ to regenerate $Pd(0)L_n$ with the release of zinc carboxylate **V**. It would then be protonated during workup and methylated with $TMSCHN_2$, affording desired compound **2a**. 3-Methylindole **3a** would be generated from intermediate **III**.

To demonstrate the synthetic utility of this carboxylation, we investigated the derivatization of **2a** into 3-substituted indole-2-carboxylates by taking advantage of the reactive *exo*-olefin at the 3-position of **2a** (Figure 6).[20] First, DBU-promoted isomerization of **2a** proceeded quantitatively to give 3-methylindole **2a″**. When epoxidation of **2a** with DMDO was conducted, 3-indolylmethanol **5** was obtained in excellent yield via an epoxide opening/aromatization sequence. By using the $Zn_4(OCOCF_3)_6O$/DMAP system,[21] **5** could be converted into furoindolone **6**, which is a known intermediate for the synthesis of carbazole alkaloids (e.g., clausamine E and furanoclausamine B).[22] Halogenation with NBS and NIS[23] resulted in the introduction of a bromo and an iodo group, respectively, at the benzylic position of 3-substituted indoles, affording **7** (X = Br) and **8** (X = I). In addition, a one-pot process involving the bromination and addition of nucleophiles such as H_2NBn and KCN[23] proceeded, and corresponding products **9** and **10** were obtained in good to high yields. Moreover, **2a** was heated at 80 °C in the presence of *N*,*N*-dimethylmethyleneiminium chloride[24] to form *N*,*N*-dimethyltryptamine derivative **11** in 95% yield. C–C bond formation by Heck reactions of the *exo*-olefin in **2a** using electron-neutral, -deficient, and -rich aryldiazonium salts[25] proceeded efficiently to afford the arylated products **12**–

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14. Not only indole derivatives but also oxindole **15** was accessed from **2a** by ozonolysis.

We then turned our attention to the synthesis of strychnocarpine (**16**), a biologically active β-carboline alkaloid.[3] After formation of dimethyltryptamine **11** from **2a**, thermal Boc deprotection and lactam formation[26] were conducted at 200 °C in one pot, affording **16** in 87% yield (eq 3).

In conclusion, we successfully developed palladium-catalyzed intramolecular arylative carboxylation of allenes with CO_2. The generated η^1-allylethylpalladium should be a key intermediate for dearomative carboxylation with CO_2. The resulting 3-methyleneindoline-2-carboxylates (**2a**–**j**) serve as useful precursors of 3-substituted indole-2-carboxylates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b01055.

Experimental details and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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