OL | Organic Letters

Cite This: Org. Lett. XXXX, XXX, XXX−XXX

Letter

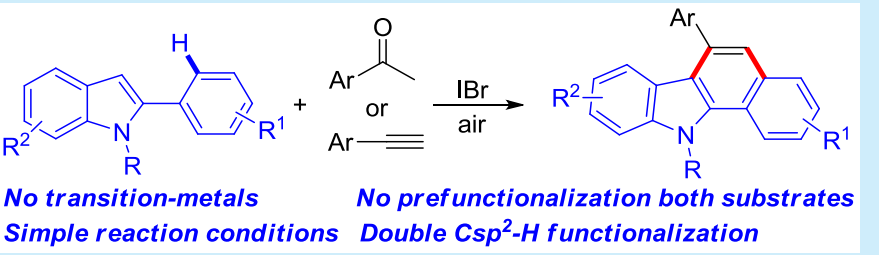
pubs.acs.org/OrgLett

Metal-Free Double Csp^2−H Bond Functionalization: Strategy for Synthesizing Benzo[*a*]carbazoles from 2-Arylindoles and Acetophenones/Alkynes

Penghui Ni, Jing Tan, Wenqi Zhao, Huawen Huang, Fuhong Xiao,* and Guo-Jun Deng*

Key Laboratory for Green Organic Synthesis and Application of Hunan Province, Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China

Supporting Information



ABSTRACT: A metal-free strategy for the synthesis of benzocarbazoles from 2-arylindoles and aryl ketones is developed. Various 2-aryl-3-vinyl-indoles were generated in situ through dehydrative condensation of aryl ketones and indoles. These key intermediates could be selectively converted into the corresponding benzo[*a*]carbazoles via a direct cyclization process between two Csp^2−H bonds. Furthermore, terminal alkynes also could be used as the versatile C2 source to afford the corresponding products in good yields.

As a class of important fused nitrogen-containing heterocycles, carbazole and its derivatives are privileged molecular structures and exhibit a wide range of biological activities.[1] Furthermore, they are also important building blocks for the synthesis of functional materials such as organic light-emitting diodes (OLEDs).[2] Traditionally, carbazoles are constructed via the well-known Fisher−Borsche,[3] Bucherer,[4] Graebe−Ullmann,[5] and Cadogan carbazole syntheses.[6] In recent years, carbazole synthesis based on transition metal-catalyzed methodologies provides a useful and efficient alternative approach.[7] However, a majority of these methods are targeted to the construction of the five-membered pyrrole ring in carbazoles. Methods for the construction of the benzene ring are less developed. Recently, an indole-to-carbazole strategy has become a very powerful synthetic approach for the construction of a new benzene ring in carbazoles because many substituted indole derivatives are commercially available.[8] Furthermore, 2,3-unsubstituted indoles can be directly used as the starting materials for carbazole construction via the C−H functionalization protocol.[9]

As a subclass of carbazoles, benzo[*a*]carbazoles have also gained considerable attention from both synthetic and medicinal chemists due to their wide range of applications in medicinal and material chemistry.[10] Because these compounds are rarely found in nature, a number of synthetic methods for the preparation of benzo[*a*]carbazoles have been developed and most of them involve transition metal-catalyzed cyclization of functionalized alkynes.[11] Furthermore, 2-nitrobiaryls, 2-aminebiaryls, and α-azidobiaryls also could be used as the substrates for benzo[*a*]carbazole synthesis via a C−H amination strategy.[12] Recently, the transition metal-catalyzed benzannulation of 2-arylindole derivatives has emerged as one of the most powerful tools for the synthesis of benzo[*a*]-carbazoles bearing unique substitution patterns. Precious metals such as Pt or Ru were used as the catalysts to convert 2-(2-alkynylphenyl)indole derivatives into benzo[*a*]carbazoles via intramolecular cyclization reaction.[13] More importantly, Tsuchimoto and Shirakawa found that readily accessible 2-arylindoles could smoothly couple with propargyl ethers catalyzed by indium to afford annulated benzo[*a*]carbazole with ether as the leaving group (Scheme 1a).[14] In 2009, Jiao and co-workers found that less reactive internal alkynes could be used as the coupling partners when palladium was used as the catalyst with oxygen as the oxidant (Scheme 1b).[15] Very recently, Gu and co-workers developed bismuth trichloride-catalyzed formation of a benzo[*a*]carbazole from 2-arylindoles and 2-bromoacetaldehydes with Friedel−Crafts alkylation as the initial step.[16] Aryl ketones are easy to handle and commercially available; therefore, these compounds are ideal C2 sources for the [2+4] annulation process. However, there is only one example using acetophenones and 2-(2-bromoaryl)-indoles as the starting materials (Scheme 1c).[17] When less reactive 2-arylindoles were used, the aryl ketones need to be initially activated to more reactive α-diazo carbonyls or

Received: April 1, 2019

DOI: 10.1021/acs.orglett.9b01138
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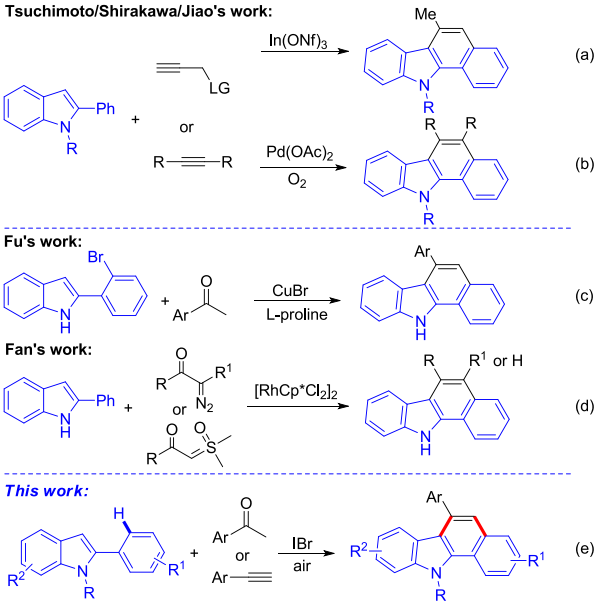
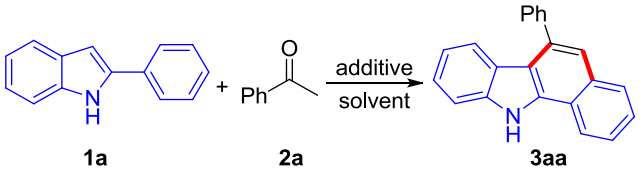
Scheme 1. Benzo[*a*]carbazole Synthesis Based on 2-Arylindoles



sulfoxonium ylides using expensive rhodium as the catalyst (Scheme 1d).[18] In our recent research, we found that 3-vinylindoles could be generated in situ from acetophenones and indoles promoted by an iodide-containing additive.[9j] We envisioned that CDC reaction (cross-dehydrogenative coupling) may occur between the vinyl group and the phenyl group in 3-vinyl-indoles, thus leading to the desired benzo[*a*]carbazole products, although CDC reaction between two Csp^2–H bonds under metal-free conditions is quite challenging. As part of our continuing interest in the preparation of indole-based heterocycles,[19] we herein report an efficient synthesis of benzo[*a*]carbazoles from 2-arylindoles and acetophenones under metal-free conditions. Furthermore, terminal alkynes also could be used as the versatile C2 source in this kind of reaction (Scheme 1e).

With this hypothesis in mind, we started our investigation by using 2-phenyl-1*H*-indole (**1a**) and acetophenone (**2a**) as the model reagents. Unfortunately, no product was obtained when NH_4I or KI was added as the additive using toluene as the solvent (Table 1, entries 1 and 2). Gratifyingly, the reaction proceeded smoothly in the promotion of molecular iodine to give desired product **3aa** in 29% yield (entry 3). Inspired by this finding, we investigated several iodide-containing additives to further improve the reaction yield, and among them, IBr showed the best efficiency to afford the product in 55% yield (entries 4–7). The solvent has an obvious effect on the yield of the reaction. In general, a better yield was achieved in less polar solvents such as benzene, chlorobenzene, *o*-xylene, and mesitylene, whereas no product could be observed in polar solvents such as DMF, NMP, and DMSO (entries 8–16). Chlorobenzene was found to be the best solvent giving desired product **3aa** in 76% yield (entry 9). However, no other byproducts were observed by GC–MS. A control experiment showed that the addition of IBr is indispensable for this kind of transformation (entry 17). After extensive screening of different parameters, optimized reaction conditions for construction of benzo[*a*]carbazoles were established: IBr (1 equiv), PhCl (0.5 mL), 130 °C, 4 h under an air atmosphere.

Table 1. Screening the Reaction Conditions[a]



entry	additive	solvent	yield (%)[b]
1	NH_4I	toluene	nd
2	KI	toluene	nd
3	I_2	toluene	29
4	HI	toluene	27
5	ICl	toluene	46
6[c]	IBr	toluene	55
7	ICl_3	toluene	38
8	IBr	toluene	62
9	IBr	chlorobenzene	76
10	IBr	*o*-xylene	47
11	IBr	*m*-xylene	51
12	IBr	mesitylene	64
13	IBr	nitrobenzene	19
14	IBr	DMF	nd
15	IBr	NMP	nd
16	IBr	DMSO	nd
17		chlorobenzene	nd

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), additive (0.2 mmol), solvent (0.5 mL), 130 °C, 4 h, under air. Abbreviations: nd, not detected; DMF, *N*,*N*-dimethylformamide; NMP, *N*-methylpyrrolidone; DMSO, dimethyl sulfoxide. [b]Isolated yield based on **2a**. [c]**Caution:** The IBr is a highly toxic compound. Please be careful.

As shown in Scheme 2, the substrate scope of the reaction with respect to various aromatic ketones (**2**) with 2-phenyl-1*H*-indole (**1a**) was investigated under the optimized conditions. First, a series of *para*-substituted acetophenones bearing electron-donating groups (Me and butyl) were smoothly converted into the corresponding products in good yields (**3ab**–**3ad**). When 4-acetylbiphenyl (**2e**) was used, **3ae** was obtained in 88% yield. To our delight, aromatic ketones with electron-withdrawing groups (CO_2CH_3, OCF_3, NO_2, and SO_2CH_3) were also reactive to involve this kind of reaction (**3af**, **3ag**, **3al**, and **3am**). Halogen-substituted substrates, including relatively reactive 4′-iodoacetophenone (**2k**), were compatible to give products **3ah**–**3ak** in good yields. **3aj** could be achieved in good yield when a gram-scale reaction was carried out. Furthermore, *meta*-substituted acetophenones were suitable reactants to give the desired products in good to high yields (**3an**–**3as**). A steric hindrance effect was observed when halogen substituents were located at the *ortho* position in acetophenone, and moderate yields were obtained (**3at** and **3au**). This kind of steric effect is more pronounced in the acetonaphthones. For example, **3aw** could be obtained in 78% yield when 2′-acetonaphthone (**2w**) was used. However, in stark contrast, **3av** could be achieved in only 40% yield. Bulky aromatic ketones such as 2-acetylphenanthrene (**2x**) and 1-acetylpyrene (**2y**) also could be used as the substrates for this kind of conversion. Furthermore, hetero-aromatic ketones such as 2-acetylbenzo[*b*]thiophene (**2aa**) underwent the reaction to give the corresponding product **3aaa** in 45% yield. Aliphatic ketones such as 1-cyclohexylethanone and 3-methylbutan-2-one failed to afford the desired product under the current conditions.

DOI: 10.1021/acs.orglett.9b01138
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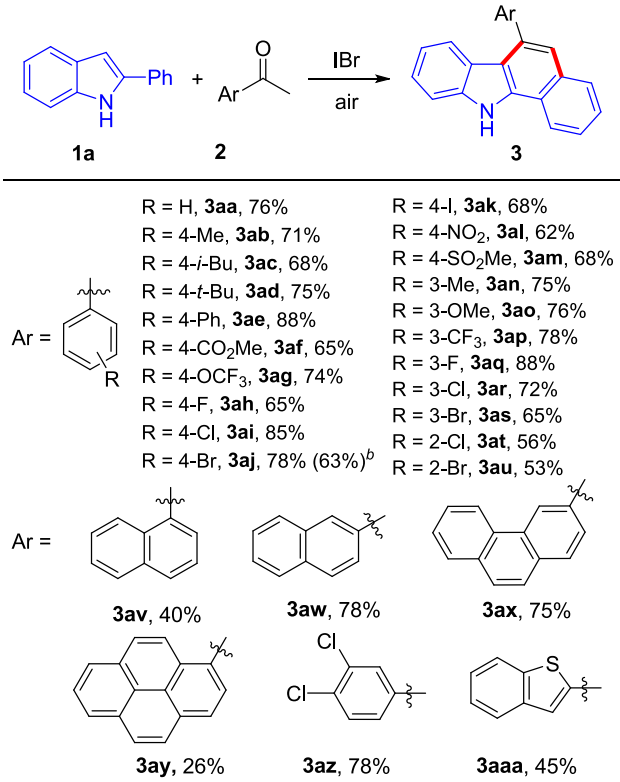
Scheme 2. Substrate Scope with Respect to the Ketones[a]

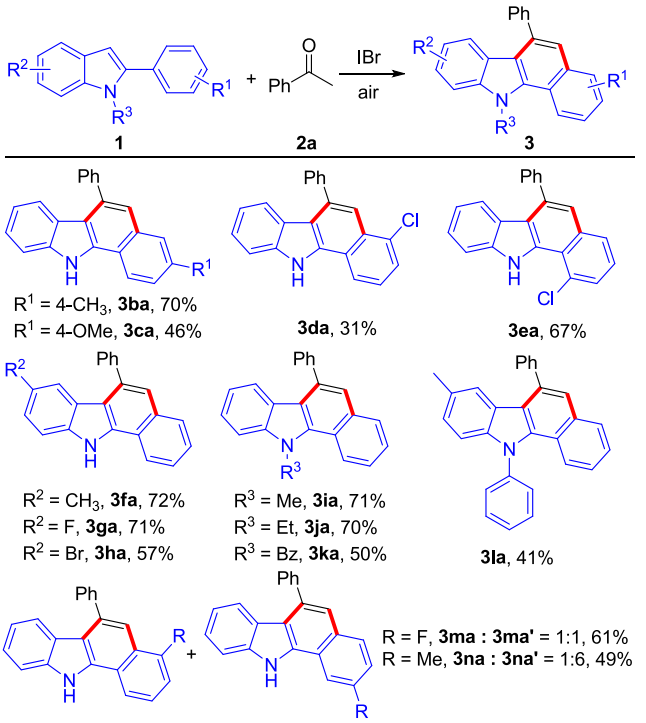


[a]Conditions: **1a** (0.3 mmol), **2** (0.2 mmol), IBr (0.2 mmol), PhCl (0.5 mL), 130 °C, 4 h, under an air atmosphere. Yields of isolated products. [b]On a 6 mmol scale.

Subsequently, the generality and limitation of 2-arylindole components were studied (Scheme 3). First, different substituents on the 2-phenyl ring were surveyed for the reaction with acetophenone (**3ba**−**3ea**). The corresponding product **3ea** was obtained in 67% yield even when the chloro substituent was presented at the *ortho* position. In addition, the substituent positions on the indole ring significantly affected the reaction. 2-Phenylindoles with substituents (methyl, chloro, and bromo) located at the C5 position were effectively involved in this reaction to give the products in reasonable yields (**3fa**−**3ha**). Besides free NH 2-arylindoles, other N-substituted indoles are also involved in this kind of reaction (**3ia**−**3la**). Finally, a mixture of isomers was obtained in 61% combination yield when a fluoro group was located at the *meta* position in the phenyl ring. A mixture of two isomers in 49% yield (1:6 **3na**:**3na′**) was obtained when (*m*-tolyl)-1*H*-indole was used as the substrate.

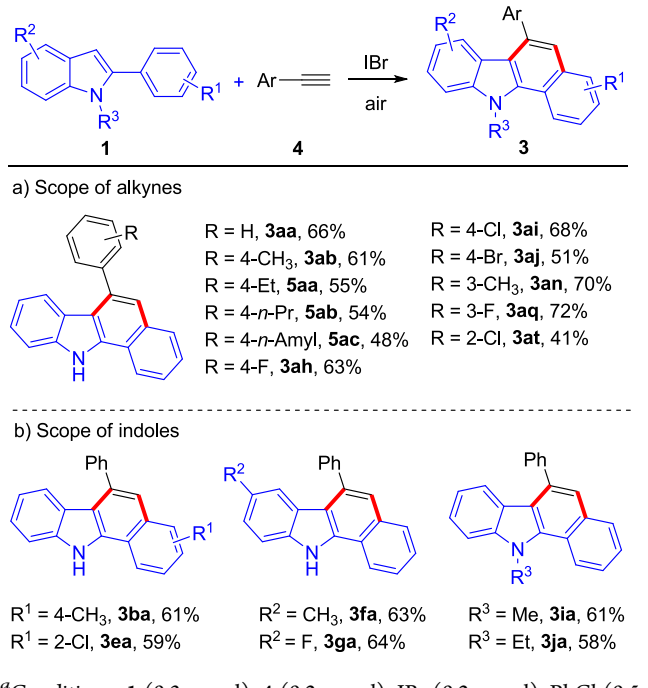
More importantly, terminal aromatic alkynes also could be used as the versatile C2 source for construction of benzo[*a*]-carbazole derivatives without the aid of a transition metal catalyst. As shown in Scheme 4, the reaction showed good regioselectivity when terminal alkynes were used to give the aryl group at the C6 position in the benzo[*a*]carbazole moiety. In general, moderate to good yields could be obtained when electron-donating substituted phenylacetylenes were used (**3ab**−**5ac**). Halogen functional groups (**3ah**−**3aj** and **3aq**−**3at**). A lower yield was obtained when the Cl group was located at the *ortho* position (**3at** vs **3ai**). Alkyl alkynes such as oct-1-yne and ethyl propiolate were not suitable substrates. Using phenylacetylene as the condensation partner, several

Scheme 3. Substrate Scope with Respect to the Indoles[a]



[a]Conditions: **1** (0.3 mmol), **2a** (0.2 mmol), IBr (0.2 mmol), PhCl (0.5 mL), 130 °C, 4 h, under an air atmosphere. Yields of isolated products.

Scheme 4. Terminal Alkyne Involved in Benzo[*a*]carbazole Formation[a]



[a]Conditions: **1** (0.3 mmol), **4** (0.2 mmol), IBr (0.2 mmol), PhCl (0.5 mL), 130 °C, 6 h, under an air atmosphere. Yields of isolated products.

indole derivatives were also screened for this transformation. In general, good yields were obtained whether the substituents were on the 2-phenyl ring or in the indole skeleton (**3ba**−**3ga**).

DOI: 10.1021/acs.orglett.9b01138
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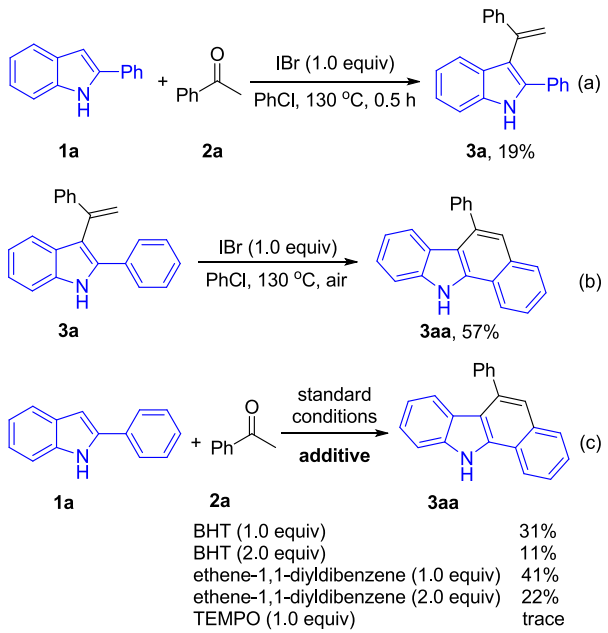
Again, besides free NH indoles, *N*-methyl- and *N*-ethylindoles were also smoothly engaged in this type of cyclization process (**3ia** and **3ja**).

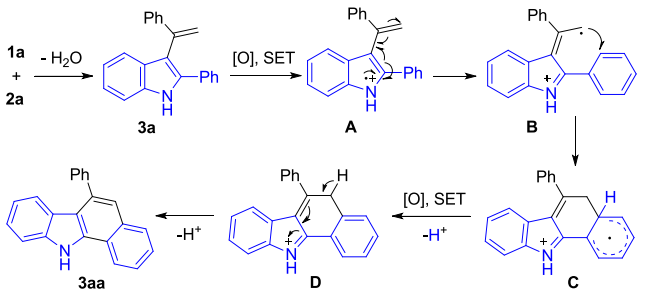
Several control experiments were designed to obtain more information about the mechanism (Scheme 5). The key intermediate 3-vinyl-indole **3a** could be obtained in 19% yield in 30 min under the standard conditions (Scheme 5a). Isolated **3a** could be smoothly converted into **3aa** in 57% yield in an IBr/air system (Scheme 5b). Inhibition experiments were conducted by addition of butylated hydroxytoluene (BHT), ethene-1,1-diyldibenzene, and 2,2,4,4-tetramethyl-1-piperidinyloxy (TEMPO) to the standard reaction mixture (Scheme 5c), and the results showed that a radical cyclization pathway was possibly involved because the reaction was completely suppressed by 1 equiv of TEMPO.

Scheme 5. Control Experiments under Various Conditions



On the basis of the experimental observations and related references presented above,[20] we proposed a plausible mechanism in Scheme 6. Dehydrative condensation of 2-phenyl-1*H*-indole (**1a**) and acetophenone (**2a**) generates intermediate **3a**. A radical intermediate **A** is generated via single-electron transfer promoted by an IBr/air oxidation system. This intermediate can further convert into vinyl radical intermediate **B** via an isomerization step. Radical abstraction of the proton on the phenyl ring generates cyclized intermediate **C**. Further single-electron oxidation and deprotonation of **C** form intermediate **D**. The final product **3aa** can be obtained by a deprotonation step.

Scheme 6. Possible Reaction Mechanism



In summary, we have developed a versatile strategy for the synthesis of benzo[*a*]carbazoles from readily available starting materials. The key 3-vinyl-indole intermediates were generated in situ through dehydrative condensation of aryl ketones and 2-arylindoles under metal-free conditions. This kind of intermediate could further convert into the final products via CDC reaction between two Csp^2–H bonds without the aid of any metal catalyst. Furthermore, terminal aromatic alkynes also could be used as the condensation partners under these metal-free conditions. This method provides an efficient approach for the versatile construction of various substituted benzo[*a*]-carbazoles from readily available raw materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01138.

Experimental procedures, characterization data, and ^1H and ^{13}C NMR spectra for all new products (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: fhxiao@xtu.edu.cn.
*E-mail: gjdeng@xtu.edu.cn.

ORCID

Huawen Huang: 0000-0001-7079-1299
Guo-Jun Deng: 0000-0003-2759-0314

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (21871226 and 21572194), the Collaborative Innovation Center of New Chemical Technologies for Environmental Benignity and Efficient Resource Utilization, and the Hunan Provincial Innovative Foundation for Postgraduate (CX2018B362).

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DOI: 10.1021/acs.orglett.9b01138
Org. Lett. XXXX, XXX, XXX−XXX