

## Tandem Synthesis of Benzo[*b*]carbazoles and Their Photoluminescent Properties

Yanpeng Xing, Binbin Hu, Qijun Yao, Ping Lu,\* and Yanguang Wang\*[a]

**Abstract:** 5*H*-Benzo[*b*]carbazoles were prepared through a tandem reaction between 2-ethynyl-*N*-triphenylphosphoranylidene anilines and  $\alpha$ -diazoketones through ketenimine intermediates in moderate-to-good yields. By using this approach, benzo[*b*]benzo[5,6]indolo[3,2-*h*]carbazoles, fluoreno[9,1-*ab*]carbazoles, and fluoreno[9,1-*ab*]fluoreno[1',9':5,6,7]indolo[3,2-*h*]carbazoles were constructed in one pot. Moreover, the resulting products emitted light within the range 410–521 nm, with quantum yields of up to 62 %.

**Keywords:** benzocarbazoles • cyclization • photoluminescence • rearrangement • tandem reactions

### Introduction

In the blossoming field of optoelectronics, a large number of efforts have been made to create new molecules and to optimize their corresponding devices to yield stable working devices with excellent performance.<sup>[1]</sup> As one type of privileged organic semiconductor, linear fused acenes, such as pentacene, have been attracting extensive attention, owing to their unique optical and electronic properties, typically for application in thin-film organic field-effect transistors (OFET)s.<sup>[2a,b]</sup> To enable the fine-tuning of the device parameters to afford higher efficiencies, modification of the structurally simple acenes is necessary. One of the useful methods for such modification is to introduce heteroatoms onto the backbone to form heteroacenes, of which sulfur<sup>[2c]</sup> and nitrogen heteroatoms<sup>[2d,e]</sup> have received the most attention. Hybrid nitrogen acenes, termed N-heteroacenes, offer the benefit of further elaboration for various purposes. For instance, substituted benzo[*a*]carbazoles have been revealed to have low-lying LUMOs and might be used as potential *n*-type or bipolar organic semiconductors (Figure 1).<sup>[3a]</sup> Similar properties of carbazolo[1,2-*a*]carbazoles have also been observed.<sup>[3b]</sup> Indolo[3,2-*b*]carbazoles exhibited both high mobility and high stability.<sup>[3c,d]</sup> Although a longer extension to benzo[1,2-*b*:5,4-*b'*]dicarbazole and benzo[1,2-*b*:4,5-*b'*]dicarbazole was achieved through multiple steps, the yields were low.<sup>[3e]</sup>

Recently, cascade reactions have been attracting much attention, owing to their high efficiency in forming new bonds. Ketene is a versatile intermediate in organic synthesis

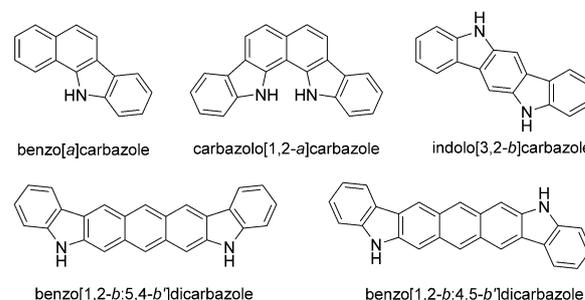


Figure 1. Representative carbazole-based fused heteroacenes.

that could be used to construct various carbocycles and heterocycles by trapping with other reagents in a cascade manner.<sup>[4]</sup> A large number of methods for the in situ generation of ketenimines have been reported. One widely used method to generate ketenimines involves the decomposition of *N*-tosyl triazole, which is formed by a copper-catalyzed alkyne–azide cycloaddition (CuAAC) reaction.<sup>[4,5]</sup> Furthermore, ketenimines can be also formed through an aza-Wittig reaction between a ketene and an aza-Wittig reagent.<sup>[4,6]</sup>

Prompted by the value of N-heteroacenes in the field of optoelectronics and by our previous investigations on the thriving chemistry of ketenimines in cascade reactions,<sup>[4,6]</sup> we were interested in the synthesis of benzo[*b*]carbazoles through ketenimine intermediates. Based on the traditional retrosynthetic analysis, the four fused rings of benzo[*b*]carbazole are commonly constructed from either substituted indoles<sup>[7a-c]</sup> or substituted naphthalenes,<sup>[7d-f]</sup> as shown in Figure 2. Exceptionally, Schmittel et al.<sup>[8a]</sup> and Shi and Wang<sup>[8b]</sup> independently reported a strategy in which three of the four fused rings of benzo[*b*]carbazoles could be constructed in a single step through a biradical cyclization reaction of the isolated *N*-(2-alkynylphenyl) ketenimines. Although this reaction offers high bond-formation efficiency, the diversity of the products is much limited, owing to the instability of the ketenimines.

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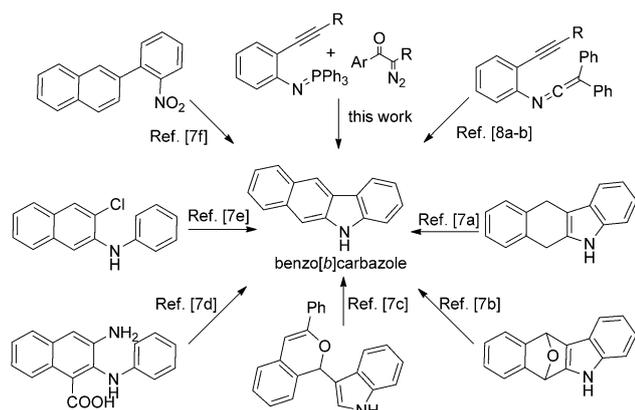


Figure 2. Synthetic routes to benzo[*b*]carbazoles.

Herein, we report a concise strategy for the construction of the benzo[*b*]carbazole skeleton and its extension to benzo[*b*]benzo[5,6]indolo[3,2-*h*]carbazole, fluoreno[9,1-*ab*]carbazole, and fluoreno[9,1-*ab*]fluoreno[1',9':5,6,7]indolo[3,2-*h*]carbazole skeletons (Figure 3), with an illustration of their photoluminescence properties.

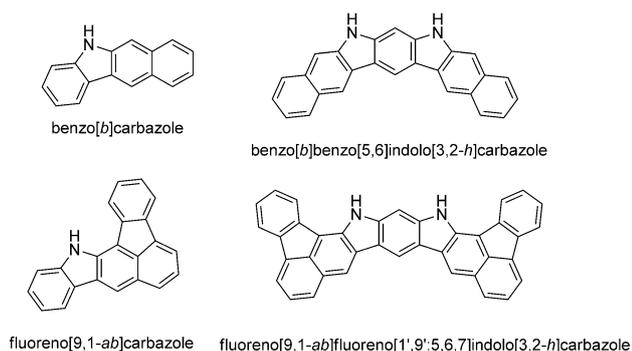
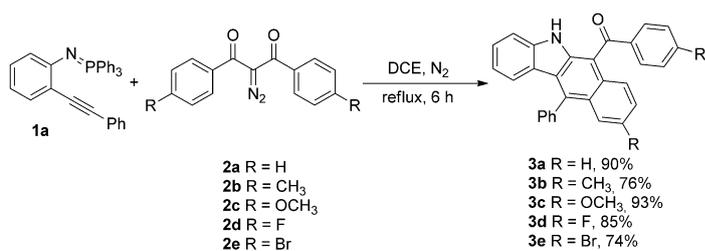


Figure 3. Carbazole-based skeletons that were synthesized in this work.

## Results and Discussion

Because  $\alpha$ -diazo-1,3-dicarbonyl compounds, which are typically prepared through a Regitz diazo-transfer reaction, could be smoothly transferred into ketenes through a well-known Wolff rearrangement reaction under thermal conditions,<sup>[6]</sup> compound **2a** was initially selected as the substrate for the in situ generation of ketenes. The reaction between compounds **1a** and **2a** was carried out in toluene under a nitrogen atmosphere at 90 °C for 6 h (Scheme 1). Compound **3a** was isolated in 83% yield and its benzo[*b*]carbazole structure was confirmed by analogy to the X-ray crystallographic analysis of its analogue **3i**.<sup>[9]</sup> Delighted by this result, we optimized the reaction conditions (for detailed optimization studies, see the Supporting Information, Table S1). By screening the solvent, reaction temperature, reaction time, and reaction atmosphere, the optimal reaction conditions were established. Thus, heating a mixture of com-

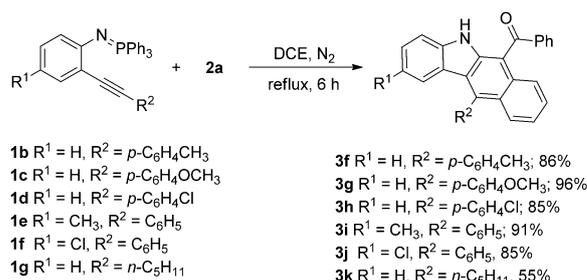


Scheme 1. Preparation of compounds **3a–3e**: Scope of the reaction with respect to compounds **2a–2e**.

pounds **1a** and **2a** in a 1:1 molar ratio in 1,2-dichloroethane (DCE) under a nitrogen atmosphere for 6 h afforded compound **3a** in 90% yield.

With the optimized reaction conditions in hand, we tested the substrate diversity. Firstly, the substituent effects of 2-diazo-1,3-diphenylpropane-1,3-dione on the reaction (Scheme 1) were investigated. No apparent electronic effects were observed. Both electron-donating (such as OCH<sub>3</sub>) and electron-withdrawing groups (such as F) on the phenyl rings of compounds **2a–2e** afforded their corresponding products (**3a–3e**) in moderate yields.

*N*-(triphenylphosphoranylidene) anilines **1b–1g** also gave the desired products in good-to-excellent yields (Scheme 2).

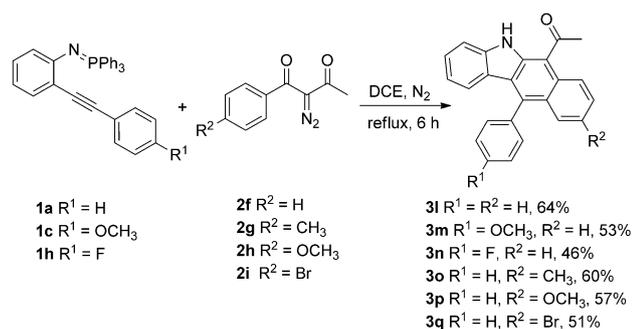
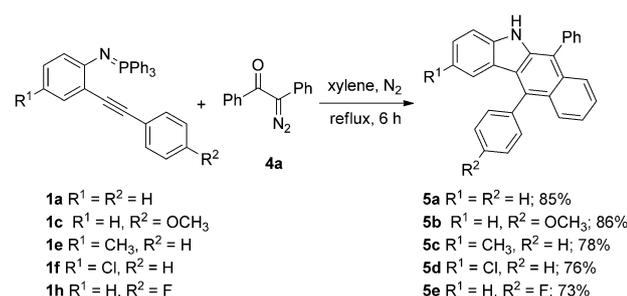
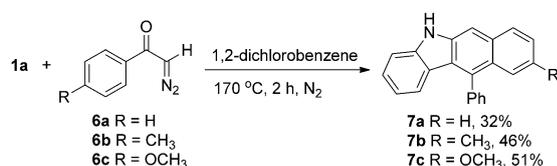


Scheme 2. Preparation of compounds **3f–3k**: Scope of the reaction with respect to compounds **1b–1g**.

Notably, 2-diazo-1-phenylbutane-1,3-diones **2f–2i** were also tolerated in this reaction and furnished their corresponding acetylated benzo[*b*]carbazoles in 46–64% yield (Scheme 3).

However, the reaction of 2-diazo-1,2-diphenylethaneone (**4a**) with compound **1a** did not occur in toluene at 90 °C (the starting materials were recovered), thus suggesting that a higher temperature was required for the Wolff rearrangement of compound **4a**. Later, compound **5a** was obtained in 85% yield from the reaction between compounds **4a** and **1a** at reflux in xylene for 6 h. In this way, analogous compounds **5b–5e** were also obtained in moderate yields (Scheme 4). Above all, benzoyl, acetyl, and phenyl groups were successfully installed at the 6-position of benzo[*b*]carbazole.

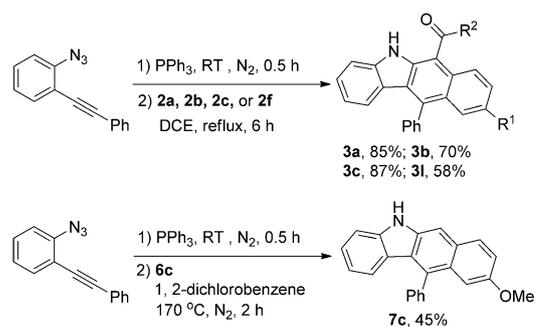
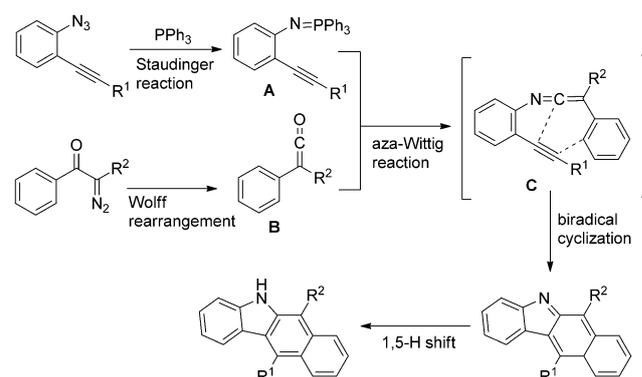
When 2-diazo-3-oxo-3-phenylpropanals **6a–6c** were applied to the reaction, the corresponding compounds (**7a–7c**) were afforded in relatively lower yields (Scheme 5). In these

Scheme 3. Preparation of compounds **3l–3q**: Scope of the reaction with respect to compounds **1** and **2f–2i**.Scheme 4. Preparation of compounds **5a–5e**: Scope of the reaction with respect to compound **1**.Scheme 5. Preparation of compounds **7a–7c**: Scope of the reaction with respect to compounds **6a–6c**.

cases, the substituent effect was apparent. The presence of electron-donating groups (such as 4-MeO) on the phenyl ring of 2-diazo-3-oxo-3-phenylpropanal promoted the reaction and afforded the product in 51% yield, whereas electron-withdrawing groups (such as 4-Br) did not afford any detectable product. These results may be attributed to a relatively low stability of the hydrogen-substituted ketenimines under high temperatures. Thus, various benzo[*b*]carbazoles without a substituent at their 6-position were prepared.

More conveniently, iminophosphoranes could be used without isolation and purification. After the direct treatment of the azide with triphenylphosphine in a 1:1 molar ratio at room temperature under a nitrogen atmosphere for 30 min,  $\alpha$ -diazo carbonyl was added. The reactions could be performed in one pot and afforded compounds **3a**, **3b**, **3c**, **3l**, and **7c** in moderate-to-good yields (Scheme 6).

Based on these results, a possible mechanism for this reaction is shown in Scheme 7: Firstly, the Staudinger reaction between phenyl azide and triphenylphosphine affords imino-

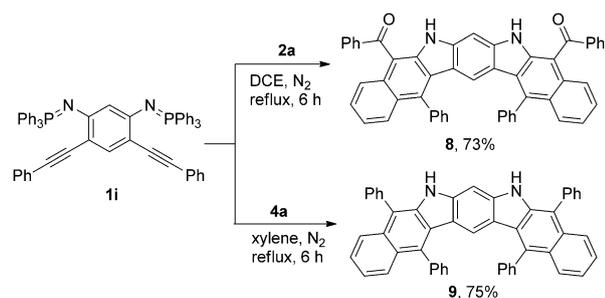
Scheme 6. One-pot preparation of compounds **3** and **7** from azides.Scheme 7. Proposed mechanism for the formation of benzo[*b*]carbazoles.

phosphorane **A**,<sup>[10]</sup> accompanied by the evolution of nitrogen gas. Meanwhile, the Wolff rearrangement of  $\alpha$ -diazo ketone generates ketene **B**, as expected. With both iminophosphorane **A** and ketene **B** in solution, a subsequent aza-Wittig reaction occurs to afford enyne-ketenimine intermediate **C**. Finally, intermediate **C** undergoes a biradical cyclization<sup>[8]</sup> and a sequential 1,5-H shift to furnish benzo[*b*]carbazoles.

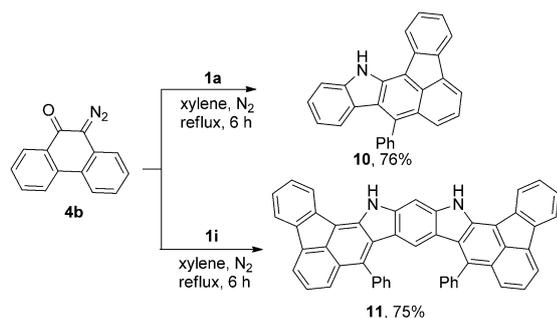
To achieve more-extended conjugation in the heteroarenes, compound **1i** was prepared. On treatment of this compound with compound **2a** at reflux in DCE under a nitrogen atmosphere for 6 h, a brand new backbone, benzo[*b*]benzo[5,6]indolo[3,2-*h*]carbazole (**8**), was efficiently constructed in 73% yield. Similarly, when compound **1i** was reacted with compound **4a**, benzo[*b*]benzo[5,6]indolo[3,2-*h*]carbazole (**9**), with four attached phenyl groups, was produced in 75% yield (Scheme 8).

Notably, 10-diazophenanthren-9(10H)-one (**4b**) could be prepared and used for the formation of the enyne-ketenimine. In these cases, compounds **10** and **11**, which contained a fluoreno[9,1-*ab*]carbazole substructure, were synthesized in 76% and 75% yield, respectively (Scheme 9).

Next, we investigated the photophysical properties of these benzo[*b*]carbazoles (Table 1). Compounds **3a–3k** absorbed light within the range 433–444 nm, which was ascribed to the  $\pi$ - $\pi^*$  transition of the benzo[*b*]carbazole backbone. These compounds emitted light within the range 490–



Scheme 8. Preparation of compounds **8** and **9**.



Scheme 9. Preparation of compounds **10** and **11**.

Table 1. Absorption and emission properties of the synthesized compounds.<sup>[a]</sup>

Compound	$\lambda_{\text{abs}}$ [nm] ( $\epsilon \times 10^{-3}$ ) <sup>[b]</sup>	$\lambda_{\text{ex}}$ [nm]	$\lambda_{\text{em}}$ [nm]	$\Phi$ [%] <sup>[c]</sup>
<b>3a</b>	433 (7.2)	433	507	0.05
<b>3b</b>	439 (6.7)	439	503	0.21
<b>3c</b>	441 (7.3)	441	503	0.31
<b>3d</b>	439 (8.3)	440	494	0.17
<b>3e</b>	444 (8.3)	440	516	0.03
<b>3f</b>	433 (8.1)	433	505	0.16
<b>3g</b>	436 (8.8)	436	508	0.13
<b>3h</b>	434 (8.4)	434	497	0.10
<b>3i</b>	440 (7.3)	440	511	0.21
<b>3j</b>	438 (8.4)	434	490	0.10
<b>3k</b>	435 (7.7)	435	521	0.19
<b>5a</b>	400 (8.1)	400	420	50.2
<b>5b</b>	400 (6.8)	395	422	62.5
<b>5c</b>	406 (7.9)	405	428	54.9
<b>5d</b>	407 (7.8)	407	428	51.5
<b>5e</b>	400 (6.4)	399	420	48.8
<b>7a</b>	392 (5.8)	389	410	28.7
<b>7b</b>	396 (5.3)	393	415	32.3
<b>7c</b>	403 (5.7)	402	432	41.4
<b>8</b>	445 (7.4)	422	471	0.11
<b>9</b>	421 (7.6)	412	441	48.9
<b>10</b>	444 (11.2)	444	471	35.0
<b>11</b>	436 (30.3)	436	509	22.8

[a] UV and FL spectra were recorded at a concentration of  $1 \times 10^{-5}$  M in  $\text{CH}_2\text{Cl}_2$ . [b] In  $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$ . [c] Quantum yields were calculated by using 9,10-diphenylethynylanthracene as an external standard.

521 nm, with quantum yields of 0.03–0.31 % in  $\text{CH}_2\text{Cl}_2$  (see the Supporting Information, Figure S1). Blue-shifted absorptions and emissions were observed for compounds **5a–5e** in comparison with those of compounds **3a–3k**. Compounds

**5a–5e** absorbed light at about 400 nm and emitted light at about 420 nm (see the Supporting Information, Figure S2). Without an electron-withdrawing carbonyl group at the 6-position of the benzo[*b*]carbazoles, intramolecular charge transfer was not observed in compounds **5a–5e**, which showed blue-shifted absorptions and emissions. However, the quantum yields of compounds **5a–5e** were significantly improved to 48.8–62.5%. The quantum yields were about 500-times higher in comparison to those substituted with a carbonyl groups. Without the phenyl group at the 6-position of benzo[*b*]carbazole, compounds **7a** and **7b** absorbed light at 392 and 396 nm and emitted light at 410 and 415 nm, respectively (see the Supporting Information, Figure S3). Compound **7c**, which contained a methoxy group at the 9-position of benzo[*b*]carbazole, absorbed light at 403 nm and emitted light at 432 nm; the quantum yields of compounds **7a–7c** were within the range 28.7–41.4%. Although compounds **8** and **9** possessed similar backbones, compound **9** emitted light at a shorter wavelength, yet with a much higher quantum yield (see the Supporting Information, Figure S4). This phenomenon was similar to the pair of compounds **5** and **3**. The molar absorptivities were significantly increased as the  $\pi$ -conjugation was extended in compounds **10** and **11**. Compound **11** absorbed light at a shorter wavelength, although it possessed a much-larger conjugation system (see the Supporting Information, Figure S5); compound **11** emitted light at 509 nm, with a larger Stokes shift.

Furthermore, compounds **5**, **7**, and **9–11** provided a wide range of maximum emission wavelengths (Figure 4), thus indicating that the emission from this family of compounds could be color-tunable for multipurpose applications.

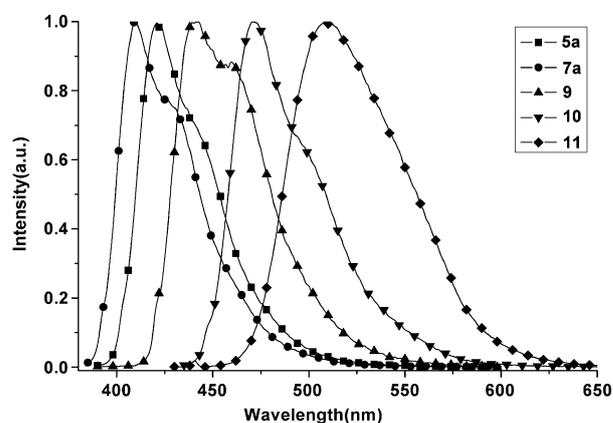


Figure 4. Normalized emission spectra of compounds **5a**, **7a**, and **9–11** in dilute  $\text{CH}_2\text{Cl}_2$ .

## Conclusion

We have developed a concise and efficient synthesis of benzo[*b*]carbazoles, benzo[*b*]benzo[5,6]indolo[3,2-*h*]carbazoles, fluoreno[9,1-*ab*]carbazoles, and fluoreno[9,1-*ab*]fluoreno[1',9':5,6,7]indolo[3,2-*h*]carbazoles. The one-pot reaction involved a tandem Wolff-rearrangement/aza-Wittig-

reaction/biradical-cyclization/1,5-H shift process. A variety of substrates were suitable for this reaction. The products have been demonstrated to emit light within the range 410–521 nm, with quantum yields of up to 62% in CH<sub>2</sub>Cl<sub>2</sub>. We believe that these compounds could find applications in optoelectronics devices for material science studies or as new fluorophores for the development of new fluorescent chemosensors in the life sciences.

## Experimental Section

**Typical procedure for the synthesis of phenyl(11-phenyl-5*H*-benzo[*b*]carbazol-6-yl)methanone (3a):** To an oven-dried Schlenk tube that was equipped with a magnetic stirrer bar were sequentially added compound **1a** (0.5 mmol), compound **2a** (0.6 mmol, 1.2 equiv), and DCE (2 mL) under a nitrogen atmosphere. Then, a condenser was fixed and the mixture was heated at reflux for 6 h. Upon completion of the reaction, the reaction system was cooled to RT. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 10:1) to give compound **3a** (179 mg, 90%) as a yellow solid. M.p. 205–206°C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 9.56 (s, 1H; NH), 7.81 (d, *J* = 7.0 Hz, 2H; CH), 7.76–7.74 (m, 2H; CH), 7.69–7.64 (m, 3H; CH), 7.58 (t, *J* = 7.3 Hz, 1H; CH), 7.54–7.53 (m, 2H; CH), 7.44 (t, *J* = 7.8 Hz, 2H; CH), 7.38–7.36 (m, 2H; CH), 7.29–7.25 (m, 2H; CH), 6.96–6.93 (m, 1H; CH), 6.83–6.82 ppm (d, *J* = 8.0 Hz, 1H; CH); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 198.0, 142.0, 140.7, 140.4, 139.1, 138.3, 132.7, 130.8, 129.8, 129.6, 129.0, 128.6, 128.2, 127.5, 127.0, 125.9, 125.5, 124.1, 123.1, 122.7, 122.6, 119.9, 112.7, 110.5 ppm; IR (neat):  $\tilde{\nu}$  = 3740, 3397, 3059, 1631, 1600, 1464, 1338, 1165, 746, 701 cm<sup>-1</sup>; HRMS (EI): *m/z* calcd for C<sub>29</sub>H<sub>19</sub>NO: 397.1467; found: 397.1464.

**Typical procedure for the synthesis of 6,11-diphenyl-5*H*-benzo[*b*]carbazole (5a):** To an oven-dried Schlenk tube that was equipped with a magnetic stirrer bar were sequentially added compound **1a** (0.5 mmol), compound **4a** (0.6 mmol, 1.2 equiv), and xylene (2 mL) under a nitrogen atmosphere. Then, a condenser was fitted and the mixture was heated at reflux for 6 h. Upon completion of the reaction, the reaction system was cooled to RT. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 20:1) to give compound **5a** (157 mg, 85%) as a white solid. M.p. 237–238°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.86 (d, *J* = 8.8 Hz, 1H; CH), 7.79–7.77 (m, 2H; NH, CH), 7.63–7.57 (m, 7H; CH), 7.55–7.51 (m, 3H; CH), 7.37 (t, *J* = 7.2 Hz, 1H; CH), 7.29–7.26 (m, 2H; CH), 7.17 (d, *J* = 8.0 Hz, 1H; CH), 6.88–6.87 ppm (m, 2H; CH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 142.0, 139.1, 137.1, 136.9, 133.4, 130.9, 130.6, 130.2, 129.3, 128.9, 127.84, 127.80, 127.7, 127.0, 126.6, 125.0, 124.4, 123.5, 123.2, 123.0, 122.5, 119.1, 117.6, 109.9 ppm; IR (neat):  $\tilde{\nu}$  = 3434, 1671, 1596, 1485, 1392, 1314, 1210, 1161, 1070, 1024, 744, 701 cm<sup>-1</sup>; HRMS (EI): *m/z* calcd for C<sub>28</sub>H<sub>19</sub>N: 369.1517; found: 369.1518.

**Typical procedure for the synthesis of 11-phenyl-5*H*-benzo[*b*]carbazole (7a):** To an oven-dried Schlenk tube that was equipped with a magnetic stirrer bar were sequentially added compound **1a** (0.5 mmol), compound **6a** (0.6 mmol, 1.2 equiv), and 1,2-dichlorobenzene (2 mL) under a nitrogen atmosphere. Then, a condenser was fitted and the mixture was stirred at 170°C for 2 h. Upon completion of the reaction, the reaction mixture was cooled to RT and purified directly by column chromatography on silica gel (petroleum ether/CH<sub>2</sub>Cl<sub>2</sub>, 5:1) to give compound **7a** (47 mg, 32%) as a white solid. M.p. 229–230°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.91 (d, *J* = 8.4 Hz, 1H; CH), 7.86 (brs, 1H; NH), 7.73–7.69 (m, 2H; CH), 7.64–7.58 (m, 3H; CH), 7.51–7.44 (m, 3H; CH), 7.38–7.34 (m, 1H; CH), 7.31–7.28 (m, 2H; CH), 6.93–6.86 ppm (m, 2H; CH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 142.1, 138.9, 133.9, 132.5, 130.1, 128.9, 127.8, 127.5, 127.0, 126.9, 126.3, 125.0, 123.6, 123.3, 123.1, 122.7, 119.1, 109.9, 104.8 ppm; IR (neat):  $\tilde{\nu}$  = 3403, 2923, 1628, 1470, 1402, 1343, 1316, 1269, 1146, 1079, 746, 703 cm<sup>-1</sup>; HRMS (EI): *m/z* calcd for C<sub>22</sub>H<sub>15</sub>N: 293.1204; found: 293.1201.

**Typical procedure for the synthesis of phenyl(11-phenyl-5*H*-benzo[*b*]carbazol-6-yl)methanone (3a) in one-pot manner by using an azide as a starting material:** To an oven-dried Schlenk tube that was equipped with a magnetic stirrer bar were sequentially added 1-azido-2-(phenylethynyl)-benzene (0.5 mmol), triphenylphosphine (0.5 mmol), and DCE (2 mL) under a nitrogen atmosphere. The mixture was stirred at RT for 0.5 h. Then, compound **2a** (0.6 mmol, 1.2 equiv) was added to the system and a condenser was fitted. The reaction mixture was continually stirred at reflux for 6 h. Upon completion of the reaction, the reaction mixture was cooled to RT. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 10:1) to give compound **3a** (169 mg, 85%) as a yellow solid.

**Procedure for the synthesis of (14,16-diphenyl-6,8-dihydrobenzo[*b*]benzo[5,6]indolo[3,2-*h*]carbazole-5,9-diyl)bis(phenylmethanone) (8):** To an oven-dried Schlenk tube that was equipped with a magnetic stirrer bar were sequentially added compound **1i** (0.5 mmol), compound **2a** (1.1 mmol, 2.2 equiv), and DCE (3 mL) under a nitrogen atmosphere. Then, a condenser was fitted and the mixture was heated at reflux for 6 h. Upon completion of the reaction, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>) to give compound **8** (262 mg, 73%) as a yellow solid. M.p. > 300°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 9.54 (s, 2H; NH), 7.80 (d, *J* = 7.2 Hz, 4H; CH), 7.63 (d, *J* = 8.4 Hz, 2H; CH), 7.59–7.52 (m, 4H; CH), 7.42 (t, *J* = 7.6 Hz, 4H; CH), 7.36 (t, *J* = 7.8 Hz, 4H; CH), 7.21–7.10 (m, 9H; CH), 7.05–7.01 (t, *J* = 7.6 Hz, 2H; CH), 6.81 ppm (s, 1H; CH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 198.4, 142.9, 141.1, 140.2, 137.5, 137.2, 132.8, 129.9, 129.3, 129.0, 128.7, 128.6, 128.1, 126.7, 125.5, 125.0, 123.7, 122.5, 118.0, 116.8, 112.3, 91.5 ppm; IR (neat):  $\tilde{\nu}$  = 3673, 1736, 1701, 1620, 1562, 1513, 1459, 1332, 1255, 1140, 755, 697 cm<sup>-1</sup>; HRMS (EI): *m/z* calcd for C<sub>52</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub>: 716.2464; found: 716.2486.

**Procedure for the synthesis of 5,9,14,16-tetraphenyl-6,8-dihydrobenzo[*b*]benzo[5,6]indolo[3,2-*h*]carbazole (9):** To an oven-dried Schlenk tube that was equipped with a magnetic stirrer bar were sequentially added compound **1i** (0.5 mmol), compound **4a** (1.1 mmol, 2.2 equiv), and xylene (2 mL) under a nitrogen atmosphere. Then, a condenser was fitted and the mixture was heated at reflux for 6 h, during which time, the product often precipitated from the reaction system. Upon completion of the reaction, the mixture was cooled to RT and filtered. The solid was washed with petroleum ether (3 × 5 mL) and dried in vacuum at 40°C for 2 h to give compound **9** (248 mg, 75%) as a yellow solid. M.p. > 300°C; <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO, 55°C): δ = 10.49 (s, 2H; NH), 7.69–7.65 (m, 6H; CH), 7.58–7.56 (m, 8H; CH), 7.50–7.47 (m, 5H; CH), 7.29–7.22 (m, 9H; CH), 7.16–7.13 ppm (t, *J* = 7.5 Hz, 2H; CH); <sup>13</sup>C NMR (125 MHz, [D<sub>6</sub>]DMSO, 55°C): δ = 144.0, 137.59, 137.57, 136.4, 130.9, 130.7, 129.4, 129.1, 128.8, 128.7, 128.6, 127.3, 127.1, 125.3, 123.9, 123.4, 122.7, 121.5, 117.1, 116.3, 115.9, 91.3 ppm; IR (neat):  $\tilde{\nu}$  = 3461, 2987, 1632, 1442, 1403, 1367, 1312, 1284, 1153, 1073, 753, 698 cm<sup>-1</sup>; HRMS (EI): *m/z* calcd for C<sub>50</sub>H<sub>32</sub>N<sub>2</sub>: 660.2565; found: 660.2545.

**Procedure for the synthesis of 8-phenyl-13*H*-fluoreno[9,1-*ab*]carbazole (10):** To an oven-dried Schlenk tube that was equipped with a magnetic stirrer bar were sequentially added compound **1a** (0.5 mmol), compound **4b** (0.6 mmol, 1.2 equiv), and xylene (2 mL) under a nitrogen atmosphere. Then, a condenser was fitted and the mixture was heated at reflux for 6 h. Upon completion of the reaction, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 20:1) to give compound **10** (140 mg, 76%) as a yellow solid. M.p. 224–225°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.32 (brs, 1H; NH), 8.05 (d, *J* = 6.8 Hz, 2H; CH), 7.92 (d, *J* = 7.2 Hz, 1H; CH), 7.70 (d, *J* = 8.0 Hz, 1H; CH), 7.59–7.58 (m, 3H; CH), 7.53–7.49 (m, 3H; CH), 7.45 (t, *J* = 7.2 Hz, 1H; CH), 7.40–7.34 (m, 3H; CH), 7.02 (d, *J* = 8.0 Hz, 1H; CH), 6.85 ppm (t, *J* = 7.4 Hz, 1H; CH); <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO): δ = 12.01 (s, 1H; NH), 8.62 (d, *J* = 7.6 Hz, 1H; CH), 8.30 (dd, <sup>1</sup>*J* = 5.6 Hz, <sup>2</sup>*J* = 2.4 Hz, 1H; CH), 8.23 (d, *J* = 7.2 Hz, 1H; CH), 7.74–7.68 (m, 3H; CH), 7.66–7.56 (m, 6H; CH), 7.48–7.44 (m, 2H; CH), 6.98–6.92 ppm (m, 2H; CH); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 142.0, 138.6, 137.9, 137.8, 135.3, 135.1, 134.8, 131.0, 130.3, 128.5, 128.0, 127.02, 126.97, 126.0, 125.8, 125.6, 124.7, 124.5, 123.4, 123.1, 121.7, 120.0, 113.4, 110.5 ppm; IR (neat):  $\tilde{\nu}$  = 3436, 2987, 1634, 1611, 1447, 1373, 1313,

1216, 1104, 1068, 1047, 741, 703 cm<sup>-1</sup>; HRMS (EI): *m/z* calcd for C<sub>28</sub>H<sub>17</sub>N: 367.1361; found: 367.1370.

**Procedure for the synthesis of 8,10-diphenyl-18,20-dihydrofluoreno[9,1-*ab*]fluoreno[1',9':5,6,7]indolo[3,2-*h*]carbazole (11):** To an oven-dried Schlenk tube that was equipped with a magnetic stirrer bar were sequentially added compound **1i** (0.5 mmol), compound **4b** (1.1 mmol, 2.2 equiv), and xylene (2 mL) under a nitrogen atmosphere. Then, a condenser was fitted and the mixture was heated at reflux for 6 h, during which time, the product often precipitated from the reaction system. Upon completion of the reaction, the mixture was cooled to RT and filtered. The solid was washed with petroleum ether (3 × 5 mL) and dried under vacuum at 40 °C for 2 h to give compound **11** (246 mg, 75%) as a brown solid. M.p. > 300 °C; <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO): δ = 12.03 (s, 2H; NH), 8.64 (d, *J* = 7.6 Hz, 2H; CH), 8.21 (t, *J* = 6.2 Hz, 4H; CH), 7.83 (s, 1H; CH), 7.66 (t, *J* = 7.4 Hz, 2H; CH), 7.62–7.58 (m, 3H; CH), 7.55–7.51 (m, 2H; CH), 7.48–7.44 (m, 6H; CH), 7.39 (s, 1H; CH), 7.37–7.35 ppm (m, 5H; CH); <sup>13</sup>C NMR (100 MHz, [D<sub>6</sub>]DMSO): δ = 144.0, 137.6, 137.2, 136.1, 135.9, 134.0, 133.5, 129.5, 129.4, 129.2, 128.5, 127.0, 125.6, 125.5, 125.1, 124.3, 124.2, 122.5, 121.7, 119.7, 117.4, 116.7, 111.9, 92.3 ppm; IR (neat):  $\tilde{\nu}$  = 3431, 2988, 1623, 1437, 1309, 1232, 1155, 1106, 1044, 751, 700 cm<sup>-1</sup>; HRMS (EI): *m/z* calcd for C<sub>50</sub>H<sub>28</sub>N<sub>2</sub>: 656.2252; found: 656.2232.

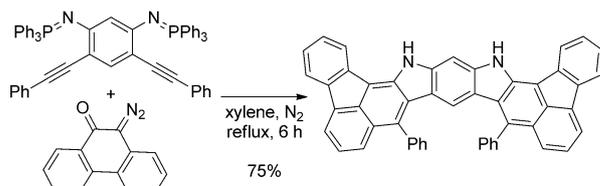
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 [9] For ORTEPs of compound **3i**, see the Supporting Information. CCDC-934436 (**3i**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/datarequest/cif](http://www.ccdc.cam.ac.uk/datarequest/cif).  
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**Lord of the rings:** A series of benzo[*b*]carbazoles were synthesized through a tandem Wolff-rearrangement/aza-Wittig-reaction/biradical-

ketenimine-cyclization/1,5-H-shift process. The products emitted intense light with high emission quantum yields (see scheme).

### Tandem Reactions

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*Y. Wang\** ..... ■■■■-■■■■

### Tandem Synthesis of Benzo[*b*]carbazoles and Their Photoluminescent Properties

