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Transition-Metal-Controlled Synthesis of 11*H*-Benzo[*a*]carbazoles and 6-Alkylidene-6*H*-isoindo[2,1-*a*]indoles via Sequential Intermolecular/Intramolecular Cross-Dehydrogenative Coupling from 2-Phenylindoles

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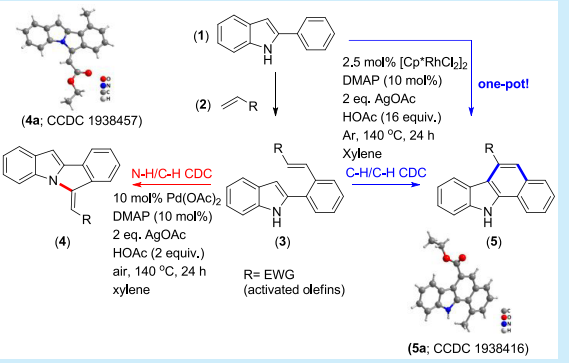
Supporting Information

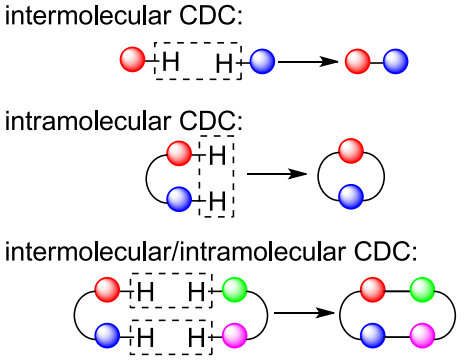
ABSTRACT: A catalyst-controlled synthesis of 11*H*-benzo[*a*]carbazoles and 6-alkylidene-6*H*-isoindo[2,1-*a*]indoles is described. $Pd(OAc)_2$ favored 6-alkylidene-6*H*-isoindo[2,1-*a*]indoles via intramolecular C−H/N−H CDC reaction, while $[Cp^*RhCl_2]_2$ led to 11*H*-benzo[*a*]carbazoles through intramolecular C−H/C−H CDC reaction. Moreover, the synthesis of 11*H*-benzo[*a*]carbazoles via sequential intermolecular *ortho* C−H/olefin coupling and intramolecular C3-H/olefin coupling from 2-phenylindoles and alkenes can be operated in one pot.



Cross-coupling reaction via C−H activation has proved to be a powerful method for the construction of carbon−carbon bonds and carbon−heteroatom bonds.[1] In particular, transition-metal-catalyzed cross-dehydrogenative-coupling (CDC) is highly attractive because both two coupling partners do not require prefunctionalization.[2] Though intermolecular[3] or intramolecular[4] CDC reactions have undergone tremendous development in recent years, methods for developing intermolecular/intramolecular sequential CDC reactions to build up polycyclic structures are rare (Scheme 1).[5] On the other hand, the fused-polycyclic molecular frameworks containing indole units are highly appealing to many organic chemists because they have been found in a broad spectrum of pharmacologically and biologically active compounds.[6] Synthesis of fused polycyclic indoles usually requires multistep approaches.[7] Thus, the development of divergent and more economical methods for the production of these compounds is highly promising.[8] Recently, we have reported a rhodium-catalyzed regioselective *ortho* C−H olefination of 2-phenylindoles.[9] For a further study, we disclose our new research in combination with the intermolecular CDC reaction (C−H/C−H CDC reaction) and intramolecular CDC reaction (C−H/C−H or C−H/N−H CDC reaction) from the same starting materials, 2-phenylindoles, and alkenes. The divergent products, 11*H*-benzo[*a*]carbazoles[10] and 6-alkylidene-6*H*-isoindo[2,1-*a*]indoles,[11] were obtained in good to excellent yields with the control of transition-metal catalysts. Notably, the sequential intermolecular *ortho* C−H olefination and intramolecular C3−H olefination can be operated in one pot (Scheme 2).

The intramolecular CDC reaction of (*E*)-ethyl 3-(2-(1*H*-indol-2-yl)-3-methylphenyl)acrylate (**3a**) was initiated as a model case (Table 1). The first attempt used palladium acetate, which is the most utilized catalyst in C3−H cross-

Scheme 1. Transition-Metal-Catalyzed CDC Reactions



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Scheme 2. Synthesis of 11*H*-Benzo[*a*]carbazoles and 6-Alkylidene-6*H*-isoindo[2,1-*a*]indoles via Sequential Intermolecular/Intramolecular Cross-Dehydrogenative Coupling from 2-Phenylindoles

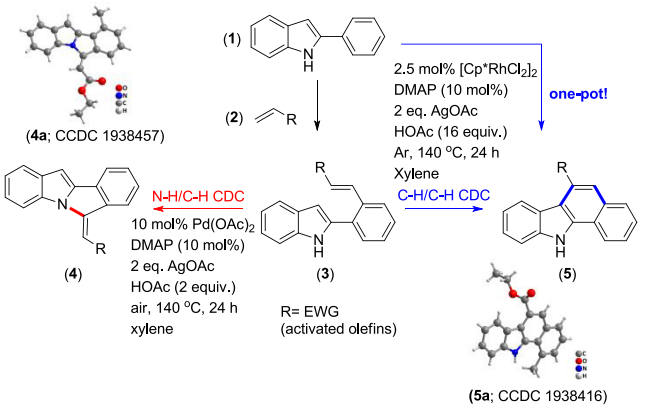
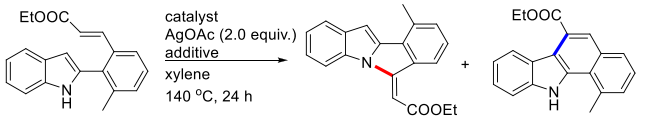


Table 1. Optimization of the Reaction Conditions[a]



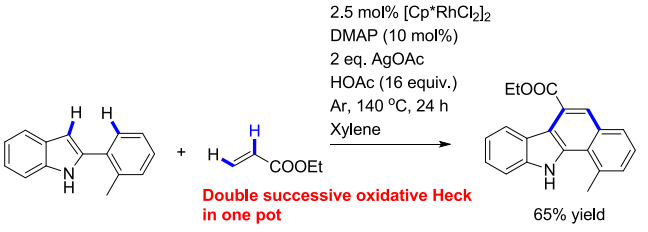
3a 4a 5a

		additive		yield[b] (%)	
entry	catalyst	HOAc (equiv)	DMAP (mol %)	4a	5a
1	$Pd(OAc)_2$ (10 mol %)	0	0	30	
2	$Pd(OAc)_2$ (10 mol %)	2	0	45	
3	$Pd(OAc)_2$ (10 mol %)	2	10	82	
4	$Pd(OAc)_2$ (10 mol %)	0	10	32	
5	$Pd(OAc)_2$ (10 mol %)	1	10	49	
6	$Pd(OAc)_2$ (10 mol %)	4	10	52	
7	$Pd(OAc)_2$ (10 mol %)	2	20	65	
8	$Pd(OAc)_2$ (10 mol %)	2	10	81 (80)	
9[c]	$[Cp^*RhCl_2]_2$ (2.5 mol %)	2	10		33
10	$[Cp^*RhCl_2]_2$ (2.5 mol %)	16	10		70 (68)
11	$[Cp^*RhCl_2]_2$ (2.5 mol %)	16	20		55

[a]Reaction conditions: **3a** (0.3 mmol), catalyst, AgOAc (2 equiv), additives, xylene (2 mL), argon atmosphere, 140 °C, 24 h. [b]^{1}H NMR yield on the basis of the amount of **3a** used, Number in parentheses is isolated yield. [c]The reaction was carried out under air atmosphere.

dehydrogenative Heck reaction for indoles.[12] To our surprise, it did not afford 11*H*-benzo[*a*]carbazole (**5a**) via the C3−H/C−H (olefin partner) CDC reaction but gave 6-alkylidene-6*H*-isoindo[2,1-*a*]indole (**4a**) via N1−H/C−H (olefin partner) CDC reaction exclusively in 30% yield (Table 1, entry 1), whose structure was confirmed by X-ray crystal diffraction (see the Supporting Information). HOAc can be employed to enhance the electrophilicity ability of the transition-metal ion.[13] We were able to increase the yield to 45% when acetic acid (HOAc) was used as a cosolvent (Table 1, entry 2). Inspired by recent reports using pyridine ligands to enhance reactivity in Pd-catalyzed Fujiwara−Moritani reactions,[14] we examined $Pd(OAc)_2$ in conjunction with a pyridine ligand. Indeed, the addition of a catalytic amount of DMAP (10 mol %) increased the yield of **4a** to ca. 82% (Table 1, entry 3). Then the quantity of HOAc was screened. It revealed that the best ratio for the reaction was 2 equiv of HOAc. The conversion of **3a** decreased if the amount of HOAc changed (Table 1, entries 5 and 6). On the other hand, an increase of the amount of DMAP also led to a decreased conversion (Table 1, entry 7). This transformation can also be performed in an air atmosphere; the isolated yield of **4a** is 80% (Table 1, entry 8). Intriguingly, when the reaction was carried out using $[Cp^*RhCl_2]_2$ as a catalyst, a completely different selectivity was observed that resulted in C−N bond formation exclusively leading to 11*H*-benzo[*a*]carbazole **5a** (Table 1, entry 9). The structure of **5a** was also confirmed by X-ray crystallography (see the Supporting Information). Further optimization showed that the use of 16 equiv of HOAc and 10 mol % of DMAP improved the yield of **5a** (Table 1, entries 10 and 11). It is worth noting that the sequential intermolecular *ortho* C−H/olefin coupling and intramolecular C3−H/olefin coupling leading to **5a** can be operated in one pot from 2-phenylindole and ethyl acrylate as starting materials. The isolated yield of **5a** is 65% (Scheme 3).

Scheme 3. Synthesis of 11*H*-Benzo[*a*]carbazoles via Double-Successive Oxidative Heck in One Pot



With the optimized conditions in hand, the generality of the N−H/C−H CDC reaction was first explored (Table 2). Regarding the olefin-coupling partner, activated alkenes such as ethyl acrylate (**4a**), 2-methoxyethyl acrylate (**4b**), *tert*-butyl acrylate (**4c**), and *n*-butyl acrylate (**4d**) could be employed to produce the desired products in good yields. Diethyl vinylphosphonate furnished the product **4e** in a synthetically useful yield (45%). Furthermore, the nonactivated alkene styrene was not suitable for this transformation (**4f**). The scope of the 2-phenylindoles was also examined. A variety of 2-phenylindole derivatives with substituents at the indole ring or benzene ring were successfully transformed to desired products in excellent yields. The CDC reaction of 2-phenyl-1*H*-indoles (**1**) with alkenes (**2**) can not stop after mono-olefination, and overalkenylation product was formed. Undoubtedly, diolefination products from 2-phenylindoles can also be transformed to annulated products (**4m**−**4r**). However, for the sake of simplicity, one of the two *ortho*-C−H bonds was blocked with methyl or chlorine. The experiment results showed that the electronic and steric properties had no effect on the reaction efficiency. As seen from Table 2, functional groups such as chloro (**4h**, **4l**), bromo (**4i**), fluoro (**4r**), and ether (**4o**, **4p**) were well tolerated under the reaction conditions.

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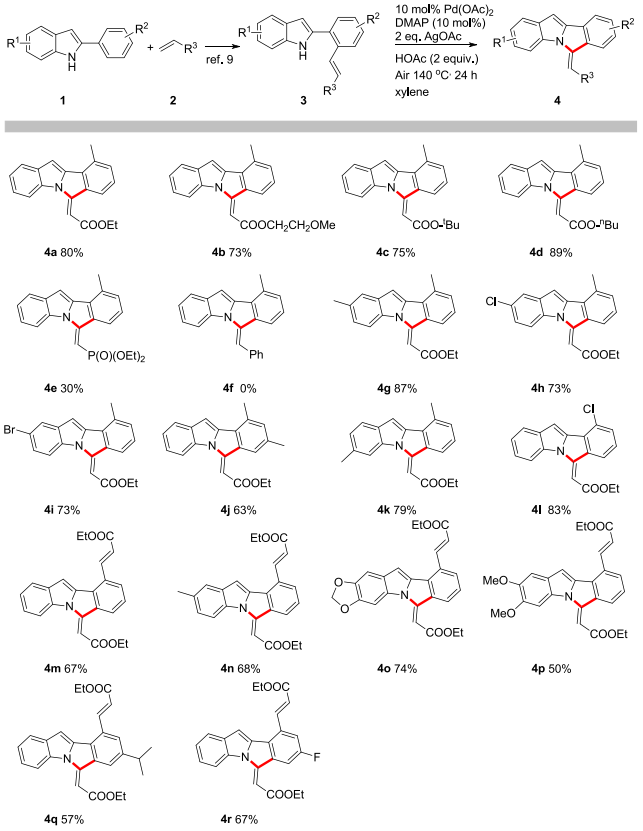
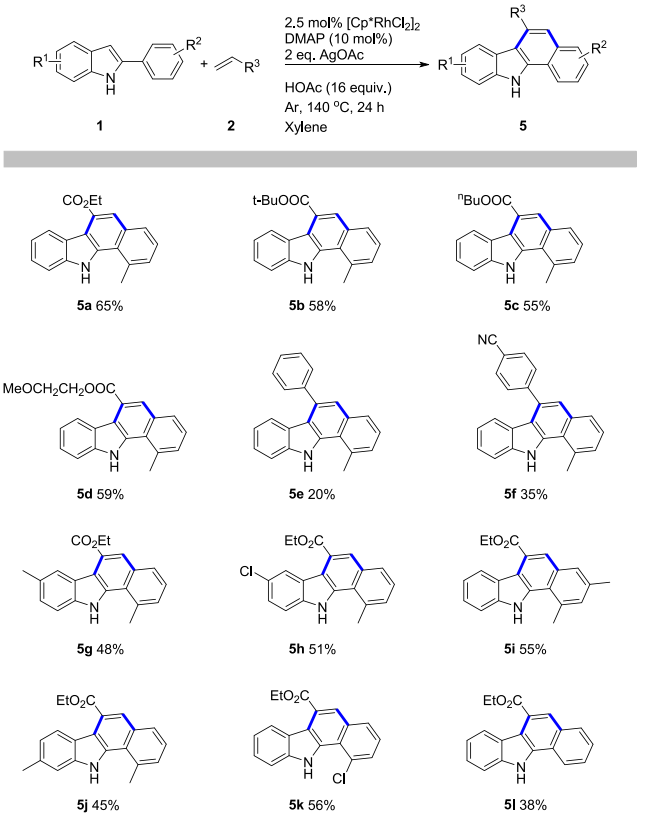
Table 2. Substrate Scope for the Synthesis of 6-Alkylidene-6*H*-isoindo[2,1-*a*]indole[a]s



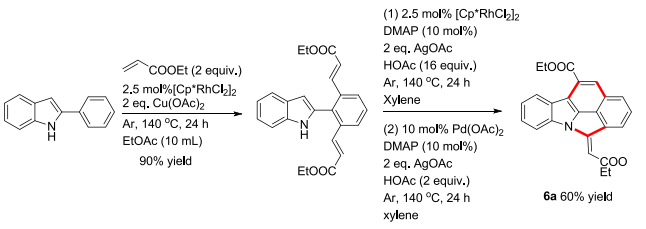
[a]Reaction conditions: **3** (0.3 mmol), $Pd(OAc)_2$ (10 mol %), AgOAc (2 equiv), DMAP (10 mol %), HOAc (2 equiv), xylene (2 mL), air atmosphere, 140 °C, 24 h. Isolated yield.

Table 3. Substrate Scope for the Synthesis of 11*H*-Benzo[*a*]carbazoles[a]



[a]Reaction conditions: **1** (0.3 mmol), 2 (0.3 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol %), AgOAc (2 equiv), DMAP (10 mol %), HOAc (16 equiv), xylene (2 mL), argon atmosphere, 140 °C, 24 h. Isolated yield.

Scheme 4. Synthesis of Fused-Pentacyclic Ring via Quadruple CDC Reaction from 2-Phenylindole



Next, we examined the one-pot, 2-fold oxidative Heck reaction of 2-phenyl-1*H*-indole derivatives with alkenes (Table 3). When 2-phenylindole was employed as the substrate, competitive intermolecular diolefination of two *ortho*-C−H bonds and subsequent intramolecular C3−H/C−H (olefin) coupling would give rise to a product which is difficult to separate from the complicate mixture. Only 38% yield of **5l** was obtained after careful isolation. Therefore, we turned our attention to investigating the reaction of 2-(*o*-tolyl)-1*H*-indole with alkenes. Various acrylates performed smoothly to give corresponding desired products **5a**−**5d** in good yields (55−65%). In contrast to palladium-catalyzed intramolecular C−H/N−H CDC, rhodium-catalyzed intramolecular C−H/C−H CDC reaction could occur with styrenes delivering 6-phenyl-11*H*-benzo[*a*]carbazoles (**5e**, **5f**), although the yields need to be further improved. We suspect that a large conjugated structure of corresponding product is beneficial for this transformation. A variety of 2-(*o*-tolyl)-1*H*-indoles reacted with ethyl acrylate to provide functionalized carbazoles in 50−55% yield (**5g**−**5j**). Blockage one of the *ortho* positions with chlorine atom was also acceptable, as demonstrated by the formation of ethyl 1-chloro-11*H*-benzo[*a*]carbazole-6-carboxylate (**5k**). Additionally, a fused-pentacyclic ring **6a** could be efficiently synthesized in three steps with an overall yield of 54% from 2-phenyl-1*H*-indole via quadruple CDC reactions (Scheme 4). In addition, when compound **4a** was subjected to the Rh-catalyzed reaction conditions [$[Cp^*RhCl_2]_2$ (2.5 mol %), AgOAc (2 equiv), DMAP (10 mol %), HOAc (16 equiv), xylene (2 mL)] no reaction occurred, and compound **4a** were recovered. This result likely indicates that the intramolecular C−H/N−H cross-dehydrogenative-coupling reaction is irreversible.

In conclusion, a catalyst-controlled switch of regioselectivity in the intramolecular CDC reaction of *ortho*-alkenylated 2-phenylindole was developed. $Pd(OAc)_2$ catalyst favored 6-alkylidene-6*H*-isoindo[2,1-*a*]indoles via intramolecular C−H/N−H CDC reaction, while $[Cp^*RhCl_2]_2$ led to 11*H*-benzo[*a*]carbazoles through an intramolecular C−H/C−H CDC reaction. Moreover, a variety of 11*H*-benzo[*a*]carbazoles can be assembled in two C−H/C−H CDC steps from 2-phenylindoles and alkenes in one pot. Further investigation on the application of the developed methods is currently underway in our laboratory.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02476.

Experimental procedures and spectral data (PDF)

Accession Codes

CCDC 1938416 and 1938457 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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