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$Cu(OAc)_2$-Mediated Cascade Annulation of Diarylalkyne Sulfonamides through Dual C−N Bond Formation: Synthesis of 5,10-Dihydroindolo[3,2-*b*]indoles

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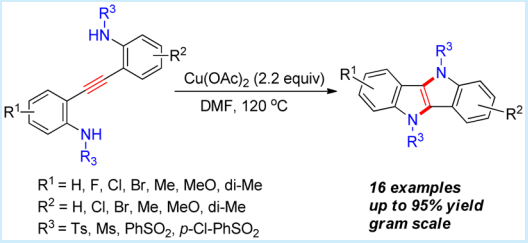
Supporting Information

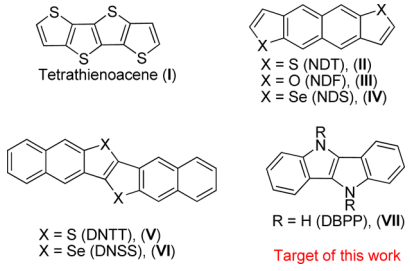
ABSTRACT: An unusual cascade reaction featuring annulation of diarylalkyne sulfonamides to form 5,10-dihydroindolo[3,2-*b*]indoles has been realized with $Cu(OAc)_2$ as the sole oxidant. This unprecedented process encompasses two sequential C−N bond formations, allowing for an efficient synthesis of the biologically important indoloindole derivatives.



Acene- and heteroacene-based materials have found wide applications in organic field-effect transistors (OFET), organic light-emitting diodes (OLED), and organic photovoltaic cell designs due to the extensively delocalized π-electrons in the fused aromatic structures.[1] Besides, the heteroacenes are expected to exhibit potential biological activities due to the existence of the heterocyclic motif.[2] In heteroacenes, the type and positions of the hetero atoms can not only significantly improve the stability of the materials[1b] but also effectively fine-tune the electronic properties and molecular packing of the single crystal. For these reasons, developing new heterotetracenes has received much attention in the past several years.

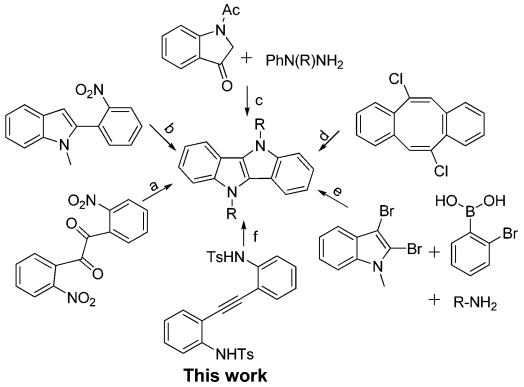
Our literature research offered a few reports on the synthesis of heteroacenes bearing a pyrrolo[3,2-*b*]pyrrole core, although their OFET properties have been claimed in recent reviews.[3] Pyrrolo[3,2-*b*]pyrrole has been generally identified as the most efficient electron donor among 10π-electron systems,[4] although it is unstable and very difficult to synthesize.[5] On the other hand, 5,10-dihydroindolo[3,2-*b*]indole (**VII** also known as dibenzopyrrolo[3,2-*b*]pyrrole, DBPP; Scheme 1), a well-known extended heteroacene also bearing a pyrrolo[3,2-*b*]pyrrole core, has been widely adopted as a building block for preparing various high-spin organic polymers[6] and OLED polymers.[7]

Scheme 1. Representative Heteroacene Compounds in OFET



Several synthetic approaches have been developed for the formation of 5,10-dihydroindolo[3,2-*b*]indoles, with most of them requiring the formation of a C−N bond as the key step.[8] Among the first syntheses of 5,10-dihydroindolo[3,2-*b*]indole reported were the reduction of *o*,*o*-dinitrobenzil with tin(II) chloride under acidic conditions (Scheme 2, path a)[9] and that of 2-(*o*-nitrophenyl)indoles with $P(OEt)_3$ (Scheme 2, path b).[10] The indoloindole skeleton can also be assembled through Fischer condensation of indolones with hydrazine derivatives (Scheme 2, path c)[11] or through the reduction of 6,12-dichlorodibenzo[*b*,*f*][1,5]-diazocines in the presence of excess

Scheme 2. Synthetic Strategies toward the Construction of DBPP Skeleton



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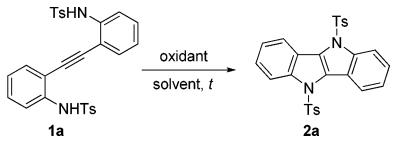
zinc under acidic conditions (Scheme 2, path d).[12] Recently, Pd-catalyzed cross-couplings between 2,3-dibromo-1-methyl-1*H*-indole, *m*-bromophenyl-boronic acid, and amines with subsequent cyclization provided a two-step strategy to access this privileged molecule (Scheme 2, path e).[13] Although these strategies all have their respective merits in the construction of the indoloindole skeleton, we believe developing additional methods, those being more convenient, efficient, and/or economical, is still in high demand. In this letter, we report an unusual reaction featuring a cascade reaction consisting of double cyclization of diarylalkyne sulfonamides in forming 5,10-dihydroindolo[3,2-*b*]indoles (Scheme 2, path f).

Currently, cascade reactions, especially those performed in one pot during which multistep reactions proceed in a single manipulation without isolation or purification of any of the intermediates, have received much attention due to the obvious reasons of high efficiency and convenience during the assembly of complex molecular structures.[14,15] Such reactions has been adopted and proven to be powerful synthetic means for the conversion of internal alkynes into bioactive polycyclic heterocycles.[16] Literature survey on intramolecular *trans*-addition of nitrogens across triple bonds showed only two examples: (1) Pd(II)/I(III)-based intramolecular annulation of internal alkyne through successive C−N bond formations leading to the formation of annelated indoles;[16a] (2) Pd(II)-catalyzed intramolecular diamination of diarylacetylene accompanied by a C(sp^3)−N bond cleavage, affording the bioactive indoloisoquinolinones.[16b] To the best of our knowledge, there has not yet been any report on direct addition of nitrogen atoms across the diarylalkyne triple bond leading to a fused polycyclic indoloindole derivative.

Owing to the many promising applications of indoloindoles in material science, we aimed to develop a new method for efficient syntheses of various functionalized 5,10-dihydroindolo-[3,2-*b*]indoles from diarylalkyne compounds. Built upon our previous work, we first explored the feasibility of hypervalent iodine reagent, PIDA as the oxidant in the presence of BF_3·Et_2O in carrying out the postulated transformation, but unfortunately, no desired product was obtained (Table 1, entry 1). The reaction did not occur either when other hypervalent iodine reagents of PIFA and PhIO were applied, even at elevated temperatures (not shown). We also carried out several experiments under standard conditions formulated in relevant literatures,[16] but no desired product was obtained in any of the cases (Table 1, entries 2 and 3).

After many trials to identify an effective oxidation system, we came across the first satisfactory yield of 56% in a system consisting of $Cu(OAc)_2$[17] as the oxidant and MeCN as solvent (Table 1, entry 4). The solvent screening study showed that DMF remained as the most appropriate solvent, in comparison to AcOH, MeCN, toluene, and DCE (Table 1, entries 4−8). To our delight, increasing the temperature to 120 °C shortened the reaction time and improved the yield to 82% (Table 1, entry 9). Further increasing the temperature to 140 °C only slightly lowered the yield (Table 1, entry 10). Using other types of copper oxidants such as $CuCl_2$ and $Cu(OTf)_2$[18] resulted in either sluggish reactions or no conversion at all (Table 1, entries 11 and 12). We further conducted the reaction with triphenylphosphine added as ligand, but no improvement of yield was observed (Table 1, entry 13). Besides, we explored a series of conditions to probe the possibility of using a catalytic amount of $Cu(OAc)_2$ in combination with a stoichiometric amount of terminal oxidant. However, the results indicated that

Table 1. Optimization of Reaction Conditions[a]



1a 2a

entry	oxidant	solvent	*t* (°C)	yield (%)[b]
1[c,d]	PIDA	DCE	80	n.d.[e]
2[f]	PIDA	DMF	120	n.d.
3[g]	$Pd(OAc)_2$	DMSO	80	n.d.
4	$Cu(OAc)_2$	MeCN	80	56
5	$Cu(OAc)_2$	DMF	80	74
6	$Cu(OAc)_2$	AcOH	100	62
7	$Cu(OAc)_2$	toluene	110	68
8	$Cu(OAc)_2$	DCE	120	65
9	$Cu(OAc)_2$	DMF	120	82
10	$Cu(OAc)_2$	DMF	140	73
11	$CuCl_2$	DMF	120	64
12	$Cu(OTf)_2$	DMF	120	72
13[h]	$Cu(OAc)_2$	DMF	120	75

[a]Reaction conditions: all reactions were carried out with **1a** (0.4 mmol), oxidant (0.88 mmol) in solvent (4.0 mL) for 2 h, unless otherwise stated. [b]Isolated yield. [c]The reaction was conducted at rt to 80 °C. [d]The reaction was conducted using 0.4 mmol of BF_3·Et_2O. [e]No desired product. [f]$Pd(OAc)_2$ (20 mmol %) was added. [g]The reaction was conducted using 0.04 mmol of TBAI and 0.8 mmol of AcOH. [h]PPh_3 (10 mmol %) was added.

catalytic conditions are not applicable to this transformation (see Supporting Information (SI) for details).

Under optimized conditions (Table 1, entry 9), a series of diarylalkyne sulfonamides **1** were subjected to these conditions to investigate the scope of this newly established method. The results are listed in Scheme 3. We first evaluated the electronic effect of substituent R^1 (Scheme 3, **2a**−**g**). It was found that substrates with a singly substituted aryl moiety improved the yield, with electron-donating groups (MeO, Me, di-Me) slightly more favored than electron-withdrawing groups (F, Cl, Br). In sharp contrast, substrates containing disubstituted aryl groups all resulted in lower yields than the unsubstituted **1a**, except for the cases with the two substituents being −Me and −OMe, which gave the same yield (Scheme 3, **2h**−**m**).

Substrates containing the R^3 substituent rather than the tosyl group, including phenylsulfonyl and *p*-Cl-phenylsulfonyl, gave similar yields as that of **1a** (Scheme 3, **2n**−**p**). However, no desired product was obtained with R^3 being an acetyl or *tert*-butyloxy carbonyl group (not shown), probably due to the less electron-withdrawing ability of the acetyl or *tert*-butyloxy carbonyl groups. These results implied that the sulfonyl group was essential for the transformation, acting as the protecting group for the N−H moiety as well as a strong electron-withdrawing group to enhance the nucleophilicity in this reaction.

The remarkable easy-to-handle nature of the process allows this one-pot protocol to be suitable for gram-scale production. Product **2a** (1 g) was successfully achieved in the one-pot fashion under the standard conditions in 80% yield. The structure of **2i** was unambiguously established by X-ray crystallography (see SI for details).

The mechanism of the reaction is depicted in Scheme 4.[19−22] The overall process consists of two steps. In step 1, $Cu(OAc)_2$ acted as a catalyst,[19] first, through ligation of the acetylene accompanied by the loss of the acetate ion (**1a** → **4** → **5**), then

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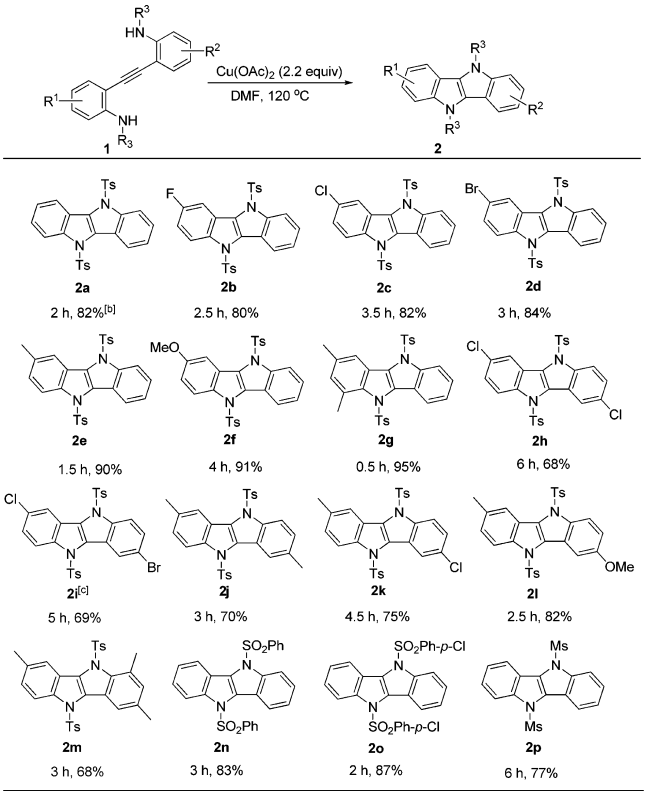
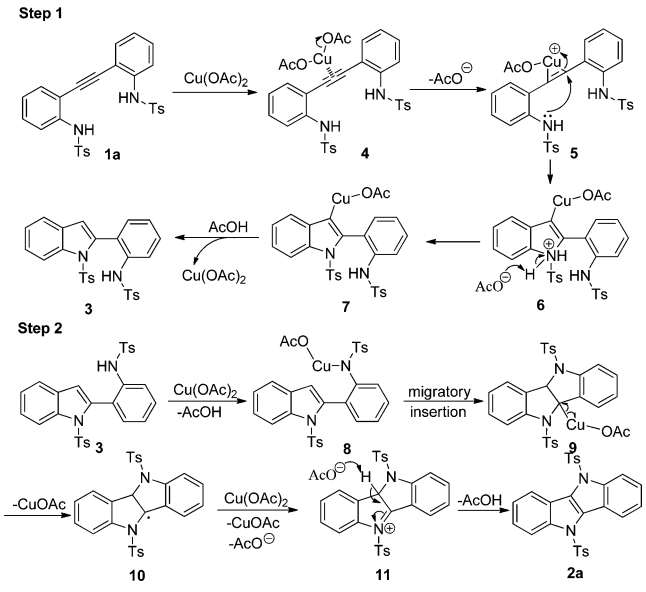
Scheme 3. Oxidative Cyclization of Diaryalkynes 1 to Indoloindole Derivatives 2[a]



[a]Reaction conditions: all reactions were carried out with **1** (0.4 mmol), oxidant (0.88 mmol) in DMF (4.0 mL) at 120 °C unless otherwise stated. [b]Isolated yield. [c]The structure of **2i** was confirmed by X-ray crystallography.

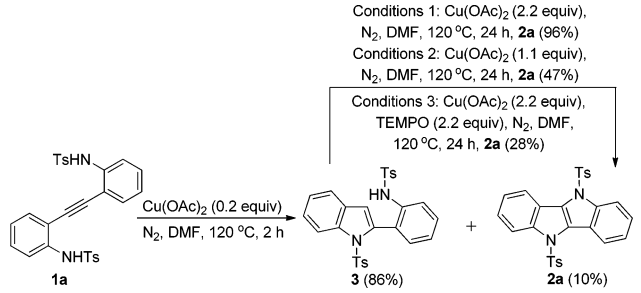
Scheme 4. Proposed Mechanistic Pathway



intramolecular nucleophilic substitution by the nitrogen moiety followed by deprontonation of **6** by the acetate ion (**5** → **6** → **7**), and finally exchange of ligands leading to intermediate **3**, and, at the same time, regeneration of the catalyst.

The proposal of the cascade reaction consisting of two distinct steps is confirmed by the following control experiment: when the amount of $Cu(OAc)_2$ was decreased to only 0.2 equiv, the reaction of **1a** afforded the indole **3**, isolated and its structure verified, in a high yield of 86%, with an additional 10% of the doubly cyclized product **2a** (Scheme 5).

Scheme 5. Mechanistic Studies



Step 2 of the mechanism[20] started with the formation of intermediate **8** due to H-abstraction at the amine moiety by the acetoxy radical, generated from $Cu(OAc)_2$. Due to the instability of the Cu-OAc moiety as well as the high-temperature conditions, the *cis*-aminocupration of the Cu-OAc moiety to a C−C double bond via intramolecular migratory insertion[21,22] led to intermediate **9**. Subsequent departure of CuOAc resulted in the benzyl radical **10**, which was oxidized to the iminium **11** by a second acetoxy radical, released again from a $Cu(OAc)_2$ molecule while forming the acetate ion. Deprotonation of **11** by the acetated anion led to the title product **2a**.

The radical pathway in step 2 was well supported by the observations that when intermediate **3** was subjected to the standard conditions in the presence of 2.2 equiv of TEMPO, the yield of **2a** was found to be only 28%. Second, the requirement of two $Cu(OAc)_2$ molecules for the reactions in step 2 as portrayed in the mechanism was also consistent with our experimental result: when only 1.1 equiv of $Cu(OAc)_2$ was used to react with intermediate **3** under standard conditions, incomplete conversion to **2a** was observed even after a more prolonged reaction time.

In summary, we have discovered a novel cascade reaction which provides a novel approach for the construction of 5,10-dihydroindolo[3,2-*b*]indoles, namely, through $Cu(OAc)_2$-mediated cascade annulation of internal diarylalkyne sulfonamides.[22] The new methodology not only carries desirable benefits such as good functional group tolerance and ligand-free conditions but also supports gram-scale synthesis of the products in good yields. The proposed mechanism describes this unprecedented process as consisting of two sequential cyclizations with two C−N bond formations during which $Cu(OAc)_2$ serves as a catalyst during the first step and an oxidant during the second step.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01343.

Experimental procedures, data of compounds characterization (PDF)

X-ray data for **2i** (CIF)

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Notes

The authors declare no competing financial interest.

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(22) During the revision of this manuscript, we read about work on $Cu(hfacac)_2/O_2$-mediated intramolecular oxidative diamination of bis(2-aminophenyl)acetylene for the synthesis of the 5,10-dihydro-indolo[3,2-*b*]indole. For details, see: Ho, H. E.; Oniwa, K.; Yamamoto, Y.; Jin, T. *Org. Lett.* **2016**, *18*, 2487.

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