Synlett H. H. Do et al. Letter

One-Pot Palladium-Catalyzed Synthesis of Benzo[*b*]carbazolediones

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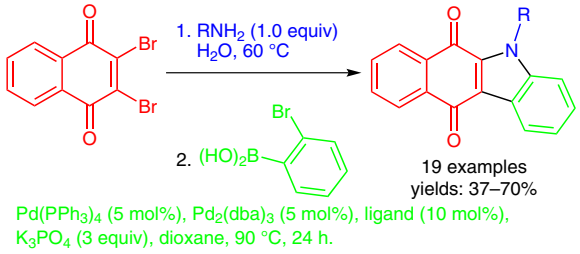


Received: 24.06.2015
Accepted after revision: 09.08.2015
Published online: 23.09.2015
DOI: 10.1055/s-0035-1560212; Art ID: st-2015-d0467-l

Abstract A palladium-catalyzed one-pot reaction for the synthesis of benzo[*b*]carbazolediones is described which proceeds by amination of 2,3-dibromonaphthoquinone, Suzuki cross-coupling with (2-bromophenyl)boronic acid, and subsequent intramolecular C–N Buchwald–Hartwig cyclization with amines.

Key words cyclizations, one-pot reaction, Suzuki–Miyaura reaction, Buchwald–Hartwig reaction, palladium

Many heterocyclic quinone derivatives are of considerable pharmacological relevance. They show, for example, antitumoral, antiprotozoal, and antibiotic activities.[1–3] Benzo[*b*]carbazoles combine the structural features of quinones and carbazoles and show excellent anticancer activities. The quinone moiety has a strong impact on the electronic properties of the carbazole system,[4] which has been demonstrated to play an important role with regard to the pharmacological activity. Benzo[*b*]carbazoles occur in various natural products, such as calothrixin B,[5] murrayaquinone A, ellipticine quinone,[6] and koeniginequinone A,[7] which exhibit strong anticancer activities (Figure 1).

For instance, calothrixin B, firstly isolated from *Calothrix* cyanobacteria in 1999, shows promising activity against human Hela cancer cells at a nanomolar scale.[5,8] 5*H*-Benzo[*b*]carbazoles have been previously prepared by radical cyclization reactions,[8a,b] lithiations,[8c] Friedel–Crafts acylations,[8d,e] or direct alkylations at a C–C double bond.[8f] In 2009, Sridharan et al. reported the synthesis of benzocarbazolediones by a palladium(II)-catalyzed oxidative biaryl coupling using copper(II) acetate as an oxidant.[8g] Most of these methodologies suffer from a limited substrate scope, tedious synthetic procedures, time-consuming purification

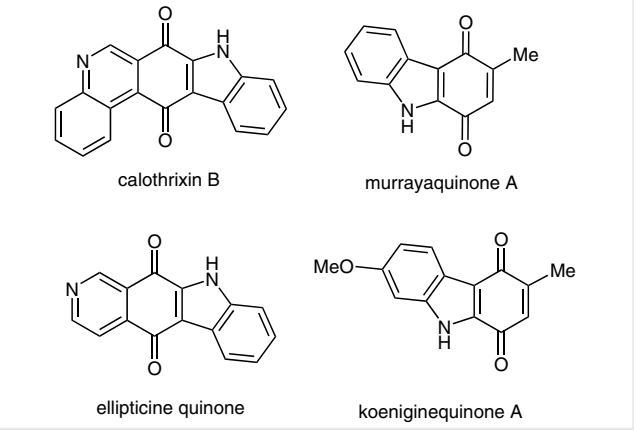


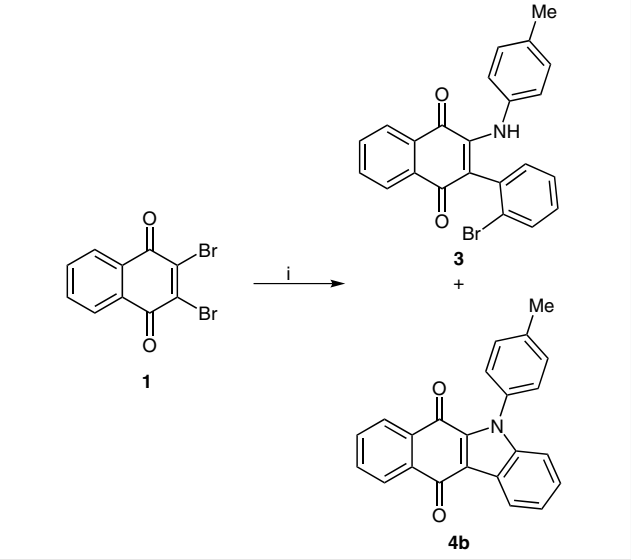
Figure 1 Structures of carbazolequinone alkaloids

of intermediates, or limited availability of the starting materials. Because of the great importance of benzo[*b*]carbazoles in medicinal and natural product chemistry, there is a considerable need for the development of convenient and efficient synthetic approaches to this type of molecule.

Recently, with the advance of palladium-catalyzed multicomponent reactions, synthesis of heterocycles is more approachable.[9a,b] We have previously reported the synthesis of diindolo[3,2-*b*:4,5-*b*′]thiophenes, indolo[2,3-*b*]quinoxalines,[9c] and 5-methyl-5,10-dihydroindolo[3,2-*b*]indoles[9d] based on the reaction of *o*-bromophenylboronic acid with tetrabromothiophene and 2,3-dibromoquinoxaline, and 2,3-dibromo-1-methyl-1*H*-indole, respectively,[9e] and subsequent cyclization by palladium-catalyzed twofold C–N coupling.[9f] Vanelle and co-workers recently reported the synthesis of 5-substituted 5*H*-benzo[*b*]carbazole-6,11-diones by a double Buchwald–Hartwig reaction.[9g] Herein, we wish to report a new and efficient two-step strategy for the chemoselective synthesis of benzo[*b*]carbazolediones

from readily available starting materials. While the application of our original strategy proved to be unsuccessful, we developed a new and convenient synthesis of benzo[*b*]carbazolediones based on the reaction of 2,3-dibromonaphthoquinone with amines in the first step and subsequent cyclization by domino C–C/C–N reactions in the second step.

Our initial idea was to carry out a onefold Suzuki–Miyaura reaction of 2,3-dibromonaphthoquinone with *o*-bromophenylboronic and to subsequently cyclize the intermediate. We have previously reported the synthesis of 2,3-diarylnaphthoquinones by double Suzuki–Miyaura reactions of 2,3-dibromonaphthoquinone.[10] Unfortunately, despite many efforts, the selective introduction of only one aryl group was not possible under a variety of conditions. Therefore, we changed the strategy by reversing the order of reactions. Our new procedure involves a catalyst-free amination of 2,3-dibromonaphthoquinone (**1**) in water, a Suzuki cross-coupling reaction, and a subsequent C–N cross-coupling reaction. The conditions were optimized for the synthesis of benzo[*b*]carbazoledione **4b** from **1** and *p*-toluidine (Scheme 1,Table 1). The first step proceeded, as previously reported,[11] in excellent yield and gave intermediate **2** without the need of any purification (Figure 2). Intermediate **2** could be isolated and characterized and, thus, presumably represents an intermediate of the reaction.



Scheme 1 Optimization of the synthesis of **4b**. *Reagents and conditions*: *i*) *p*-toluidine (1 equiv), H_2O (1 mL), 60 °C; *ii*) (2-bromophenyl)boronic acid (1.1 equiv), catalyst (5 mol%), ligand (10 mol%), K_3PO_4 (3 equiv), dioxane (10 mL), 90 °C, 24 h.

We next focused on the optimization of the Suzuki coupling and subsequent C–N cyclization. We initially applied the same conditions which we earlier used in reactions of (2-bromophenyl)boronic acid (Table 1, entry 1).[9] The catalyst $Pd(PPh_3)_4$, K_3PO_4, water, and dioxane were poured immediately into the reaction vessel after formation of intermediate **2**[12] in the initial step, and the mixture was stirred at 90 °C for 24 hours. Indeed, the reaction afforded the desired benzo[*b*]carbazoledione **4b**,[12] albeit in only 28% yield. In contrast, product **3** was isolated as the major product in 47% yield. This product was formed by Suzuki reaction, but the cyclization did not take place. Treatment of pure **3**[12] with the catalyst, following identical conditions, resulted in the formation of **4b** in 47% yield. This result suggested that **3** indeed represents an intermediate of the one-pot reaction and that the cyclization step represents the crucial step of the one-pot reaction which required further optimization.

Table 1 Optimization of the Synthesis of **4b**

Entry	Catalyst	Co-catalyst/ligand	Yield of **3** (%)[a]	Yield of **4b** (%)[a]
1	$Pd(PPh_3)_4$	–	47	28
2	$Pd(PPh_3)_4$	$Pd_2(dba)_3$ + SPhos	36	35
3	$Pd(PPh_3)_4$	$Pd_2(dba)_3$ + dppe	28	37
4	$Pd(PPh_3)_4$	RuPhos	42	31
5	$Pd(PPh_3)_4$	$Pd_2(dba)_3$ + RuPhos	17	47
6[b]	$Pd(PPh_3)_4$	$Pd_2(dba)_3$ + RuPhos	52	13
7[c]	$Pd(PPh_3)_4$	$Pd_2(dba)_3$ + RuPhos	24	26
8	–	$Pd_2(dba)_3$ + RuPhos	31	17
9[d]	$Pd(PPh_3)_4$	$Pd_2(dba)_3$ + RuPhos	24	16
10[e]	$Pd(PPh_3)_4$	$Pd_2(dba)_3$ + RuPhos	33	39
11[f]	$Pd(PPh_3)_4$	$Pd_2(dba)_3$ + RuPhos	16	19

[a] Isolated yield.
[b] 60 °C in the second step.
[c] 120 °C in the second step.
[d] THF as solvent.
[e] DMF as solvent.
[f] Toluene as solvent.

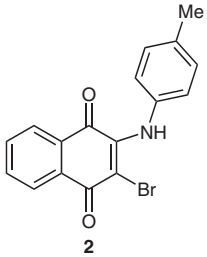


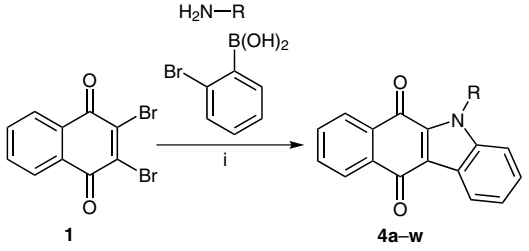
Figure 2 Structure of intermediate **2**

To promote the intramolecular C–N coupling, we decided to use $Pd_2(dba)_3$ as a co-catalyst together with common ligands used for C–N Buchwald–Hartwig cross-coupling reactions (Table 1, entries 2–5).[11] The isolated yields of **4b** obtained in the one-pot reaction of **1** could be improved to up to 47% (Table 1, entry 5) when $Pd_2(dba)_3$ and RuPhos were

used as co-catalyst along with $Pd(PPh_3)_4$ which was used for the Suzuki reaction (Table 1, entry 5). Interestingly, the yield decreased to 17% when the reaction was carried out without $Pd(PPh_3)_4$ (Table 1, entry 8). Besides, other solvents were used instead of dioxane, but none of them gave better results (Table 1, entries 9–11). The temperature was varied as well (Table 1, entries 5–7). When the reaction was carried out at 60 °C, **3** was isolated in 52% yield, while **4b** was isolated in only 13% yield (Table 1, entry 6). When the temperature was increased to 90 °C, the yield of desired product **4b** could be increased to 47%, while **3** was isolated in only 17% yield after 24 hours reaction time. The yield of **4b** was low when the temperature was increased to 120 °C (Table 1, entry 7).

To extend the scope of the reaction, we studied the reaction of **1** with various aromatic and aliphatic amines using our optimized conditions (Scheme 2,Table 2). The reactions of **1** with various amines worked gave the desired benzo[*b*]carbazolediones **4a**–**w**[12] in 37–70% yield. The reactions of **1** with aniline derivatives (Table 2, entries 1–7) gave moderate to good yields. Anilines substituted with an electron-withdrawing fluoro group (Table 2, entry 3) gave higher yields (60%) than anilines containing electron-donating substituents, although the latter represent better nucleophiles. However, 4-nitroaniline gave only 37% yield (Table 2, entry 4). No products at all could be isolated when 4-aminophenol, *m*-(trifluoromethyl)aniline, or *p*-cyanoaniline were employed, presumably due to their low nucleophilicity (Table 2, entries 8–10). Aliphatic and benzylic amines again worked well under our reaction conditions (Table 2, entries 11–22). The highest yield was achieved starting with 2-(3,4-dimethoxyphenyl)ethanamine to give product **4w** in 70% yield (Table 2, entry 22). The structure of product **4c** was independently confirmed by crystal-structure analysis (Figure 3).[13]

In summary, we have described a new and convenient synthesis of benzo[*b*]carbazolediones which relies on the three-component consecutive reaction of 2,3-dibromonaphthoquinone (**1**) with (2-bromophenyl)boronic acid and various amines. Benzo[*b*]carbazolediones represent an important type of core structure in medicinal and natural product chemistry.



Scheme 2 Synthesis of benzo[*b*]carbazolediones **4a**–**w**. *Reagents and conditions*: *i*, 1) *p*-toluidine (1 equiv), H_2O (1 mL), 60 °C; 2) (2-bromophenyl)boronic acid (1.1 equiv), $Pd(PPh_3)_4$ (5 mol%), $Pd_2(dba)_3$ (5 mol%), ligand (10 mol%), K_3PO_4 (3 equiv), dioxane (10 mL), 90 °C, 24 h.

Table 2 Synthesis of Benzo[*b*]carbazolediones **4a**–**w**

Entry	4	R	Yield (%)[a]
1	**4a**	Ph	51
2	**4b**	4-MeC_6H_4	49
3	**4c**	4-FC_6H_4	60
4	**4d**	4-$O_2NC_6H_4$	37
5	**4e**	4-$MeOC_6H_4$	47
6	**4f**	3,5-$Me_2C_6H_3$	47
7	**4g**	4-*t*-BuC_6H_4	48
8	**4h**	3-$F_3CC_6H_4$	0
9	**4i**	4-NCC_6H_4	0
10	**4j**	4-HOC_6H_4	0
11	**4k**	*n*-Bu	42
12	**4l**	*n*-C_5H_{11}	48
13	**4m**	*n*-C_6H_{13}	57
14	**4o**	*n*-C_7H_{15}	44
15	**4p**	*n*-C_8H_{17}	40
16	**4q**	Bn	52
17	**4r**	$Ph(CH_2)_2$	55
18	**4s**	$Ph(CH_2)_3$	48
19	**4t**	4-$FC_6H_4CH_2$	52
20	**4u**	4-$MeOC_6H_4CH_2$	64
21	**4v**	4-$F_3CC_6H_4CH_2$	59
22	**4w**	3,4-$(MeO)_2C_6H_3(CH_2)_2$	70

[a] Isolated yield.

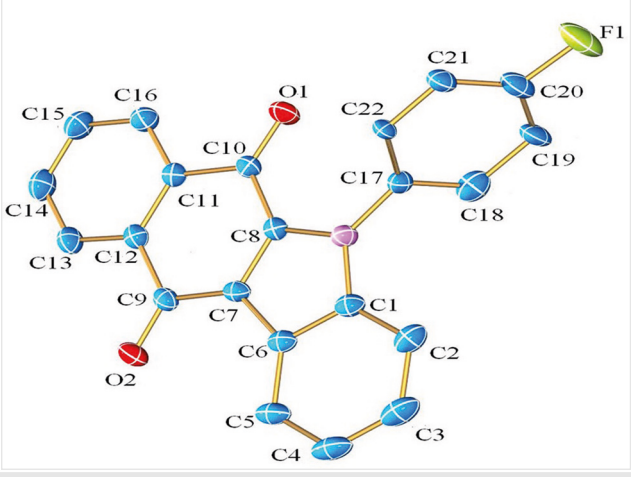


Figure 3 Crystal structure of **4c**[13]

Acknowledgment

Financial support by the State of Mecklenburg-Vorpommern (Landesgraduiertenstipendium for H.H.D.) and by the State of Vietnam (MOET scholarship for H.Q.T.) is gratefully acknowledged.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1560212.

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(12) **General Procedures for the Synthesis of 4a–w**
2,3-Dibromo-1,4-naphthoquinone 1 (0.3 mmol), the appropriate amine (0.3 mmol), and H_2O (1 mL) were poured into a pressure tube. The reaction was set up at 60 °C for 6 h, then, 2-bromophenylboronic acid (0.3 mmol), $Pd(PPh_3)_4$ (5 mol%), $Pd_2(dba)_3$ (5 mol%), RuPhos (10 mol%), K_3PO_4 (0.9 mmol), and 1,4-dioxane (10 mL) were added under argon. The tube was sealed with a Teflon valve and stirred at 90 °C. After 24 h, the mixture was allowed to reach r.t., diluted with H_2O, and extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude material was purified by flash column chromatography on silica gel.
2-Bromo-3-(*p*-tolylamino)naphthalene-1,4-dione (2)
Dark red solid; mp 157–158 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.19 (dd, ^3J = 7.6 Hz, ^4J = 1.3 Hz, 1 H), 8.14–8.05 (m, 1 H), 7.81–7.60 (m, 3 H), 7.15 (d, ^3J = 8.2 Hz, 2 H), 7.00 (d, ^3J = 8.3 Hz, 2 H), 2.36 (s, 3 H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 180.3, 177.4 (C=O), 144.4, 136.0 (C), 135.1 (CH), 135.0 (C), 133.0 (CH), 132.6, 130.0 (C), 129.2 (2CH), 127.5, 127.2 (CH), 125.0 (2 CH), 107.0 (C), 21.2 (CH_3). IR (ATR): ν = 3302 (m), 3223 (w), 3095 (w), 3024 (w), 2916 (w), 1672 (s), 1645 (m), 1630 (m), 1591 (m), 1581 (m), 1566 (m), 1547 (s), 1516 (m), 1497 (m), 1479 (m), 1454 (m), 1410 (m), 1369 (w), 1329 (m), 1298 (m), 1282 (m), 1263 (s), 1234 (s), 1188 (m), 1174 (m), 1161 (m), 1124 (s), 1111 (s), 1097 (m), 1078 (m), 1043 (m), 1026 (m), 1012 (m), 974 (m), 960 (m), 941 (m), 908 (m), 895 (m), 845 (m), 831 (m), 818 (m), 804 (m), 787 (s), 773 (s), 752 (m), 717 (s), 700 (vs), 679 (s), 660 (m), 636 (m), 625 (s), 604 (m), 542 (s), 530 (m) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 341 (73) [M$^+$], 326 (4), 262 (100), 247 (12), 219 (9), 178 (10), 158 (3), 130 (5), 105 (13), 91 (29), 76 (14), 65 (21), 50 (7), 39 (6). HRMS (EI): *m/z* calcd for $C_{17}H_{12}BrNO_2$ [M$^+$]: 341.00459; found: 341.00382.
2-(2-Bromophenyl)-3-(*p*-tolylamino)naphthalene-1,4-dione (3)
Red solid (21 mg, 17%); mp 175–176 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.23–8.11 (m, 2 H), 7.82–7.66 (m, 3 H), 7.27–7.20 (m, 1 H), 7.04–6.81 (m, 3 H), 6.78–6.62 (m, 4 H), 2.14 (s, 3 H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 182.9, 181.5 (C=O), 142.2, 135.2 (C), 135.1 (CH), 134.6, 134.3, 133.6 (C), 132.9, 132.4, 132.2 (CH), 130.4 (C), 128.7 (CH), 128.5 (2 CH), 126.9, 126.5, 126.5 (CH), 125.3 (C), 124.6 (2 CH), 115.9 (C), 20.9 (CH_3). IR (ATR): ν = 3331 (w), 3298 (s), 3064 (w), 3045 (w), 3010 (w), 2920 (w), 1674 (s), 1633 (m), 1612 (w), 1595 (m), 1569 (s), 1516 (s), 1505 (s), 1469 (s), 1425 (m), 1407 (m), 1379 (w), 1328 (s), 1294 (s), 1279 (s), 1253 (s), 1211 (m), 1173 (m), 1156 (m), 1133 (m), 1106 (s), 1052 (m), 1040 (m), 1029 (m), 1018 (s), 1006 (s), 966 (m), 942 (m), 920 (m), 863 (m), 850 (m), 835 (m), 811 (s), 795 (s), 748 (vs), 727 (s), 714 (vs), 670 (s), 655 (s), 647 (s), 632 (s), 599 (s), 578 (s), 530.5 (s) cm^{-1}. MS (EI, 70 eV): *m/z* (%) = 419 (4), 417 (5) [M$^+$], 339 (27), 338 (100), 324 (7), 323 (26), 295 (3) 294 (5), 281 (2), 266 (2), 239 (2), 221 (1), 204 (2), 190 (6), 176 (7), 169 (3), 165 (6), 161 (9), 147 (2), 139 (1), 104 (3), 91 (4), 76 (5), 65 (4), 51 (1), 39 (2). HRMS (EI): *m/z* calcd for $C_{23}H_{16}BrNO_2$ [M$^+$]: 417.03589; found: 417.03524; *m/z* calcd for $C_{23}H_{16}{}^{81}BrNO_2$ [M$^+$]: 419.03385; found: 419.03478.
5-(*p*-Tolyl)-5*H*-benzo[*b*]carbazole-6,11-dione (4b)
Orange solid (48 mg, 49%); mp 266–268 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.56–8.46 (m, 1 H), 8.30–8.19 (m, 1 H), 8.10–7.96 (m, 1 H), 7.79–7.58 (m, 2 H), 7.46–7.29 (m, 6 H), 7.21–7.09 (m, 1 H), 2.52 (s, 3 H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 181.7, 177.7 (C=O), 141.3, 139.4, 135.7, 134.3 (C), 134.2 (C), 133.8 (CH), 133.7 (C), 133.1 (CH), 130.3 (2 CH), 127.7 (CH), 127.4 (2 CH), 126.6 (CH), 126.4 (CH), 124.9 (CH), 124.0 (C), 123.8 (CH),119.9 (C), 112.3 (CH), 21.5 (CH_3). IR (ATR): ν = 3062 (w), 3050 (w), 2956 (w), 2921 (m), 2851 (m), 1732 (w), 1660 (m), 1641 (m), 1612 (w), 1588 (m), 1516 (s), 1488 (m), 1458 (s), 1418 (m), 1401 (m), 1350 (w), 1318 (m), 1310 (w), 1282 (m), 1158 (m), 1149 (m), 1131 (m), 1111 (m), 1095 (m), 1045 (s), 1017 (s), 1003 (s), 971 (m), 961.3 (m), 947 (m), 937 (m), 894 (m), 877 (m), 847 (m), 832 (s), 799 (s), 790 (s), 744 (vs), 725 (m), 709 (s), 697 (s), 664 (m), 648 (m), 640 (m), 610 (m), 596 (s), 571 (m) cm^{-1}. MS (EI, 70

eV): *m/z* (%) = 337 (100) [M$^+$], 322 (38), 308 (9), 278 (12), 252 (2), 239 (1), 204 (1), 190 (3), 176 (1), 168 (11), 163 (5), 152 (2), 147 (2), 139 (4), 132 (7), 126 (2), 113 (1), 91 (2), 76 (2), 65 (3), 51 (1), 39 (2). HRMS (EI): *m/z* calcd for $C_{23}H_{15}NO_2$ [M$^+$]: 337.10973; found: 337.10925.

(13) CCDC 1002799 contains all crystallographic details of this publication and is available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or can be ordered from the following address: Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: +44(1223)336033; or deposit@ccdc.cam.ac.uk.