

# A One-Pot Approach to 2-(N-Substituted Amino)-1,4-naphthoquinones with Use of Nitro Compounds and 1,4-Naphthoquinones in Water

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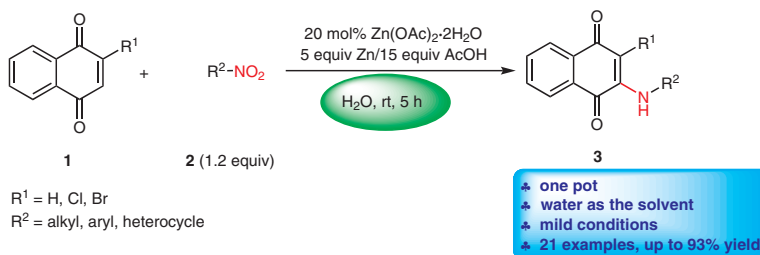
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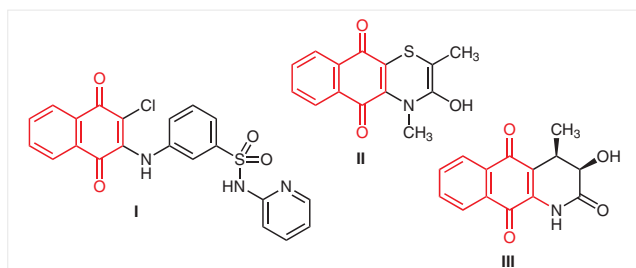
**Abstract** A one-pot synthesis of 2-(N-substituted amino)-1,4-naphthoquinones from 1,4-naphthoquinones and nitro compounds in water has been developed. This method features mild reaction conditions and provides aromatic nitro compounds with various functional groups such as halogens, methylthio, ester, amide, even allyl, propargyl, and heterocycles, as well as aliphatic nitro compounds that are well tolerated. This method can be scaled up and we conducted further transformation of the obtained 2-(N-substituted amino)-1,4-naphthoquinones to synthesize carbazolequinone derivatives.

**Key words** amines, 1,4-naphthoquinones, nitro compounds, one-pot reactions, reactions in water, carbazolequinones

Amines, especially secondary amines are prevalent in medicinal chemistry<sup>1</sup> and the development of new methods for their construction under mild conditions has received increasing attention in the past few years. Among numerous approaches there are alkylation,<sup>2</sup> amine-carbonyl reductive amination,<sup>3</sup> and C–N cross coupling.<sup>4</sup> Recently, Baran's group reported an amine synthesis by hydroamination utilizing olefins and nitroarenes.<sup>5</sup>

Despite the recent development, it is desirable to pursue the distant pathway to secondary amines. The secondary amine, 2-(N-substituted amino)-1,4-naphthoquinone motif is widespread in natural compounds and biologically active molecules (Figure 1).<sup>6</sup> It has been demonstrated that substituents such as the amino group in the naphthoquinone structure can change the electron-accepting capacity and therefore result in increased biological activities.<sup>7</sup> What's more, this type of compounds have shown interesting biological properties such as antibacterial,<sup>8</sup> antifungal,<sup>9</sup> antimalarial,<sup>10</sup> and anticancer activities.<sup>11</sup> Additionally, 2-(N-substituted amino)-1,4-naphthoquinone is also important as an intermediate for the synthesis of biologically active compounds.<sup>12</sup> Therefore, the synthesis of 2-(N-substituted amino)-1,4-naphthoquinone has drawn considerable attention. Generally, 2-(N-substituted amino)-1,4-naphthoquinones are prepared by 1,4-nucleophilic addition of amines to naphthoquinones in the presence of catalysts such as CeCl<sub>3</sub>·7H<sub>2</sub>O,<sup>13</sup> FeCl<sub>3</sub>,<sup>14</sup> Cu(OAc)<sub>2</sub>,<sup>14</sup> I<sub>2</sub>,<sup>15</sup> and HClO<sub>4</sub>–SiO<sub>2</sub>.<sup>16</sup> Nucleophilic substitution of amines with 2-halogen-atom-substituted 1,4-naphthoquinones also can afford 2-(N-substituted amino)-1,4-naphthoquinones.<sup>17,18</sup> Moreover, the synthesis of 2,3-diamino-1,4-naphthoquinone through palladium-catalyzed coupling of 2-amino-3-chloro-1,4-naphthoquinones with amines has been reported.<sup>19</sup> However, in

the previously reported methods, the source of the nitrogen atom of 2-(N-substituted amino)-1,4-naphthoquinone is limited to amines. It is important to further broaden the range of substrates for the synthesis of 2-(N-substituted amino)-1,4-naphthoquinones. In continuation of the research about the reduction of nitro compounds,<sup>20</sup> we attempted to combine the nitro reduction with the 1,4-nucleophilic addition of amines to 1,4-naphthoquinones. Fortunately, 2-(N-substituted amino)-1,4-naphthoquinones were obtained in good yield in one-pot reactions under very mild conditions. Most importantly, utilizing this protocol to prepare complex natural product structures can avoid the external protection and deprotection steps of amine substrates. Recently, with an objective to develop environmentally benign reaction conditions, water has been shown to be an attractive solvent because of its non-toxicity, cost effectiveness, and eco-friendly properties.<sup>21</sup> Herein, we report the one-pot synthesis of 2-(N-substituted amino)-1,4-naphthoquinones from 1,4-naphthoquinones and nitro compounds with water as the solvent.



**Figure 1** Biological compounds containing a naphthoquinone skeleton

We commenced our study with the reaction of 1,4-naphthoquinone **1a** and nitrobenzene **2a** using different catalysts, hydrogen sources, metals, and solvents (Table 1). Initially, in the presence of Lewis acid  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Zn}/\text{AcOH}$  system, various solvents were investigated. Low yields were obtained in the case of MeOH, EtOH, THF, and DCM (entries 1, 2, 4, 5). When HFIP (hexafluoroisopropanol) and  $\text{H}_2\text{O}$  were employed, compound **3aa** was obtained in similar yields (entries 3, 6). However,  $\text{H}_2\text{O}$  was preferred over HFIP because of the very low price and environmental friendliness. What's more, several Lewis acids were examined as the catalysts for the reaction and they were less effective than  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (entries 7–10). When we carried out the reaction in the absence of a catalyst, the product **3aa** was observed in 22% yield (entry 11). No reaction occurred when  $\text{Zn}$  dust was replaced by  $\text{Fe}$  powder (entry 12). Additionally, the utilization of other hydrogen sources such as  $\text{CF}_3\text{COOH}$  and 2 N HCl solution did not provide the desired product (entries 13, 14). When the amount of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  was decreased to 15 and 10 mol%, the product was obtained in 75 and 50% yield, respectively (entries 15 and 16). Finally, we chose the reaction of 1,4-naphthoquinone **1a** (1.0 equiv) with nitrobenzene **2a** (1.2 equiv) in

the presence of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (20 mol%) and  $\text{Zn}$  (5 equiv)/ $\text{AcOH}$  (15 equiv) in  $\text{H}_2\text{O}$  at room temperature for five hours as the optimized conditions.

**Table 1** Optimization Experiments<sup>a</sup>

Entry	Catalyst (mol%)	Metal	[H] <sup>b</sup>	Solvent (0.5 M)	Yield (%) <sup>c</sup>
1	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (20)	Zn	AcOH	MeOH	25
2	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (20)	Zn	AcOH	EtOH	37
3	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (20)	Zn	AcOH	HFIP	92
4	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (20)	Zn	AcOH	THF	39
5	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (20)	Zn	AcOH	DCM	28
6	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (20)	Zn	AcOH	$\text{H}_2\text{O}$	93
7	$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (20)	Zn	AcOH	$\text{H}_2\text{O}$	59
8	$\text{FeCl}_3$ (20)	Zn	AcOH	$\text{H}_2\text{O}$	66
9	$\text{Zn}(\text{OTf})_2$ (20)	Zn	AcOH	$\text{H}_2\text{O}$	44
10	$\text{ZnCl}_2$ (20)	Zn	AcOH	$\text{H}_2\text{O}$	36
11	–	Zn	AcOH	$\text{H}_2\text{O}$	22
12	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (20)	Fe	AcOH	$\text{H}_2\text{O}$	–
13	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (20)	Zn	$\text{CF}_3\text{COOH}$	$\text{H}_2\text{O}$	–
14	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (20)	Zn	2 N HCl	$\text{H}_2\text{O}$	–
15	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (15)	Zn	AcOH	$\text{H}_2\text{O}$	75
16	$\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (10)	Zn	AcOH	$\text{H}_2\text{O}$	50

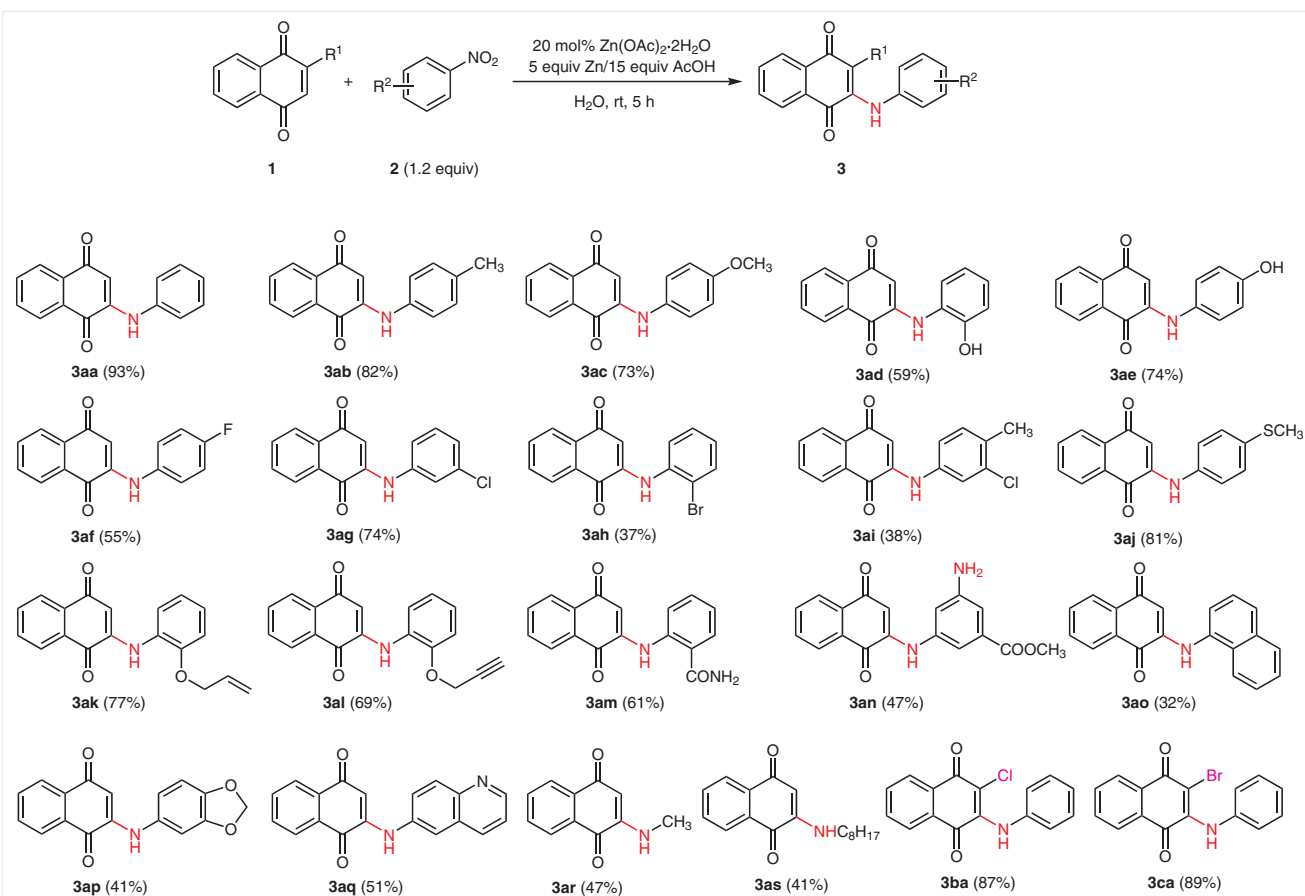
<sup>a</sup> Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol, 1.2 equiv),  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.6 mmol, 20 mol%),  $\text{Zn}$  dust (1.5 mmol, 5 equiv), AcOH (4.5 mmol, 15 equiv),  $\text{H}_2\text{O}$  (0.6 mL), rt, 5 h.

<sup>b</sup> Hydrogen source.

<sup>c</sup> Isolated yield.

Having the optimal reaction conditions in hand, we investigated a series of nitro compounds as the substrates (Scheme 1). Nitrobenzene could engage in this process to deliver the corresponding product **3aa** in 93% yield and nitrobenzene with substituents such as methyl, methoxy, and hydroxyl were also amenable to this protocol, furnishing the desired products in moderate to good yield (**3ab–ae**).

Compared with 4-nitrophenol, the reactivity of 2-nitrophenol was lower, which could be attributed to the hindering effect of the neighboring hydroxyl group. Nitro compounds containing halogen atoms were compatible with this transformation and delivered the products in low to moderate yields without dehalogenation (**3af–ai**). In the presence of a methylthio group, the reaction proceeded smoothly to deliver compound **3aj** in 81% yield. Notably, reducible functionalities such as allyl and propargyl were also tolerated in this process (**3ak, 3al**). Nitrobenzene with an



**Scheme 1** Substrate scope for the synthesis of 2-(N-substituted amino)-1,4-naphthoquinones. Reaction conditions: **1** (0.3 mmol), **2** (0.36 mmol, 1.2 equiv),  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.6 mmol, 20 mol%), Zn dust (1.5 mmol, 5 equiv),  $\text{AcOH}$  (4.5 mmol, 15 equiv),  $\text{H}_2\text{O}$  (0.6 mL), rt, 5 h. Isolated yields are given.

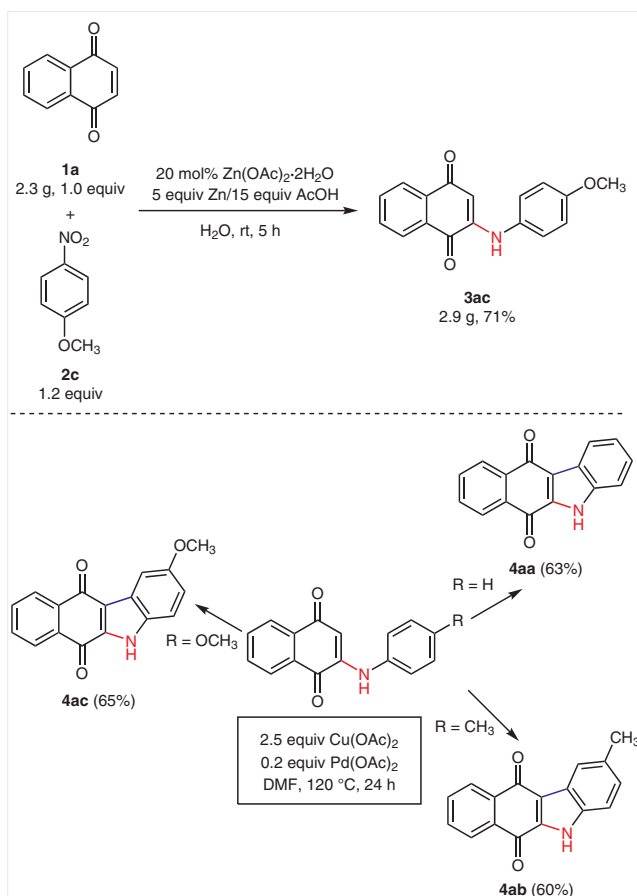
amide functional group could give the desired product **3am** in 61% yield. In the case of methyl 3,5-dinitrobenzoate, compound **3an** was obtained in 47% yield with two nitro groups being transformed to amino groups. Compound **3ao** could be prepared with use of 1-nitronaphthalene in 32% yield. This transformation could also be successfully extended to heterocyclic nitro compounds to form the desired products (**3ap**, **3aq**). It is noteworthy that aliphatic nitro compounds could also serve as viable acceptor in this process providing the desired products (**3ar**, **3as**). Subsequently, several substituted 1,4-naphthoquinones as the substrates were also studied. It is known that the halogen atoms on the quinonoid ring are very reactive toward nucleophiles.

Particularly, the reaction of 2-halogen-atom-substituted 1,4-naphthoquinones with nitrobenzene proceeded effectively to provide the desired products in high yields with the halogen atom remaining unchanged, thus offering opportunities for further derivatization (**3ba**, **3ca**). Furthermore, a scale-up reaction was conducted to evaluate the applicability of the protocol (Scheme 2). When we performed the reaction with 1,4-naphthoquinone **1a** and 1-methoxy-

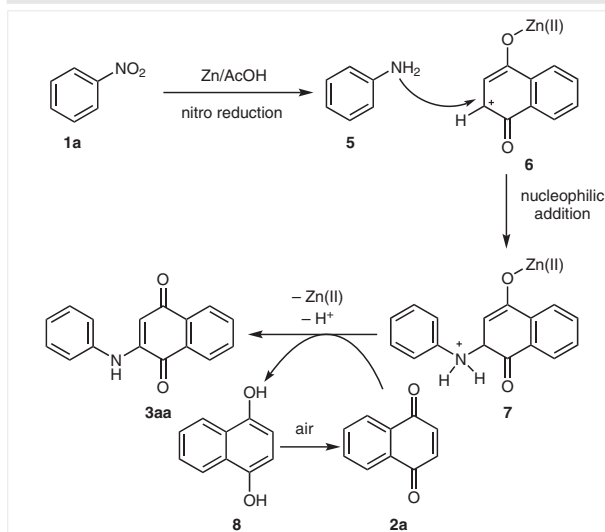
4-nitrobenzene **2c** on gram scale, the corresponding product **3ac** was isolated in 71% yield. Furthermore, a Pd-catalyzed oxidative coupling reaction of the obtained 2-amino-1,4-naphthoquinones allowed the generation of carbazole-quinone derivatives in moderate yields (Scheme 2).<sup>22</sup> Hence, we provided a rapid route for the synthesis of carbazolequinone derivatives with nitro compounds as the nitrogen source. The carbazolequinone derivatives have several bioactivities such as anticancer and GSK $\beta$  (a serine kinase) inhibition activities.<sup>23,24</sup>

On the basis of previous literature,<sup>13–16</sup> a plausible mechanism is proposed (Scheme 3). First, in the presence of  $\text{Zn}/\text{AcOH}$  system, the nitro compound **1a** is reduced to the corresponding amine **5**. With Lewis acid  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ , 1,4-naphthoquinone is activated to generate the complex **6**, and the intermediate reacts with aniline through 1,4-nucleophilic addition to give the adduct **7**. Then, compound **7** can be oxidized to afford **3aa** in the presence of molecular oxygen along with losing a proton and the Lewis acid.

In summary, an efficient protocol for the preparation of 1,4-naphthoquinone derivatives in one pot with use of 1,4-naphthoquinone and nitro compounds has been developed.



**Scheme 2** Scale-up reaction and application to carbazolequinones with 2-(N-substituted amino)-1,4-naphthoquinones



**Scheme 3** Proposed mechanism

This protocol features mild conditions and water as the solvent. The reaction conditions are suitable for aromatic nitro compounds containing various functional groups and ali-

phatic nitro compounds. Additionally, a scale-up reaction was conducted and carbazolequinone derivatives were obtained successfully.

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## Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0037-1610689>.

## References and Notes

- (1) Ishihara, Y.; Montero, A.; Baran, P. S. *The Portable Chemist's Consultant*; Apple Publishing Group: Cupertino CA, **2013**.
- (2) (a) Marson, C. M.; Savy, P. In *Comprehensive Organic Functional Group Transformations II*; Ramsden, C., Ed.; Elsevier: Oxford, **2005**, 255. (b) Guillena, G.; Ramón, D. J.; Yus, M. *Chem. Rev.* **2010**, *110*, 1611.
- (3) Baxter, E. W.; Reitz, A. B. *Org. React.* **2004**, *59*, 1.
- (4) (a) Surry, D. S.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2008**, *47*, 6338. (b) Hartwig, J. F. *Acc. Chem. Res.* **2008**, *41*, 1534.
- (5) Gui, J.; Pan, C.-M.; Jin, Y.; Qin, T.; Lo, J. C.; Lee, B. J.; Spengel, S. H.; Mertzman, M. E.; Pitts, W. J.; La Cruz, T. E.; Schmidt, M. A.; Darvatar, N.; Natarajan, S. R.; Baran, P. S. *Science* **2015**, *348*, 886.
- (6) (a) Morton, R. A. *Biochemistry of Quinones*; Academic Press: New York, **1965**. (b) Kapadia, G. J.; Azuine, M. A.; Balasubramanian, V.; Sridhar, R. *Pharmacol. Res.* **2001**, *43*, 363.
- (7) (a) Jordao, A. K.; Novais, J.; Leal, B.; Escobar, A. C.; dos Santos, H. M.; Castro, H. C.; Ferreira, V. F. *Eur. J. Med. Chem.* **2013**, *63*, 196. (d) Wellington, K. W.; Kolesnikova, N. I. *Bioorg. Med. Chem.* **2012**, *20*, 4472.
- (8) (a) Aguilar-Martínez, M.; Cuevas, G.; Jiménez-Estrada, M.; González, I.; Lotina-Hennsen, B.; Macías-Ruvalcaba, N. J. *Org. Chem.* **1999**, *64*, 3684.
- (9) (a) Brandelli, A.; Bizani, D.; Martinelli, M.; Stefani, V.; Gerbase, A. E. *Rev. Bras. Cienc. Farm.* **2004**, *40*, 247. (b) Neves, A. P.; Barbosa, C. C.; Greco, S. J.; Vargas, M. D.; Visentin, L. C.; Pinheiro, C. B.; Mangrich, A. S.; Barbosa, J. P.; Da Costa, G. L. *J. Braz. Chem. Soc.* **2009**, *20*, 712.
- (10) (a) Tandon, V. K.; Chor, R. B.; Singh, R. V.; Raib, S.; Yadava, D. B. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 1079. (b) Tandon, V. K.; Yadav, D. B.; Singh, R. V.; Chaturvedi, A. K.; Shukla, P. K. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 5324.
- (11) Kapadia, G. J.; Azuine, M. A.; Balasubramanian, V.; Sridhar, R. *Pharmacol. Res.* **2001**, *43*, 363.
- (12) Francisco, A. I.; Casellato, A.; Neves, A. P.; de Mesquita Carneiro, J. W.; Vargas, M. D.; do Canto Visentin, L.; Magalhães, A.; Câmara, C. A.; Pessoa, C.; Costa-Lotufo, L. V.; Marinho-Filho, J. D. B.; De Moraes, M. O. *J. Braz. Chem. Soc.* **2010**, *21*, 169.
- (13) Aristoff, P. A.; Johnston, P. D. *J. Org. Chem.* **1992**, *57*, 6234.
- (14) Leyva, E.; López, L. I.; Loredó-Carrillo, S. E.; Rodríguez-Kessler, M.; Montes-Rojas, A. *J. Fluorine Chem.* **2011**, *132*, 94.

- (14) (a) Leyva, E.; Baines, K. M.; Espinosa-González, C. G.; Magaldi-Lara, D. A.; Loredó-Carrillo, S. E.; De Luna-Méndez, T. A.; López, L. I. *J. Fluorine Chem.* **2015**, *180*, 152. (b) da Silva Lisboa, C.; Santos, V. G.; Vaz, B. G.; de Lucas, N. C.; Eberlin, M. N.; Garden, S. *J. J. Org. Chem.* **2011**, *76*, 5264.
- (15) Huang, H.-M.; Li, Y.-J.; Dai, Y.-P.; Yu, W.-B.; Ye, Q.; Gao, J.-R. *J. Chem. Res.* **2013**, *37*, 34.
- (16) Sharma, U.; Katoch, D.; Sood, S.; Kumar, N.; Singh, B.; Thakur, A.; Gulati, A. *Indian J. Chem.* **2013**, *52B*, 1431.
- (17) Couladouros, E. A.; Plyta, A. F.; Papageorgiou, V. P. *J. Org. Chem.* **1996**, *61*, 3031.
- (18) Leyva, E.; Baines, K. M.; Espinosa-González, C. G.; López, L. I.; Magaldi-Lara, D. A.; Leyva, S. *Tetrahedron Lett.* **2015**, *56*, 5248.
- (19) Wang, X. L.; Zheng, X. F.; Wang, L.; Reiner, J.; Xie, W. L.; Chang, J. B. *Synthesis* **2007**, 989.
- (20) Chen, X.-L.; Ai, B.-R.; Dong, Y.; Zhang, X.-M.; Wang, J.-Y. *Tetrahedron Lett.* **2017**, *58*, 3646.
- (21) (a) Li, C. *J. Chem. Rev.* **1993**, *93*, 2023. (b) Butler, R. N.; Coyne, A. G. *Chem. Rev.* **2010**, *110*, 6302. (c) Simon, M.-O.; Li, C.-J. *Chem. Soc. Rev.* **2012**, *41*, 1415.
- (22) Sridharan, V.; Martín, M. A.; Menéndez, J. C. *Eur. J. Org. Chem.* **2009**, 4614.
- (23) Singh, P. P.; Aithagani, S. K.; Yadav, M.; Singh, V. P.; Vishwakarma, R. A. *J. Org. Chem.* **2013**, *78*, 2639.
- (24) Moon, Y.; Jeong, Y.; Kook, D.; Hong, S. *Org. Biomol. Chem.* **2015**, *13*, 3918.
- (25) Sieveking, I.; Thomas, P.; Estévez, J. C.; Quiñones, N.; Cuéllar, M. A.; Villena, J.; Espinosa-Bustos, C.; Fierro, A.; Tapia, R. A.; Maya, J. D.; López-Muñoz, R.; Cassels, B. K.; Estévez, R. J.; Salas, C. O. *Bioorg. Med. Chem.* **2014**, *22*, 4609.
- (26) Mandal, A.; Mondal, S. K.; Jana, A.; Manna, S. K.; Ali, S. K.; Samanta, S. *J. Heterocyclic Chem.* **2017**, *54*, 2529.
- (27) **Typical Procedure: Preparation of 2-(Phenylamino)naphthalene-1,4-dione (3aa)**<sup>25</sup>  
To a solution of 1,4-naphthoquinone (0.3 mmol, 1 equiv), nitrobenzene (0.36 mmol, 1.2 equiv), Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.06 mmol, 20 mol%), Zn (1.5 mmol, 5 equiv) in H<sub>2</sub>O (0.6 mL) was added AcOH (4.5 mmol, 15 equiv). The resulting mixture was stirred for 5 h at rt. Then, the reaction mixture was diluted with water, filtered to remove the residual Zn dust, extracted with EtOAc (3×5 mL). The combined organic layers were washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting crude product was then purified by column chromatography (petroleum ether/EtOAc 5:1) on silica gel to afford the desired product **3ac** (yield: 2.9 g, 71%).
- (28) **Reaction on Gram Scale**  
To a solution of 1,4-naphthoquinone (**1a**) (2.3 g, 15 mmol, 1 equiv), 1-methoxy-4-nitrobenzene (**2c**) (18 mmol, 1.2 equiv), Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (3 mmol, 20 mol%), Zn (75 mmol, 5 equiv) in H<sub>2</sub>O (30 mL) was added AcOH (0.2 mol, 15 equiv). The resulting mixture was stirred for 5 h at rt. Then, the reaction mixture was diluted with water and extracted with EtOAc (3×80 mL). The combined organic layers were washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting crude product was then purified by column chromatography (petroleum ether/EtOAc 5:1) on silica gel to afford the desired product **3ac** (yield: 2.9 g, 71%).
- (29) **Synthesis of 2-Methoxy-5H-benzo[b]carbazole-6,11-dione (4ac)**<sup>26</sup>  
To a solution of 2-(4-methoxyphenylamino)naphthalene-1,4-dione (**3ac**) (0.13 g, 0.5 mmol, 1 equiv) in DMF (2.0 mL) were added Pd(OAc)<sub>2</sub> (0.1 mmol, 0.2 equiv) and Cu(OAc)<sub>2</sub> (1.25 mmol, 2.5 equiv). The resulting mixture was stirred for 24 h at 120 °C. Then, the reaction mixture was cooled to rt, diluted with water and extracted with EtOAc (3×20 mL). The combined organic layers were washed with water, brine, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The resulting crude product was then purified by column chromatography (petroleum ether/EtOAc 1:1) on silica gel to afford the desired product **4ac** as a yellow solid (yield: 90.1 mg, 65%), mp 300–305 °C. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 13.00 (s, 1 H), 8.08 (t, *J* = 7.3 Hz, 2 H), 7.81 (d, *J* = 19.1 Hz, 2 H), 7.59 (d, *J* = 2.1 Hz, 1 H), 7.47 (d, *J* = 9.0 Hz, 1 H), 7.07 (dd, *J* = 9.0, 2.3 Hz, 1 H), 3.84 (s, 3 H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>): δ = 180.06, 177.02, 156.76, 136.82, 133.98, 133.25, 132.96, 132.55, 125.83, 124.65, 118.24, 116.82, 114.80, 101.91, 55.20.