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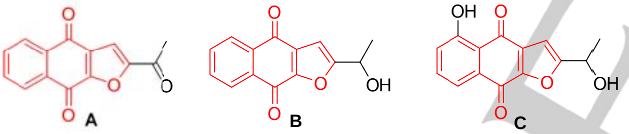
NIS-Induced Enones Difunctionalization for the Synthesis of Naphtho[2,3-*b*]furan-4,9-diones

Yun Liu,*[a] Wen-Hui Ge,[a] You-Quan Zhu,[b] Hua-You Hu,[c] Hui Fan,[a] Yan-Hui Shi[a] and Hui Wu*[a]

Abstract: An efficient synthesis of naphtho[2,3-*b*]furan-4,9-diones has been developed via *N*-Iodosuccinimide (NIS)-induced enones difunctionalization reaction with 2-hydroxy-1,4-naphthoquinones. This reaction involved sequential Michael addition, intramolecular oxidative cyclization and dehydrogenative aromatization to form new C-C and C-O bonds at *α*- and *β*-position of enones. Various enones survived under the reaction conditions and the corresponding products were obtained in moderate to excellent yields.

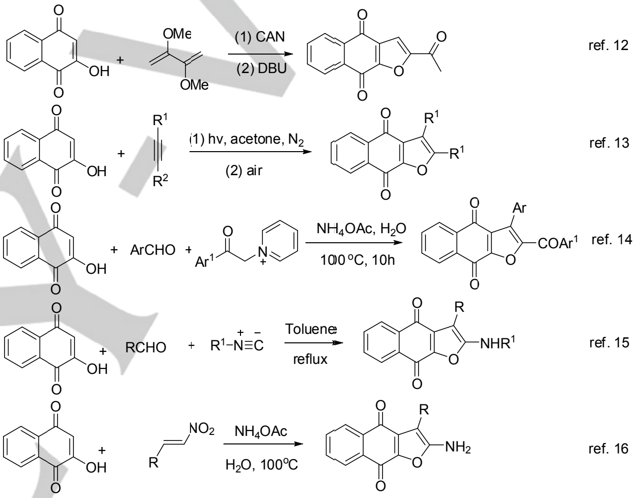
Introduction

Naturally occurring quinones constitute an important class of natural products.[1,2] As annulated quinones, naphtho[2,3-*b*]furan-4,9-diones have been found in many natural plants.[3] For examples, compounds **A**, **B** and **C** were isolated from *Tabebuia cassinoides* (Scheme 1).[3a-3c] Furthermore, naphtho[2,3-*b*]furan-4,9-diones have exhibited significant biological activities, such as anticancer,[4] antitumoral,[5] antiproliferative,[6] trypanocidal,[7] and against the growth of human keratinocyte.[8] Consequently, the synthesis of naphtho[2,3-*b*]furan-4,9-dione derivatives have drawn much attention in the past decades.[9-17]



Scheme 1 Examples of natural products bearing naphtho[2,3-*b*]furan-4,9-dione skeleton

2-Hydroxy-1,4-naphthoquinone is an important precursor for naphtho[2,3-*b*]furan-4,9-diones synthesis. As shown in Scheme 2, the major synthetic protocols include CAN-mediated oxidative cycloaddition with special alkene;[12] photochemical cycloaddition with alkenes or alkynes;[13] three-component reaction with aromatic aldehydes and pyridinium salt;[14] or with isocyanides and aldehydes;[15] and domino reaction with *β*-nitrostyrenes.[16] However, there are some shortcomings associated with these methods such as limited substituent scope, not easily available substrates, or low yields. Therefore, it is still highly desirable to develop more convenient synthetic protocols for the preparation of diverse naphtho[2,3-*b*]furan-4,9-diones from 2-hydroxy-1,4-naphthoquinone.



Scheme 2 Previous routes to naphtho[2,3-*b*]furan-4,9-diones from 2-hydroxy-1,4-naphthoquinone

Iodine or low valent iodine(I)-promoted C-H oxidative coupling in tandem reaction has been reported as an effective approach for the construction of heterocyclic compounds.[18-19] Recently, Gao uncovered the synthesis of 2,3-dihydropyrroles by I_2-mediated reaction of chalcones with enamine ketones;[19a] Park developed a mild synthesis of 3-arylimidazo[1,2-*a*]pyridines via NIS-oxidation;[19b] and Huang described I_2-mediated oxidative cyclization for the synthesis of indolizines.[19c] From our own interest in iodine and *N*-iodosuccinimide (NIS)-mediated reaction herein, we report an effective synthesis of naphtho[2,3-*b*]furan-4,9-diones via NIS-induced difunctionalization reaction of enones with 2-hydroxy-1,4-naphthoquinones.

Results and Discussion

The reaction of 2-hydroxy-1,4-naphthoquinone **1a** with chalcone **2a** was studied initially. To our delight, by heating the mixture of **1a** (0.5 mmol) and **2a** (0.5 mmol), NIS (0.5 mmol) and Et_3N (1.0 equiv) in acetonitrile at 100 °C for 12 h, we obtained **3a** in 48% yield (entry 1 in Table 1).

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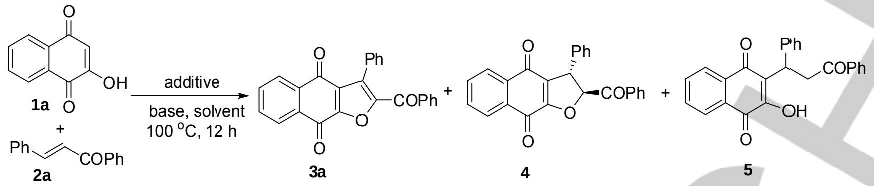
Table 1 Optimization of reaction conditions[a]



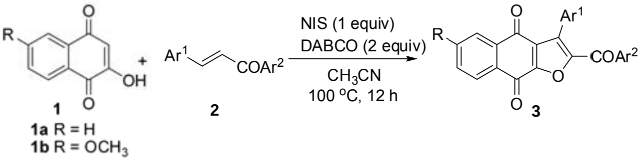
Entry	Additive (equiv)	Solvent	Base (equiv)	2a (% conversion)	3a (% yield)[b]	4 (% yield)[b]	5 (% yield)[b]
1	NIS (1)	CH_3CN	Et_3N (2)	55	48	0.	0
2	NIS (0.5)	CH_3CN	Et_3N (2)	53	38	0	trace
3	NIS (1.5)	CH_3CN	Et_3N (2)	56	43	0	0
4	none	CH_3CN	Et_3N (2)	52	0	0	45
5	I_2 (1)	CH_3CN	Et_3N (2)	52	42	0	0
6	ICl (1)	CH_3CN	Et_3N (2)	54	46	0	0
7	NIS (1)	CH_3CN	none	0	0	0	0
8	NIS (1)	CH_3CN	K_2CO_3 (2)	8	0	0	trace
9	NIS (1)	CH_3CN	Cs_2CO_3 (2)	10	0	0	trace
10	NIS (1)	CH_3CN	Pyridine (2)	54	46	0	0
11	NIS (1)	CH_3CN	DABCO (2)	66	59	0	0
12	NIS (1)	CH_3CN	DABCO (2.5)	68	59	0	0
13	NIS (1)	CH_3CN	DABCO (1.5)	50	36,	0	trace
14	NIS (1)	Dioxane	DABCO (2)	33	26	0	0
15	NIS (1)	benzene	DABCO (2)	28	22	0	0
16	NIS (1)	DMF	DABCO (2)	41	33	0	0
17	NIS (1)	C_2H_5OH	DABCO (2)	32	25	0	0
18	NIS (1)	DCE	DABCO (2)	10	trace	0	0
19[c]	NIS (1)	CH_3CN	DABCO (2)	90	78	0	0
20[d]	NIS (1)	CH_3CN	DABCO (2)	91	78	0	0
21[c,e]	NIS (1)	CH_3CN	DABCO (2)	91	77	0	0
22[c,f]	NIS (1)	CH_3CN	DABCO (2)	88	23	0	51
23[c,g]	NIS (1)	CH_3CN	DABCO (2)	87	51	28	0
24[c,h]	NIS (1)	CH_3CN	DABCO (2)	17	0	0	10

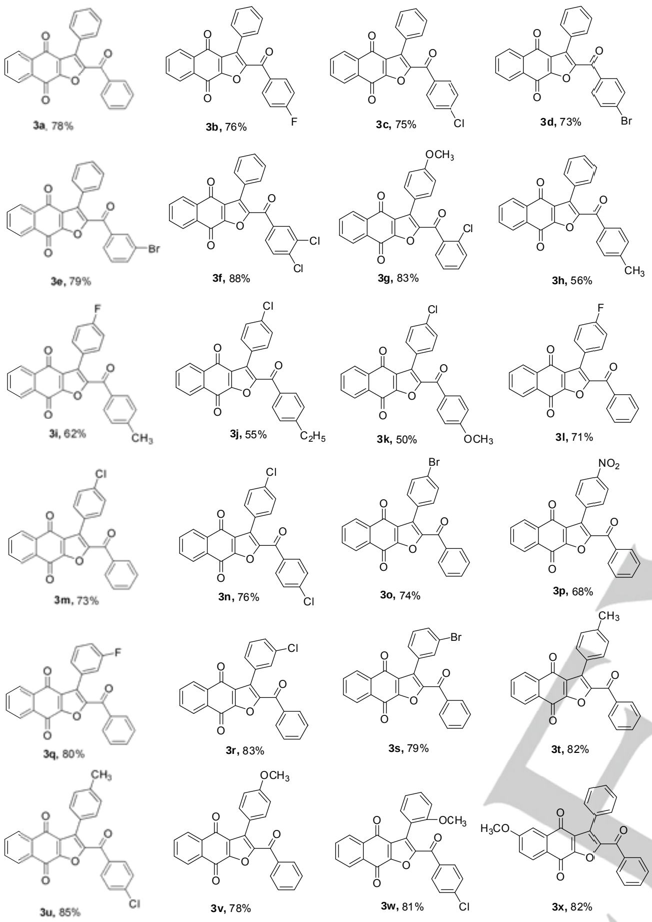
[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), additive, base, solvent (5 mL), sealed tube, 100 °C, 12 h. [b] Isolated yields based on added **2a**. [c] 0.75 mmol of **1a**. [d] 1.0 mmol of **1a**. [e] Under O_2. [f] Under N_2. [g] 80 °C. [h] 60 °C.

Inspired by this promising result, we began to optimize the reaction conditions (Table 1). It was found the amount of NIS, the use of base and solvent, the ratio of reactants, as well as reaction temperature all played critical roles on the reaction efficiency. To this reaction, one equiv of NIS was needed but further increase of its amount could not provide better yield (entry 1-3). Without NIS, only Michael adduct **5** was generated (entry 4). Using iodine or ICl instead of NIS also led to low yields of **3a** (entry 5-6). Organic bases could promote this reaction, and 2.0 equiv of DABCO (1,4-diazabicyclo[2.2.2]octane) gave the best result of them (entry 7-13). With 2.0 equiv of DABCO as base, different solvents were screened and acetonitrile was found to be a superior solvent compared to dioxane, benzene, alcohol, DMF, and DCE (entry 11, 14-18). For the ratio of substrates, 1.5 equiv of **1a** worked most effectively and the yield of **3a** was improved to 78% (entry 19-20). Under oxygen atmosphere, a similar yield of **3a** was given (entry 21). While under nitrogen atmosphere, a significant amount of Michael adduct **5** was detected (entry 22). Reducing the reaction temperature to 80 °C or 60 °C led to mixture of **3** and **4**[20] or Michael adduct (entry 23-24). Therefore, the optimal conditions were set to heating **1a** (0.75 mmol), **2a** (0.5 mmol) and NIS (0.5 mmol) in acetonitrile at 100 °C for 12 h using DABCO (1.0 mmol) as base.

With the optimized reaction conditions in hand, the scope of enone was then surveyed (Table 2). The result showed that a range of chalcones **2** reacted with **1a** smoothly under the optimal conditions. For instance, chalcones with electron-deficient groups (F, Cl and Br) on *ortho-*, *meta-*, or *para*-position of Ar^2 ring provided the desired products **3b-3g** in good to excellent yields (73-88%). Meanwhile, chalocones with electron-donating groups (Me, Et and OMe) on Ar^2 ring gave the products **3h-3k** in moderate yields (50%-62%). Similarly, for chalcones with different groups at Ar^1 ring, products **3l-3w** were formed in 68% to 85% yields. Using chalcone **2a** to react with substituted 2-hydroxy-1,4-naphthoquinone **1b** gave satisfied result as well (**3x**, 82%). Except for NMR and HRMS, the structure of the products was further supported by X-ray crystallographic structure of **3q**.

Table 2 Scope of chalcone **2**[a,b]

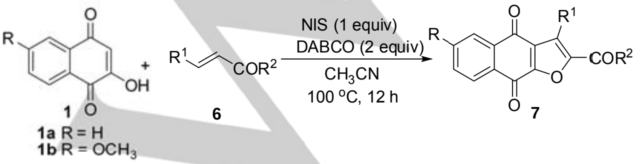


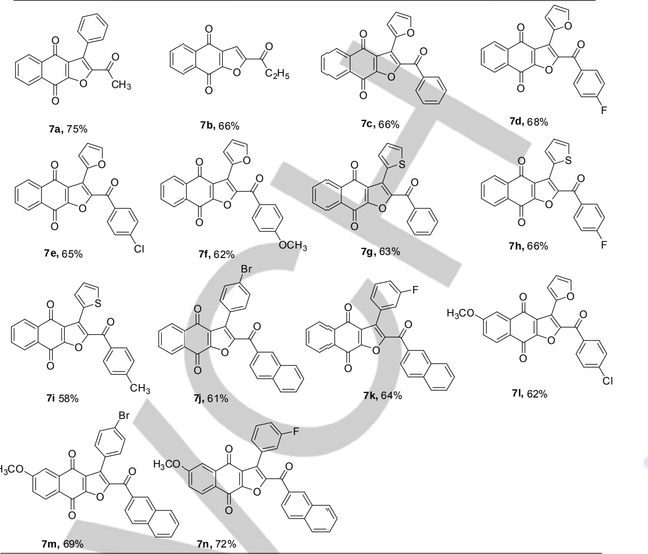


[a] Reaction conditions: **1** (0.75 mmol), **2** (0.5 mmol), NIS (0.5 mmol), DABCO (1.0 mmol), acetonitrile (5 mL), sealed tube, 100 °C, 12 h. [b] Isolated yields based on added **2**.

To further extend the utility of this reaction, we then turned our attention to other enones, including benzalacetone**,** penten-3-one, and furyl-, thienyl-, and naphthyl-substituted enones (Table 3). It was observed that various enones **6** participated in this reaction well, forming the corresponding naphtho[2,3-*b*]furan-4,9-diones **7a-7n** in 58%-75% yields.

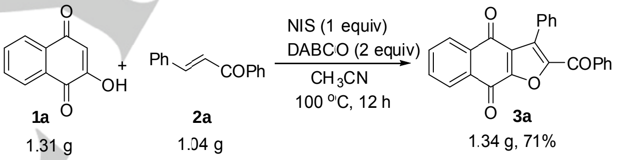
Table 3 Scope of other enone **6**[a,b]





[a] Reaction conditions: **1** (0.75 mmol), **6** (0.5 mmol), NIS (0.5 mmol), DABCO (1.0 mmol), acetonitrile (5 mL), sealed tube, 100 °C, 12 h. [b] Isolated yields based on added **6**..

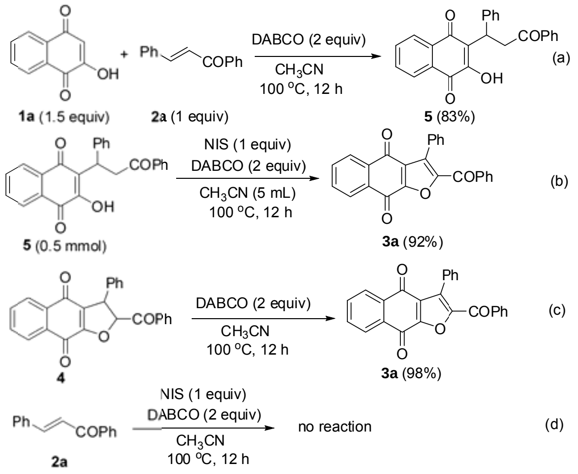
To demonstrate the feasibility of this method in practical organic synthesis, we carried out this reaction on gram scale (Scheme 3). Heating **1a** (7.5 mmol, 1.31 g), **2a** (5 mmol, 1.04 g) under the optimal reaction conditions, 1.34 g of **3a** was obtained, meaning a 71% yield.



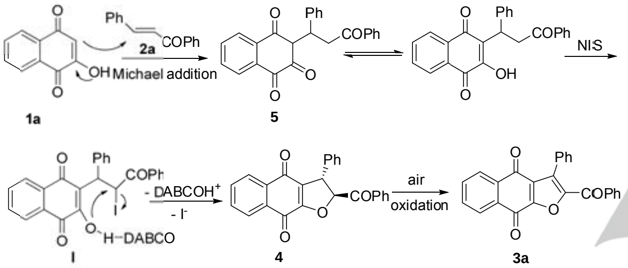
Scheme 3 Gram-scale synthesis

To shed light on the reaction mechanism, three control experiments were carried out. Firstly, Michael adduct **5** prepared under basic condition without NIS could be tansformed completely under the standard conditions, and **3a** was isolated in 92% yield (Scheme 4a, 4b). This illustrated that **5** was a possible intermediate of this reaction. Secondly, preparing **4** from **1a** and **2a** at 80 °C (entry 23, Table 1) and then heating **4** with DABCO but without NIS in acetonitrile provided **3a** in 98% yield, which confirmed that NIS is not involved in the aromatization step (Scheme 4c). Thirdly, mixing chalcone **2a** with NIS and DABCO, no reaction occurred after heating in acetonitrile at 100 °C for 12 h (Scheme 4d). This ruled out the possibility of initial chalcone iodination.

Based on these results and previous literatures,[19] a possible mechanism for this reaction is suggested (Scheme 5). At first, Michael addition of 2-hydroxy-1,4-naphthoquinone **1a** with chalcone **2a** yielded the tautomeric intermediate **5.** Subsequently, in the aid of NIS, **5** was transformed into iodinated intermediate **I**. Finally, in the presence of base, intermediate **I** underwent intramolecular nucleophilic cyclization to afford **4**, which generated **3a** via air oxidation.



Scheme 4 Control experiments



Scheme 5 Proposed mechanism

Conclusions

In summary, we have described an efficient methodology for the synthesis of naphtho[2,3-*b*]furan-4,9-dione derivatives via NIS-induced enones difunctionalization reaction with 2-hydroxy-1,4-naphthoquinones. In this reaction process, new C-C and C-O bonds were formed in one pot. This synthesis enjoys easy availability of starting materials, wide substrate scope and mild reaction conditions. A variety of enones tolerated the reaction conditions and the corresponding products were obtained in moderate to excellent yields.

Experimental Section

General: Melting points are uncorrected. ^{1}H NMR spectra were measured on 400 MHz with $CDCl_3$ as solvent. The chemical shifts (δ) are reported in parts per million relative to the residual deuterated solvent signal, and coupling constants (J) are given in Hertz. ^{13}C NMR spectra were measured on 100 MHz with $CDCl_3$ as solvent. HRMS (ESI) data were obtained in the electron impact (EI) mode. All reagents and solvent used were obtained commercially and used without further purification unless indicated otherwise. Chalcones **2**, furyl-, thienyl-, or naphthyl-substituted enones **6**, and 2-hydroxy-6-methoxy-1,4-naphthoquinone **1b** were prepared according to literature 21 and 22.

General Procedure for the Preparation of Naphtho[2,3-*b*]furan-4,9-dione 3 (Table 2): 2-Hydroxy-1,4-naphthoquinone **1** (0.75 mmol), chalcone **2** (0.5 mmol), NIS (0.5 mmol), and DABCO (1.0 mmol) were mixed in 5 mL of CH_3CN in a sealed tube and heated at 100 °C for 12 h. After completion of the reaction, the mixture was cooled to room temperature and separated by flash column chromatography (ethyl acetate/hexane) on silica gel to afford product **3**.

2-Benzoyl-3-phenylnaphtho[2,3-*b*]furan-4,9-dione (3a): Yellow solid; mp 140–142 °C; yield 147 mg, 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.43 (m, 5H), 7.48–7.49 (m, 2H), 7.55 (t, J = 7.6 Hz, 1H), 7.78–7.80 (m, 2H), 7.89 (d, J = 8.0 Hz, 2H), 8.16–8.18 (m, 1H), 8.25–8.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8, 180.0, 174.1, 152.4, 150.5, 135.9, 134.6, 134.1, 133.8, 133.7, 132.3, 132.0, 130.2, 129.9, 129.2, 128.5, 128.2, 128.0, 127.8, 127.4, 126.9. HRMS (ESI) m/z calcd for $C_{25}H_{15}O_4$ $[M+H]^+$ 379.0970, found 379.0966.

2-(4-Fluorobenzoyl)-3-phenylnaphtho[2,3-*b*]furan-4,9-dione (3b): Yellow solid; mp 133–135 °C; yield 151 mg, 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (t, J = 8.4 Hz, 2H), 7.39–7.41 (m, 3H), 7.47–7.49 (m, 2H), 7.78–7.81 (m, 2H), 7.94–7.97 (m, 2H), 8.15–8.17 (m, 1H), 8.25–8.27 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.7, 179.5, 173.7, 165.6 (d, J = 250 Hz), 152.1, 149.9, 134.2, 133.8, 133.3, 132.3 (d, J = 9 Hz), 131.9, 131.8, 131.7, 129.8, 128.9, 127.7, 127.6, 127.4, 127.0, 126.6, 115.4 (d, J = 22 Hz). HRMS (ESI) m/z calcd for $C_{25}H_{14}FO_4$ $[M+H]^+$ 397.0876, found 397.0870.

2-(4-Chlorobenzoyl)-3-phenylnaphtho[2,3-*b*]furan-4,9-dione (3c): Yellow solid; mp 194–195 °C; yield 154 mg, 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.43 (m, 5H), 7.47–7.49 (m, 2H), 7.79–7.81 (m, 2H), 7.86 (d, J = 8.8 Hz, 2H), 8.16–8.18 (m, 1H), 8.26–8.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.3, 179.7, 174.0, 152.4, 150.1, 140.2, 134.5, 134.2, 134.1, 133.6, 132.3, 132.1, 131.2, 130.6, 130.1, 129.3, 129.2, 128.8, 127.9, 127.7, 127.3, 126.9. HRMS (ESI) m/z calcd for $C_{25}H_{14}ClO_4$ $[M+H]^+$ 413.0581, found 413.0569.

2-(4-Bromobenzoyl)-3-phenylnaphtho[2,3-*b*]furan-4,9-dione (3d): Yellow solid; mp 190–192 °C; yield 166 mg, 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.50 (m, 5H), 7.57 (d, J = 8.4 Hz, 2H), 7.78–7.82 (m, 4H), 8.16–8.19 (m, 1H), 8.27–8.29 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.6, 179.8, 174.1, 152.5, 150.1, 134.7, 134.6, 134.2, 133.7, 132.5, 132.2, 131.9, 131.3, 130.1, 130.0, 1294, 129.1, 128.1, 128.0, 127.8, 127.4, 127.3, 127.0. HRMS (ESI) m/z calcd for $C_{25}H_{14}BrO_4$ $[M+H]^+$ 457.0075, found 457.0077.

2-(3-Bromobenzoyl)-3-phenylnaphtho[2,3-*b*]furan-4,9-dione (3e): Yellow solid; mp 131–133 °C; yield 180 mg, 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, J = 8.0 Hz, 1H), 7.39–7.48 (m, 5H), 7.65 (d, J = 8.0 Hz, 1H), 7.80–7.82 (m, 3H), 7.96 (d, J = 1.6 Hz, 1H), 8.17–8.19 (m, 1H), 8.27–8.29 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.3, 179.8, 174.0, 152.6, 149.8, 137.5, 136.4, 134.6, 134.1, 133.7, 132.7, 132.5, 132.2, 130.1, 130.0, 129.3, 128.3, 128.0, 127.9, 127.7, 127.3, 126.9, 122.6. HRMS (ESI) m/z calcd for $C_{25}H_{14}BrO_4$ $[M+H]^+$ 457.0075, found 457.0083.

2-(3,4-Dichlorobenzoyl)-3-phenylnaphtho[2,3-*b*]furan-4,9-dione (3f): Yellow solid; mp 210–212 °C; yield 196 mg, 88%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.50 (m, 6H), 7.75 (dd, J = 8.4, 2.0 Hz, 1H), 7.80–7.82 (m, 2H), 7.95 (d, J = 2.0 Hz, 1H), 8.16–8.18 (m, 1H), 8.27–8.29 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.2, 179.7, 174.0, 152.6, 149.6, 138.3, 135.4, 134.6, 134.2, 133.7, 133.2, 132.9, 132.2, 131.7, 130.6, 130.0, 129.4, 128.7, 128.0, 127.8, 127.7, 127.4, 127.0. HRMS (ESI) m/z calcd for $C_{25}H_{13}Cl_2O_4$ $[M+H]^+$ 447.0191, found 447.0197.

2-(2-Chlorobenzoyl)-3-(4-methoxyphenyl)naphtho[2,3-*b*]furan-4,9-dione (3g): Yellow solid; mp 185–187 °C; yield 183 mg, 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.86 (d, *J* = 8.8 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.36 (td, *J* = 7.2, 0.8 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 3H), 7.77–7.80 (m, 2H), 8.15–8.17 (m, 1H), 8.24–8.26 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.7, 180.0, 174.1, 160.3, 152.9, 149.9, 136.9, 134.5, 134.1, 133.8, 132.6, 132.5, 132.3, 132.1, 131.7, 130.2, 130.1, 127.9, 127.3, 127.0, 126.9, 119.5, 113.3, 55.3. HRMS (ESI) *m/z* calcd for $C_{26}H_{16}ClO_5$ $[M+H]^+$ 443.0686, found 443.0679.

2-(4-Methylbenzoyl)-3-phenylnaphtho[2,3-*b*]furan-4,9-dione (3h): Yellow solid; mp 178–180 °C; yield 110 mg, 56%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.39–7.42 (m, 3H), 7.49–7.51 (m, 2H), 7.78–7.84 (m, 4H), 8.16–8.18 (m, 1H), 8.25–8.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.4, 180.0, 174.1, 152.3, 150.8, 144.9, 134.5, 134.1, 133.8, 133.4, 132.3, 131.5, 130.2, 129.3, 129.1, 128.3, 128.0, 127.8, 127.3, 126.9, 21.8. HRMS (ESI) *m/z* calcd for $C_{26}H_{17}O_4$ $[M+H]^+$ 393.1127, found 393.1136.

3-(4-Fluorophenyl)-2-(4-methylbenzoyl)naphtho[2,3-*b*]furan-4,9-dione (3i): Yellow solid; mp 215-216 °C; yield 127 mg, 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 7.10 (t, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.49–7.53 (m, 2H), 7.80–7.85 (m, 4H), 8.17–8.19 (m, 1H), 8.26–8.29 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.2, 180.1, 174.0, 163.1 (d, *J* = 248 Hz), 152.2, 150.8, 145.0, 134.5, 134.1, 133.7, 133.2, 132.2 (d, *J* =9 Hz), 130.6, 130.1, 129.3, 127.7, 127.3, 126.9, 124.1, 115.1 (d, *J* = 22 Hz), 21.8. HRMS (ESI) *m/z* calcd for $C_{26}H_{16}FO_4$ $[M+H]^+$ 411.1033, found 411.1043.

2-(4-Ethylbenzoyl)-3-(4-chlorophenyl)naphtho[2,3-*b*]furan-4,9-dione (3j): Yellow solid; mp 195–196 °C; yield 121 mg, 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.6 Hz, 3H), 2.71 (q, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.79–7.81 (m, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 8.16–8.18 (m, 1H), 8.26–8.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.2, 180.0, 174.0, 152.2, 151.2, 150.9, 135.2, 134.5, 134.2, 133.6, 133.4, 132.2, 131.6, 130.5, 130.2, 128.2, 128.1, 127.6, 127.3, 126.9, 126.7, 29.1, 15.2. HRMS (ESI) *m/z* calcd for $C_{27}H_{18}ClO_4$ $[M+H]^+$ 441.0894, found 441.0890.

3-(4-Chlorophenyl)-2-(4-methoxybenzoyl)naphtho[2,3-*b*]furan-4,9-dione (3k): Yellow solid; mp 219–220 °C; yield 111 mg, 50%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (s, 3H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.80–7.82 (m, 2H), 7.98 (d, *J* = 8.8 Hz, 2H), 8.16–8.18 (m, 1H), 8.26–8.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.8, 180.0, 174.0, 164.4, 152.1, 151.1, 135.2, 134.5, 134.1, 133.7, 132.6, 132.2, 131.5, 130.1, 128.6, 128.2, 127.7, 127.3, 126.9, 114.0, 55.6. HRMS (ESI) *m/z* calcd for $C_{26}H_{16}ClO_5$ $[M+H]^+$ 443.0686, found 443.0693.

2-Benzoyl-3-(4-fluorophenyl)naphtho[2,3-*b*]furan-4,9-dione (3l): Yellow solid; mp 166–167 °C; yield 140 mg, 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (t, *J* = 8.8 Hz, 2H), 7.40–7.49 (m, 5H), 7.79–7.81 (m, 2H), 7.94–7.97 (m, 2H), 8.15–8.18 (m, 1H), 8.25–8.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.7, 180.0, 174.1, 163.0 (d, *J* = 250 Hz), 152.4, 150.5, 135.9, 134.6, 134.2, 133.9, 133.7, 132.3, 132.2 (d, *J* = 9 Hz), 131.1, 129.9, 128.6, 127.5 (d, *J* = 26 Hz), 127.0, 124.1, 124.0, 115.1 (d, *J* = 22 Hz). HRMS (ESI) *m/z* calcd for $C_{25}H_{14}FO_4$ $[M+H]^+$ 397.0876, found 397.0871.

2-Benzoyl-3-(4-chlorophenyl)naphtho[2,3-*b*]furan-4,9-dione (3m): Yellow solid; mp 240–242 °C; yield 151 mg, 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.45–7.47 (m, 4H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.79–7.82 (m, 2H), 7.93 (d, *J* = 7.6 Hz, 2H), 8.16–8.18 (m, 1H), 8.25–8.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.6, 180.0, 174.0, 152.4, 150.5, 135.8, 135.4, 134.6, 134.2, 133.9, 133.6, 132.2, 131.6, 130.9, 130.0, 128.7, 128.3, 127.7, 127.4, 127.0, 126.6. HRMS (ESI) *m/z* calcd for $C_{25}H_{14}ClO_4$ $[M+H]^+$ 413.0581, found 413.0569.

2-(4-Chlorobenzoyl)-3-(4-chlorophenyl)naphtho[2,3-*b*]furan-4,9-dione (3n): Yellow solid; mp 225–226 °C; yield 169 mg, 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.48 (m, 6H), 7.81–7.83 (m, 2H), 7.93 (dd, *J* = 6.8, 1.6 Hz, 2H), 8.16–8.19 (m, 1H), 8.26–8.29 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.0, 179.8, 173.9, 152.3, 150.0, 140.5, 135.5, 134.7, 134.2, 134.1, 133.6, 132.1, 131.5, 131.3, 130.7, 129.5, 129.4, 129.0, 128.3, 127.4, 127.0, 126.4. HRMS (ESI) *m/z* calcd for $C_{25}H_{13}Cl_2O_4$ $[M+H]^+$ 447.0191, found 447.0191.

2-Benzoyl-3-(4-bromophenyl)naphtho[2,3-*b*]furan-4,9-dione (3o): Yellow solid; mp 244–246 °C; yield 168 mg, 74%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.80–7.82 (m, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 8.16–8.19 (m, 1H), 8.26–8.29 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.6, 179.8, 174.1, 152.5, 150.1, 134.7, 134.2, 133.7, 132.5, 132.2, 131.9, 131.3, 130.1, 129.4, 1291.1, 128.0, 127.9, 127.8, 127.4, 127.0. HRMS (ESI) *m/z* calcd for $C_{25}H_{14}BrO_4$ $[M+H]^+$ 457.0075, found 457.0079.

2-Benzoyl-3-(4-nitrophenyl)naphtho[2,3-*b*]furan-4,9-dione (3p): Yellow solid; mp 234–236 °C; yield 143 mg, 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (t, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.82–7.84 (m, 2H), 7.99 (d, *J* = 7.2 Hz, 2H), 8.15–8.18 (m, 1H), 8.27–8.30 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.6, 179.3, 173.4, 151.9, 150.3, 147.6, 135.0, 134.8, 134.3, 134.0, 133.8, 133.0, 131.7, 130.8, 129.5, 129.4, 128.4, 127.1, 127.0, 126.6. 122.7. HRMS (ESI) *m/z* calcd for $C_{25}H_{14}NO_6$ $[M+H]^+$ 424.0821, found 424.0828.

2-Benzoyl-3-(3-fluorophenyl)naphtho[2,3-*b*]furan-4,9-dione (3q): Yellow solid; mp 202–204 °C; yield 158 mg, 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (td, *J* = 8.0, 1.6 Hz, 1H), 7.24–7.28 (m, 2H), 7.35–7.41 (m, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.81–7.85 (m, 2H), 7.94 (d, *J* = 7.6 Hz, 2H), 8.18–8.21 (m, 1H), 8.28–8.30 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.5, 179.8, 174.0, 162.2 (d, *J* = 250 Hz), 152.3, 150.7, 135.8, 134.6, 134.2, 133.9, 133.6, 132.2, 130.5, 130.4, 130.2 (d, *J* = 9 Hz), 129.9, 129.4 (d, *J* = 8 Hz), 128.6, 127.7, 127.4, 127.0, 125.9 (d, *J* = 3 Hz), 117.3 (d, *J* = 23 Hz), 116.1 (d, *J* = 21 Hz). HRMS (ESI) *m/z* calcd for $C_{25}H_{14}FO_4$ $[M+H]^+$ 397.0876, found 397.0865.

2-Benzoyl-3-(3-chlorophenyl)naphtho[2,3-*b*]furan-4,9-dione (3r): Yellow solid; mp 144–146 °C; yield 171 mg, 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.40 (m, 3H), 7.44–7.49 (m, 3H), 7.59 (t, *J* = 7.2 Hz, 1H), 7.80–7.82 (m, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 8.17–8.19 (m, 1H), 8.26–8.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.5, 179.8, 174.0, 152.3, 150.7, 135.8, 134.7, 134.3, 133.9, 133.8, 133.6, 132.2, 130.5, 130.2, 130.0, 129.9, 129.3, 129.2, 128.7, 128.4, 127.7, 127.4, 127.0. HRMS (ESI) *m/z* calcd for $C_{25}H_{14}ClO_4$ $[M+H]^+$ 413.0581, found 413.0579.

2-Benzoyl-3-(3-bromophenyl)naphtho[2,3-*b*]furan-4,9-dione (3s): Yellow solid; mp 179–181 °C; yield 180 mg, 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 8.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 3H), 7.52–7.64 (m, 3H), 7.80–7.82 (m, 2H), 7.92 (dd, *J* = 8.4, 1.2 Hz, 2H), 8.16–8.19 (m, 1H), 8.26–8.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.7, 180.1, 174.2, 152.6, 150.9, 136.0, 134.9, 134.5, 134.2, 133.9, 133.3, 132.5, 132.4, 130.6, 130.5, 130.2, 129.7, 129.2, 129.1, 128.9, 127.9, 127.7, 127.3, 122.1. HRMS (ESI) *m/z* calcd for $C_{25}H_{14}BrO_4$ $[M+H]^+$ 457.0075, found 457.0070.

2-Benzoyl-3-*p*-tolylnaphtho[2,3-*b*]furan-4,9-dione (3t): Yellow solid; mp 153–155 °C; yield 161 mg, 82%. ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 2.39 (s, 3H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.39–7.45 (m, 4H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.79–7.81 (m, 2H), 7.92 (dd, *J* = 8.8, 1.6 Hz, 2H), 8.17–8.19 (m, 1H), 8.26–8.28 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 184.1, 180.3, 174.4, 152.7, 150.8, 139.5, 136.3, 134.8, 134.3, 134.1, 133.9, 132.6, 130.3, 130.2, 129.5, 129.3, 129.0, 128.8, 127.8, 127.6, 127.2, 125.4, 21.8. HRMS (ESI) *m/z* calcd for $C_{26}H_{17}O_4$ [M+H]$^+$ 393.1127, found 393.1118.

2-(4-Chlorobenzoyl)-3-*p*-tolylnaphtho[2,3-*b*]furan-4,9-dione (3u): Yellow solid; mp 232–234 °C; yield 182 mg, 85%. ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 2.39 (s, 3H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.39 (t, *J* = 8.0 Hz, 4H), 7.78–7.80 (m, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 8.15–8.18 (m, 1H), 8.25–8.27 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 182.3, 179.7, 174.0, 152.3, 149.9, 140.1, 139.3, 134.5, 134.2, 134.0, 133.6, 132.5, 132.1, 131.2, 129.9, 128.8, 128.6, 127.7, 127.4, 127.3, 126.8, 124.8, 21.4. HRMS (ESI) *m/z* calcd for $C_{26}H_{16}ClO_4$ [M+H]$^+$ 427.0737, found 427.0739.

2-Benzoyl-3-(4-methoxyphenyl)naphtho[2,3-*b*]furan-4,9-dione (3v): Orange solid; mp 164–165 °C; yield 159 mg, 78%. ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 3.84 (s, 3H), 6.92 (d, *J* = 8.8 Hz, 2H), 7.41–7.48 (m, 4H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.79–7.81 (m, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 8.18–8.20 (m, 1H), 8.26–8.28 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 183.9, 180.1, 174.1, 160.3, 152.4, 150.3, 136.1, 134.5, 134.0, 133.8, 133.6, 132.3, 132.0, 131.8, 129.9, 128.6, 128.5, 127.7, 127.3, 126.9, 120.0, 113.4, 55.3. HRMS (ESI) *m/z* calcd for $C_{26}H_{17}O_5$ [M+H]$^+$ 409.1076, found 409.1088.

3-(2-Methoxyphenyl)-2-(4-chlorobenzoyl)naphtho[2,3-*b*]furan-4,9-dione (3w): Yellow solid; mp 178 mg, 85–86 °C; yield 81%. ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 3.63 (s, 3H), 6.85 (d, *J* = 8.8 Hz, 1H), 7.01 (t, *J* = 7.2 Hz, 1H), 7.34–7.40 (m, 4H), 7.78–7.84 (m, 4H), 8.14–8.16 (m, 1H), 8.26–8.28 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 182.5, 179.7, 174.0, 156.5, 152.5, 150.7, 139.9, 134.4, 134.2, 133.9, 133.7, 132.3, 131.3, 130.9, 130.8, 128.6, 128.5, 127.4, 127.2, 126.9, 120.3, 117.5, 110.6, 55.2. HRMS (ESI) *m/z* calcd for $C_{26}H_{16}ClO_5$ [M+H]$^+$ 443.0686, found 443.0691.

2-Benzoyl-6-methoxy-3-phenylnaphtho[2,3-*b*]furan-4,9-dione (3x): Yellow solid; mp 182–184 °C; yield 167 mg, 82%. ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 3.94 (s, 3H), 7.22 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.38–7.43 (m, 5H), 7.47–7.49 (m, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 2.8 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 2H), 8.20 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 183.7, 179.9, 173.3, 164.7, 152.9, 150.2, 136.1, 136.0, 133.6, 132.0, 130.1, 129.9, 129.4, 129.1, 128.5, 128.3, 127.9, 127.6, 127.5, 125.6, 119.9, 111.5, 56.0. HRMS (ESI) *m/z* calcd for $C_{26}H_{17}O_5$ [M+H]$^+$ 409.1076, found 409.1066.

General Procedure for the Preparation of Naphtho[2,3-*b*]furan-4,9-dione 7 (Table 3): 2-Hydroxy-1,4-naphthoquinones **1** (0.75 mmol), enone **6** (0.5 mmol), NIS (0.5 mmol), and DABCO (1.0 mmol) were mixed in 5 mL of CH_3CN in a sealed tube and heated at 100 °C for 12 h. After completion of the reaction, the mixture was cooled to room temperature and separated by flash column chromatography (ethyl acetate/hexane) on silica gel to afford product 7.

2-Acetyl-3-phenylnaphtho[2,3-*b*]furan-4,9-dione (7a): Yellow solid; mp 154–156 °C; yield 118 mg, 75%. ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 2.56 (s, 3H), 7.50 (s, 5H), 7.78–7.80 (m, 2H), 8.13–8.15 (m, 1H), 8.25–8.28 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 188.0, 179.8, 174.2, 152.0, 149.9, 134.6, 134.1, 133.7, 132.2, 130.8, 129.9, 129.4, 128.0, 127.9, 127.3, 126.9, 28.3. HRMS (ESI) m/z calcd for $C_{20}H_{13}O_4$ [M+H]$^+$ 317.0814, found 317.0810.

2-Propionylnaphtho[2,3-*b*]furan-4,9-dione (7b): Red solid; mp 189–191 °C; yield 84 mg, 66%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.26 (t, *J* = 7.2 Hz, 3H), 3.06 (q, *J* = 7.2 Hz, 2H), 7.61 (s, 1H), 7.80–7.82 (m, 2H), 8.22–8.27 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 190.8, 179.8, 173.9, 155.4, 152.7, 134.4, 134.3, 133.1, 132.6, 130.7, 127.3, 127.2, 111.9, 32.6, 7.4. HRMS (ESI) *m/z* calcd for $C_{15}H_{11}O_4$ [M+H]$^+$ 255.0657, found 255.0661.

2-Benzoyl-3-(furan-2-yl)naphtho[2,3-*b*]furan-4,9-dione (7c): Red solid; mp 167–169 °C; yield 122 mg, 66%. ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 6.50–6.52 (m, 1H), 7.32 (d, *J* = 1.6 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 3.2 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.82–7.84 (m, 2H), 7.90 (d, *J* = 7.6 Hz, 2H), 8.26–8.28 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 184.3, 179.6, 173.8, 152.6, 150.0, 143.8, 142.1, 136.1, 134.5, 134.0, 133.8, 133.7, 132.0, 129.7, 128.6, 127.4, 126.9, 126.2, 119.6, 115.3, 111.8. HRMS (ESI) *m/z* calcd for $C_{23}H_{13}O_5$ [M+H]$^+$ 369.0763, found 369.0752.

2-(4-Fluorobenzoyl)-3-(furan-2-yl)naphtho[2,3-*b*]furan-4,9-dione (7d): Red solid; mp 190–191 °C; yield 132 mg, 68%. ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 6.52–6.53 (m, 1H), 7.15 (t, *J* = 8.4 Hz, 2H), 7.34 (s, 1H), 7.52 (d *J* = 3.2 Hz, 1H), 7.81–7.83 (m, 2H), 7.94–7.97 (m, 2H), 8.25–8.27 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 182.6, 179.5, 173.8, 166.1 (d, *J* = 255 Hz), 152.7, 149.6, 143.9, 142.0, 134.6, 134.1, 133.7, 132.6 (d, *J* = 2.9 Hz), 132.4 (d, *J* = 10 Hz), 131.9, 127.5, 126.9, 126.2, 119.8, 115.9 (d, *J* = 22 Hz), 115.5, 111.9. HRMS (ESI) *m/z* calcd for $C_{23}H_{12}FO_5$ [M+H]$^+$ 387.0669, found 387.0672.

2-(4-Chlorobenzoyl)-3-(furan-2-yl)naphtho[2,3-*b*]furan-4,9-dione (7e): Red solid; mp 177–179 °C; yield 130 mg, 65%. ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 6.53–6.54 (m, 1H), 7.34 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 3.6 Hz, 1H), 7.81–7.84 (m, 2H), 7.86 (d, *J* = 8.8 Hz, 2H), 8.25–8.27 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 183.0, 179.5, 173.8, 152.7, 149.5, 143.9, 142.0, 140.4, 134.6, 134.5, 134.1, 133.7, 131.9, 131.0, 129.0, 127.5, 126.9, 115.6, 112.0. HMRS (ESI) *m/z* calcd for $C_{23}H_{12}ClO_5$ [M+H]$^+$ 403.0373, found 403.0381.

3-(Furan-2-yl)-2-(4-methoxybenzoyl)naphtho[2,3-*b*]furan-4,9-dione (7f): Red solid; mp 60–62 °C; yield 123 mg, 62%. ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 3.89 (s, 3H), 6.50–6.51 (m, 1H), 6.94 (d, *J* = 8.8 Hz, 2H), 7.36 (s, 1H), 7.50 (d, *J* = 3.6 Hz, 1H), 7.79–7.81 (m, 2H), 7.92 (d, *J* = 8.4 Hz, 2H), 8.23–8.25 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 182.7, 179.6, 173.8, 164.3, 152.3, 150.5, 143.7, 142.3, 134.4, 134.0, 133.7, 132.3, 132.0, 129.0, 127.4, 126.8, 126.2, 118.8, 115.0, 114.0, 111.7, 55.6. HMRS (ESI) *m/z* calcd for $C_{24}H_{15}O_6$ [M+H]$^+$ 399.0869, found 399.0876.

2-Benzoyl-3-(thiophen-2-yl)naphtho[2,3-*b*]furan-4,9-dione (7g): Red solid; mp 150–152 °C; yield 121 mg, 63%. ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.06 (t, *J* = 8.0 Hz, 1H), 7.43–7.47 (m, 3H), 7.52 (d, *J* = 3.6 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.80–7.82 (m, 2H), 7.91 (d, *J* = 7.6 Hz, 2H), 8.21–8.23 (m, 1H), 8.25–8.27 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 183.8, 179.7, 174.0, 152.4, 150.6, 135.9, 134.6, 134.1, 133.9, 133.8, 132.0, 131.8, 129.9, 128.6, 128.5, 127.6, 127.5, 127.4, 126.9, 126.8, 124.5. HRMS (ESI) *m/z* calcd for $C_{23}H_{13}O_4S$ [M+H]$^+$ 385.0535, found 385.0539.

2-(4-Fluorobenzoyl)-3-(thiophen-2-yl)naphtho[2,3-*b*]furan-4,9-dione (7h): Red solid; mp 125–127 °C; yield 133 mg, 66%. ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.07–7.15 (m, 3H), 7.48 (d, *J* = 5.2 Hz, 1H), 7.52 (d, *J* = 3.6 Hz, 1H), 7.81–7.83 (m, 2H), 7.96–7.99 (m, 2H), 8.22–8.24 (m, 1H), 8.26–8.28 (m, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) *δ* 182.1, 179.7, 173.9, 166.1 (d, *J* = 255 Hz), 152.4, 150.3, 134.6, 134.1, 133.8, 132.6 (d, *J* = 10 Hz), 132.3, 132.2, 132.0, 131.9, 128.7, 127.5, 127.4, 127.3, 126.9, 126.8, 124.7, 115.9 (d, *J* = 22 Hz). HRMS (ESI) *m/z* calcd for $C_{23}H_{12}FO_4S$ [M+H]$^+$ 403.0440, found 403.0449.

2-(4-Methylbenzoyl)-3-(thiophen-2-yl)naphtho[2,3-*b*]furan-4,9-dione (7i): Red solid; mp 157–159 °C; yield 115 mg, 58%. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 2.42 (s, 3H), 7.07 (t, *J* = 4.8 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 5.2 Hz, 1H), 7.53 (d, *J* = 3.6 Hz, 1H), 7.79–7.84 (m, 4H), 8.21–8.23 (m, 1H), 8.25–8.27 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 183.4, 179.8, 174.0, 152.3, 150.9, 145.1, 134.5, 134.1, 133.8, 133.3, 132.1, 131.7, 130.1, 129.4, 128.5, 127.6, 127.4, 126.9, 124.0, 21.8. HRMS (ESI) *m/z* calcd for $C_{24}H_{15}O_4S$ [M+H]$^+$ 399.0691, found 399.0681.

2-(2-Naphthoyl)-3-(4-bromophenyl)naphtho[2,3-*b*]furan-4,9-dione (7j): Yellow solid; mp 194–195 °C; yield 154 mg, 61%. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.43 (d, *J* = 8.4 Hz, 2H), 7.52–7.59 (m, 3H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.81–7.83 (m, 2H), 7.88–8.00 (m, 4H), 8.18–8.20 (m, 1H), 8.27–8.30 (m, 1H), 8.51 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 183.3, 180.0, 174.0, 152.4, 150.7, 135.8, 134.6, 134.2, 133.7, 133.0, 132.7, 132.2, 131.8, 131.2, 129.9, 129.2, 128.7, 127.8, 127.4, 127.2, 127.0, 126.9, 124.7, 123.7. HRMS (ESI) *m/z* calcd for $C_{29}H_{16}BrO_4$ [M+H]$^+$ 507.0232, found 507.0221.

2-(2-Naphthoyl)-3-(3-fluorophenyl)naphtho[2,3-*b*]furan-4,9-dione (7k): Yellow solid; mp 179–180 °C; yield 143 mg, 64%. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.05 (t, *J* = 8.0 Hz, 1H), 7.27–7.35 (m, 3H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.80–7.83 (m, 2H), 7.86–7.99 (m, 4H), 8.18–8.20 (m, 1H), 8.27–8.30 (m, 1H), 8.48 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 183.4, 179.8, 174.0, 162.0 (d, *J* = 246 Hz), 152.3, 150.9, 135.8, 134.6, 134.2, 133.6, 133.0, 132.7, 132.2 (d, *J* = 3 Hz), 130.4, 129.8, 129.5 (d, *J* = 8 Hz), 129.2, 128.6, 127.8, 127.4, 127.0, 126.9, 125.9 (d, *J* = 3 Hz), 124.7, 117.3 (d, *J* = 23 Hz), 116.1 (d, *J* = 21 Hz). HMRS (ESI) *m/z* calcd for $C_{29}H_{16}FO_4$ [M+H]$^+$ 447.1033, found 447.1039.

2-(4-Chlorobenzoyl)-3-(furan-2-yl)-6-methoxynaphtho[2,3-*b*]furan-4,9-dione (7l): Red solid; mp 93–95 °C; yield 134 mg, 62%. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 3.99 (s, 3H), 6.52–6.53 (m, 1H), 7.24 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.35 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 2.8 Hz, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 8.19 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 182.8, 179.4, 172.9, 164.8, 153.2, 149.1, 143.9, 142.0, 140.3, 136.0, 134.6, 131.0, 129.4, 129.0, 125.2, 120.0, 119.8, 115.6, 111.9, 111.7, 56.0. HMRS (ESI) *m/z* calcd for $C_{24}H_{14}ClO_6$ [M+H]$^+$ 433.0479, found 433.0473.

2-(2-Naphthoyl)-3-(4-bromophenyl)-6-methoxynaphtho[2,3-*b*]furan-4,9-dione (7m): Yellow solid; mp 199–201 °C; yield 185 mg, 69%. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 3.96 (s, 3H), 7.24 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.62–7.65 (m, 2H), 7.87–7.99 (m, 4H), 8.20 (d, *J* = 8.8 Hz, 1H), 8.51 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 183.3, 179.9, 173.1, 164.8, 152.9, 150.4, 136.0, 135.8, 133.1, 132.7, 132.2, 131.8, 131.1, 130.8, 129.8, 129.5, 129.1, 128.6, 127.8, 127.3, 127.2, 127.0, 125.6, 124.7, 123.6, 120.0, 111.5, 56.0. HMRS (ESI) *m/z* calcd for $C_{30}H_{18}BrO_5$ [M+H]$^+$ 537.0338, found 537.0328.

2-(2-Naphthoyl)-3-(3-fluorophenyl)-6-methoxynaphtho[2,3-*b*]furan-4,9-dione (7n): Yellow solid; mp 208–210 °C; yield 171 mg, 72%. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 3.96 (s, 3H), 7.03–7.07 (m, 1H), 7.24 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.27–7.35 (m, 3H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.60–7.64 (m, 2H), 7.86–7.98 (m, 4H), 8.21 (d, *J* = 8.8 Hz, 1H), 8.50 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 183.4, 179.8, 173.2, 164.8, 162.3 (d, *J* = 245 Hz), 152.9, 150.6, 136.0, 135.8, 133.1, 132.6, 132.2, 130.5 (d, *J* = 8 Hz), 129.8, 129.5, 129.1, 128.6, 127.8, 127.4, 126.9, 125.9 (d, *J* = 3 Hz), 125.6, 124.7, 120.0, 117.3 (d, *J* = 23 Hz), 116.0 (d, *J* = 21 Hz), 111.5, 56.0. HMRS (ESI) *m/z* calcd for $C_{30}H_{18}FO_5$ [M+H]$^+$ 477.1138, found 477.1149.

Procedure for the Preparation of 4: 2-Hydroxy-1,4-naphthoquinone **1a** (0.75 mmol), chalcone **2a** (0.5 mmol), NIS (0.5 mmol), and DABCO (1.0 mmol) were mixed in 5 mL of CH_3CN in a sealed tube and heated at 80 °C for 12 h. After completion of the reaction, the mixture was cooled to room temperature and separated by flash column chromatography (ethyl acetate/hexane) on silica gel to afford product **4**.

***trans*-2-Benzoyl-3-phenyl-2,3-dihydronaphtho[2,3-*b*]furan-4,9-dione (4):** Yellow solid; mp 168–170 °C; yield 54 mg, 28%. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 4.96 (d, *J* = 5.2 Hz, 1H), 6.08 (d, *J* = 5.2 Hz, 1H), 7.33–7.41 (m, 5H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.68–7.70 (m, 2H), 7.93 (d, *J* = 7.2 Hz, 2H), 7.95–7.97 (m, 1H), 8.12–8.14 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 191.7, 181.2, 177.6, 159.2, 139.3, 134.5, 134.4, 133.2, 132.9, 131.7, 129.4, 129.3, 129.1, 128.3, 127.7, 126.4, 126.3, 126.2, 91.5, 49.6. HRMS (ESI) *m/z* calcd for $C_{25}H_{17}O_4$ [M+H]$^+$ 381.1127, found 381.1128.

Procedure for the Preparation of 5: 2-Hydroxy-1,4-naphthoquinone **1a** (1.5 mmol), chalcone **2a** (1.0 mmol), and DABCO (2.0 mmol) were mixed in 10 mL of CH_3CN in a sealed tube and heated at 100 °C for 12 h. After completion of the reaction, the mixture was cooled to room temperature and separated by flash column chromatography (ethyl acetate/hexane) on silica gel to afford Michael adduct **5**.

2-Hydroxy-3-(3-oxo-1,3-diphenylpropyl)naphthalene-1,4-dione (5): Yellow solid; mp 138–139 °C; yield 317 mg, 83%. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 3.72 (dd, *J* = 18.0, 5.6 Hz, 1H), 4.43 (dd, *J* = 18.0, 10.0 Hz, 1H), 5.16 (dd, *J* = 10.0, 5.2 Hz, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.53–7.65 (m, 5H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.97–8.03 (m, 3H), 8.10 (d, *J* = 7.6 Hz, 1H).

Procedure for the Preparation of Naphtho[2,3-*b*]furan-4,9-dione 3a in Gram Scale: 2-Hydroxy-1,4-naphthoquinone **1a** (1.31 g, 7.5 mmol), chalcone **2a** (1.04 g, 5 mmol), NIS (1.13 g, 5 mmol), and DABCO (1.12 g, 10 mmol) were mixed in 30 mL of CH_3CN in a sealed tube and heated at 100 °C for 12 h. After completion of the reaction, the mixture was cooled to room temperature and separated by flash column chromatography (ethyl acetate/hexane) on silica gel to afford **3a** (1.34 g, 71% yield).

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