

# Divergent Construction of Nitrogen-Containing Polycyclic Compounds with a Dearomatization Strategy

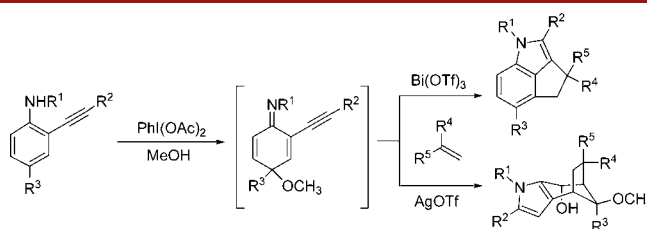
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## ABSTRACT



The oxidative dearomatization of para-substituted *o*-alkynylanilines afforded 2-alkynyl cyclohexadienimines, which can act as active substrates for reaction with electron-rich styrenes. The reaction is metal-controlled. Bi(OTf)<sub>3</sub>-catalyzed reactions afforded 3,4-dihydro-cyclopenta[*c,d*]indoles, and AgOTf-catalyzed reactions provided tricyclic pyrrole derivatives.

Dearomatization of aromatic compounds provides an economical and efficient way to build architecturally complex molecules as a result of the inherent functionalities

(1) Reviews, see: (a) Quideau, S.; Pouységu, L. *Org. Prep. Proced. Int.* **1999**, *31*, 617. (b) Pape, A. R.; Kaliappan, K. P.; Kündig, E. P. *Chem. Rev.* **2000**, *100*, 2917. (c) Smith, P. L.; Chordia, M. D.; Harman, W. D. *Tetrahedron* **2001**, *57*, 8203. (d) Magdziak, D.; Meek, S. J.; Pettus, T. R. R. *Chem. Rev.* **2004**, *104*, 1383. (e) López Ortiz, F.; Iglesias, M. J.; Fernández, I.; Andújar Sánchez, C. M.; Gómez, G. R. *Chem. Rev.* **2007**, *107*, 1580. (f) Quideau, S.; Pouységu, L.; Deffieux, D. *Synlett* **2008**, 467. (g) Pouységu, L.; Deffieux, D.; Quideau, S. *Tetrahedron* **2010**, *66*, 2235. (h) Roche, S. P.; Porco, J. A., Jr. *Angew. Chem., Int. Ed.* **2011**, *50*, 4068.

(2) Recent examples, see: (a) Mejjorado, L. H.; Pettus, T. R. R. *J. Am. Chem. Soc.* **2006**, *128*, 15625. (b) Dohi, T.; Maruyama, A.; Takenaga, N.; Senami, K.; Minamitsuji, Y.; Fujioka, H.; Caemmerer, S. B.; Kita, Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 3787. (c) Pouységu, L.; Chassaing, S.; Dejugnac, D.; Lamidey, A.-M.; Miqueu, K.; Sotiropoulos, J.-M.; Quideau, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 3552. (d) Quideau, S.; Lyvinec, G.; Marguerit, M.; Bathany, K.; Ozanne-Beaudenon, A.; Buffeteau, T.; Cavagnat, D.; Chénéde, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 4605. (e) Li, F.; Tartakoff, S. S.; Castle, S. L. *J. Am. Chem. Soc.* **2009**, *131*, 6674. (f) Guérard, K. C.; Sabot, C.; Racicot, L.; Canesi, S. J. *J. Org. Chem.* **2009**, *74*, 2039. (g) Dong, S.; Hamel, E.; Bai, R.; Covell, D. G.; Beutler, J. A.; Porco, J. A., Jr. *Angew. Chem., Int. Ed.* **2009**, *48*, 1494. (h) Qi, J.; Beeler, A. B.; Zhang, Q.; Porco, J. A., Jr. *J. Am. Chem. Soc.* **2010**, *132*, 13642. (i) Frie, J. L.; Jeffrey, C. S.; Sorensen, E. J. *Org. Lett.* **2010**, *12*, 5394. (j) Trzuppek, J. D.; Lee, D.; Crowley, B. M.; Marathias, V. M.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2010**, *132*, 8506. (k) Liang, H.; Ciufolini, M. A. *Org. Lett.* **2010**, *12*, 1760. (l) Lian, Y.; Davies, H. M. L. *J. Am. Chem. Soc.* **2010**, *132*, 440. (m) Uyanik, M.; Yasui, T.; Ishihara, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 2175. (n) Rudolph, A.; Bos, P. H.; Meetsma, A.; Minnaard, A. J.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2011**, *50*, 5834.

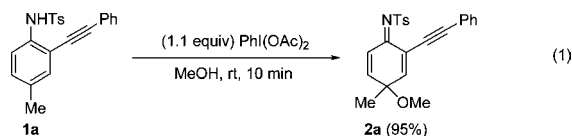
stored within the aromatic systems.<sup>1</sup> The appeal of such an approach has drawn significant attention in the past decades. Most of the reports focus on the oxidative dearomatization of phenols and their derivatives.<sup>2,3</sup> Another family of significance in aromatic compounds, anilines, is also interesting using materials in organic synthesis. Dearomatization of anilines will provide a powerful tool to construct complex nitrogen-containing molecules. However, to date the dearomatization of anilines has been concentrated on the oxidation of para- or ortho-aminophenols or phenylenediamines<sup>4</sup> and the subsequent conversion of the corresponding quinonemoides and diimides.<sup>5</sup> Compared with the extensive investigation of reactions of para-substituted phenols,

(3) Recent examples, see: (a) Imbos, R.; Minnaard, A. J.; Feringa, B. L. *J. Am. Chem. Soc.* **2002**, *124*, 184. (b) Hayashi, Y.; Gotoh, H.; Tamura, T.; Yamaguchi, H.; Masui, R.; Shoji, M. *J. Am. Chem. Soc.* **2005**, *127*, 16028. (c) Ladziata, U.; Kuposov, A. Y.; Lo, K. Y.; Willging, J.; Nemykin, V. N.; Zhdankin, V. V. *Angew. Chem., Int. Ed.* **2005**, *44*, 7127. (d) Liu, Q.; Rovis, T. *J. Am. Chem. Soc.* **2006**, *128*, 2552. (e) Vo, N. T.; Pace, R. D. M.; O'Hara, F.; Gaunt, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 404. (f) Lu, S.; Xu, Z.; Bao, M.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 4366. (g) Garcia-Fortanet, J.; Kessler, F.; Buchwald, S. L. *J. Am. Chem. Soc.* **2009**, *131*, 6676. (h) Gu, Q.; Rong, Z.-Q.; Zheng, C.; You, S.-L. *J. Am. Chem. Soc.* **2010**, *132*, 4056. (i) Wu, Q.-F.; Liu, W.-B.; Zhuo, C.-X.; Rong, Z.-Q.; Ye, K.-Y.; You, S.-L. *Angew. Chem., Int. Ed.* **2011**, *50*, 4455.

(4) Recent developments in the chemistry of quinoneimides, see: Nair, V.; Dhanya, R.; Rajesh, C.; Devipriya, S. *Synlett* **2005**, 2407.

the dearomatization of para-substituted anilines has only been investigated in a few cases.<sup>6</sup> Under oxidizing conditions, dearomatization of para-substituted anilines results in cyclohexadienimines. Compared with cyclohexadienones, cyclohexadienimines are less reactive for further conversion due to the existence of the carbon–nitrogen double bond. In our dearomatization strategy (Scheme 1), an alkynyl group is introduced at the ortho-position of para-substituted anilines. The corresponding dearomatization product could be stabilized by the conjugated effect. More importantly, the dearomatization might be followed by a transition metal catalyzed cyclization to afford a more reactive intermediate **I**.<sup>7</sup> The coexistence of an electrophilic center (C-4) and a nucleophilic center (C-3) in its structure could make intermediate **I** act as a 1,3-dipole. For example, it might react with alkenes via a cycloaddition<sup>8</sup> to access 3,4-dihydro-cyclopenta[*c,d*] indole, which is structurally related to the orchid alkaloid dendrobine.<sup>9,10</sup> Additionally, this scaffold appears as the core structure in some organic electroluminescent components.<sup>11</sup>

To test the feasibility of our strategy, compound **1a** was selected as the standard substrate. After screening various oxidants, nucleophiles (ROH), temperature and solvents, the optimized dearomatization condition was established (eq 1).



The reaction between 1-methoxy-4-vinylbenzene **3a** and compound **2a** was done in order to investigate the cascade reaction. Gold(III) chloride was tested as the first catalyst. We were pleased to observe that the reaction proceeded well, and the desired product **4aa** was isolated in a 39% yield (Table 1, entry 1). Interestingly, the formation of compound **4aa** was not observed from the reaction

(5) Examples on the reactions of quinoneimides, see: (a) Engler, T. A.; Wanner, J. *J. Org. Chem.* **2000**, *65*, 2444. (b) Parker, K. A.; Mindt, T. L. *Org. Lett.* **2002**, *4*, 4265. (c) Nair, V.; Dhanya, R.; Rajesh, C.; Bhadbhade, M. M.; Manoj, K. *Org. Lett.* **2004**, *6*, 4743. (d) Tichenor, M. S.; Kastrinsky, D. B.; Boger, D. L. *J. Am. Chem. Soc.* **2004**, *126*, 8396. (e) Jackson, S. K.; Banfield, S. C.; Kerr, M. A. *Org. Lett.* **2005**, *7*, 1215.

(6) (a) Jackson, S. K.; Banfield, S. C.; Kerr, M. A. *Org. Lett.* **2005**, *7*, 1215. (b) Quideau, S.; Pouységou, L.; Ozanne, A.; Gagnepain, J. *Molecules* **2005**, *10*, 201. (c) Giroux, M.-A.; Guérard, K. C.; Beaulieu, M.-A.; Sabot, C.; Canesi, S. *Eur. J. Org. Chem.* **2009**, 3871. (d) Salomon, R. J.; Todd, M. A.; Sabat, M.; Myers, W. H.; Harman, W. D. *Organometallics* **2010**, *29*, 707.

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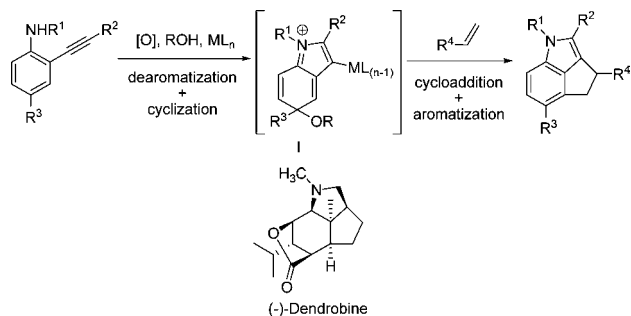
(8) (a) Dohi, T.; Hu, Y.; kamitanaka, T.; Washimi, N.; Kita, Y. *Org. Lett.* **2011**, *13*, 4814. (b) Fan, R.; Li, W.; Ye, Y.; Wang, L. *Adv. Synth. Catal.* **2008**, *350*, 1531.

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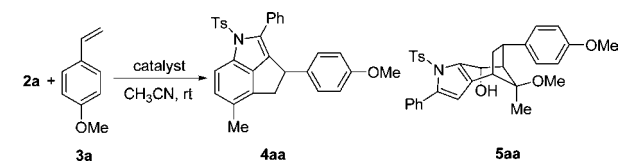
(10) The synthesis of 3,4-dihydro-cyclopenta[*c,d*]indole, see: Rousseaux, S.; Davi, M.; Sofack-Kreutzer, J.; Pierre, C.; Kefalidis, C. E.; Clot, E.; Fagnou, K.; Baudoin, O. *J. Am. Chem. Soc.* **2010**, *132*, 10706.

(11) Takahashi, H.; Iizumi, Y. Organic Electroluminescent Component. Jpn. Kokai Tokkyo Koho JP 2000268961 A 20000929, 2000.

**Scheme 1.** Synthesis of 3,4-Dihydro-cyclopenta[*c,d*]indoles



**Table 1.** Selection of Catalyst for the Cascade Reaction<sup>a</sup>

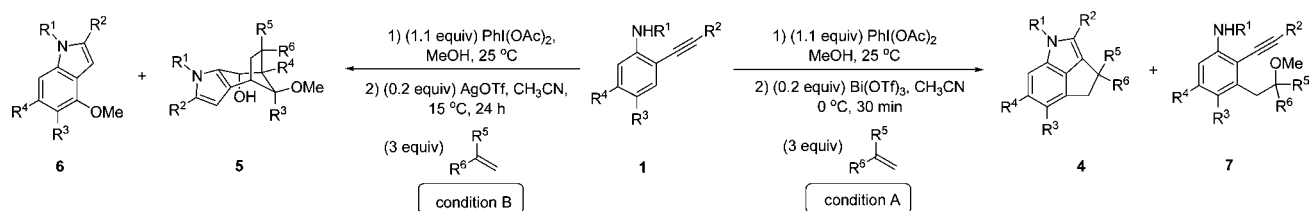


entry	catalyst	4aa		5aa			
		(%) <sup>b</sup>	(%) <sup>b</sup>	entry	catalyst	(%) <sup>b</sup>	(%) <sup>b</sup>
1	AuCl <sub>3</sub>	39	0	12	Yb(OTf) <sub>3</sub>	0	0
2	AuCl	0	17	13	In(OTf) <sub>3</sub>	38	0
3	CuCl	0	0	14	Bi(OTf) <sub>3</sub>	62	0
4	CuI	0	0	15	AgOTf	0	91
5	CuCl <sub>2</sub>	0	0	16	Rh(OAc) <sub>2</sub>	0	0
6	CuBr <sub>2</sub>	0	0	17	Pd(OAc) <sub>2</sub>	46	0
7	Cu(OAc) <sub>2</sub>	0	0	18	PdCl <sub>2</sub>	38	0
8	Cu(OTf) <sub>2</sub>	49	0	19	PtCl <sub>2</sub>	20	0
9	Zn(OTf) <sub>2</sub>	0	0	20	RuCl <sub>3</sub>	48	0
10	Ni(OTf) <sub>3</sub>	0	0	21	FeCl <sub>3</sub>	52	0
11	Sc(OTf) <sub>3</sub>	0	0	22	FeCl <sub>2</sub>	0	0

<sup>a</sup> General reaction conditions: reactions performed on 0.1 mmol scale using 2 equiv of **3a**, 20 mol % catalyst in CH<sub>3</sub>CN (2 mL) at 25 °C. <sup>b</sup> Reported yields are of the isolated product based on compound **2a**.

catalyzed by gold(I) chloride. Instead, a new fused heterocyclic compound **5aa** was obtained in a 17% yield (Table 1, entry 2). The structures of compounds **4aa** and **5aa** were confirmed by their single-crystal diffraction analysis (see the Supporting Information). Encouraged by these results, a variety of metal salts were explored. For various copper catalysts (Table 1, entries 3–8), only Cu(OTf)<sub>2</sub> proved effective to catalyze the formation of compound **4aa**, and the yield was improved to 49%. Further screening of other metal triflates revealed that Bi(OTf)<sub>3</sub> and AgOTf were the best catalysts for generating products **4aa** and **5aa**, respectively (Table 1, entries 9–15). Some other Lewis acids [Pd(II), Pt(II), Ru(III), and Fe(III)] exhibited lower catalytic activities in the formation of compound **4aa**, but they could not catalyze the generation of compound **5aa** (Table 1, entries 17–21).

In an attempt to make this approach more efficient, oxidative dearomatization and the subsequent cascade

**Table 2.** Reaction Scope Investigation<sup>a</sup>


entry	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	R <sup>6</sup>	condition A product (%) <sup>b</sup>	condition B product (%) <sup>b</sup>
1	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	Me	H	4-MeOC <sub>6</sub> H <sub>4</sub>	H	<b>4aa</b> (63)	<b>5aa</b> (93)
2	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	Me	H	4-MeOC <sub>6</sub> H <sub>4</sub>	H	<b>4ba</b> (50)	<b>5ba</b> (51)
3	MeSO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	Me	H	4-MeOC <sub>6</sub> H <sub>4</sub>	H	<b>4ca</b> (62)	<b>5ca</b> (92)
4	CF <sub>3</sub> SO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	Me	H	4-MeOC <sub>6</sub> H <sub>4</sub>	H	<b>4da</b> (0)	<b>5da</b> (0)
5	C <sub>6</sub> H <sub>5</sub> CO	C <sub>6</sub> H <sub>5</sub>	Me	H	4-MeOC <sub>6</sub> H <sub>4</sub>	H	<b>4ea</b> (0)	<b>5ea</b> (0)
6	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	4-MeOC <sub>6</sub> H <sub>4</sub>	Me	H	4-MeOC <sub>6</sub> H <sub>4</sub>	H	<b>4fa</b> (52)	<b>5fa</b> (81)
7	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	4-MeC <sub>6</sub> H <sub>4</sub>	Me	H	4-MeOC <sub>6</sub> H <sub>4</sub>	H	<b>4ga</b> (54)	<b>5ga</b> (84)
8	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	4-ClC <sub>6</sub> H <sub>4</sub>	Me	H	4-MeOC <sub>6</sub> H <sub>4</sub>	H	<b>4ha</b> (47)	<b>5ha</b> (80)
9	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	2-thiophyl	Me	H	4-MeOC <sub>6</sub> H <sub>4</sub>	H	<b>4ia</b> (50)	<b>5ia</b> (92)
10	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	2-pyridyl	Me	H	4-MeOC <sub>6</sub> H <sub>4</sub>	H	<b>4ja</b> (0), <b>7ja</b> (45)	<b>5ja</b> (76)
11	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	cyclopropyl	Me	H	4-MeOC <sub>6</sub> H <sub>4</sub>	H	<b>4ka</b> (0)	<b>5ka</b> (72)
12	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	H	Me	H	4-MeOC <sub>6</sub> H <sub>4</sub>	H	<b>4la</b> (0)	<b>5la</b> (75)
13	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	Et	H	4-MeOC <sub>6</sub> H <sub>4</sub>	H	<b>4ma</b> (60)	<b>5ma</b> (0), <b>6m</b> (88)
14	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	<i>n</i> -Bu	H	4-MeOC <sub>6</sub> H <sub>4</sub>	H	<b>4na</b> (55)	<b>5na</b> (0), <b>6n</b> (85)
15	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	Me	Me	4-MeOC <sub>6</sub> H <sub>4</sub>	H	<b>4oa</b> (60)	<b>5oa</b> (0)
16	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	Me	H	C <sub>6</sub> H <sub>5</sub>	H	<b>4ab</b> (0)	<b>5ab</b> (0)
17	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	Me	H	4-BnOC <sub>6</sub> H <sub>4</sub>	H	<b>4ac</b> (53)	<b>5ac</b> (82)
18	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	Me	H	3,4-(MeO) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	H	<b>4ad</b> (55)	<b>5ad</b> (85)
19	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	Me	H	2-Br-4,5-(MeO) <sub>2</sub> -C <sub>6</sub> H <sub>2</sub>	H	<b>4ae</b> (39)	<b>5ae</b> (92)
20	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	Me	H	4-MeOC <sub>6</sub> H <sub>4</sub>	Me	<b>4af</b> (70)	<b>5af</b> (0), <b>4af</b> (71)
21	4-MeC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	Me	H	4-MeC <sub>6</sub> H <sub>4</sub>	Me	<b>4ag</b> (74)	<b>5ag</b> (0), <b>4ag</b> (70)

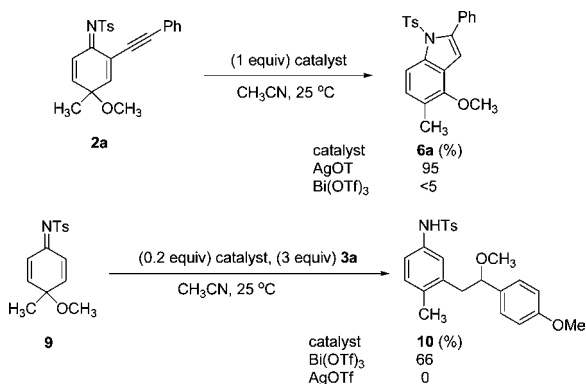
<sup>a</sup> Reactions performed on 0.1 mmol scale. <sup>b</sup> Reported yields are of the isolated products based on compound **1** over two steps.

reaction were conducted in a one-pot fashion. However, the formation of compound **4aa** or **5aa** was not observed, and 4-methoxy substituted indole **6a** was isolated as the major product from both Bi(OTf)<sub>3</sub> and AgOTf catalyzed reactions. After a workup process to remove methanol, the crude oxidative dearomatization mixture was used in the cascade reaction. Either Bi(OTf)<sub>3</sub> or AgOTf catalyzed cascade proceeded well and afforded compound **4aa** or **5aa** in a 58 or 85% yield over two steps, respectively. Further optimization of the cascade processes revealed that acetonitrile was the best solvent for both conversions. Compared with Bi(OTf)<sub>3</sub>-catalyzed reaction (the optimized conditions: 0.2 equiv of Bi(OTf)<sub>3</sub>, 3 equiv of **3a**, CH<sub>3</sub>CN, 0 °C, 30 min), a higher reaction temperature (15 °C) and a longer reaction time (24 h) were required for AgOTf-catalyzed reaction.

The protecting group of nitrogen atoms played a significant role on the transformations (Table 2, entries 1–5). Ts and Ms groups proved to be the best choices. When *N*-Tf protected substrate **1d** was used, it was unreactive toward the oxidant under the dearomatization conditions. When *N*-Bz protected substrate **1e** was used, the oxidative dearomatization proceeded well, but further conversions did not occur. The substituent at the alkynyl group also affected the reactions. Compounds **1f–1i** bearing an aryl

group or a thiophen group as the R<sup>2</sup> substituent were suitable substrates for both conversions (Table 2, entries 6–9). When the R<sup>2</sup> group was a pyridine, a cyclopropyl, or a hydrogen, the formation of products **4ja**, **4ka**, and **4la** were not observed from Bi(OTf)<sub>3</sub>-catalyzed reactions, but AgOTf-catalyzed reaction proceeded well and afforded products **5ja**, **5ka**, and **5la** in good yields (Table 2, entries 10–12). When the methyl group at the para position was replaced by an ethyl or a butyl group, AgOTf-catalyzed reaction did not afford the desired product **5ma** or **5na**. However, this change had no influence on the Bi(OTf)<sub>3</sub>-catalyzed reactions (Table 2, entries 13 and 14). When the 5-position of compound **1** was blocked by a methyl group, the formation of compound **5oa** was not observed in the AgOTf-catalyzed reaction (Table 2, entry 15). Electron-rich styrenes are suitable partners in this process, as we expected (Table 2, entries 16–19). When 1-methoxy- or 1-methyl-4-(prop-1-en-2-yl)benzene **3f** or **3g** was utilized, AgOTf-catalyzed reaction also provided compounds **4af** or **4ag** as the major products (Table 2, entries 20 and 21). Notably, the formation of products **4** or **5** is completely selective under the conditions **A** or **B**, respectively. 4-Methoxy substituted indole **6** or acyclic addition product **7** was isolated from the reaction as the major by-product when AgOTf or Bi(OTf)<sub>3</sub> was used as the catalyst,

## Scheme 2. Control Experiments

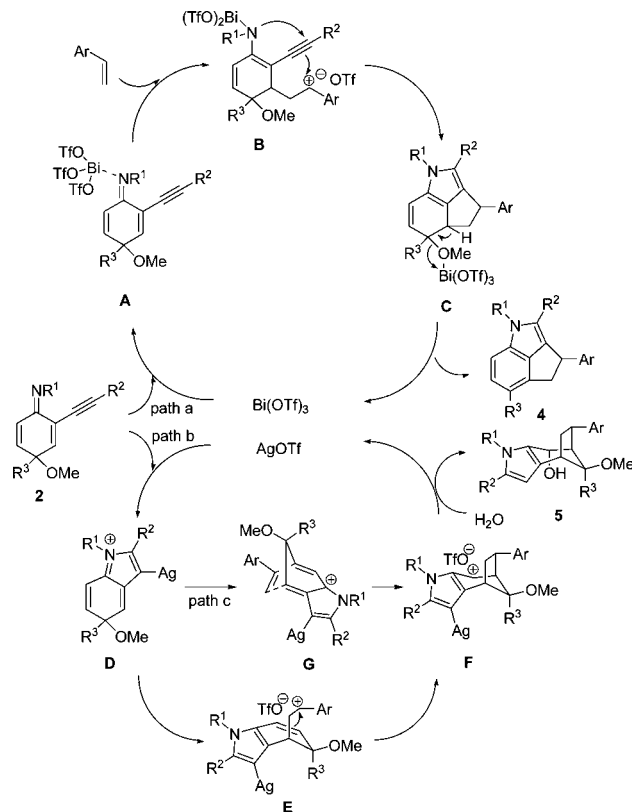


respectively. For example, Bi(OTf)<sub>3</sub>-catalyzed reaction of substrate **1j** provided compound **7ja** in a 45% yield. In the AgOTf-catalyzed reactions of substrates **1m** and **1n**, 4-methoxy substituted indoles **6m** and **6n** were isolated as the major products (Table 2, entries 13 and 14).

Treatment of compound **2a** with 1 equiv of AgOTf in acetonitrile at 25 °C led to the complete conversion to compound **6a**. But the conversion was not observed in the presence of Bi(OTf)<sub>3</sub> under the same conditions (Scheme 2, eq 1). When the alkynyl group was removed from compound **2a**, Bi(OTf)<sub>3</sub> could still catalyze the corresponding reaction to afford meta-substituted aniline derivative **10**;<sup>12</sup> however, AgOTf failed (Scheme 2, eq 2). These results indicated that the activating mode of Bi(OTf)<sub>3</sub> or AgOTf in the cascade reaction was different.

A plausible reaction pathway is depicted in Scheme 3. The reaction between 2-alkynyl cyclohexadienimine and the electron-rich alkene proceeds in two different pathways depending on the employed Lewis acid.<sup>7</sup> In path a, Bi(OTf)<sub>3</sub> works as a Lewis acid to promote the Michael addition of the electron-rich alkene to compound **2** to generate intermediate **B**. After a tandem cyclization and a succeeding Bi(OTf)<sub>3</sub>-catalyzed aromatization, compound **4** is formed. In path b, AgOTf acts as a  $\pi$  acid to coordinate with the triple bond of compound **2** and facilitates the intramolecular nucleophilic attack of the nitrogen on the triple bond to yield an iminium ion **D**. The nucleophilic attack by the electron-rich alkene at the C-4 position of intermediate **D** yields an intermediate **E**, which undergoes a cyclization at the C-6 position to produce an intermediate **F**. Alternatively, the intermediate **D** can also undergo a 5 + 2 ( $4\pi + 2\pi$ ) cycloaddition with the electron-rich alkene to afford the intermediate **F** (path c).<sup>13</sup> In the presence of a trace amount of water in the reaction system, intermediate **F** is hydrolyzed to form compound **5** and regenerate the silver catalyst. In the case of 1-(prop-1-en-2-yl)benzene **3f**

## Scheme 3. Plausible Reaction Pathway



or **3g**, the  $4\pi + 2\pi$  cycloaddition or the cyclization at the C-6 position is not preferred due to steric factors, and the corresponding AgOTf-catalyzed reaction also provided compound **4af** or **4ag** as the major product.

In summary, we have explored a strategy of building nitrogen-containing polycyclic compounds from simple aniline derivatives. Our strategy relies on the dearomatization of para-substituted *o*-alkynylanilines and the subsequent metal-controlled cascade reactions of the corresponding 2-alkynyl cyclohexadienimines. Two fine-tuned metal-controlled conditions were established. Further studies on the reaction mechanism and synthetic applications of this methodology are currently under investigation at our laboratory.

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**Supporting Information Available.** Experimental procedures, characterization data, copies of <sup>1</sup>H NMR and <sup>13</sup>C NMR of new compounds, and crystallographic data of compounds **4aa** and **5aa** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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