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Indium-catalyzed annulation of 3-aryl- and 3-heteroarylindoles with propargyl ethers: synthesis and photoluminescent properties of aryl- and heteroaryl[c]carbazoles†

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Treatment of 3-aryl- and 3-heteroarylindoles with propargyl ethers under indium catalysis successfully provided aryl- and heteroaryl[c]carbazoles, which were found to be more efficient emitters compared with the corresponding [a]-analogs.

Aryl- and heteroaryl-annulated carbazoles (AHACs) are key constituents found in natural products, biologically active molecules and drugs¹ as well as optoelectronic materials.² AHACs are classified into [a]-, [b]- and [c]-types based on the position at which the (hetero)aryl ring is fused to the carbazole nucleus. Among the three types, we firstly developed a new synthetic strategy for the [a]-type, by the indium-catalyzed annulation of 2-(hetero)arylindoles with propargyl ethers.³ The strategy features a two carbon-carbon bond-forming cascade in one batch, where direct use of two C-H bonds of 2-(hetero) arylindoles for an addition-substitution sequence to propargyl ethers is included as a key ingredient. Our prime concern in this research project is to refine the strategy so as to be a more practical and general tool capable of synthesizing other types of AHACs. We now found that the strategy works well also for [c]-types, simply by replacing 2-(hetero)arylindoles with their 3analogs. Diverse synthetic methods for AHACs have thus far been developed due to their importance in a variety of aspects.^{1,2} However, a powerful strategy with a broad substrate scope applicable to both [a]- and [c]-types has yet to be explored.4-11 Taking advantage of this strategy which allows us to access the two types, we also disclose interesting structureproperty correlations by evaluating their photoluminescent properties.

Due to the potent activity of $In(ONf)_3$ (Nf = $SO_2C_4F_9$) found in our preceding research,³ study on this topic began with its testing in the reaction of 3-phenylindole (1a) with methyl propargyl ether (2a) (Table 1). Thus, the reaction with $In(ONf)_3$ (30 mol%) in Bu₂O at 70 °C for 15 h gave 6-methyl-7*H*-benzo[*c*]carbazole (3a) in 54% yield as a single isomer (entry 1).¹² The non-formation of the other isomer (4a) is noteworthy. Although the use of propargyl alcohol (2b) instead of 2a provided no improvement in the yield, 3-trimethylsilyloxy-1-propyne (2c) reacted with 1a more efficiently (entries 2 and 3). With 2c, the reaction under higher dilution conditions raised the yield to 71% (entry 4). Interestingly, using 2 with a good leaving functionality was found to afford 4a predominantly. Among such types of 2d–2f examined, the highest selectivity for 4a was achieved in the use of 2f with OCO₂Et as

Table 1Indium-catalyzed annulation of 3-phenylindole with propargyl alcoholderivatives 2^a



Entry	R	Solvent	Conv. ^{<i>b</i>} (%) of 1a	Yield ^{<i>b</i>} (%) of 3a and 4a	3a : 4a ^c
1	Me (2a)	Bu ₂ O	79	54	>99:1
2	H (2b)	Bu_2O	70	54	>99:1
3	$SiMe_3$ (2c)	Bu_2O	84	66	>99:1
$4^{d,e}$	$SiMe_3$ (2c)	Bu_2O	93	71	>99:1
5	COBu (2d)	Bu_2O	84	13	48:52
6	$SO_2Me(2e)$	Bu_2O	68	33	32:68
7	$CO_2Et(2f)$	Bu_2O	77	21	13:87
8	$CO_2Et(\mathbf{2f})$	PhCl	83	41	9:91
9^d	$CO_2Et(\mathbf{2f})$	PhCl	88	53	10:90

^{*a*} Reagents: **1a** (0.20 mmol), **2** (0.22 mmol), In(ONf)₃ (60 µmol), solvent (3.0 mL). ^{*b*} Determined by ¹H NMR. ^{*c*} Determined by GC. ^{*d*} The solvent (3.5 mL) was used. ^{*e*} Reaction time = 12 h.

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the leaving group (entries 5–7). In this case, replacing Bu_2O with PhCl improved both the yield and selectivity (entry 8). Here again, increasing the solvent volume enhanced the yield of the products (entry 9).

With both sets of the suitable reaction conditions in hand, we examined the substrate scope of the reaction (Table 2). Besides **1a**, Me-, MeO-, or Br-substituted 3-phenylindole reacted with **2c** to give **3b–3g** in a regioselective fashion (entries 1–7). Aryl groups on the nitrogen atom of substrates did not participate in the annulation, thus showing remarkable reaction-site selectivity (entries 8–9).¹³ Using propargyl ethers with a substituent at the propargylic position allows us to introduce an additional carbon framework regioselectively (entries 10–11). With **2f** instead of **2c** as a C3 source, **4b** and **4d** were obtained selectively as in the case of **4a** (entries 12–14). The strategy can be also applied to synthesis of heteroaryl derivatives. The predominant formation of thieno[*c*]carbazole



^{*a*} Conditions A: **1** (0.20 mmol), **2c** (0.22 or 0.26 mmol), $In(ONf)_3$ (40 or 60 μmol, 20 or 30 mol%), Bu_2O (3.5 mL); conditions B: **1** (0.20 mmol), **2f** (0.22 mmol), $In(ONf)_3$ (60 μmol, 30 mol%), PhCl (3.5 mL). See ESI for further details. ^{*b*} Isolated yield based on **1**. ^{*c*} Determined by GC. ^{*d*} PhCl instead of Bu_2O was used as a solvent. ^{*e*} 3-Trimethylsilyloxy-1-butyne instead of **2c** was used. ^{*f*} 5-Ethyl-7*H*-benzo[*c*]carbazole was also formed in 1% yield. ^{*g*} 3-Trimethylsilyloxy-1-octyne instead of **2c** was used. ^{*h*} 5-(1-Hexyl)-7*H*-benzo[*c*]carbazole was also formed in 1% yield.

3l was thus attained in the reaction of thienylindole **1b** with **2c** [eqn (1)]. For the synthesis of indolo[*c*]carbazole **3m**, **2a** was a superior electrophile [eqn (2)]. The reaction of benzothienylindole **1d** with **2f** provided **4n** as a single regioisomer [eqn (3)].



Plausible reaction mechanisms based on our earlier studies are shown as paths A and B in Scheme 1.³ Path A in which 2c acts as the C3 unit starts with addition of the indolyl C-H bond to the C=C bond activated by the indium salt (*In*).¹⁴ The next stage is intramolecular S_N^2 cyclization followed by aromatization to provide 3. On the other hand, substitution between 1 and the 2f-*In* complex would precede addition in path B because 2f has OCO₂Et as a good leaving group.¹⁵ The final step is aromatization leading to 4. Considering such reversed order of the addition and substitution processes in paths A and B, the regiochemistry concerning the methyl group of 3 and 4 would be rationally understood.

Finally, we investigated the photoluminescent properties of some (hetero)aryl[*c*]carbazoles, and compared them to those of the corresponding [*a*]-type (Table 3).^{3,16} The emission maxima of the [*c*]-types ranged from 360 to 400 nm, similarly to [*a*]-analogs. Methyl and electron-rich aryl groups including a phenyl group on the nitrogen atom (**3f**, **3h** and **3i**) contributed



Scheme 1 Plausible reaction mechanisms.

 Table 3
 Photoluminescent properties of (hetero)aryl[c]- and -[a]carbazoles^a



^{*a*} Fluorescence spectra excited at 265 nm were measured in CH_2Cl_2 ($c = 1.5 \times 10^{-6}$ M). Photoluminescent data of [*a*]-types collected herein were derived from ref. 3*b*. ^{*b*} (H)A[*c*]C = (hetero)aryl[*c*]carbazole. ^{*c*} sh = shoulder. ^{*d*} Determined with reference to the quantum yield of *p*-terphenyl. ^{*e*} (H)A [*a*]C = (hetero)aryl[*a*]carbazole.

to enhancing quantum efficiency in comparison to basic structure **3a**, as observed in the [a]-types (**5a** vs. **5f**, **5h** or **5i**). Interestingly, the quantum yields of each [c]-type were found to be always higher than those of the corresponding [a]-type. These structure-property correlations for AHACs might be a useful guide to create optoelectronic devices.

In closing, we have developed a new synthetic method for (hetero)aryl[c]carbazoles, which can be efficiently constructed by the two carbon–carbon bond-forming cascade in one batch through the annulation of 3-(hetero)arylindoles with propargyl ethers. One important aspect is the selective synthesis of 3 and 4 by the appropriate choice of the C3 source. The development of this reaction gave us a great opportunity to evaluate emission properties of the product, thereby showing that the [c]-type is more emissive than the [a]-type. As the finale of this research project, the application of this strategy to the [b]-type that remains unaddressed would be suitable. We believe that elucidation of structure–property correlations reflecting all three types of AHACs would be worthy of future research.

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