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Palladium-Catalyzed Regioselective Decarboxylative Alkylation of Arenes and Heteroarenes with Aliphatic Carboxylic Acids

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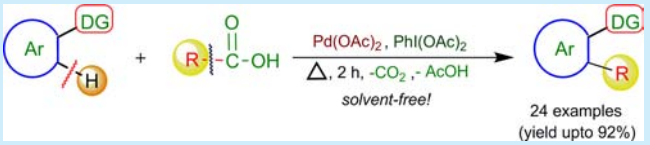
Supporting Information

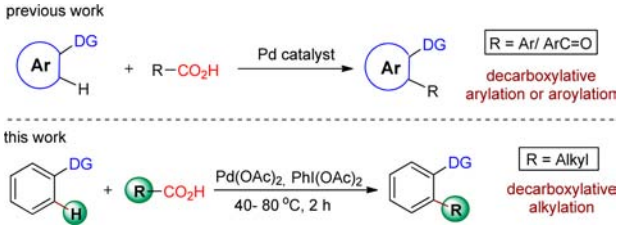
ABSTRACT: An unprecedented $Pd(OAc)_2$-catalyzed decarboxylative alkylation of unactivated arenes, with aliphatic carboxylic acids as inexpensive alkyl sources, is reported. The alkylation, controlled by the directing group, is regioselective, shows high functional group tolerance, and provides mild access to alkylated indolines, 2-phenylpyridines, and azobenzenes under solvent-free conditions in moderate to high yields.



Palladium-catalyzed C−H functionalization has evolved as an atom-economic strategy for the formation of carbon−carbon and carbon−heteroatom bonds.[1,2] The presence of Lewis basic groups in these C−H bond activations is known to enhance reactivity and control selectivity.[3] A number of reports on Pd-catalyzed and directing group assisted alkylation,[4] arylation,[5] alkenylation,[6] alkynylation,[7] alkoxylation,[8] acylation,[9] nitrogenation,[10] and halogenation[11] have appeared in the past decade. Most of the successful sp^2 C−H alkylations have been performed using transition metals as catalysts and organoboron reagents,[12] alkyl halides,[13] Grignard reagents,[14] and *N*-tosylhydrazones[15] under very harsh reaction conditions. Compared with the C−H bond arylation, C−H bond alkylation is more challenging since oxidative addition of alkyl halides is unfavorable and the resulting alkyl metal intermediates tend to undergo β-hydride elimination reactions. In this context, the use of carboxylic acids as alkylating agents in transition-metal-assisted decarboxylative coupling is of contemporary interest since this method avoids the preparation and use of stoichiometric organometallic reagents and produces CO_2 as the waste instead of toxic metal salts. Also, carboxylic acid derivatives as cross-coupling partners are minimally toxic, low cost, and stable. Therefore, extensive studies on Pd-catalyzed decarboxylative Heck reaction of alkenes with benzoic acids[16] and decarboxylative arylation[17] and acylation[18] of arene C−H bonds with aromatic carboxylic acids and α-oxocarboxylic acids, respectively, exist in literature. While silver has been used for a decarboxylative alkylation of heterocycles,[19] there is no single report on a Pd-catalyzed regioselective alkylation of unactivated sp^2 C−H bonds using aliphatic carboxylic acids (Scheme 1).

Herein, we report palladium-catalyzed formation of C_{sp2}−C_{sp3} bonds through decarboxylative cross-coupling using a range of secondary or tertiary α-substituted, cyclic, and acylic aliphatic carboxylic acids as the alkyl source under solvent-free conditions. The reaction involves breaking of the C_{sp3}−COOH bond of aliphatic carboxylic acid and pyrimidine, pyridine, and azo group directed regioselective alkylation of the arene/heteroarene C−H bond to yield the alkylated indolines, 2-phenylpyridines, and azobenzenes, respectively.

Scheme 1. Palladium-Catalyzed Directing Group Assisted C−C Bond Formation via Decarboxylation Pathway



We began our investigation with the indoline nucleus since it is a ubiquitous motif in nature, and direct C−C bond formation at the arene C−H bonds with control of site selectivity is a challenging goal. Addressing the C-7 position by C−H arylation, alkylation, and alkenylation is attractive but rare.[20] There is only one previous report by Sanford and co-workers in which a C-7 methylation of acetylated indoline has been demonstrated with alkyl borates under Pd(II) catalysis using MnF_3 as the stoichiometric oxidant.[21] We initiated the alkylation of *N*-pyrimidylindoline (**1a**) with commercially available pivalic acid (**2a**). When **2a** (2 equiv) was reacted with **1a** in the presence of 2 equiv of $PhI(OAc)_2$ and 10 mol % of $Pd(OAc)_2$ at 130 °C, we were delighted to see that, as desired, a C-7 selective alkylation of indoline took place and the product, 7-*tert*-butyl-1-(pyrimidin-2-yl)indoline (**3a**) was formed in 46% yield along with *N*-pyrimidylindole as the oxidation product of **1a**. Further, with unprotected indoline, no alkylation took place under oxidative Pd(II) catalysis, while with *N*-phenyl-substituted indoline oxidation to the corresponding *N*-phenylindole took place suggesting that the C-7 site activation and selectivity was being controlled by the pyrimidyl unit. With this preliminary success, we were enthused to have achieved an unprecedented Pd(II)-catalyzed decarboxylative alkylation via C−H bond activation.

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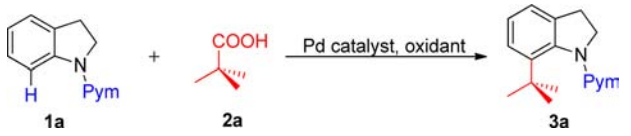
The only other preceding report on a decarboxylative alkylation on a C−H bond was demonstrated using silver as the catalyst and benzothiazoles and benzoxazoles as substrates.[19]

We next moved toward optimizing the reaction with respect to catalyst, oxidant, solvent, temperature, and time (Table 1). While substrate conversion was found to be 100% at 100 °C, 80 °C, as well as 40 °C, lowering the reaction temperature showed an improvement in yield of the desired product and suppressed the formation of byproduct generated by oxidation of indoline at high temperatures (Table 1, entry 1−3). Therefore, it was decided to carry out further studies at 40 °C. Lowering the catalytic loading of $Pd(OAc)_2$ to 8 and 5 mol % substantially reduced the yield to 62% and 45%, respectively (entry 3), while increasing it to 12 mol % did not alter the yield of **3a**. Use of other palladium precatalysts like $PdCl_2$ and $Pd(dba)_2$ was also examined. Both were found to be active and yielded **3a** in 82 and 88% yields, respectively, (entries 4 and 5). Since $Pd(OAc)_2$ was found to have the highest activity, it was used for further optimizations. Addition of solvents was found to be detrimental for the reaction. With DCE, CH_3CN, and toluene, the yield was reduced to 45−59% (entry 6−8) with the formation of unidentified side products, while with polar solvents like DMF and DMSO, the effect worsened (31−33%) (entries 9 and 10). Thus, it was decided to conduct alkylation under solvent-free conditions. Screening of oxidants such as $PhI(OAc)_2$, benzoquinone (BQ), and $K_2S_2O_8$ demonstrated that $PhI(OAc)_2$ was highly specific and catalyzed the reaction with high yield, while no trace of product was seen with the other two oxidants (entries 11 and 12). Moreover, control reactions in the absence of $Pd(OAc)_2$ or $PhI(OAc)_2$ did not yield any product, suggesting each of them to be a critical requirement for alkylation (entries 13 and 14). Further, varying the equivalents of $PhI(OAc)_2$ to 1.0, 1.5, and 3.0 did not help the reaction either, and lower yields were obtained with 1.0 and 1.5 equiv (entry 15). Furthermore, reducing the amount of **2a** to 1.0 equiv dropped the product yield to 50%, while increasing it to 3.0 equiv resulted in a similar yield as with 2.0 equiv (entry 16). The reaction time was also optimized. In 1 h, reaction was found to be incomplete and only 42% yield of **3a** was obtained, while extending it up to 3 h did not bring about any change in the reaction profile (entry 17). Therefore, optimal reaction conditions involved heating 1 equiv of **1a**, 2 equiv of **2a**, 10 mol % of $Pd(OAc)_2$, and 2 equiv of $PhI(OAc)_2$ at 40 °C for 2 h in the absence of any solvent.

Table 1. Optimization of Reaction Conditions for Decarboxylative Alkylation[a]



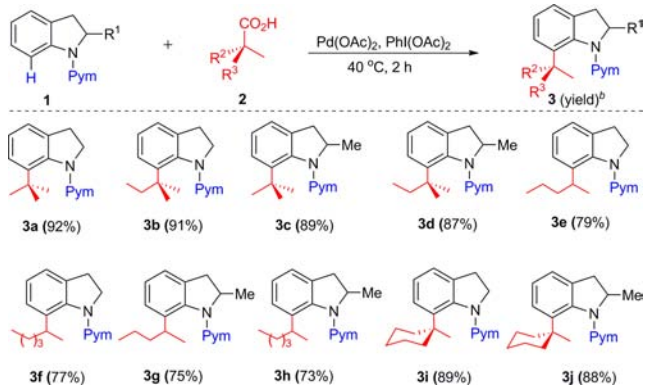
1a 2a 3a

entry	catalyst	oxidant	temp (°C)	solvent	yield %[b] (conversion%)[c]
1	$Pd(OAc)_2$	$PhI(OAc)_2$	100	-----	52 (100)
2	$Pd(OAc)_2$	$PhI(OAc)_2$	80	-----	67 (100)
3	$Pd(OAc)_2$	$PhI(OAc)_2$	40	-----	92 (100), 62 (76)[d], 45 (52)[e]
4	$PdCl_2$	$PhI(OAc)_2$	40	------	82 (90)
5	$Pd(dba)_2$	$PhI(OAc)_2$	40	------	88 (96)
6	$Pd(OAc)_2$	$PhI(OAc)_2$	40	DCE	59 (72)
7	$Pd(OAc)_2$	$PhI(OAc)_2$	40	CH_3CN	56 (74)
8	$Pd(OAc)_2$	$PhI(OAc)_2$	40	toluene	45 (65)
9	$Pd(OAc)_2$	$PhI(OAc)_2$	40	DMF	33 (58)
10	$Pd(OAc)_2$	$PhI(OAc)_2$	40	DMSO	31 (58)
11	$Pd(OAc)_2$	BQ	40	-----	0 (0)
12	$Pd(OAc)_2$	$K_2S_2O_8$	40	-----	0 (0)
13	-----	$PhI(OAc)_2$	40	-----	0 (0)
14	$Pd(OAc)_2$	-----	40	-----	0 (0)
15	$Pd(OAc)_2$	$PhI(OAc)_2$	40	-----	90 (100)[f], 62 (70)[g], 42 (54)[h]
16	$Pd(OAc)_2$	$PhI(OAc)_2$	40	-----	40 (50)[i]
17	$Pd(OAc)_2$	$PhI(OAc)_2$	40	-----	42 (50)[j], 92 (100)[k]

[a]Reaction conditions: **1a** (1.0 equiv), **2a** (2.0 equiv), oxidant (2.0 equiv), Pd catalyst (10 mol %) heated for 2 h. [b]Isolated yield. [c]Based on **1a**. [d]8 mol % of $Pd(OAc)_2$. [e]5 mol % of $Pd(OAc)_2$. [f]3.0 equiv of $PhI(OAc)_2$. [g]1.5 equiv of $PhI(OAc)_2$. [h]1.0 equiv of $PhI(OAc)_2$. [i]1.0 equiv of **2a**. [j]Reaction time is 1 h. [k]Reaction time is 3 h. Pym: pyrimidine.

With the optimized reaction conditions, scope of this transformation was investigated. The reactivity of *N*-pyrimidylindoline toward different tertiary and secondary α-substituted aliphatic carboxylic acids was seen (Scheme 2). With acyclic tertiary carboxylic acids, **1a** and alkylated indoline (**1b**) gave high yield of the corresponding C-7 alkylated products (**3a−d**). Selective alkylation on **1a** and **1b** could also be achieved using secondary carboxylic acids, though slightly lower yields were obtained in these cases (**3e−h**). Notably, the palladium catalysis could also be applied to cyclic carboxylic acids, and **3i** and **3j** were synthesized from **1a** and **1b** in excellent yield. However, with primary carboxylic acids such as acetic acid, no alkylation was seen, and the entire starting material was converted into unidentified polymeric products within 2 h of reaction time.

Scheme 2. Scope of Decarboxylative Alkylation with Indolines[a]



1 2 3 (yield)[b]

[a]Reaction conditions: **1** (1.0 equiv), **2** (2.0 equiv), $PhI(OAc)_2$ (2.0 equiv), $Pd(OAc)_2$ (10 mol %), 40 °C, 2 h. [b]Isolated yield.

To explore the generality of this method, we attempted this to other sp^2 C−H systems in which regioselectivity was being controlled by a different directing group. For this, 2-phenylpyridine (**4a**) was chosen as it is the most extensively studied system for Pd catalyzed C−H activation.[22] However, no reports on a Pd assisted decarboxylative alkylation on **4** exist in literature. It was found that using **2a**, alkylation on **4a** was achieved exclusively at C-2 position to yield 2-(2-*tert*-butylphenyl)-

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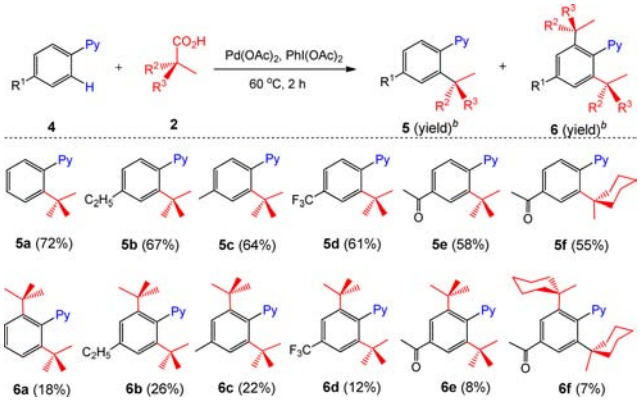
pyridine (**5a**) in 72% yield. The reaction, however, had to be conducted at slightly higher temperature (60 °C), yet it did not go to completion.

The reactivity of different substituted 2-phenylpyridines toward acyclic and cyclic tertiary carboxylic acids was examined (Scheme 3). To our delight, the monoalkylated 2-phenyl-

Scheme 3. Scope of Decarboxylative Alkylation with 2-Phenylpyridines[a]



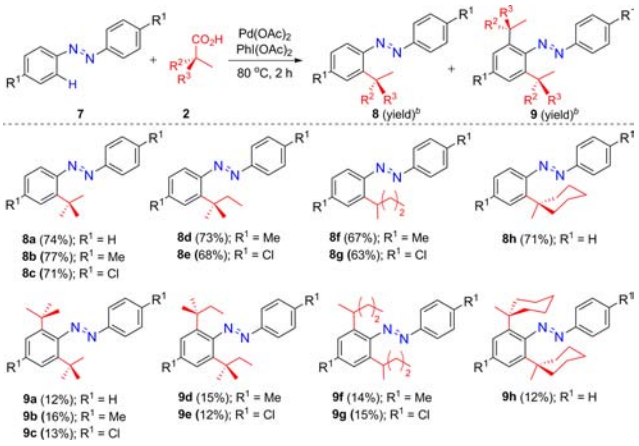
[a]Reaction conditions: **4** (1.0 equiv), **2** (2.0 equiv), $PhI(OAc)_2$ (2.0 equiv), $Pd(OAc)_2$ (10 mol %), 60 °C, 2–4 h. [b]Isolated yield.

pyridines **5a–f** were obtained in moderate yields (55–72%). However, we noticed that dialkylation was inevitable in all these cases, and **6a–f** were isolated as minor products of the reaction. The electronic effect showed some obvious influence on the decarboxylative coupling reactions. 2-Phenylpyridine with electron-donating ethyl and methyl groups gave higher yields of the products (**5b,c**), while with electron-withdrawing CF_3 and $COCH_3$ substituents relatively lower yields were obtained (**5d–f**).

Next, we decided to extend this methodology for selective alkylation of aromatic azo compounds, which hold immense significance in many fields such as nonlinear optics, dyes, indicators, photochemical switches, and therapeutic agents.[23] It was found that azo-directed *ortho*-alkylation required higher temperature (80 °C) and gave monoalkylated products (**8a–h**) in 63–77% yield along with dialkylated products (**9a–h**) in 12–16% yield (Scheme 4). We emphasize that the present methodology offers very good selectivity in affording mono-alkylated unsymmetrical azobenzenes. It is also of interest to note that the halo group in products **8c,e,g** may be utilized as a handle for further functionalization.

To ascertain the involvement of free-radical species in the reaction; quenching studies with TEMPO were carried out. As anticipated, the reaction did not take place on addition of TEMPO to the reaction mixture, and the starting substrate **1a** was left as such, along with the formation of a new species identified as the TEMPO-pivalyl adduct (see the Supporting Information). We surmised that the reaction involved a pivalyl radical. This was verified by replacing indoline with styrene as the substrate, and then performing the reaction under the optimized conditions. If the reaction was to follow a free-radical path, addition of pivalyl group on styrene was the expected outcome due to the high affinity of π-bonds toward the radical. We found that a facile addition of pivalyl radical on to the styrene double bond indeed took place. Moreover, the reaction between styrene

Scheme 4. Azo-Directed Decarboxylative Alkylation[a]

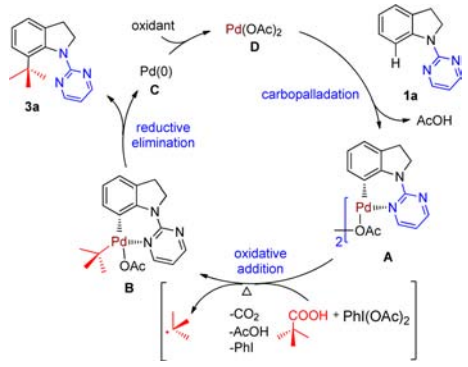


[a]Reaction conditions: **7** (1.0 equiv), **2** (2.0 equiv), $PhI(OAc)_2$ (2.0 equiv), $Pd(OAc)_2$ (10 mol %), 80 °C, 2 h. [b]Isolated yield.

and **2a** was also found to cease on addition of TEMPO, indicating it to be mediated through a free-radical path.

On the basis of these observations, we propose that the decarboxylative alkylation begins by directing-group assisted cyclopalladation yielding a six-membered pallacycle complex **A** by coordination of **1a** to palladium(II) (Scheme 5). This is

Scheme 5. Plausible Mechanism



followed by oxidative addition of the pivalyl radical to **A** to form **B** in which palladium might exist in the form of palladium (III or IV) intermediate. Apparently, generation of pivalyl radical is facilitated by thermal decomposition of $PhI(OAc)_2$[24] followed by abstraction of hydrogen radical and then release of CO_2. This role of $PhI(OAc)_2$ also explains its specificity for the reaction, and requirement in 2.0 equiv. Finally reductive elimination of **B** yields the alkylated product **3a** and Pd(0). Pd(II) is regenerated back into the catalytic cycle with the help of the external oxidant. Consistent with the radical mechanism, radical scavengers such as ascorbic acid were found to reduce the product yield in a dose-dependent manner (Table 2).

In conclusion, we have developed a useful method for regioselective alkylation of unactivated sp^2 C–H bonds through an auxiliary-assisted Pd-catalyzed decarboxylative reaction. This method enables us to address several of the key limitations of prior C–H alkylation processes. The current transformation proceeds under mild solvent-free conditions, produces CO_2 as an innocuous byproduct, and is effective for installation of secondary and tertiary acyclic and cyclic alkyl substitutents into substrates bearing pyridyl, azo, and pyrimidine directing groups.

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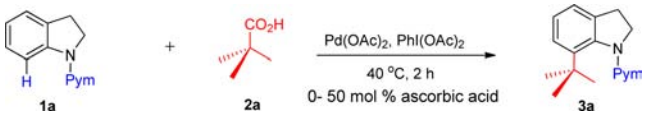
Table 2. Inhibition by Ascorbic Acid[a]



no.	ascorbic acid (mol %)	% yield[b]
1	0	92
2	10	51
3	25	29
4	50	6

[a]Reaction conditions: **1a** (1.0 equiv), **2a** (2.0 equiv), Pd catalyst (10 mol %), $PhI(OAc)_2$ (2.0 equiv), 40 °C, 2 h. [b]Isolated yield.

The reaction exhibits high generality, excellent selectivity toward *ortho* C−H bonds, and good functional group tolerance. Through mechanistic studies, we propose that the protocol involves an in situ generation of alkyl radical and has been demonstrated for synthesis of alkylated indolines, 2-phenylpyridines, and unsymmetrical azobenzenes in moderate to high yields.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H NMR and ^{13}C NMR for all synthesized compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b00878.

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Notes

The authors declare no competing financial interest.

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