Novel Synthesis of 5-Substituted 5*H*-Benzo[*b*]carbazole-6,11-diones via Double Buchwald–Hartwig Reaction

Khrystyna Bolibrukh,[a] Omar Khoumeri,[b] Svyatoslav Polovkovych,[a] Volodymyr Novikov,[a] Thierry Terme,[b] Patrice Vanelle*[b]

[a] Department of Technology of Biologically Active Substances, Pharmacy and Biotechnology, Lviv Polytechnic National University, Bandera Str. 12, Lviv, 79013, Ukraine
Fax +38(32)2582478; E-mail: vnovikov@polynet.lviv.ua

[b] Aix-Marseille Univ, CNRS, Institut de Chimie Radicalaire ICR, UMR 7273, Laboratoire de Pharmaco-Chimie Radicalaire, Faculté de Pharmacie, 27 Bd J. Moulin, Marseille Cedex 05, 13385, France
Fax +33(4)91794677; E-mail: patrice.vanelle@univ-amu.fr

Received: 23.07.2014; Accepted after revision: 11.09.2014

Abstract: 2-Bromo-3-(2-bromophenyl)naphthalene-1,4-dione was synthesized as a key precursor to obtain a number of functionalized benzo[*b*]carbazole-6,11-diones by double Buchwald–Hartwig coupling reaction.

Key words: quinone, anilines, Buchwald–Hartwig reaction, carbazole, one-pot

Quinones are not only important for synthesis but also possess a wide range of biological activities.[1] Nitrogen-containing heterocyclic quinones are known to demonstrate antibacterial, antifungal,[2] and cytotoxic activities.[3] The clinical significance of these heterocyclic quinones and the strong biological activity of some natural compounds of this group is raising interest in the synthesis of quinonoid compounds.[4] As a result of isolation and structural determination of a number of antibiotics and pigments, it has been established that heterocyclic quinones are widely distributed in nature.[5] This privileged core structure is common to numerous antitumor drugs and plays an important role in DNA intercalation.[6] Doxorubicin, mitomycin, actinomycin D, and streptonigrin are significant examples of these DNA-damaging agents (Figure 1). Moreover, several studies in vitro have shown that calothrixin[7] and renieramycin[8] have antiproliferative activity in different cancer cell lines.

Palladium-catalyzed coupling reactions have been widely used in organic chemistry and their success can be attributed to cost and to the tolerance of many functional groups.[9] In particular, the palladium-catalyzed Suzuki reaction, for the synthesis of biaryl compounds from aryl halides and boronic acids, has been successfully exploited in medicinal chemistry.[10] Furthermore, C–N bond formation via Buchwald–Hartwig reaction has recently emerged as an effective synthetic methodology for preparing aromatic and heteroaromatic amines.[11] However, only a few examples of double Buchwald–Hartwig coupling reactions have been reported.[12]

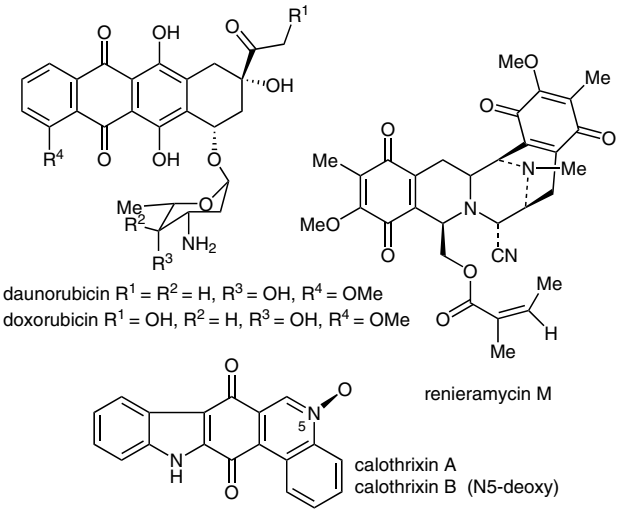


Figure 1 Structure of DNA-damaging agents

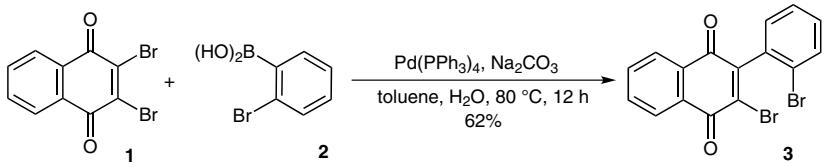
In continuation of our research program centered on the design and synthesis of novel bioactive molecules,[13] we were interested in developing a new approach utilizing quinone-based substrates to allow access to the corresponding functionalized benzo[*b*]carbazole-6,11-diones.

We report herein the first one-pot double palladium-catalyzed Buchwald–Hartwig coupling reaction in a quinonoid series for the synthesis of 5-substituted 5*H*-benzo[*b*]carbazole-6,11-diones.

The required starting material for this coupling reaction, 2-bromo-3-(2-bromophenyl)naphthalene-1,4-dione **3**, was synthesized by Suzuki–Myaura reaction between 2,3-dibromo-1,4-naphthoquinone (**1**) and 2-bromophenylboronic acid (**2**) using $Pd(PPh_3)_4$ as a catalyst and Na_2CO_3 as a base in a toluene–water mixture at 80 °C for 12 hours (Scheme 1).[14] Only the monoaryl product was obtained due to the sterically hindered bromine atom in the *ortho* position.[15]

We used this key 2-bromo-3-(2-bromophenyl)naphthalene-1,4-dione for the one-pot coupling reaction with aniline derivatives catalyzed by palladium. Heating by

SYNLETT 2014, 25, 2765–2768
Advanced online publication: 16.10.2014
DOI: 10.1055/s-0034-1379235; Art ID: st-2014-d0622-l



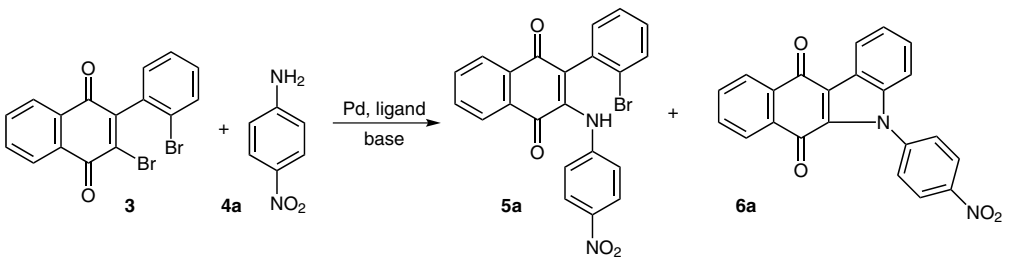
Scheme 1 Preparation of 2-bromo-3-(2-bromophenyl)naphthalene-1,4-dione

microwave irradiation was applied to decrease reaction time.

Depending on the conditions, the reaction gave a mixture of two products, the substituted naphthoquinone **5a** and the ring-closed benzocarbazoloquinone **6a** (Scheme 2). We initiated this study with 4-nitroaniline (**4a**) in the presence of $Pd(OAc)_2$ (15 mol%), BINAP (15 mol%), and K_2CO_3 (2 equiv) as a base at 80 °C in toluene for two hours (Table 1, entry 1). The reaction furnished only the cyclic 5-(4-nitrophenyl)-5*H*-benzo[*b*]-carbazole-6,11-dione (**6a**) in 83% yield. To optimize the one-pot coupling reaction, we employed different catalysts [$Pd(OAc)_2$, $Pd(PPh_3)_4$], in the presence of bases (K_2CO_3, Cs_2CO_3) at different temperatures and times of reaction. The best yield of 5-(4-nitrophenyl)-5*H*-benzo[*b*]carbazole-6,11-dione (**6a**, 85%) was observed using $Pd(OAc)_2$ (15 mol%), BINAP (15 mol%), and K_2CO_3 (2 equiv) as a base at 100 °C in toluene for two hours (Table 1, entry 2).[16] The same reaction conducted under conventional heating furnished the compound **6a** in 68% yield after 24 hours. Thus, microwave irradiation gave a superior yield in a shorter reaction time than conventional heating. It was observed that the formation of the 5-substituted 5*H*-benzo[*b*]carbazole-6,11-diones involved a stage where the intermediate product **5a** was formed. Increasing the reaction time to two hours led to the main product **6a**, instead of a mixture of **5a** and **6a**. When cesium carbonate was used as a base it gave a good yield of uncondensed product **5a**.

To determine the structure of intermediate compound **5a** we determined the X-ray structure of its analogue **5b** (Figure 2), which was obtained from 2-bromo-3-(2-bromophenyl)-naphthalene-1,4-dione (**3**) and aniline **4b** using $Pd(OAc)_2$ (15 mol%), BINAP (15 mol%), and K_2CO_3 (2 equiv) as a base at 100 °C in toluene for two hours (Table 1, entry 4).[17] This proved the attack by the aniline nitrogen on the C–Br bond in the quinone fragment, due to the higher reactivity of this position. The aryl substituents are twisted out of the plane of the naphthoquinone moiety.

To widen the scope of this method, the reaction of 2-bromo-3-(2-bromophenyl)naphthalene-1,4-dione (**3**) with a number of substituted anilines was performed under microwave irradiation. Interactions were carried out using optimized conditions (Table 1, entry 2), and the corresponding 5-substituted 5*H*-benzo[*b*]carbazole-6,11-di-



Scheme 2 Reaction of 2-bromo-3-(2-bromophenyl)naphthalene-1,4-dione (**3**) and 4-nitroaniline (**4a**)

Table 1 Optimization of the Reaction between 2-Bromo-3-(2-bromophenyl)naphthalene-1,4-dione and 4-Nitroaniline[a]

Entry	Temp (°C)	Time (h)	Catalyst, ligand	Base	Heating	Yield of **5a** (%)	Yield of **6a** (%)[b]
1	80	2	$Pd(OAc)_2$, BINAP	K_2CO_3	MW	0	83
2	100	2	$Pd(OAc)_2$, BINAP	K_2CO_3	MW	0	85
3	100	1	$Pd(OAc)_2$, BINAP	K_2CO_3	MW	34	52
4	100	2	$Pd(OAc)_2$, BINAP	Cs_2CO_3	MW	74	0
5	100	24	$Pd(OAc)_2$, BINAP	K_2CO_3	conventional	0	68
6	100	2	$Pd(PPh_3)_4$	K_2CO_3	MW	0	0

[a] All reactions are performed using 10 mol% Pd, 15 mol% ligand, and 2 equiv of base.
[b] All yields refer to chromatographically pure products based on substrate **3**.

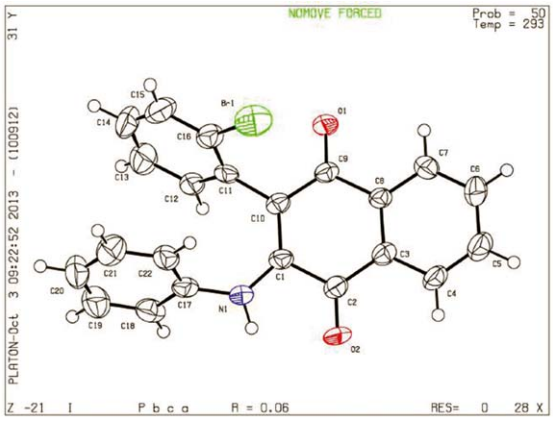


Figure 2 ORTEP view of intermediate **5b**

Table 2 Reaction of 2-Bromo-3-(2-bromophenyl)naphthalene-1,4-dione (**3**) with some Aniline Derivatives[a]

Entry	Aromatic amine	R	Product **6**	Yield (%)[b]
1	4-nitroaniline	4-NO_2	**6a**	85
2	aniline	H	**6b**	61
3	3-chloroaniline	3-Cl	**6c**	73
4	4-methyl-3-nitroaniline	3-NO_2, 4-Me	**6d**	75
5	3,4-dichloroaniline	3,4-Cl	**6e**	62
6	2-chloroaniline	2-Cl	**6f**	52
7	3-nitroaniline	3-NO_2	**6g**	85
8	2-cyano-4-nitroaniline	2-CN, 4-NO_2	**6h**	83
9	4-(trifluoromethyl)aniline	4-F_3C	**6i**	63
10	4-methoxy-2-nitroaniline	2-NO_2, 4-MeO	**6j**	70
11	2-methyl-3-nitroaniline	2-Me, 3-NO_2	**6k**	71

[a] All reactions were performed using 10 mol% Pd(OAc), 15 mol% BINAP, and 2 equiv of K_2CO_3 in toluene for 2 h at 100 °C under MW irradiation.
[b] All yields refer to chromatographically pure products based on substrate **3**.

ones **6a–k** were obtained in good yields (52–85%, Scheme 3, Table 2). The best yields were obtained with 3- and 4-nitroaniline (85%) or 2-cyano-4-nitroaniline (83%). Intermediate yields were obtained with methyl- or methoxy-substituted anilines (70–75%). With halogenated anilines (**4c**,**e**,**f**,**i**) yields of 52–73% were obtained.

In conclusion, in this study we prepared 2-bromo-3-(2-bromophenyl)naphthalene-1,4-dione (**3**) by Suzuki–Miyaura reaction from 2,3-dibromo-1,4-naphthoquinone and 2-bromoboronic acid. This product was a good candidate for the one-pot palladium-catalyzed double Buchwald reaction with substituted anilines to synthesize the corresponding 5-substituted 5*H*-benzo[*b*]carbazole-6,11-diones **6a–k**.

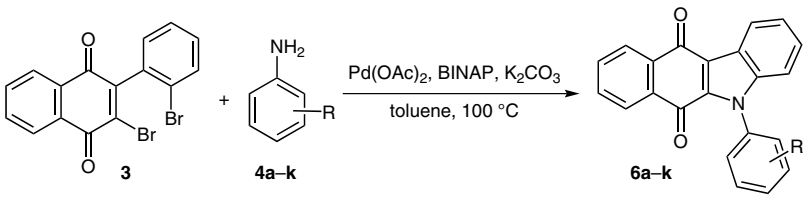
Acknowledgment

This work was supported by the Centre National de la Recherche Scientifique, Aix-Marseille University and Lviv Polytechnic National University. We express our thanks to V. Remusat for recording ^{1}H NMR and ^{13}C NMR spectra and T. Schembri for recording mass spectra. We are also grateful to the Ministry of Education and Science of Ukraine for supporting K. Bolibrukh's internship at Aix-Marseille University.

Supporting Information for this article is available online at http://www.thieme-connect.com/products/ejournals/journal/10.1055/s-00000083.

References and Notes

(1) Thomson, R. H. *Naturally Occurring Quinones IV*; Chapman and Hall: London, **1997**, 583.
(2) (a) Hong, S. Y.; Chung, K. H.; You, H. J.; Choi, I. H.; Chae, M. J.; Han, J. Y.; Jung, O. J.; Kang, S. J.; Ryu, C. K. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 3563. (b) Tandon, V. K.; Yadav, D. B.; Chaturvedi, A. K.; Shukla, P. K. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 3288. (c) Ryu, C. K.; Kang, H. Y.; Yi, Y. J.; Shin, K. H.; Lee, B. H. *Bioorg. Med. Chem.* **2000**, *10*, 1589. (d) Ryu, C. K.; Choi, K. U.; Shim, J. Y.; You, H. J.; Choi, I. H.; Chae, M. J. *Bioorg. Med. Chem.* **2003**, *11*, 4003. (e) Ryu, C. K.; Han, J. Y.; Jung, O. J.; Lee, S. K.; Lee, J. Y.; Jeong, S. H. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 679.
(3) (a) Kuo, S. C.; Ibuka, T.; Huang, L. J.; Lien, J. C.; Yean, S. R.; Hung, S. C.; Lednicer, D.; Morris-Natschke, S.; Lee, K. H. *J. Med. Chem.* **1996**, *39*, 1447. (b) Gomez-Monterrey, I. M.; Campiglia, P.; Mazzoni, O.; Novellino, E.; Diurno, M. V. *Tetrahedron Lett.* **2001**, *42*, 5755. (c) Gomez-Monterrey, I. M.; Grieco, P.; Diurno, M. V.; Bolongnese, A.; Colla, P. L.; Novellino, E. *Bioorg. Med. Chem.* **2003**, *11*, 3769. (d) Lee, H. J.; Kim, J. S.; Park, S. Y.; Suh, M. E.; Kim, H. J.; Seo, E. K.; Lee, C. O. *Bioorg. Med. Chem.* **2004**, *12*, 1623. (e) Manzanaro, S.; Vicent, M. J.; Martín, M. J.; Salvador-Tormo, N.; Pérez, J. M.; Blanco, M. M.; Avendaño, C.; Menéndez, J. C.; Fuente, J. A. *Bioorg. Med. Chem.* **2004**, *12*, 6505. (f) Benites, J.; Valderrama, J. A.; Rivera, P.; Rojo, L.;



Scheme 3 Synthesis of 5-substituted 5*H*-benzo[*b*]carbazole-6,11-diones **6a–k**

Campos, N.; Pedro, M.; Nascimento, M. S. *J. Bioorg. Med. Chem.* **2008**, *16*, 862.

(4) (a) Tandon, V. K.; Chhor, R. B.; Singh, R. V.; Rai, S.; Yadav, D. B. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 1079. (b) Tandon, V. K.; Singh, R. V.; Yadav, D. B. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 2901. (c) Tandon, V. K.; Yadav, D. B.; Singh, R. V.; Yaish, M.; Chaturvedi, A. K.; Shukla, P. K. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 3463. (d) Tandon, V. K.; Yadav, D. B.; Singh, R. V.; Chaturvedi, A. K.; Shukla, P. K. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 5324.

(5) Thomson, R. H. *Naturally Occuring Quinones IV*; Blackie Academic: London, **1997**.

(6) (a) Lin, A. J.; Cosby, L. A.; Shansky, C. W.; Sartorelli, A. C. *J. Med. Chem.* **1972**, *15*, 1247. (b) Moore, H. W. *Science* **1977**, *197*, 527. (c) Arcamone, F. *Cancer Res.* **1985**, *45*, 5995. (d) Monneret, C. *Eur. J. Med. Chem.* **2001**, *36*, 483.

(7) (a) Chen, X.; Smith, G. D.; Waring, P. *J. Appl. Phycol.* **2003**, *15*, 269. (b) Bernardo, P. H.; Chai, Ch. L. L.; Heath, G. A.; Mahon, P. J.; Smith, G. D.; Waring, P.; Wilkes, B. A. *J. Med. Chem.* **2004**, *47*, 4958.

(8) Cheun-Arom, T.; Chanvorachote, P.; Sirimangkalakitti, N.; Chuanasa, T.; Saito, N.; Abe, I.; Suwanborirux, K. *J. Nat. Prod.* **2013**, *76*, 1468.

(9) (a) Diederich, F.; Stang, P. J. *Metal-catalyzed cross-coupling reactions*; Wiley-VCH: Weinheim, **1998**. (b) King, A. O.; Yasuda, N. *Top. Organomet. Chem.* **2004**, *6*, 205. (c) Carey, J. S.; Laffan, D.; Thomson, C.; Williams, M. T. *Org. Biomol. Chem.* **2006**, *4*, 2337.

(10) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147. (c) Chemler, S. R.; Trauner, D.; Danishefsky, S. J. *Angew. Chem. Int. Ed.* **2001**, *40*, 4544.

(11) (a) Kosugi, M.; Kameyama, M.; Migita, T. *Chem. Lett.* **1983**, 927. (b) Wolfe, J. P.; Rennels, R. A.; Buchwald, S. L. *Tetrahedron* **1996**, *52*, 7525. (c) Hartwig, J. F. *Angew. Chem. Int. Ed.* **1998**, *37*, 2046. (d) Wolfe, J. P.; Wagaw, S.; Marcoux, J. F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805. (e) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852. (f) Hartwig, J. F. *Pure Appl. Chem.* **1999**, *71*, 1417. (g) Yang, B. H.; Buchwald, S. L. *J. Organomet. Chem.* **1999**, *576*, 125. (h) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2002**, *219*, 131.

(12) (a) Nozaki, K.; Takahashi, K.; Nakano, K.; Hiyama, T.; Tang, H.-Z.; Fujiki, M.; Yamaguchi, S.; Tamao, K. *Angew. Chem. Int. Ed.* **2003**, *42*, 2051. (b) Kitawaki, T.; Hayashi, Y.; Ueno, A.; Chida, N. *Tetrahedron* **2006**, *62*, 6792. (c) Zhou, Y.; Verkade, J. G. *Adv. Synth. Catal.* **2010**, *352*, 616.

(13) (a) Vanelle, P.; Maldonado, J.; Madadi, N.; Gueiffier, A.; Teulade, J.-C.; Chapat, J.-P.; Crozet, M. P. *Tetrahedron Lett.* **1990**, *31*, 3013. (b) Crozet, M. P.; Giraud, L.; Sabuco, J.-F.; Vanelle, P.; Barreau, M. *Tetrahedron Lett.* **1991**, *32*, 4125. (c) Delmas, F.; Gasquet, M.; Timon-David, P.; Madadi, N.; Vanelle, P.; Vaille, A.; Maldonado, J. *Eur. J. Med. Chem.* **1993**, *28*, 23. (d) Amiri-Attou, O.; Terme, T.; Vanelle, P. *Molecules* **2005**, *10*, 545. (e) Amiri-Attou, O.; Terme, T.; Vanelle, P. *Synlett* **2005**, 3047. (f) Montana, M.; Terme, T.; Vanelle, P. *Tetrahedron Lett.* **2006**, *47*, 6573. (g) Curti, C.; Laget, M.; Ortiz Carle, A.; Gellis, A.; Vanelle, P. *Eur. J. Med. Chem.* **2007**, *42*, 880. (h) Crozet, M. D.; Botta, C.; Gasquet, M.; Curti, C.; Remusat, V.; Hutter, S.; Chapelle, O.; Azas, N.; De Meo, M. P.; Vanelle, P. *Eur. J. Med. Chem.* **2009**, *44*, 653.

(14) **2-Bromo-3-(2-bromophenyl)naphthalene-1,4-dione (3)**
To a mixture of 2,3-dibromonaphthalene-1,4-dione (0.786 g, 2.49 mmol) and boronic acid (0.5 g, 2.49 mol%) in toluene (10 mL) was added $Pd(PPh_3)_4$ (0.172 g, 0.15 mmol) and 2 M aq Na_2CO_3 solution (5 mL). The resulting mixture was stirred at 80 °C overnight. After cooling the mixture was diluted with CH_2Cl_2, washed 3 times with H_2O, and dried over $MgSO_4$. After filtration and evaporation, the crude product was purified by silica gel chromatography (CH_2Cl_2–PE, 5:5) giving **3** as yellow crystals, mp 126 °C, yield 1.2 g (62%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.22 (dd, 1 H, *J* = 7.4, 1.8 Hz, ArH), 7.30–7.49 (m, 2 H, ArH), 7.7 (dd, 1 H, *J* = 7.9, 1.2 Hz, ArH), 7.76–7.85 (m, 2 H, Ar), 8.14–8.27 (m, 2 H, ArH). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 122.0 (C), 127.6 (2 × CH), 127.8 (CH), 128.3 (C), 129.9 (CH), 130.8 (CH), 131.3 (C), 131.7 (C), 132.9 (CH), 134.3 (CH), 134.7 (CH), 136.2 (C), 140.4 (C), 150.2 (C), 178.0 (CO), 180.6 (CO). Anal. Calcd for $C_{16}H_8Br_2O_2$: C, 49.02; H, 2.06. Found: C, 49.65; H, 1.98.

(15) (a) Best, W. M.; Sims, C. G.; Winslade, M. *Aust. J. Chem.* **2001**, *54*, 401. (b) Molina, T. M.; Navarro, C.; Moreno, A.; Csaky, A. G. *Org. Lett.* **2009**, *11*, 4938.

(16) **General Procedure for the Double Buchwald–Hartwig Reaction for the Synthesis of 5-Substituted 5*H*-benzo[*b*]carbazole-6,11-diones 6a–k**
A mixture of 2-bromo-3-(2-bromophenyl)naphthalene-1,4-dione (**3**, 0.1 g, 0.25 mmol), aniline (1.5 g, 0.38 mmol equiv) in toluene (10 mL), K_2CO_3 (105 g, 0.76 mmol), $Pd(OAc)_2$ (0.0098 g, 0.05 mmol), and BINAP (0.042 g, 0.06 mmol) was placed in a 4 mL sealed vial in a Biotage microwave-reactor cavity. The mixture was irradiated at 100 °C for 2 h. After cooling, the reaction mixture was diluted with CH_2Cl_2, washed with H_2O (3 × 40 mL), and dried over $MgSO_4$. After filtration and evaporation, the crude product was purified by silica gel chromatography (CH_2Cl_2–PE, 5:5).
5-(4-Nitrophenyl)-5*H*-benzo[*b*]carbazole-6,11-dione (6a)
Yellow solid; mp 287 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.15–7.20 (m, 1 H, ArH), 7.44–7.50 (m, 2 H, ArH), 7.65–7.79 (m, 5 H, ArH), 8.05 (dd, 2 H, *J* = 7.0, 1.7 Hz, ArH), 8.25 (dd, 2 H, *J* = 7.0, 1.0 Hz, ArH), 8.46–8.56 (m, 2 H, ArH). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 111.5 (CH), 124.1 (C), 124.2 (CH), 124.9 (2 × CH), 125.3 (CH), 126.7 (2 × CH), 128.4 (CH), 129.0 (2 × CH), 133.3 (2 × C), 133.5 (CH), 133.9 (C), 134.3 (CH), 135.3 (C), 140.5 (C), 142.5 (C), 147.9 (C), 177.7 (CO), 181.7 (CO). Anal. Calcd for $C_{22}H_{12}N_2O_4$: C, 71.74; H, 3.28; N, 7.61. Found: C, 71.66; H, 3.22; N, 7.61..

(17) Compounds **5a**,**b** were formed by the same protocol but using Cs_2CO_3 as base.
2-(2-Bromophenyl)-3-(4-nitrophenylamino)naphthlene-1,4-dione (5a)
Orange solid; mp 220 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.84 (d, 2 H, *J* = 8.9 Hz, ArH), 6.89–7.14 (m, 3 H, ArH), 7.31 (dd, 1 H, *J* = 8.0, 0.7 Hz, ArH), 7.70–7.87 (m, 4 H, ArH), 7.89 (s, 1 H, NH), 8.20 (dd, 2 H, *J* = 7.6, 1.4 Hz, ArH). ^{13}C NMR (50 MHz, $CDCl_3$) :δ = 119.4 (C), 122.8 (2 × CH), 123.5 (2 × CH), 124.6 (CH), 126.7 (CH), 127.2 (CH), 127.3 (CH), 129.9 (CH), 130.2 (C), 132.3 (CH), 133.0 (CH), 133.1 (C), 133.2 (C), 134.0 (C), 134.4 (CH), 140.8 (C), 143.1 (C), 143.7 (C), 181.6 (CO), 182.4 (CO). Anal. Calcd for $C_{22}H_{13}BrN_2O_4$: C, 58.82; H, 2.92; N, 6.24. Found: C, 85.77; H, 2.87; N, 6.33.
2-(2-Bromophenyl)-3-(phenylamino)naphthalene-1,4-dione (5b)
Red solid; mp 161 °C.^{1}H NMR (200 MHz, $CDCl_3$): δ = 6.78–6.99 (m, 7 H, ArH), 7.24 (d, 1 H, *J* = 9.6 Hz, ArH), 7.69–7.82 (m, 3 H, ArH), 8.18 (dd, 2 H, *J* = 7.6, 1.4 Hz, ArH). ^{13}H NMR (50 MHz, $CDCl_3$): δ = 116.3 (C), 124.5 (2 × CH), 125.2 (CH), 125.3 (C), 126.5 (CH), 126.6 (CH), 127.0 (CH), 127.9 (2 × CH), 129.0 (CH), 130.4 (C), 132.3 (CH), 132.5 (CH), 132.8 (CH), 133.5 (C), 134.5 (C), 135.1 (CH), 136.9 (C), 141.9 (C), 181.6 (CO), 188.9 (CO).

