Synthetic Methods

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Palladium(II)-Catalyzed Tandem Synthesis of Acenes Using Carboxylic Acids as Traceless Directing Groups

*Kiho Kim, Dhananjayan Vasu, Honggu Im, and Sungwoo Hong**

Dedicated to Professor Steven M. Weinreb on the occasion of his 75th birthday

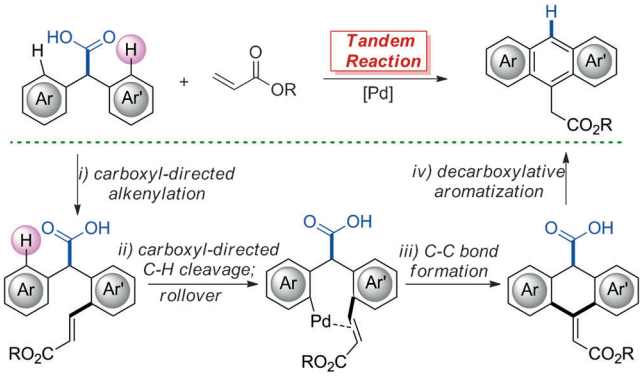
Abstract: *A straightforward synthetic strategy for generating useful anthracene derivatives was developed involving palladium(II)-catalyzed tandem transformation with carboxylic acids as traceless directing groups. Carboxyl-directed C-H alkenylation, carboxyl-directed secondary C-H activation and rollover, intramolecular C–C bond formation, and decarboxylative aromatization are proposed as the key steps in the tandem reaction pathway. This novel synthetic route utilizes a broad range of substrates and provides a convenient synthetic tool that allows access to acenes.*

Linearly fused polycyclic aromatic hydrocarbons (PAHs) are highly important structural motifs in various areas of organic chemistry,[1] medicinal chemistry,[2] and materials science.[3] The electron-rich nature of heteroacenes has attracted considerable attention, with applicability as versatile synthetic precursors and building blocks for optoelectronic applications.[4] Moreover, heteroacene derivatives such as indolocarbazoles, exhibit a wide range of pharmacological properties, including antitumor and antibiotic activities.[5] Consequently, the development of efficient and selective syntheses of such aromatic structures is a topic of intensive research.[6,7] Although many impressive synthetic strategies have been developed, the scope of reactions has often been limited by a requirement for prefunctionalization, the difficulty of incorporating heteroatoms, or harsh reaction conditions. In this context, an expedient synthetic method that produces heteroacene skeletons in a new type of efficient catalytic transformation is highly desirable.

While transition metal-catalyzed direct C-H functionalization has evolved into an efficient and versatile strategy for modern transformative developments in organic synthesis,[8,9] its power and efficiency could be dramatically enhanced by combining such catalytic transformations into a one-pot process. From the perspective of step- and atom-economy, a one-pot catalytic approach is appealing for the construction of complicated motifs from simple starting materials.[10]

Recently, the use of carboxylic acids as traceless directing groups for decarboxylative coupling was investigated as a highly efficient route for the synthesis of diversely substituted arenes.[11,12] We were intrigued by the possibility of a tandem transformation employing removable carboxylic acid directing groups, which simultaneously afforded catalytic control and efficiency. In particular, we speculated that the olefinated intermediate generated in situ as a result of the Pd(II)-catalyzed, carboxyl-directed alkenylation of a diaryl carboxylic acid, could be further utilized for another C-H activation in the context of the same directing group. The sequential C-H functionalization approach is a highly efficient method for intramolecular cyclization of diaryl compounds.[13] Subsequently, we hypothesized that rollover of the palladated intermediate might enable coordination to an alkene moiety,[14] which would set the stage for intramolecular C–C bond formation. Finally, the carboxylate group could be removed in a traceless fashion by decarboxylative aromatization, affording the desired anthracene products. If successful, this strategy represents a novel approach to step-economical synthesis of diversely functionalized anthracene and heteroacene derivatives (Scheme 1).

In line with our hypothesis, we began our studies by investigating the tandem reaction of diphenyl carboxylic acid (**1a**), which can be easily obtained from the arylation of ethyl acetate[15] with ethyl acrylate **2a**, employing a catalytic system consisting of $Pd(OAc)_2$ and an amino acid-derived ligand (Table 1).[16] Our initial attempts with $KHCO_3$ were discour-



Scheme 1. Pd(II)-catalyzed tandem transformation using carboxylic acids as traceless directing groups: i) carboxyl-directed C-H alkenylation, ii) carboxyl-directed C-H activation and rollover, iii) intramolecular C–C bond formation, and iv) decarboxylative aromatization.

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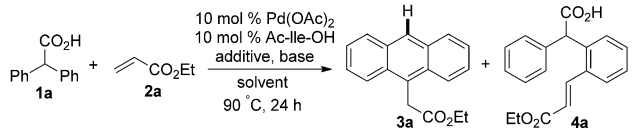
Table 1: Optimization of the reaction conditions.[a]

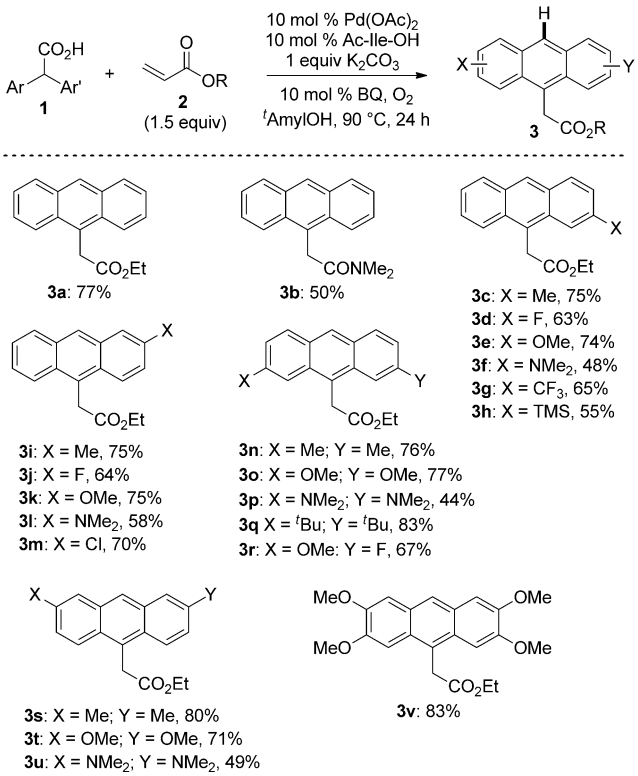


Entry	Base [1 equiv]	Additive [10 mol %]	Solvent	Yield [%] 3a	4a
1	$KHCO_3$	–	*t*-amylOH	trace	45
2	Na_2CO_3	–	*t*-amylOH	5	42
3	Li_2CO_3	–	*t*-amylOH	–	15
4	Cs_2CO_3	–	*t*-amylOH	44	5
5	K_3PO_4	–	*t*-amylOH	52	8
6	K_2CO_3	–	*t*-amylOH	66	–
7	K_2CO_3	–	1.2-DCE	–	5
8	K_2CO_3	–	1.6-dioxane	38	22
9	K_2CO_3	DMSO	*t*-amylOH	62	–
10	K_2CO_3	*i*-Pr_2S	*t*-amylOH	65	–
11	K_2CO_3	benzoquinone	*t*-amylOH	77	–

[a] **1a** (1.0 equiv), **2a** (1.5 equiv), $Pd(OAc)_2$ (10 mol %), Ac-Ile-OH (10 mol %), additive (10 mol %), base (1.0 equiv), O_2 (1 atm) in *t*-amylOH (0.5 M) at 90 °C for 24 h. Yields of isolated products. DMSO = dimethyl sulfoxide, DCE = 1,2-dichloroethane.

aging because of a lack of reactivity of the resulting olefinated intermediate **4a** under the reaction conditions (entry 1). Further investigations revealed that the base fundamentally influences the efficiency of the sequential reactions, and a remarkable countercation (Li^+, K^+, Na^+, and Cs^+) effect[17] was also observed. Catalytic efficacy was considerably improved using Cs_2CO_3 as the base; anthracene **3a** was obtained in 44 % yield, thus indicating that an overall tandem process was operating effectively. After extensive screenings, K_2CO_3 was found to be the optimal base, and the product yield further increased to 66 % with only a negligible amount of the intermediate **4a** (entry 6). Use of the preformed sodium or potassium salts of **1a** as the starting materials did not improve the overall outcome. Among the palladium sources tested, $Pd(OAc)_2$ displayed the best catalytic reactivity. A control experiment confirmed that the amino acid-derived ligand is essential, and that Ac-Ile-OH is the most appropriate ligand. The use of tert-amyl alcohol (*t*-amylOH) as the solvent was necessary to achieve a higher conversion; other solvents gave poor yields. Additives such as DMSO and i-Pr_2S were investigated to minimize the precipitation of palladium black, but no beneficial effects were observed. Further screening studies revealed that an optimal result could be obtained with $Pd(OAc)_2$ (10 mol %), Ac-Ile-OH (10 mol %), benzoquinone (10 mol %), and K_2CO_3 (1 equiv) in *t*-amylOH using 1 atm O_2 as the oxidant, generating anthracene product **3a** in the highest yield (entry 11, 77 %).

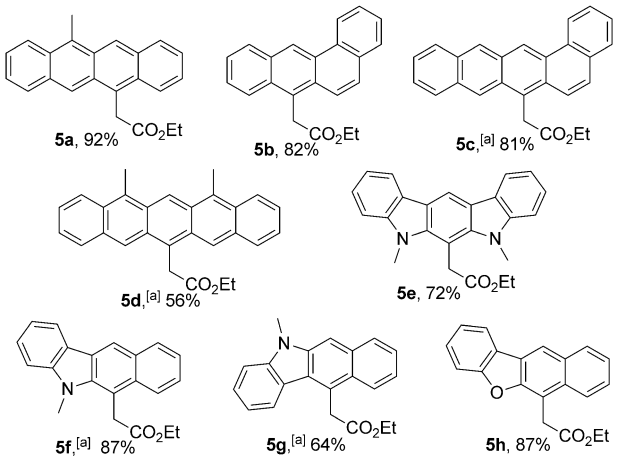
Having established that construction of anthracene occurs by the tandem reaction, the substrate scope was studied with a range of functional groups, such as alkyl, methoxy, halide, trifluoromethyl, and amino groups. We envisaged that these groups could be a useful synthetic handle. We were delighted to observe that substitution with both electron-donating (Me-, *t*-Bu-, MeO-, and Me_2N-) and electron-withdrawing groups (F-, Cl-, and, CF_3-) on the aryl moieties afforded the corresponding products with moderate to good yields under the reaction conditions (summarized in Scheme 2). Additionally, the substrate bearing a silyl group was compatible with



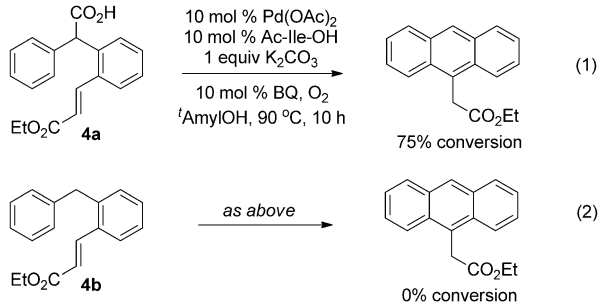
Scheme 2. Substrate scope of anthracenes. Reaction conditions: **1** (1.0 equiv), **2** (1.5 equiv), $Pd(OAc)_2$ (10 mol %), Ac-Ile-OH (10 mol %), additive (10 mol %), K_2CO_3 (1.0 equiv), O_2 (1 atm) in *t*-amylOH (0.5 M) at 90 °C for 24 h. Yields of isolated products.

the coupling conditions, enabling production of **3h**. Notably, the chlorine-substituted substrate can be employed in the tandem reaction, thus enabling further functionalization at this position (**3m**). Further exploration demonstrated that a starting material bearing an unsymmetrical substitution pattern (MeO- and F-) was a suitable substrate (**3r**). This method was also compatible with the dimethoxyphenyl group, affording the tetramethoxy-substituted anthracene **3v**. Thus, the process was used to synthesize anthracene derivatives with substituents at various positions, providing considerable advantages in both simplicity and efficiency.

For broad utility, we turned our attention to the scope of the polyacenes, as shown in Scheme 3. For example, tetracene **5a** was produced in 92 % yield when 2-(naphthalen-2-yl)-2-phenylacetic acid was employed as the substrate. Similarly, the bent polyacene, benzoanthracene **5b**, was synthesized in excellent yield. Employment of a substrate bearing 1-naphthyl and 2-naphthyl groups resulted in the formation of the corresponding dibenzoanthracene **5c**, which indicates that the reaction occurred at the sterically less hindered β-position of the naphthyl group. Importantly, pentacene derivative **5d** was also accessible by this method. Considering



Scheme 3. Substrate scope of polyacene and heteroacene derivatives. Reaction conditions: substrate (1.0 equiv), ethyl acrylate (1.5 equiv), $Pd(OAc)_2$ (10 mol %), Ac-Ile-OH (10 mol %), benzoquinone (10 mol %), K_2CO_3 (1.0 equiv), O_2 (1 atm) in *t*-amylOH (0.5 M) at 90°C for 24 h. [a] $Pd(OAc)_2$ (20 mol %).



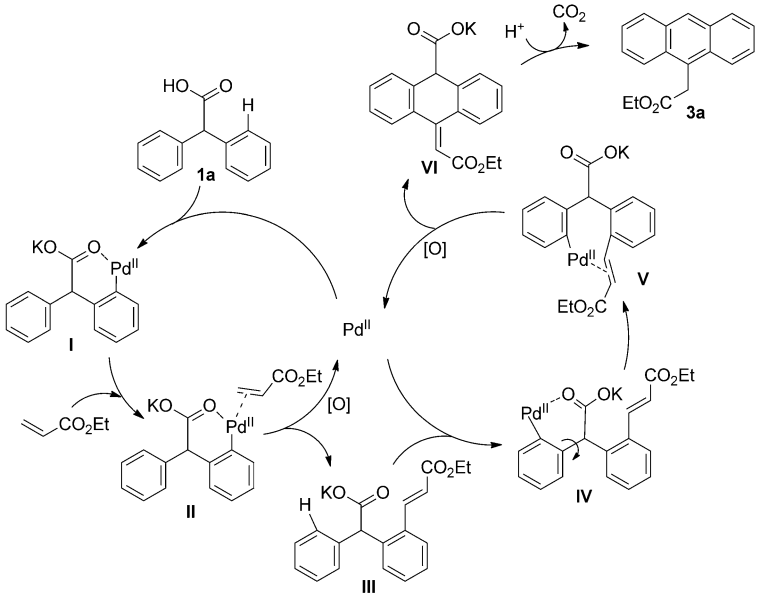
Scheme 4. Control experiments.

the importance of indolocarbazole[5,18] as a key moiety within various biologically active molecules and optoelectronic materials, we subsequently assessed the applicability of our method with respect to substrates bearing heteroaromatic units. Indeed, the utility of the present method was further demonstrated by providing convenient access to prominent heteroacene structural motifs, featuring indole units fused to the benzenoid ring (**5e**, **5f**, and **5g**).[19] Expanding the scope to a benzofuran-containing substrate was also possible, affording benzonaphthofuran **5h**.

Although **4a** is believed to be the key reaction intermediate for the tandem process, another mechanistic possibility involving an early protodecarboxylation pathway is conceivable. To gain insight into the mechanism of the tandem process, two possible reaction intermediates **4a** and **4b** were subjected to the standard reaction conditions without adding ethyl acrylate. Indeed, the reaction of **4a** proceeded smoothly, leading to the formation of the corresponding anthracene (Scheme 4). On the other hand, substrate **4b** was not converted into the desired product, indicating that the intramolecular C–C bond formation is likely to be initiated by carboxyl-directed C–H activation of the olefinated intermediate.

Based on the above observations, a mechanistic proposal for the tandem process is illustrated in Scheme 5. The six-membered palladacyclic intermediate **I**, derived from the initial carboxyl-directed C–H bond activation, reacts with the alkene to give olefinated intermediate **III**. Subsequently, the palladacycle complex **IV** is presumably generated by another carboxyl-directed C–H bond cleavage. Subsequent rollover from **IV** enables coordination to an alkene moiety, followed by an intramolecular cyclization to afford the cyclized intermediate **VI**. Finally, decarboxylative aromatization leads to the formation of the anthracene product, and the oxidation of Pd^0 species into a Pd(II) species by molecular oxygen completes the catalytic cycle.

In summary, we developed a Pd(II)-catalyzed tandem transformation involving carboxyl-directed C-H alkenylation/carboxyl-directed secondary C-H activation and rollover/intramolecular C–C bond formation/decarboxylative aromatization sequences. The current method is compatible with a broad range of substituents and allows the rapid generation of anthracene derivatives of high synthetic utility. The synthetic potential of this method was further highlighted by the convenient and direct synthesis of the useful structural motifs, polyacenes and heteroacenes.



Scheme 5. Proposed mechanism for Pd(II)-catalyzed tandem transformation.

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Keywords: acenes · C-H functionalization · decarboxylation · palladium · tandem reactions

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[19] CCDC 1472791 contains the supplementary crystallographic data for **5e**. This data is provided free of charge by The Cambridge Crystallographic Data Centre.

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Communications

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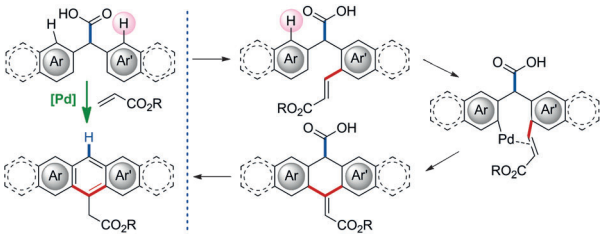
Palladium(II)-Catalyzed Tandem Synthesis of Acenes Using Carboxylic Acids as Traceless Directing Groups



Driving tandem: A tandem strategy that generates useful anthracene derivatives involves carboxyl-directed C-H alkenylation and secondary C-H activation, followed by rollover/intramolecular C–C bond formation/decarboxylative aromatization sequences. The synthetic route accommodates a broad range of substrates and their acene products.