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Palladium(II)-catalyzed Oxidative Annulation of 2-Hydroxynaphthalene-1,4-diones and Internal Alkynes via C-H Functionalization

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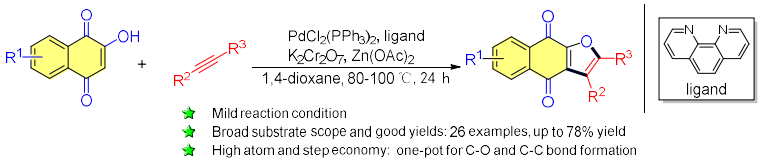
Abstract

An efficient Pd(II)-catalyzed oxidative annulation of 2-hydroxynaphthalene-1,4-diones and internal alkynes has been developed with high step efficiency. A broad range of functional groups are compatible with this reaction, thus providing a new entry to diverse naphtho[2,3-*b*]furan-4,9-dione derivatives in good to high yields.



Naphtho[2,3-*b*]furan-4,9-dione unit has been widely found in numerous natural products and synthetic analogues. As an important privileged structural motif, many of furonaphthoquinones exhibit versatile biological activities such as antitumor,[1] trypanocidal,[2] anti-leukemic activity,[3] inhibitor of HaCaT cell growth,[4] cytotoxic activity toward KB[5] and Vero cells,[6] and inhibitor of human keratinocyte hyperproliferation (**A**–**D**, Fig. 1).[7] For instance, Lapacho **A** has been used as a longtime folk medicine against inflammatory, infectious, stomach, and skin

diseases.[8] Nowadays, Lapacho **A** has been developed into an anticancer drug in clinical treatments and also used against psoriasis.[8]

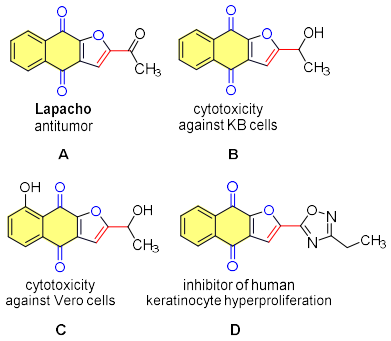


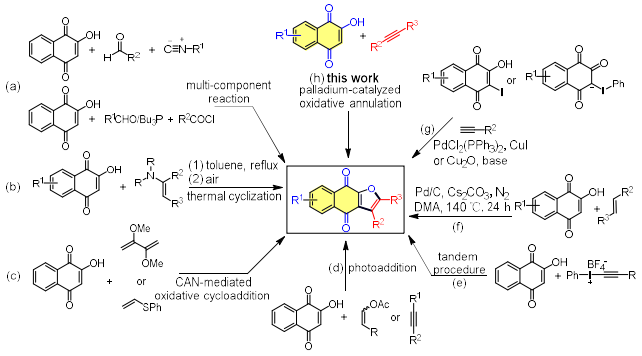
Figure 1. Biologically active furonaphthoquinones.

Substituted furonaphthoquinones are of great interest in pharmaceutical research and drug discovery, therefore, considerable efforts have been focused on the synthetic methods of naphtho[2,3-*b*]furan-4,9-diones. Over the past decades, several different approaches for furonaphthoquinone preparation have been reported (Scheme 1). Mainly starting from 2-hydroxy-1,4-naphthoquinones, multi-component reaction (Scheme 1a),[9] various [3+2] annulation strategies [thermal cyclization with enamines (Scheme 1b),[10] CAN-mediated oxidative cycloaddition with vinyl sulfide[11] and enol ether[12] (Scheme 1c), photoaddition[13] (Scheme 1d)], one-pot cascade procedure (Scheme 1e),[14] and transition-metal-catalyzed methods (Scheme 1f and 1g)[15] have been developed. In addition, other miscellaneous methods such as Diels-Alder cycloaddition/aromatization,[16] oxidative cyclization/isomerization,[17] Friedel-Crafts acylation/oxidation,[18] base-promoted oxidative coupling of 2-hydroxy-1,4-naphthoquinones with (Z)-2-ylideneimidazo[1,2-*a*]pyridin-3(2*H*)-ones,[19] and

bromine-mediated intramolecular cyclization[20] have also been developed. Despite the significant progress made in the synthesis of furonaphthoquinones, novel synthetic approaches with milder reaction conditions and enhanced reaction efficiency are still desirable. For example, Liu[15a] recently demonstrated an atom- and step-efficient approach through Pd-catalyzed reverse hydrogenolysis coupling of 2-hydroxy-1,4-naphthoquinones and olefins (Scheme 1f).

Due to improved atom and step economy, recent years have witnessed an upsurge in heterocycle synthesis based on metal-catalyzed C-H activation processes.[21] Specifically, oxidative annulation reactions between alkynes and different partners (such as phenols,[22a] thiols,[22b] anilines,[22c] and benzoic acids[22d]) set the stage for the development of practical approaches for the atom-efficient formation of heterocycles in a limited number of steps.[22] For instance, Rh- and Ru-catalyzed oxidative annulation between α-naphthol and alkynes have been independently developed for the synthesis of naphthopyrans by Miura[23] and Ackermann,[24] respectively. Ackermann[25] also demonstrated an atom- and step-economical synthesis of isocoumarins through oxidative annulations of alkynes by carboxylic acids using a ruthenium catalyst. Sahoo group developed a novel one-step synthesis of 2,3-disubstituted benzofurans through Pd-catalyzed oxidative annulations of phenols with unactivated internal alkynes.[26] More recently, Gogoi described a ruthenium(II)-catalyzed annulation of vinylnaphthols and alkynes to give spiro-pentacyclic naphthalenones through C-H activation, dearomatization, and alkyne insertion.[27] With our continuous efforts on metal-catalyzed (Cu[28] and Pd[29])

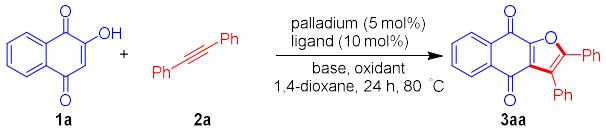
oxidative C-H functionalization, herein we envisioned that 2-hydroxy-1,4-naphthoquinones and alkynes should be suitable substrates for the synthesis of furonaphthoquinones through palladium-catalyzed oxidative [3+2] annulation reaction (Scheme 1h).



Scheme 1. Synthetic methods stating from 2-hydroxy-1,4-naphthoquinones.

2-Hydroxynaphthalene-1,4-dione (**1a**) was selected as the substrate to react with diphenylacetylene (**2a**) in the presence of different combinations of palladium catalysts, nitrogen-based ligands, and oxidants (Table 1). The blank experiment (without the catalyst and ligand) was examined in 1,4-dioxane at 80 ℃ for 24 h using NaOAc as the base, and no desired product was obtained. We then tested the reaction conditions previously used for oxidative annulations of phenols with unactivated internal alkynes.[26] However, a combination of $Pd_2(dba)_3$ (2.5 mol%), 1,10-phenanthroline (Phen, **L1**, 10 mol%), and NaOAc as the base cannot efficiently promote the reaction in 1,4-dioxane, and **3aa** was obtained in a low yield (26%, entry 1). The ^1H and ^{13}C NMR spectroscopy data and melt point of the target **3aa** were consistent with the reported literature.[15a] A survey of palladium catalysts showed that $PdCl_2(PPh_3)_2$ provided better results (35% yield) than $Pd_2(dba)_3$, $Pd(PPh_3)_4$, $Pd(OAc)_2$, $PdCl_2$, and $PdCl_2(MeCN)_2$ (15-32% yields) with Phen as the ligand and

Table 1. Condition optimization for the synthesis of **3aa**[a]



1a 2a 3aa

entry	catalyst/ligand[b]	oxidant/base	yield (%)[c]	entry	catalyst/ligand[b]	oxidant/base	yield (%)[c]
1[d]	$Pd_2(dba)_3$/L1	$Cu(OAc)_2$/NaOAc	26	16	$PdCl_2(PPh_3)_2$/L1	$K_2Cr_2O_7$/NaOMe	38
2	$Pd(PPh_3)_4$/L1	$Cu(OAc)_2$/NaOAc	32	17	$PdCl_2(PPh_3)_2$/L1	$K_2Cr_2O_7$/NaO^{t}Bu	trace
3	$PdCl_2(PPh_3)_2$/L1	$Cu(OAc)_2$/NaOAc	35	18	$PdCl_2(PPh_3)_2$/L1	$K_2Cr_2O_7$/NEt_3	N.D.
4	$Pd(OAc)_2$/L1	$Cu(OAc)_2$/NaOAc	24	19	$PdCl_2(PPh_3)_2$/L1	$K_2Cr_2O_7$/$Zn(OAc)_2$	78 (73)[e]
5	$PdCl_2$/L1	$Cu(OAc)_2$/NaOAc	18	20	$PdCl_2(PPh_3)_2$/–	$K_2Cr_2O_7$/$Zn(OAc)_2$	N.D.
6	$PdCl_2(MeCN)_2$/L1	$Cu(OAc)_2$/NaOAc	15	21	$PdCl_2(PPh_3)_2$/L2	$K_2Cr_2O_7$/$Zn(OAc)_2$	18
7	$PdCl_2(PPh_3)_2$/L1	AgOAc/NaOAc	35	22	$PdCl_2(PPh_3)_2$/L3	$K_2Cr_2O_7$/$Zn(OAc)_2$	35
8	$PdCl_2(PPh_3)_2$/L1	Ag_2CO_3/NaOAc	N.D.	23	$PdCl_2(PPh_3)_2$/L4	$K_2Cr_2O_7$/$Zn(OAc)_2$	43
9	$PdCl_2(PPh_3)_2$/L1	$K_2S_2O_8$/NaOAc	N.D.	24	$PdCl_2(PPh_3)_2$/L5	$K_2Cr_2O_7$/$Zn(OAc)_2$	trace
10	$PdCl_2(PPh_3)_2$/L1	$K_2Cr_2O_7$/NaOAc	53	25[f]	$PdCl_2(PPh_3)_2$/L1	$K_2Cr_2O_7$/$Zn(OAc)_2$	15
11	$PdCl_2(PPh_3)_2$/L1	$KMnO_4$/NaOAc	42	26[g]	$PdCl_2(PPh_3)_2$/L1	$K_2Cr_2O_7$/$Zn(OAc)_2$	trace
12	$PdCl_2(PPh_3)_2$/L1	O_2/NaOAc	N.D.	27[h]	$PdCl_2(PPh_3)_2$/L1	$K_2Cr_2O_7$/$Zn(OAc)_2$	26
13	$PdCl_2(PPh_3)_2$/L1	$Cu(OTf)_2$/NaOAc	15	28[i]	$PdCl_2(PPh_3)_2$/L1	$K_2Cr_2O_7$/$Zn(OAc)_2$	26
14	$PdCl_2(PPh_3)_2$/L1	$Cu(OAc)_2$/HCOONa	43	29[j]	$PdCl_2(PPh_3)_2$/L1	$K_2Cr_2O_7$/$Zn(OAc)_2$	47
15	$PdCl_2(PPh_3)_2$/L1	$Cu(OAc)_2$/$NaHCO_3$	45	30	$PdCl_2(PPh_3)_2$/L1	$K_2Cr_2O_7$/$Zn(OAc)_2$	79[k]/76[l]/78[m]

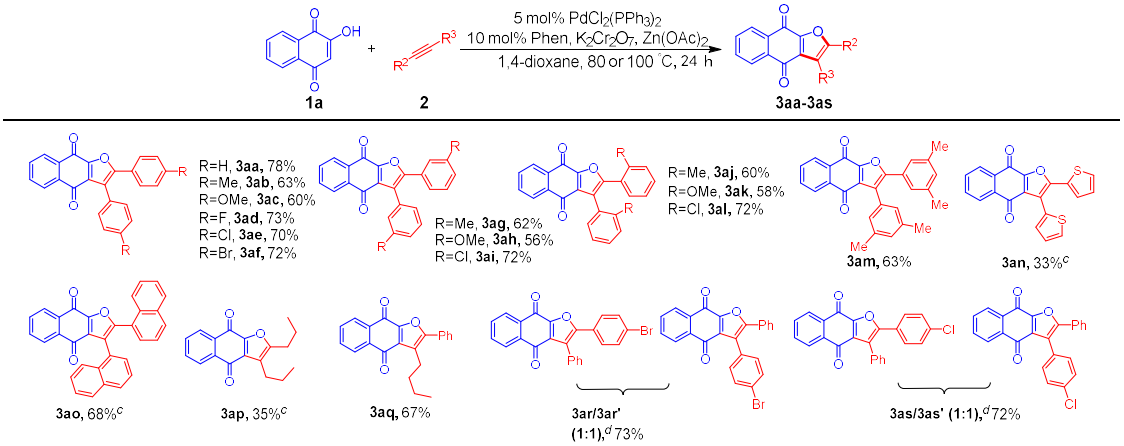
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), catalyst (0.01 mmol), ligand (0.02 mmol), oxidant (2 equiv), and base (2 equiv) in solvent (2 mL) at 80 ℃ for 24 h. [b] L1 = 1,10-phenanthroline, L2 = 2,2'-bipyridine, L3 = 4,7-diphenyl-1,10-phenanthroline, L4 = 3,4,7,8-tetramethyl-1,10-phenanthroline L5 = oxalaldehyde dioxime. [c] Isolated yield after chromatography. [d] 2.5 mol% $Pd_2(dba)_3$ was used. [e] One millimole scale. [f] DMF. [g] DMSO or DCE. [h] THF. [i] MeCN. [j] toluene. [k] 100 ℃. [l] 110 ℃. [m] 24 h.

$Cu(OAc)_2$ as the oxidant (entries 1-6). Among the range of oxidants [AgOAc, Ag_2CO_3, $K_2S_2O_8$, $K_2Cr_2O_7$, $KMnO_4$, O_2 and $Cu(OTf)_2$, entries 7-13] that were surveyed, $K_2Cr_2O_7$ appeared to be optimal and gave **3aa** with an enhanced yield (53%, entry 10). The effect of other bases such as HCOONa, $NaHCO_3$, NaOMe, NaO^{t}Bu, Et_3N, and $Zn(OAc)_2$ on the reaction was next examined (entries 14−19), $Zn(OAc)_2$ provided a better result with 78% isolated yield (entry 19) probably by the chelated 2-hydroxyketone coordination to increase the rate of deprotonation. Using $Zn(OAc)_2$ as the base, examination of nitrogen-containing bidented ligands showed that the Phen (**L1**) was most efficient (entry 19), while 2,2'-bipyridyl (**L2**), ligands with 1,10-phenanthroline scaffold (**L3** and **L4**), and oxalaldehyde dioxime (**L5**) produced lower amounts of **3aa** (from trace to 43% yield, entries 21-24). The rigid *N,N*-pincer phenanthroline-type

ligands provided better results than the acyclic ligand 2,2'-bipyridyl (78% and 18%, **L1** vs **L2**, entries 19 and 21). A survey of reaction media showed that the use of 1,4-dioxane provided better results than those obtained in DMF, DMSO, DCE, THF, acetonitrile, and toluene (entries 19 and 25−29). It is worth noting that the *N*-bearing bidented ligand is essential to this transformation and **3aa** was not produced in the absence of ligand (entry 20).[26] Finally, with increased reaction temperature and time, yields have not obviously been improved (entry 30). In addition, the reaction can be carried out on a 1.0 mmol scale without compromising the yield (78% vs 73%).

With the optimized reaction conditions in hand, the scope of this annulation reaction was then examined. A variety of diversely substituted furonaphthoquinone **3** was obtained in moderate to good yields (Tables 2 and 3). For symmetrically substituted alkyne substrates **2**, the effect of electron-rich and electron-deficient aryl-substituted alkynes was first investigated (Table 2, **2b**−**2o**, **2r**, and **2s**). A variety of substituents (Me, OMe, F, Cl, and Br) on the internal arylalkynes were applicable,

Table 2. Variation of internal alkynes[a,b]

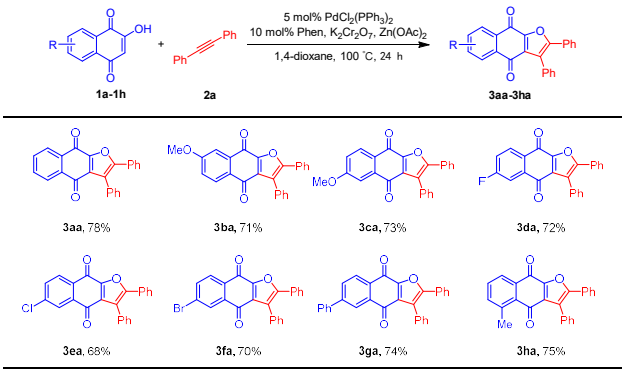


[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $PdCl_2(PPh_3)_2$ (0.01 mmol), Phen (0.02 mmol), $K_2Cr_2O_7$ (0.4 mmol), and $Zn(OAc)_2$ (0.4 mmol) in 1,4-dioxane (2 mL) at 80 ℃ for 24 h. [b] Isolated yields. [c] 100 ℃. [d] The ratio of the regioisomers was determined by NMR analysis.

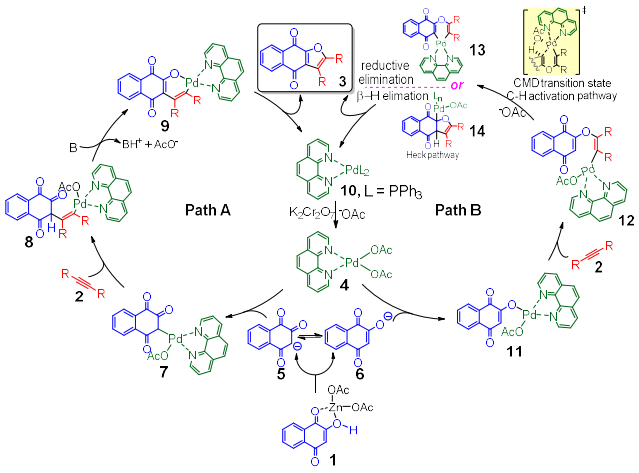
affording the corresponding products in 56−78% yields. Both electron-donating (**2b**−**c**, **2g**−**h**, **2j**−**k**, and **2m**) and electron-withdrawing (**2d**−**f**, **2i**, **2l**) substituents can be incorporated at the *para*-, *meta*-, and *ortho*-position (Table 2, **3ab**−**3al**). The electronic nature of the aromatic motifs affected the outcome to some extent, the introduction of electron-withdrawing substituents can afford higher yields. In addition, dimethyl-substituted (**2m**), hetero (**2n**), and fused aryl (α-naphthyl , **2o**) alkynes were also transformed into the corresponding products in 63%, 33%, and 68% yield, respectively. Because of the lack of conjugation, the symmetrically substituted alkyl alkyne is less reactive.[30] The desired 2,3-dialkyl-substituted furonaphthoquinone **3ap** was obtained from 4-octyne (**2p**) in only 35% yield. A similar result was also observed for asymmetrical 1,2-dialkylalkyne, for instance, 31% yield was obtained for non-4-yne. When asymmetrically substituted internal arylalkynes were used, potential regioselectivity issue exists in the oxidative annulation process. For asymmetrical 1,2-diarylalkynes (**2r**, and **2s**), a 1:1 mixture of two regioisomers was obtained in the two cases (Table 2, **3ar**/**3ar'**, and **3as**/**3as'**), indicating that the difference of electric nature between two aryl groups of unsymmetrical 1,2-diarylalkynes seem not to affect the regioselectivity. However, when alkyl, aryl-substituted alkyne, for example, phenyl- and n-butyl-substituted alkyne **2q** was used, the 3-butyl-2-phenylnaphtho[2,3-*b*]furan-4,9-dione **3aq** was exclusively formed in 67% yield, consistent with the observations of the groups of Larock,[31] Fagnou,[30b] Sahoo,[26] and Patel.[32] Finally, terminal alkynes were incompatible with the protocol due to the formation of alkyne homo-coupling products.[30b]

The generality of 2-hydroxynaphthalene-1,4-diones **1** was then examined. As shown in Table 3, a great variety of 2-hydroxynaphthalene-1,4-diones **1a**–**1h** can be smoothly converted into the corresponding products **3ba**–**3ha** in good yields (68–78%). Several functional groups, such as Me, OMe, Ph, F, Cl, and Br were tolerated in the aryl fragment of **1**. Generally, the electronic nature of the aromatic motifs does not seem to affect the efficiency of this transformation, and electron-donating (Me, OMe, and Ph) and electron-withdrawing substituents (F, Cl, and Br) can be incorporated at different positions of aryl moiety.

Table 3. Variation of 2-hydroxynaphthalene-1,4-diones[a,b]



[a] Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol), $PdCl_2(PPh_3)_2$ (0.01 mmol), Phen (0.02 mmol), $K_2Cr_2O_7$ (0.4 mmol), and $Zn(OAc)_2$ (0.4 mmol) in 1,4-dioxane (2 mL) at 100 ℃ for 24 h. [b] Isolated yields.



Scheme 2. Proposed mechanistic cycle.

Two competitive catalytic cycles for the synthesis of furonaphthoquinones have been proposed in Scheme 2. In the presence of $Zn(OAc)_2$ as the base, the deprotonation of 2-hydroxynaphthalene-1,4-dione **1** yielded two tautomeric anions which existed as either carbanion **5** in the keto-form or as oxygen anion **6** in the enol-form. At this stage, attack of anion onto the electrophilic Pd(II) species may occur in two different ways (Scheme 2, path A and B). Path A involved the attack of carbanion **5** onto catalytic active species **4** to form alkyl-Pd(II) species **7**. Subsequently, the coordination of the internal alkyne **2** to **7** would induce its carbopalladation to afford an alkenyl palladium(II) complex **8**. Base-assisted further deprotonation of the ketone α-carbon of **8** led to O−Pd bond formation, affording intermediate **9**. Palladacycle **9** underwent C−O reductive elimination to afford the desired product **3** and a Pd(0) species **10**, which was oxidized by $K_2Cr_2O_7$ to regenerate the active Pd(II) species **4** for the next catalytic cycle. On the other hand, mechanistic cycle B was initiated by the attack of enol anion **6** onto the electrophilic Pd(II) species **4**, giving the enol-type palladium(II) **11**. The coordination followed by *syn* migratory insertion of internal alkyne 2 into O-Pd bond then afforded alkenyl-Pd(II) species **12**.[33] The final product **3** can be formed possibly through two distinct pathways (C–H activation or Heck pathway). The C–H activation pathway involved a concerted metalation deprotonation (CMD) transition state[34] of alkene to form the palladacycle **13**, which underwent C−C bond-forming reductive elimination to afford the desired furonaphthoquinone **3** and regenerate a Pd(0) species **10**. The Heck pathway involved an intramolecular *syn* migratory insertion into the olefin

moiety of **12,** then was followed by an isomerization process to give the σ-alkyl-palladium(II) acetate **14** with β-hydrogen in a *syn* position relative to the palladium atom. A *syn* β-hydride elimination afforded **3** and a hydridopalladium(II) acetate, which underwent a reversible reductive elimination to regenerate a Pd(0) complex **10**. Finally, Pd(0) resulting from an elimination process was oxidized to Pd(II) by $K_2Cr_2O_7$.

In conclusion, we have developed a modular approach for rapid syntheses of diverse naphtho[2,3-*b*]furan-4,9-dione derivatives through Pd-catalyzed oxidative annulations of 2-hydroxynaphthalene-1,4-diones with readily accessible unactivated internal alkynes. The success of the reaction heavily relies on the careful selection of proper base and oxidant. The combination of $Zn(OAc)_2$ and $K_2Cr_2O_7$ was found to be essential for the efficient formation of furonaphthoquinones. This synthetic method exhibits a broad substrate scope with good yields and excellent regioselectivity for aryl, alkyl-substituted alkynes. Considering considerable valance of the products for medicinal science, this reaction could be of synthetic utility for the discovery of drugs.

EXPERIMENTAL SECTION

General Information. Chemicals were all purchased from commercial supplies and used without further purification unless otherwise stated. Solvents were dried and purified according to the standard procedures before use. Reactions were monitored by analytical thin-layer chromatography (TLC). All reactions were conducted in dried glassware. Purification of reaction products was done by flash chromatography with

230−400 mesh silica gel. Internal alkynes (**2a**–**2m**[35] and **2q**–**2s**[36]) and 2-hydroxynaphthalene-1,4-diones (**1a**–**1f**,[37] **1h**[37] and **1g**[38]) were prepared according to the literature methods. All these substrates are known compounds, and the spectroscopic and physical data are matched with those from the literature. Melting points were determined on a melting point apparatus in open capillaries and are uncorrected. ^{1}H NMR spectra were recorded on a 500 MHz spectrometer, and ^{13}C NMR spectra were recorded at 125 MHz. Unless otherwise stated, deuterochloroform ($CDCl_3$) was used as a solvent. Chemical shifts (δ) are given in parts per million downfield relative to tetramethylsilane (TMS). Chemical shifts for carbon resonances are reported in parts per million and are referenced to the carbon resonance of the solvent $CHCl_3$ (δ = 77.16 ppm). Coupling constants are given in hertz. High-resolution mass spectra were recorded on a BIO TOF Q mass spectrometer equipped with an electrospray ion source (ESI), operated in the positive mode.

General procedures for synthesis of naphtho[2,3-*b*]furan-4,9-dione derivatives. A 10 mL schlenk tube equipped with a magnetic stirring bar was charged with $PdCl_2(PPh_3)_2$ (7.0 mg, 5 mol%), phenanthroline (3.6 mg, 10 mol%), $K_2Cr_2O_7$ (117.6 mg, 2 eq) and $Zn(OAc)_2$ (73.4 mg, 2 eq), and then internal alkynes (0.4 mmol, 2 eq), α-hydroxynaphthoquinone derivative (0.2 mmol, 1 eq) were added. 1, 4-Dioxane (2.0 mL) was then added to the mixture via syringe at room temperature under air. The tube was sealed and put into a preheated oil bath at 80 or 100 ℃ for 24 h. The mixture was cooled to room temperature, quenched with water (5 mL), and diluted

with CH_2Cl_2 (10 mL). The layers were separated, and the aqueous layer was extracted with 3 × 5 mL of CH_2Cl_2. The organic layer is washed with saturated aqueous NaCl (15 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude product is purified by silica gel column chromatography, eluting with 10−20% ethyl acetate/petroleum ether.

*2,3-Diphenylnaphtho[2,3-b]furan-4,9-dione (**3aa**).*[15a] The reaction was carried out on a 1.0 mmol scale. Yellow solid, mp 262-264 ℃; yield, 73% (255.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 – 8.22 (m, 1H), 8.12 – 8.07 (m, 1H), 7.78 – 7.69 (m, 2H), 7.61 – 7.56 (m, 2H), 7.47 (br, 5H), 7.36 – 7.28 (m, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 179.8, 172.4, 154.4, 150.1, 132.8, 132.7, 132.5, 131.5, 129.2, 129.0, 128.8, 128.7, 127.7, 127.6, 127.5, 126.2, 125.9, 125.6, 120.7. HRMS-ESI: $[M + H]^+$ calcd for $C_{24}H_{15}O_3^+$ m/z 351.1016, found 351.1018.

*2,3-Di-p-tolylnaphtho[2,3-b]furan-4,9-dione (**3ab**).* Yellow solid, mp 235-237 ℃; yield, 63% (47.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.3 Hz, 1H), 8.02 (d, *J* = 7.3 Hz, 1H), 7.69 – 7.62 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.22 – 7.19 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H), 2.27 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 179.9, 172.4, 154.7, 149.9, 139.0, 137.3, 132.7, 132.6, 132.5, 131.5, 128.8, 128.4, 128.3, 126.2, 126.1, 125.8, 125.6, 124.8, 120.2, 20.5, 20.4. HRMS-ESI: $[M + H]^+$ calcd for $C_{26}H_{19}O_3^+$ m/z 379.1329, found 379.1332.

*2,3-Bis(4-methoxyphenyl)naphtho[2,3-b]furan-4, 9-dione (**3ac**).* Yellow solid, mp 233-235 ℃; yield, 60% (49.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.2 Hz, 1H), 8.09 (d, *J* = 7.2 Hz, 1H), 7.76 – 7.79 (m, 2H), 7.55 (d, *J* = 8.9 Hz, 2H), 7.38 (d, *J* = 8.6 Hz,

2H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H), 3.82 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 181.1, 173.3, 160.7, 159.7, 155.8, 150.7, 133.7, 133.64, 133.61, 132.6, 131.4, 129.9, 128.9, 126.9, 126.6, 122.4, 121.3, 120.1, 114.2, 114.1, 55.4, 55.3. HRMS-ESI: $[M + H]^+$ calcd for $C_{26}H_{19}O_5^+$ m/z 411.1227, found 411.1229.

2,3-Bis(4-fluorophenyl)naphtho[2,3-b]furan-4,9-dione ***(3ad)****.* Yellow solid, mp 267-269 ℃; yield, 73% (56.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 7.4, 1.4 Hz, 1H), 8.10 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.58 – 7.54 (m, 2H), 7.46 – 7.41 (m, 2H), 7.20 – 7.16 (m, 2H), 7.05 – 7.01 (m, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 179.8, 172.4, 162.4 (163.4, 161.4, d, $^{1}J_{C\text{-}F}$ = 252 Hz), 161.9 (162.9, 160.9, d, $^{1}J_{C\text{-}F}$ = 252 Hz), 153.7, 150.4, 132.9, 132.4, 131.4, 130.9 (130.9, 130.8, d, $^{2}J_{C\text{-}F}$ = 9 Hz), 128.5, 128.4 (128.4, 128.3, d, $^{2}J_{C\text{-}F}$ = 9 Hz), 125.9, 125.7, 124.9 (124.88, 124.86, d, $^{4}J_{C\text{-}F}$ = 2.5 Hz), 123.6 (123.61, 123.59, d, $^{4}J_{C\text{-}F}$ = 2.5 Hz), 119.4, 115.1 (115.08, 115.05, d, $^{3}J_{C\text{-}F}$ = 4 Hz), 114.9 (114.91, 114.88, d, $^{3}J_{C\text{-}F}$ = 4 Hz). HRMS-ESI: $[M + H]^+$ calcd for $C_{24}H_{13}F_2O_3^+$ m/z 387.0827, found 387.0825.

2,3-Bis(4-chlorophenyl)naphtho[2,3-b]furan-4,9-dione ***(3ae)****.* Yellow solid, mp 261-263 ℃; yield, 70% (58.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.0 Hz, 1H), 8.09 (d, *J* = 7.0 Hz, 1H), 7.80 – 7.70 (m, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 180.7, 173.4, 154.4, 151.4, 134.0, 133.4, 132.4, 132.12, 132.11, 131.7, 129.3, 128.9, 128.7, 127.1, 127.0, 126.8, 124.6, 123.2, 120.9. HRMS-ESI: $[M + H]^+$ calcd for $C_{24}H_{13}Cl_2O_3^+$ m/z 419.0236, found 419.0237.

2,3-Bis(4-bromophenyl)naphtho[2,3-b]furan-4,9-dione ***(3af)****.*[9c] Yellow solid, mp

237-238 ℃; yield, 66% (66.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 – 8.21 (m, 1H), 8.11 – 8.07 (m, 1H), 7.79 – 7.71 (m, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 180.7, 173.4, 154.4, 151.4, 136.2, 135.0, 134.0, 133.4, 132.8, 132.4, 131.4, 129.3, 129.2, 129.1, 128.5, 128.4, 127.0, 126.8, 126.7, 120.8.

*2,3-Di-m-tolylnaphtho[2,3-b]furan-4,9-dione (**3ag**).* Yellow solid, mp 235-237 ℃; yield, 62% (46.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.2 Hz, 1H), 8.09 (d, *J* = 7.0 Hz, 1H), 7.77 – 7.67 (m, 2H), 7.52 (s, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.23 (m, 4H), 7.15 (t, *J* = 6.3 Hz, 2H), 2.40 (s, 3H), 2.30 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 180.8, 173.5, 155.6, 151.0, 138.4, 138.3, 133.7, 133.6, 132.6, 130.6, 130.5, 130.3, 129.8, 129.4, 128.6, 128.5, 128.4, 127.7, 127.0, 126.9, 126.6, 124.4, 121.8, 21.5, 21.4. HRMS-ESI: $[M + H]^+$ calcd for $C_{26}H_{19}O_3^+$ m/z 379.1329, found 379.1323.

*2,3-Bis(3-methoxyphenyl)naphtho[2,3-b]furan-4,9-dione (**3ah**).* Yellow solid, mp 225-227 ℃; yield, 56% (45.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 – 8.20 (m, 1H), 8.11 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.74 – 7.68 (m, 2H), 7.52 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.34 (td, *J* = 8.3, 1.5 Hz, 2H), 7.09 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.01 – 6.93 (m, 2H), 6.89 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 8.3 Hz, 1H), 3.69 (s, 3H), 3.41 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 180.7, 173.4, 159.8, 159.5, 155.3, 151.0, 133.8, 133.5, 132.5, 131.7, 129.8, 129.7, 129.6, 126.9, 126.7, 122.3, 121.7, 119.7, 116.5, 115.5, 114.3, 111.6, 55.3, 55.2. HRMS-ESI: $[M + H]^+$ calcd for $C_{26}H_{19}O_5^+$ m/z 411.1227, found 411.1225.

*2,3-Bis(3-chlorophenyl)naphtho[2,3-b]furan-4,9-dione (**3ai**).* Yellow solid, mp 266-268 ℃; yield, 72% (60.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 7.4, 1.3 Hz,

1H), 8.11 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.80 – 7.73 (m, 2H), 7.65 (t, *J* = 1.7 Hz, 1H), 7.49 – 7.42 (m, 3H), 7.36 – 7.33 (m, 3H), 7.24 (d, *J* = 7.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 180.5, 173.5, 154.0, 151.4, 135.0, 134.7, 134.1, 134.0, 133.4, 132.3, 131.6, 130.2, 130.1, 130.0, 129.8, 129.3, 129.1, 128.2, 127.2, 127.0, 126.8, 125.3, 121.1. HRMS-ESI: $[M + H]^+$ calcd for $C_{24}H_{13}Cl_2O_3^+$ m/z 419.0236, found 419.0237.

*2,3-Di-o-tolylnaphtho[2,3-b]furan-4,9-dione (**3aj**).* Yellow solid, mp 236-238 ℃; yield, 60% (45.4 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.5 Hz, 1H), 8.06 – 8.00 (m, 1H), 7.73 – 7.62 (m, 2H), 7.23 – 7.14 (m, 4H), 7.13 – 7.04 (m, 3H), 7.00 (t, *J* = 7.4 Hz, 1H), 2.24 (s, 3H), 2.06 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 179.8, 172.6, 156.5, 150.8, 136.7, 136.2, 132.8, 132.7, 132.5, 131.5, 129.9, 129.5, 129.4, 129.2, 129.0, 128.6, 128.4, 127.5, 127.0, 125.9, 125.6, 124.7, 124.6, 121.3, 19.5, 19.0. HRMS-ESI: $[M + H]^+$ calcd for $C_{26}H_{19}O_3^+$ m/z 379.1329, found 379.1332.

*2,3-Bis(2-methoxyphenyl)naphtho[2,3-b]furan-4,9-dione (**3ak**).* Yellow solid, mp 227-229 ℃; yield, 58% (47.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.2 Hz, 1H), 8.09 (d, *J* = 7.1 Hz, 1H), 7.78 – 7.68 (m, 2H), 7.40 (t, *J* = 8.2 Hz, 1H), 7.21 (br, 2H), 7.10 (br, 1H), 7.07 – 6.97 (m, 3H), 6.87 (d, *J* = 3.4 Hz, 1H), 3.82 (s, 3H), 3.65 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 180.5, 173.6, 157.4, 157.0, 155.1, 151.8, 133.8, 133.6, 133.5, 132.6, 131.4, 130.9, 130.5, 130.0, 129.6, 126.8, 126.6, 120.6, 120.5, 120.3, 119.8, 118.3, 111.2, 110.7, 55.5, 54.9. HRMS-ESI: $[M + H]^+$ calcd for $C_{26}H_{19}O_5^+$ m/z 411.1227, found 411.1231.

*2,3-Bis(2-chlorophenyl)naphtho[2,3-b]furan-4,9-dione (**3al**).* Yellow solid, mp 227-229 ℃; yield, 72% (60.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.1 Hz, 1H),

8.04 (d, *J* = 6.6 Hz, 1H), 7.73 – 7.65 (m, 2H), 7.58 (br, 1H), 7.43 – 7.34 (m, 3H), 7.29 – 7.27 (m, 2H), 7.21 – 7.14 (m, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 179.5, 172.4, 152.9, 150.4, 133.9, 133.6, 133.0, 132.9, 132.4, 131.3, 130.6, 129.1, 129.0, 128.99, 128.97, 128.8, 128.2, 128.1, 127.2, 126.1, 126.0, 125.8, 124.2, 120.0. HRMS-ESI: $[M + H]^+$ calcd for $C_{24}H_{13}Cl_2O_3^+$ m/z 419.0236, found 4 19.0239.

*2,3-Bis(3,5-dimethoxyphenyl)naphtho[2,3-b]furan-4,9-dione (**3am**).* Yellow solid, mp 265-267 ℃; yield, 63% (51.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 7.4, 1.2 Hz, 1H), 8.03 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.70 – 7.61 (m, 2H), 7.19 (s, 1H), 7.15 (s, 2H), 7.02(br, 1H), 6.98 (s, 2H), 6.90 (s, 1H), 2.29 (s, 6H), 2.16 (s, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 179.8, 172.4, 154.8, 149.8, 137.1, 137.0, 132.6, 131.6, 130.4, 129.2, 129.1, 128.9, 127.5, 126.5, 125.9, 125.6, 123.9, 120.9, 20.3, 20.2. HRMS-ESI: $[M + H]^+$ calcd for $C_{28}H_{23}O_3^+$ m/z 407.1642, found 407.1644.

*2,3-Di(thiophen-2-yl)naphtho[2,3-b]furan-4,9-dione (**3an**).* Yellow solid, mp 183-185 ℃; yield, 33% (23.8 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 6.8 Hz, 1H), 8.04 (d, *J* = 6.9 Hz, 1H), 7.74 – 7.63 (m, 2H), 7.52 (d, *J* = 4.0 Hz, 1H), 7.46 (s, 1H), 7.32 (d, *J* = 3.8 Hz, 1H), 7.19 – 7.15 (m, 2H), 6.99 (br, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 179.4, 172.1, 152.2, 149.5, 132.9, 132.8, 132.3, 131.4, 129.1, 128.7, 128.6, 128.2, 128.1, 127.5, 127.1, 126.7, 126.5, 125.9, 125.7, 112.0. HRMS-ESI: $[M + H]^+$ calcd for $C_{20}H_{11}O_3S_2^+$ m/z 363.0144, found 363.0146.

*2,3-Di(naphthalen-1-yl)naphtho[2,3-b]furan-4,9-dione (**3ao**).* Yellow solid, mp 276-278 ℃; yield, 68% (61.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.5 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 8.06 (d, *J* = 7.5 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.87 –

7.74 (m, 5H), 7.71 (t, *J* = 7.4 Hz, 1H), 7.52 – 7.43 (m, 3H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.37 – 7.30 (m, 3H), 7.20 (t, *J* = 7.7 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 180.4, 173.8, 157.9, 152.2, 133.9, 133.8, 133.6, 133.54, 133.5, 132.6, 132.3, 131.4, 130.8, 130.4, 129.4, 129.1, 128.6, 128.5, 128.3, 127.8, 127.2, 127.1, 126.8, 126.5, 126.4, 126.0, 125.6, 125.4, 125.3, 125.2, 124.8, 122.1. HRMS-ESI: $[M + H]^+$ calcd for $C_{32}H_{19}O_3^+$ m/z 451.1329, found 451.1325.

*2,3-Dipropylnaphtho[2,3-b]furan-4,9-dione (**3ap**).* Yellow solid, mp 133-135 ℃; yield, 35% (19.7 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.7 Hz, 1H), 7.68 – 7.57 (m, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 2.62 (t, *J* = 7.4 Hz, 2H), 2.56 (t, *J* = 7.4 Hz, 2H), 1.77 – 1.68 (m, 2H), 1.64 – 1.56 (m, 3H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 181.1, 175.2, 159.0, 155.2, 135.2, 130.3, 129.4, 129.1, 128.6, 121.9, 121.7, 120.4, 27.7, 25.5, 23.0, 21.7, 13.8, 13.7. HRMS-ESI: $[M + H]^+$ calcd for $C_{18}H_{19}O_3^+$ m/z 283.1329, found 283.1330.

*2-Butyl-3-phenylnaphtho[2,3-b]furan-4,9-dione (**3aq**).* Yellow solid, mp 165-167 ℃; yield, 67% (44.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 5.8, 3.1 Hz, 1H), 8.18 (dd, *J* = 5.8, 3.1 Hz, 1H), 7.80 (d, *J* = 7.3 Hz, 2H), 7.78 – 7.71 (m, 2H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.3 Hz, 1H), 3.10 – 2.97 (m, 2H), 1.76 – 1.70 (m, 2H), 1.55 – 1.47 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 182.0, 173.3, 155.7, 151.2, 133.7, 133.6, 133.5, 132.7, 130.3, 129.6, 129.3, 128.9, 127.1, 126.8, 126.7, 122.8, 32.0, 23.9, 22.9, 13.9. HRMS-ESI: $[M + H]^+$ calcd for $C_{22}H_{19}O_3^+$ m/z 331.1329, found 331.1324.

*Mixture of 2-(4-bromophenyl)-3-phenylnaphtho [2,3-b]furan-4,9-dione (**3ar**) and*

*3-(4-bromophenyl) -2-phenylnaphtho[2,3-b]furan-4,9-dione (**3ar'**).* Yield, 73% (61.6 mg); the ratio (**3ar**:**3ar'** =1:1) is determined by ^{1}H NMR; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.3 Hz, 2H), 8.09 (d, *J* = 7.3 Hz, 2H), 7.79 – 7.68 (m, 4H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 7.0 Hz, 2H), 7.51 – 7.40 (m, 10H), 7.37 – 7.32 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 179.8, 179.6, 172.4, 172.3, 154.5, 153.3, 150.26, 150.21, 132.9, 132.84, 132.8, 132.5, 132.4, 131.39, 131.38, 131.0, 130.9, 130.8, 129.0, 128.9, 128.8, 128.6, 128.3, 128.2, 127.8, 127.7, 127.6, 127.2, 126.4, 126.3, 125.9, 125.8, 125.7, 125.6, 123.2, 121.9, 121.2, 119.4. HRMS-ESI: $[M + H]^+$ calcd for $C_{24}H_{14}BrO_3^+$ m/z 429.0121, found 429.0121, 431.0101.

*Mixture of 2-(4-chlorophenyl)-3-phenylnaphtho [2,3-b]furan-4,9-dione (**3as**) and 3-(4-chlorophenyl)- 2-phenylnaphtho[2,3-b]furan-4,9-dione (**3as'**).* Yield, 72% (55.3 mg); the ratio (**3as**:**3as'** =1:1) is determined by ^{1}H NMR; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.0 Hz, 2H), 8.05 – 7.98 (m, 2H), 7.74 – 7.64 (m, 8H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.52 (t, *J* = 8.3 Hz, 4H), 7.47 – 7.42 (m, 5H), 7.40 – 7.24 (m, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 179.7, 179.3, 172.6, 172.3, 154.9, 151.7, 150.8, 150.5, 134.4, 133.1, 133.05, 133.0, 132.9, 132.5, 132.3, 131.6, 131.4, 131.3, 130.1, 129.4, 128.7, 128.5, 128.4, 128.2, 128.0, 127.9, 126.8, 126.4, 126.3, 126.0, 125.9, 125.8, 125.7, 123.2, 118.7, 117.6, 117.2, 111.9, 111.4. HRMS-ESI: $[M + H]^+$ calcd for $C_{24}H_{14}ClO_3^+$ m/z 385.0626, found 385.0628, 387.1230.

*7-Methoxy-2,3-diphenylnaphtho[2,3-b]furan-4,9-dione (**3ba**).* Yellow solid, mp 274-276 ℃; yield, 71% (53.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.6 Hz, 1H), 7.69 (d, *J* = 2.6 Hz, 1H), 7.58 (d, *J* = 7.0 Hz, 2H), 7.46 (br, 5H), 7.34 – 7.29 (m, 3H), 7.15

(dd, *J* = 8.6, 2.6 Hz, 1H), 3.97 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 180.1, 173.4, 164.1, 155.5, 151.1, 134.7, 130.4, 130.0, 129.9, 129.8, 129.3, 128.8, 128.7, 128.62, 128.59, 127.3, 126.9, 122.0, 119.6, 110.6, 56.0. HRMS-ESI: $[M + H]^+$ calcd for $C_{25}H_{17}O_4^+$ m/z 381.1121, found 381.1128.

*6-Methoxy-2,3-diphenylnaphtho[2,3-b]furan-4,9-dione (**3ca**).* Yellow solid, mp 275-277 ℃; yield, 73% (55.5 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.5 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.47 (br, 5H), 7.34 – 7.30 (m, 3H), 7.18 (dd, *J* = 8.4, 1.8 Hz, 1H), 3.91 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 180.8, 173.0, 164.2, 154.9, 151.6, 135.9, 130.4, 130.0, 129.7, 129.4, 129.1, 128.68, 128.65, 128.61, 128.58, 127.2, 125.8, 121.6, 119.5, 111.2, 55.9. HRMS-ESI: $[M + H]^+$ calcd for $C_{25}H_{17}O_4^+$ m/z 381.1121, found 381.1127.

*6-Fluoro-2,3-diphenylnaphtho[2,3-b]furan-4,9-dione (**3da**).* Yellow solid, mp 282-284 ℃; yield, 72% (53 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 8.5, 5.3 Hz, 1H), 7.90 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 2H), 7.48 – 7.45 (m, 5H), 7.40 – 7.29 (m, 4H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 179.5, 172.1, 166.2 (167.2, 165.2, d, $^{1}J_{C\text{-}F}$ = 257 Hz), 156.0, 151.0, 135.4 (135.38, 135.32, d, $^{3}J_{C\text{-}F}$ = 7.6 Hz), 130.1, 130.04, 130.0, 129.96, 129.9, 128.8, 128.7, 128.6, 128.4, 127.3, 122.0, 120.5 (120.6, 120.4, d, $^{2}J_{C\text{-}F}$ = 23 Hz), 113.7 (113.8, 113.6, d, $^{2}J_{C\text{-}F}$ = 24 Hz). HRMS-ESI: $[M + H]^+$ calcd for $C_{24}H_{14}FO_3^+$ m/z 369.0922, found 369.0921.

*6-Chloro-2,3-diphenylnaphtho[2,3-b]furan-4,9-dione (**3ea**).* Yellow solid, mp 282-284 ℃; yield, 68% (52.2 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 1.9 Hz, 1H), 8.03 (d, *J* = 8.3 Hz, 1H), 7.66 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 2H), 7.50 –

7.44 (m, 5H), 7.36 – 7.29 (m, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 178.7, 171.1, 155.0, 149.8, 139.8, 132.8, 132.6, 130.8, 129.0, 128.9, 128.8, 127.7, 127.6, 127.5, 127.4, 126.3, 125.7, 120.9. HRMS-ESI: $[M + H]^+$ calcd for $C_{24}H_{14}ClO_3^+$ m/z 385.0626, found 385.0628, 387.1230.

*6-Bromo-2,3-diphenylnaphtho[2,3-b]furan-4,9-dione (**3fa**).* Yellow solid, mp 287-289 ℃; yield, 70% (59.9 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.84 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.58 (d, *J* = 7.3 Hz, 2H), 7.49 – 7.42 (m, 5H), 7.36 – 7.29 (m, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 179.9, 172.1, 156.0, 150.7, 136.7, 133.7, 132.2, 130.0, 129.99, 129.9, 129.7, 129.3, 128.8, 128.7, 128.6, 128.4, 127.3, 121.9. HRMS-ESI: $[M + H]^+$ calcd for $C_{24}H_{14}BrO_3^+$ m/z 429.0121, found 429.0121, 431.0101.

*2,3,6-Triphenylnaphtho[2,3-b]furan-4,9-dione (**3ga**).* Yellow solid, mp 293-295 ℃; yield, 74% (63.1 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.15 (d, *J* = 7.9 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.60 (d, *J* = 7.0 Hz, 2H), 7.54 – 7.43 (m, 8H), 7.35 –7.32 (m, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 180.6, 173.5, 155.6, 151.3, 146.6, 138.8, 133.0, 132.2, 131.8, 130.3, 130.1, 129.9, 129.8, 129.1, 128.9, 128.7, 128.7, 128.6, 127.7, 127.30, 127.29, 125.1, 121.9. HRMS-ESI: $[M + H]^+$ calcd for $C_{30}H_{19}O_3^+$ m/z 427.1329, found 427.1328.

*5-Methyl-2,3-diphenylnaphtho[2,3-b]furan-4,9-dione (**3ha**).* Yellow solid, mp 274-276 ℃; yield, 75% (54.6 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.56 (m, 2H), 7.51 – 7.46 (m, 6H), 7.34 – 7.29 (m, 3H), 2.51 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 180.7, 173.8, 155.4, 151.2, 144.9, 134.4, 132.5,

131.4, 130.4, 130.1, 129.7, 128.8, 128.7, 128.61, 128.59, 127.3, 127.2, 127.1, 121.8, 21.8. HRMS-ESI: $[M + H]^+$ calcd for $C_{25}H_{17}O_3^+$ m/z 365.1172, found 365.1176.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.

^1H and $^{13}C\{^1H\}$ NMR spectra of the products and High-resolution mass spectra of new compounds (PDF).

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Notes

The authors declare no competing financial interest.

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