Organic LETTERS

Letter

pubs.acs.org/OrgLett

Procedure for the Synthesis of Polysubstituted Carbazoles from 3-Vinyl Indoles

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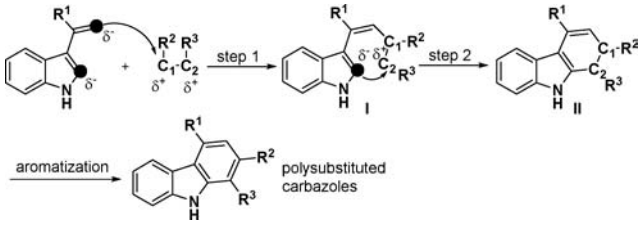
Supporting Information

ABSTRACT: A simple Brønsted acid catalyzed tandem reaction, including intermolecular nucleophilic addition, substitution and intramolecular cyclization, in a one-pot manner is described. Thirty two 2-indolyl substituted carbazoles are generated in good to excellent yields. Based on this tandem reaction strategy, the poly(1,4-carbazole) is prepared for the first time. Preliminary studies indicate that the poly(1,4-carbazole) has good thermostability and optical properties.

Carbazole units appear widely in biologically active compounds and functional materials. Many carbazole-containing molecules exhibit a wide range of biological activities,[1] such as antiviral,[2] antimalarial,[3] anti-TB activity,[4] and antitumoral properties.[5] Carbazole moieties are also found in many natural compounds.[6] Furthermore, because of their wide band gap and high luminescence efficiency, carbazoles are excellent building blocks for functional materials,[7] especially materials used in organic light-emitting diodes (OLEDs).[8] Numerous synthetic strategies have been developed for preparing functionalized carbazoles. Among reported methods, some have focused on C−C and/or C−N bond forming reactions,[9] while others have focused on the benzannulation of indoles.[10] Indole is a readily available material, and construction of carbazoles from indole derivatives would offer an attractive synthetic tool. However, current methods based on this route involve expensive transition-metal catalysts, harsh reaction conditions, and a limited substrate scope. The development of a concise, efficient synthetic route from indole derivatives to carbazoles remains highly desirable.

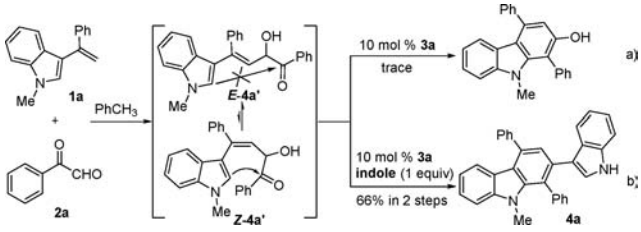
3-Vinyl indole is an important building block in organic synthesis and has been used as a dienophile,[11] diene,[12] and electrophile[13] in the literature. Recently, we reported the use of 3-vinyl indole as a nucleophile in a catalytic asymmetric addition to prochiral electrophiles and showed that the terminal carbon of 3-vinyl indole is a good nucleophile.[14] In addition to the terminal carbon, the 2-position of 3-vinyl indole is also a good nucleophile and these two nucleophilic sites are located at the ends of a 4π-electron conjugated system. We envisioned that a reactant containing two adjacent electrophilic sites reacted with 3-vinyl indole could undergo nucleophilic attack twice in tandem. This reaction model is depicted in Scheme 1. First, the terminal alkene carbon attacks one electrophilic site (C1), leading to the allylic product **I**. Then, the 2-position of indole attacks another electrophilic site (C2), giving the cyclization product **II**. This procedure is a novel utilization of 3-vinyl indole to construct indole-fused heterocycles. If product **II** can be aromatized, a substituted carbazole could be generated. In this work, we used this strategy to construct polysubstituted carbazoles via a simple Brønsted acid catalyzed tandem reaction, including intermolecular nucleophilic addition, substitution, and intramolecular cyclization, in a one-pot manner.

Scheme 1. Tandem Reaction Strategy to Carbazoles from 3-Vinyl Indoles



In the initial study, we chose the phenyl substituted 3-vinyl indole **1a** and the phenylglyoxal **2a** as reactants in the model reaction. We found that the nucleophilic addition of **1a** to **2a** proceeded smoothly in the absence of catalyst, giving the allylic product **4a′** in excellent yield. However, the following cyclization did not take place. A phosphoric acid catalyst **3a** was added to promote the cyclization; however, this also failed to give the cyclized product (Scheme 2a). We considered the

Scheme 2. Initial Studies



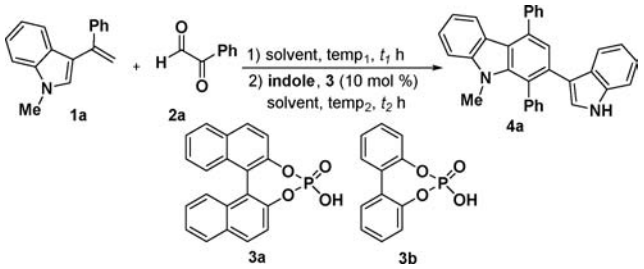
Received: October 30, 2016
Published: November 18, 2016

DOI: 10.1021/acs.orglett.6b03257
Org. Lett. 2016, 18, 6200−6203

C=C double bond configuration of **4a′** to be the main obstacle that prevented the cyclization. The *Z*-product should give the corresponding carbazole, while the *E*-product will be converted into its *Z*-conformer before the second nucleophilic attack can take place. Addressing the issue of the energy barrier of the *E*- to *Z*-conformer transition was the key step to realizing this synthetic strategy. One method to increase the transformation of *E*- to *Z*- is to decrease the stability of the *E*-isomer. We speculated that the introduction of a bulky substituent via substitution of the hydroxyl of **4a′** might achieve this goal. Hence, indole was added to the reaction after reactant **2a** was completely consumed, without separation of intermediate **4a′**. As expected, the second nucleophilic attack proceeded smoothly and the target compound **4a** was obtained in 66% total yield (Scheme 2b). Typically, the molecule structure of **4a** belongs to a '(3-indolyl)-planar' system, a common structural feature in biologically active natural and unnatural products.[15] Thus, a synthetic route to polysubstituted carbazoles, including three reaction components and three transformations, was realized by simple Brønsted acid catalysis in a one-pot manner.

After this initial success, we attempted to increase the yield by optimizing the reaction conditions. First, several commonly used Brønsted acids were tested (Table 1, entries 2−5). These results indicated that benzenesulfonic acid could give a yield comparable to that of catalyst **3a** (Table 1, entry 2 vs 1). Five Lewis acids were also examined in this reaction; however, no better results were obtained (Table 1, entries 6−10). In terms of cost effectiveness, benzenesulfonic acid was chosen as the optimal catalyst for further optimization of the reaction conditions. After screening solvents and adjusting the ratio of reactants, the yield of **4a** could be enhanced to 69% (Table 1, entry 16). These unsatisfactory results led us to turn our attention back to phosphoric acid catalysts. An analogue of **3a**, phosphoric acid **3b**, derived from 2, 2′-biphenol was prepared and used as a catalyst. Satisfyingly, product **4a** was obtained in 75% yield through promotion with **3b** (Table 1, entry 17). The total yield was further improved to 88% when 10 μL of H_2O were added as an additive in step 2 (Table 1, entry 18).

Table 1. Screening of Catalyst and the Optimization of Reaction Conditions[a]

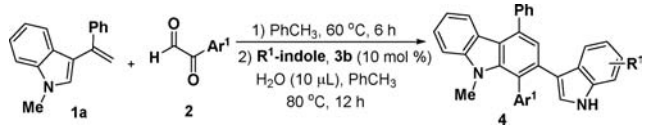


entry	3	solvent	$temp_1/temp_2$ (°C)	t_1/t_2 (h)	yield (%)[b]
1	**3a**	$PhCH_3$	60/80	12/35	66
2	$PhSO_3H$	$PhCH_3$	60/80	6/18	63
3	$TsOH·H_2O$	$PhCH_3$	60/80	6/12	33
4	CF_3COOH	$PhCH_3$	60/80	5/2	21
5	CF_3SO_3H	$PhCH_3$	60/r.t	6/12	25
6	$AlCl_3$	$PhCH_3$	60/80	6/12	52
7	$ZrCl_4$	$PhCH_3$	60/80	6/12	62
8	$ZnCl_2$	$PhCH_3$	60/80	6/12	36
9	$FeCl_3$	$PhCH_3$	60/80	6/12	20
10	$CuCl_2$	$PhCH_3$	60/80	6/12	43
11	$PhSO_3H$	$PhCH_3$	60/80	6/18	66[c]
12	$PhSO_3H$	*m*-xylene	60/80	6/21	52[c]
13	$PhSO_3H$	Et_2O	rt/rt	13/96	39[c]
14	$PhSO_3H$	DCM	rt/rt	13/96	28[c]
15	$PhSO_3H$	THF	60/60	6/40	47[c]
16	$PhSO_3H$	$PhCH_3$	60/80	6/10	69[d]
17	**3b**	$PhCH_3$	60/80	6/12	75[d]
18	**3b**	$PhCH_3$	60/80	6/12	88[d,e]

[a] **1a**:**2a**:indole = 1:1.2:1, solvent (1 mL). [b] Isolated yield. [c] **1a**:**2a**:indole = 1:1.2:2. [d] **1a**:**2a**:indole = 1.2:1:1. [e] 10 μL H_2O was added.

After optimizing the reaction, we then examined its substrate scope. First, various substituents on the indole component were examined. Satisfyingly, the position and electron properties of the indole substituents did not noticeably affect the experimental results; all substrates, except 5-Cl indole, gave the corresponding products in excellent yields (Table 2, entries 2−10). The strong electron-withdrawing properties of the chlorine group likely limited the nucleophilicity of the 5-Cl indole, decreasing the yield of product **4d** (Table 2, entry 4). We then investigated different arylglyoxals substrates. We found that arylglyoxals substituted by electron-withdrawing groups could produce the target compounds in moderate to good yields (Table 2, entries 11−16). The substituent position affected the experimental outcome slightly. For example, the 2-CF_3 phenylglyoxal yielded product **4o** in 42% yield (Table 2, entry 15), which was much lower than the yields of other substrates. This result may have been caused by the steric influence of the 2-CF_3 substituent (Table 2, entry 14).

Table 2. Substrate Scopes of Arylglyoxals and Indoles[a]



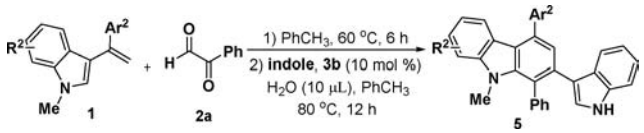
entry	4	R^1	Ar^1	yield (%)[b]
1	**4a**	H	C_6H_5	88
2	**4b**	5-Me	C_6H_5	73
3	**4c**	5-MeO	C_6H_5	73
4	**4d**	5-Cl	C_6H_5	43
5	**4e**	5-Br	C_6H_5	74[c]
6	**4f**	5-I	C_6H_5	78
7	**4g**	6-Me	C_6H_5	70
8	**4h**	6-Br	C_6H_5	75
9	**4i**	6-F	C_6H_5	78
10	**4j**	7-Me	C_6H_5	80[c]
11	**4k**	H	$4\text{-}FC_6H_4$	76
12	**4l**	H	$4\text{-}BrC_6H_4$	74
13	**4m**	H	$4\text{-}CF_3C_6H_4$	58[d]
14	**4n**	H	$4\text{-}MeOC_6H_4$	52
15	**4o**	H	$2\text{-}CF_3C_6H_4$	42[d]
16	**4p**	H	$2,4\text{-}F_2C_6H_3$	72
17	**4q**	H	$3,4\text{-}F_2C_6H_3$	81[d]

[a] **1a**:**2a**:indole =1.2:1:1, $PhCH_3$ (1 mL). [b] Isolated yield. [c] **1a**:**2a**:indole =1.2:1:1.2. [d] **1a**:**2a**:indole =1.2:1:1.5.

Next, 3-vinyl indoles bearing various substituents on the indole and phenyl rings were examined. Three substituents, 5-Me, 5-Br, and 6-Me, were introduced into the indole ring of 3-vinyl indole **1**. The 5- and 6-Me 3-vinyl indoles gave better yields than that of the 5-Br substituted substrate (Table 3,

DOI: 10.1021/acs.orglett.6b03257
Org. Lett. 2016, 18, 6200−6203

Table 3. Substrate Scope of 3-Vinyl Indoles[a]



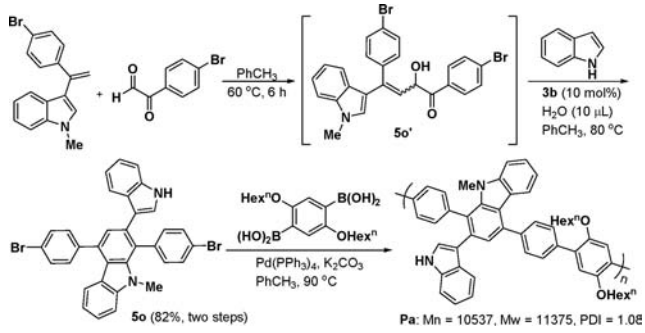
entry	5	R^2	Ar^2	yield (%)[b]
1	**5a**	5-Me	C_6H_5	67[c]
2	**5b**	5-Br	C_6H_5	54[c,d]
3	**5c**	6-Me	C_6H_5	68[c,d]
4	**5d**	H	2-MeC_6H_4	63
5	**5e**	H	2-BrC_6H_4	62[c,d]
6	**5f**	H	3,5-2MeC_6H_4	70
7	**5g**	H	3-$MeOC_6H_4$	48[c]
8	**5h**	H	3-BrC_6H_4	72
9	**5i**	H	3-ClC_6H_4	62
10	**5j**	H	4-MeC_6H_4	67[c]
11	**5k**	H	4-$MeOC_6H_4$	63
12	**5l**	H	4-BrC_6H_4	76[c]
13	**5m**	H	4-ClC_6H_4	64
14	**5n**	H	4-IC_6H_4	92

[a]**1a**:**2a**:indole = 1.2:1:1, $PhCH_3$ (1 mL). [b]Isolated yield. [c]**1a**:**2a**:indole = 1.2:1:1.2. [d]Using 20 mol % **3b**.

entries 1 and 3 vs 2). 3-Vinyl indoles bearing various substituents on different positions of the phenyl group were then tested (Table 2, entries 4−14). We found that a strong electron-donating group in the 3-position of the substituted phenyl decreased the yield slightly; for example, the 3-MeO phenyl substituted 3-vinyl indole gave the product **5g** in 48% yield (Table 3, entry 7). Other substituted phenyls bearing electron-donating or -withdrawing groups in the 2- or 4-positions could give the polysubstituted carbazoles in good to excellent yields. Notably, the 4-I phenyl substituted 3-vinyl indole produced **5n** in 92% yield (Table 3, entry 14), which is the highest yield achieved in this work. The structure of **4a** was confirmed by X-ray single-crystal analysis (see the Supporting Information).[16]

The carbazoles we obtained possessed the following features: (1) the indole unit was fixed at the 2-position, such that the nitrogen atom of the indole could be easily substituted with a wide range of functional groups to tune optical and electrical properties, as well as the solubility; (2) two phenyl groups were simultaneously installed at the 1- and 4-positions. Suitable groups, such as Br and I, could be easily introduced into these two phenyls groups for use in coupling reactions to prepare poly(1,4-carbazole)s. Carbazole-containing polymers have many attractive properties, which have led to their widespread use as photoconductors and charge-transporting materials.[17] However, the majority of research has focused on poly(3,6-carbazole)s and poly(2,7-carbazole)s. Here, 2′-(*p*-Br-phenyl)-3-vinyl indole, 4-Br phenylglyoxal, and indole were manipulated in a one-pot reaction, based on our representative procedure (see the Supporting Information), to give compound **5o**. The monomer **5o** was coupled with 1,4-phenylenediboronic acid to give poly(1,4-carbazole) **Pa** in good yield and high molecular weight (M_n = 10537, M_w = 11375), with a good polymer dispersity index (PDI = 1.08) (Scheme 3). We then evaluated the thermal stability and optical properties of the irregular polymer **Pa** (see the Supporting Information). Thermal gravimetric analysis (5% decomposition: 286 °C) and differential scanning calorimetry (Glass transition temperature: 72.0 °C) results indicated that **Pa** had good thermal stability. The UV−vis spectra of **Pa** showed absorption maxima at 244 and 338 nm. The photoluminescence spectra of **Pa** showed a blue emission with a maximum at 446 nm.

Scheme 3. Synthesis of Poly(1,4-carbazole) Pa from 3-Vinyl Indole



In conclusion, we report an efficient strategy for the synthesis of carbazoles from 3-vinyl indoles. Although three transformations were included in this procedure, the simple phosphoric acid **3b**, which was derived from 2,2′-biphenol, was sufficient to promote this tandem reaction and gave the polysubstituted carbazoles in good to excellent yields. The substrate scope was also quite broad. Additionally, we prepared a poly(1,4-carbazole) **Pa** using a carbazole monomer based on the reaction developed in this work. This preliminary study indicates that the poly(1,4-carbazole) **Pa** has good thermal stability and optical properties.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03257.

Representative experimental procedures and analytical data for all new compounds; X-ray crystalographic data for determination of the molecular structure of **4a** (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for financial support from NSFC (21272002, 21472150), the Program for New Century Excellent Talents in Universities (NCET-12-0929) and the Open Foundation of Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, Northwest University.

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(16) CCDC 1510353 (**4a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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DOI: 10.1021/acs.orglett.6b03257
Org. Lett. 2016, 18, 6200−6203