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Transition-metal-free, visible-light induced cyclization of arylsulfonyl chlorides with *o*-azidoarylalkynes: a regiospecific route to unsymmetrical 2,3-disubstituted indoles†

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A visible-light-catalyzed synthesis of unsymmetrical 2,3-diaryl-substituted indoles from arylsulfonyl chlorides and *o*-azidoarylalkynes at room temperature has been discovered. This transformation exhibits excellent substrate scope and functional group tolerance. The use of inexpensive eosin Y as the catalyst with easy operation makes this protocol very practical.

Polysubstituted indoles are not only common motifs in natural products and pharmaceuticals, but also useful building blocks for the construction of highly complex target structures.[1] The importance of indole motifs has initiated substantial research efforts directed towards the development of efficient synthetic strategies to prepare this heteroarene.[2,3] As important members of the indole family, 2,3-disubstituted indole derivatives are core structures in some bioactive natural products.[1f] In this regard, there are many reports on the synthesis of 2,3-disubstituted indole derivatives.[4] Generally, the complementary synthesis of indole derivatives with a predictable 2,3-substitution pattern meets with certain restrictions. For the case of unsymmetrical 2,3-diarylated derivatives, the use of transition-metal catalysis has enabled some elegant solutions to this problem. Recently, Zhang developed the gold-catalyzed annulation of *o*-azidoarylalkynes with electron-rich arenes for the synthesis of unsymmetrical 2,3-disubstituted indoles.[4a] Very recently, the group of Wan reported the rhodium-catalyzed C–H annulation of nitrones with alkynes for the formation of unsymmetrical 2,3-diaryl-substituted indoles.[4g] However, these reactions employ transition metals as the catalyst. To date, the synthesis of unsymmetrical 2,3-diaryl-substituted indoles under visible-light irradiation has not been realized.

Harvesting of energy from visible light, the most abundant part of the solar spectrum, is a sustainable and cost-effective approach to activate chemical transformations.[5] Many visible-light photoredox catalysts, such as Ru or Ir complexes and organic dye catalysts have been used to solve the problem of poor visible light absorption efficiency.[6] Visible-light photoredox catalysts are capable of engaging in single-electron-transfer (SET) events in their photoexcited states. Some groundbreaking studies have reported unusual chemical reactions induced by photoredox catalysis, in particular, SET-based photoredox activation processes.[7]

Given the wide availability of arylsulfonyl chlorides with some of them, such as *p*-toluenesulfonyl chloride, produced industrially on a multi-ton scale, they appear to be an attractive class of compounds for the formation of aryl radicals.[6d] Recently, we developed a visible-light induced cyclization of arylsulfonyl chlorides with 2-isocyanobiphenyls for the synthesis of phenanthridines.[8] We hypothesized that *o*-azidoarylalkynes may serve as a platform to trap aryl radicals, a transformation that to our knowledge has not previously been described. Herein, we disclose our preliminary results on the visible-light-promoted transformation of arylsulfonyl chlorides and *o*-azidoarylalkynes used for the synthesis of unsymmetrical 2,3-diaryl-substituted indoles at room temperature without the requirement for strong acids, strong bases or organometallic reagents. This new method offers rapid access to unsymmetrical 2,3-diaryl-substituted indoles from simple and readily available arylsulfonyl chlorides. The significance of the present finding is two-fold: (1) simple and readily available eosin Y emerges as an efficient catalyst, rather than a transition-metal catalyst, which is often expensive and is required to be completely removed from the products, especially in the synthesis of pharmaceutical compounds, and (2) visible-light is employed as a safe, renewable and inexpensive source of chemical energy to facilitate the construction of unsymmetrical 2,3-diaryl-substituted indoles (Scheme 1).

As an initial test reaction, the simple benzenesulfonyl chloride **1a** was treated with the *o*-azidophenylalkyne **2a** and 1,4-cyclohexadiene (1,4-CHD) in DMF in the presence of eosin Y and the inorganic base Na_2CO_3 at room temperature for 14 h. The desired 2,3-diphenyl-1*H*-indole **3aa** was obtained, albeit in a low yield

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6cc10305g

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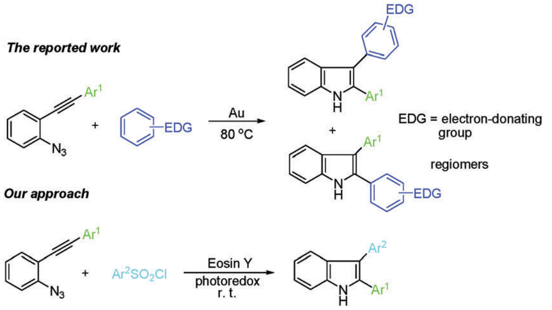
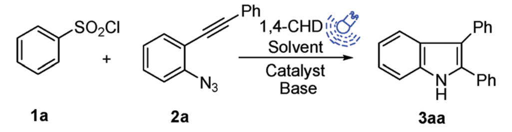


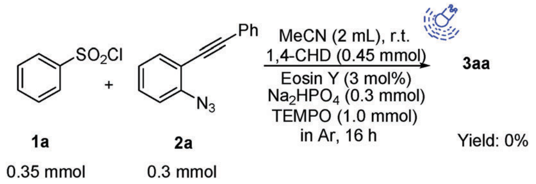
Scheme 1 The synthesis of unsymmetrically 2,3-diaryl substituted indoles *via* the cyclization of *o*-azidoarylalkynes.

Table 1 Optimization of the reaction conditions[a]



Entry	Catalyst	Solvent	Base	Yield[b] (%)
1	Eosin Y	DMF	Na_2CO_3	36
2[c]	Eosin Y	MeCN	Na_2CO_3	58
3	Eosin Y	DMSO	Na_2CO_3	30
4	Eosin Y	THF	Na_2CO_3	Trace
5	Eosin Y	EtOAc	Na_2CO_3	9
6	Eosin Y	MeCN	Na_2HPO_4	74
7	Eosin Y	MeCN	$NaHCO_3$	53
8	Eosin Y	MeCN	K_2CO_3	32
9	Eosin Y	MeCN	Et_3N	15
10	Rose Bengal	MeCN	Na_2HPO_4	12
11	$[Ru(bpy)_3Cl_2]$	MeCN	Na_2HPO_4	Trace
12	$[Ir(ppy)_3]$	MeCN	Na_2HPO_4	19
13[c]	Eosin Y	MeCN	Na_2HPO_4	26
14[d]	Eosin Y	MeCN	Na_2HPO_4	33
15[e]	Eosin Y	MeCN	Na_2HPO_4	0
16	None	MeCN	Na_2HPO_4	0

[a] Reaction conditions: **1a** (0.35 mmol), **2a** (0.3 mmol), base (0.3 mmol), catalyst (3 mol%), solvent (2.0 mL), room temperature, Ar atmosphere, 1,4-CHD (0.45 mmol), 5 W blue LED (λ_{max} = 455 nm) light for 14 h. [b] Isolated yield. [c] Hantzsch ester (0.45 mmol) was used instead of 1,4-CHD. [d] Ph_3SiH (0.45 mmol) was used instead of 1,4-CHD. [e] Without additional light.



Scheme 2 Control experiment.

(Table 1, entry 1). Extensive screening of the solvents revealed that MeCN provided the best results (Table 1, entries 2–5). Switching the base to Na_2HPO_4 resulted in a significant improvement in the yield. Other bases, such as $NaHCO_3$, K_2CO_3 and Et_3N, were less efficient than Na_2HPO_4 (Table 1, entries 6–9). It was found that eosin Y was superior to other visible-light photoredox catalysts (Table 1, entries 10–12). To improve the reaction yield, different hydrogen sources were added to the reaction (Table 1, entries 13 and 14). However, no higher yield of **2a** was observed. The reaction did not take place in the absence of either the visible-light photoredox catalysts or additional visible light (Table 1, entries 15 and 16).

With the best conditions in hand, the scope of the [eosin Y]-facilitated, visible-light induced cyclization protocol was investigated with regard to the scope of the arylsulfonyl chloride **1** and *o*-azidoarylalkyne **2**. As shown in Scheme 2, the optimal reaction conditions were applicable to a wide range of arylsulfonyl chlorides **1**. The results showed that the cyclization reaction could be realized in a good yield irrespective of the nature and the position of the aryl substituents on the arylsulfonyl chloride **1**. In addition, a variety of functional groups were tolerated and the efficiency of the reaction was not affected in the presence of halides, ethers and alkyl groups. Notably, the halogens F and Cl were tolerated under the reaction conditions, thereby facilitating additional modification at the halogenated positions. The application of naphthalene-1-sulfonyl chloride **1h** delivers the desired products in 64% yield (Table 2, entry 7). Apart from benzenesulfonyl chloride **1a**, thiophene-2-sulfonyl chloride **1i** reacted smoothly with **2a** and led to the corresponding product **3ai** in 57% yield (Table 2, entry 8). To further explore the potential of our methodology, trifluoro-methanesulfonyl chloride **1j** was subjected to the standard reaction conditions (Table 2, entry 9) and the desired product was isolated in a low yield (31%).

Subsequently, we examined the generality of this visible-light initiated cyclization reaction with respect to a range of *o*-azidoarylalkynes **2** (Table 3). Gratifyingly, both electron-donating and electron-withdrawing aromatic substituents were tolerated in the terminal alkyne. We were pleased to find that heteroaryl-substituted alkyne **2d** was also a suitable substrate and allowed the formation of **3da** in 63% yield. It was found that the reactions of **2e** with **1a** proceeded well and gave the desired indole in 69% yield. However, the optimized reaction conditions were not applicable to substrate **2f**, which bears an alkyl group in the terminal alkyne. To highlight the utility of this transformation, representative 2-phenylethynyl arylazides were selected to illustrate the tolerance for substituents on the aryl ring of the 1-(azido)benzene moiety. Electron-withdrawing-group-substituted substrates **2g–2j** were compatible with the domino sequence. Substrate **2** bearing electron-donating groups, such as methyl and methoxyl, proceeded smoothly in the reaction and gave the desired indoles in moderate to good yields (Table 3, entries 10 and 11). The visible-light initiated domino reactions can tolerate some functional groups such as an alkyl group, ethers and C–Cl bonds, which could be used for further modification at the substituted positions.

In order to gain some more information on the reaction mechanism, several control reactions were performed as shown in Scheme 2. When the reaction of **1a** with **2a** was carried out in the presence of a stoichiometric amount of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, a well-known radical-capturing species), the reaction was completely suppressed (Scheme 2). These results suggest that a radical process may be involved in this transformation. Furthermore, the product yield dropped significantly when no

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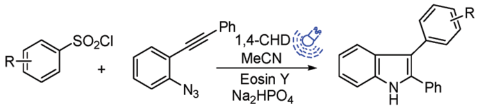
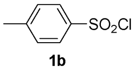
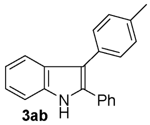
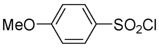
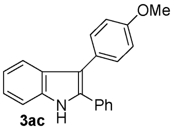
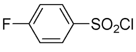
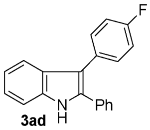
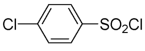
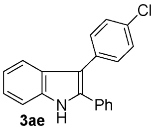
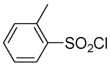
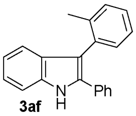
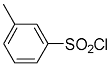
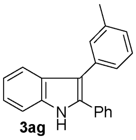
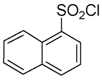
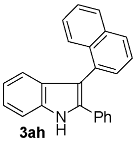
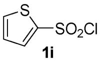
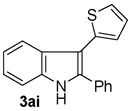
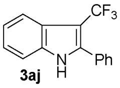
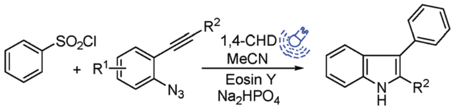
Table 2 Scope of the arylsulfonyl chloride **1**[a]

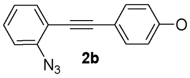
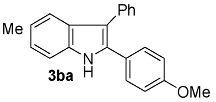
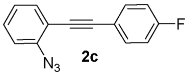
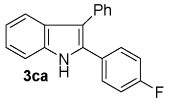
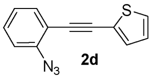
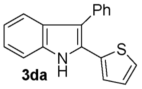
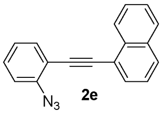
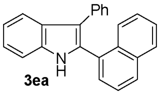
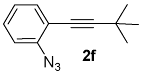
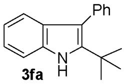
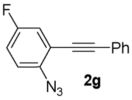
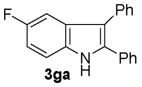
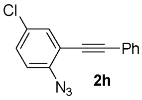
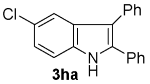
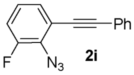
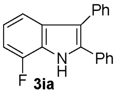
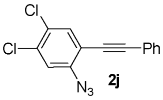
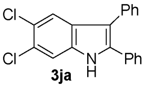
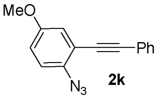
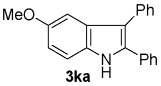
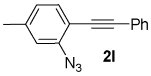
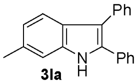


Entry	Arylsulfonyl chloride **1**	Indole **3**	Yield[b] (%)
1	 **1b**	 **3ab**	74
2	 **1c**	 **3ac**	68
3	 **1d**	 **3ad**	71
4	 **1e**	 **3ae**	70
5	 **1f**	 **3af**	62
6	 **1g**	 **3ag**	68
7	 **1h**	 **3ah**	64
8	 **1i**	 **3ai**	57
9	$F_3C{-}SO_2Cl$ **1j**	 **3aj**	31

[a] Reaction conditions: **1** (0.35 mmol), **2a** (0.3 mmol), Na_2HPO_4 (0.3 mmol), eosin Y (3 mol%), MeCN (2.0 mL), room temperature, Ar atmosphere, 1,4-CHD (0.45 mmol), 5 W blue LED (λ_{max} = 455 nm) light for 14 h. [b] Isolated yield.

Table 3 Scope of the *o*-azidoarylalkyne 2[a]



Entry	Azidoarylalkyne **2**	Indole **3**	Yield[b] (%)
1	 **2b**	 **3ba**	84
2	 **2c**	 **3ca**	77
3	 **2d**	 **3da**	63
4	 **2e**	 **3ea**	69
5	 **2f**	 **3fa**	0
6	 **2g**	 **3ga**	67
7	 **2h**	 **3ha**	51
8	 **2i**	 **3ia**	58
9	 **2j**	 **3ja**	70
10	 **2k**	 **3ka**	74
11	 **2l**	 **3la**	66

[a] Reaction conditions: **1a** (0.35 mmol), **2** (0.3 mmol), Na_2HPO_4 (0.3 mmol), eosin Y (3 mol%), MeCN (2.0 mL), room temperature, Ar atmosphere, 1,4-CHD (0.45 mmol), 5 W blue LED light (λ_{max} = 455 nm) for 14 h. [b] Isolated yield.

photocatalyst was present in the reaction and/or under dark conditions (Scheme 3).

Based on these observations, we proposed a rationale for this visible-light initiated cyclization reaction.[8–10] We reasoned that SET reduction of benzenesulfonyl chloride **1a** will occur upon photocatalyst excitation using visible light irradiation, delivering the phenyl radical ($Ph^\bullet$) and [eosin Y]$^{\bullet+}$. Subsequently, the addition of $Ph^\bullet$ to the alkynyl moiety of **2a** forms intermediate **A**, which immediately undergoes the intramolecular cyclization of the alkenyl radical with the azido moiety to produce the N-radical intermediate **B** with extrusion of N_2 gas. H-Atom abstraction from 1,4-CHD will form the desired product **3aa** and generate the radical **C**, which closes the photoredox cycle by SET with $PC^{\bullet+}$.

In conclusion, we have demonstrated a facile, transition-metal-free and direct annulation approach for access to a variety of

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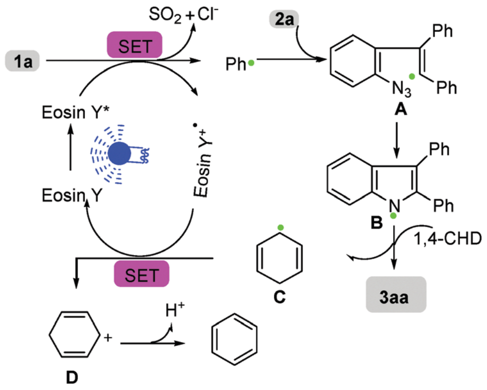

Scheme 3 Plausible reaction mechanism.

unsymmetrical 2,3-diaryl-substituted indoles *via* a visible-light initiated cascade cyclization process with predictable regioselectivity upon the reaction of a variety of arylsulfonyl chlorides with various 2-alkynyl arylazides. These reactions exhibit excellent substrate scope and functional group tolerance. The use of inexpensive eosin Y as the catalyst with easy operation makes this protocol very practical. Further investigations on the mechanism of the reaction and its application are ongoing in our laboratory.

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