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CATALYST-FREE SYNTHESIS OF 1-PHENYLNAPHTHO[2,1-*b*]FURAN DERIVATIVES UNDER MICROWAVE IRRADIATION

Baolong Wang,[1] Jinfu Zhang,[1] Jianhong Liao,[1] Yiyuan Peng,[2]* and Hua Zheng[1]*

[1]School of Chemistry, Chemical Engineering and Life Sciences, Wuhan University of Technology, Wuhan, Hubei, P. R. China. [2]School of Chemistry, Jiangxi Normal University, Nanchang, Jiangxi, P. R. China
E-mail:zhenghuawhut@163.com

Abstract – An environmentally benign and efficient method has been developed for the synthesis of naphtho[2,1-*b*]furan from (*E*)-(2-nitrovinyl)benzene and naphthalen-2-ol in brine media under catalyst-free conditions through microwave-assisted technology. The advantages of this process are that it is catalyst-free, has an easy work-up, provides good yields, and uses brine as the solvent which is considered to be relatively environmentally benign.

Green chemistry, which emphasizes the development of environmentally benign chemical processes and technologies has attracted much attention in recent years.[1] Organic solvents represent the biggest pollution problem in many synthetic organic processes.[2] Water as a green reaction medium has gained considerable interest in view of its low cost, safety, and environmentally benign properties.[3] Furthermore, catalyst-free reaction protocols in water will also be one of the most suitable strategies, which will meet the requirements of green chemistry as well as develop libraries of medicinal scaffolds.[4]

Heterocyclic rings are of remarkable biological and chemical significance in many fields,[5] including biological field and pharmaceutical field. Naphthofurans are important classes of heterocyclic compounds that are present as key structural motifs in many pharmaceuticals and biologically active natural products[6] (Figure 1). Some naturally occurring substances in this family exhibit a variety of interesting pharmacological properties such as anticancer,[7] anti-inflammatory,[8] regulators of the nuclear receptor HNF4R,[9] and imaging agents for β-amyloid plaques in the brain[10] and many others.[11]

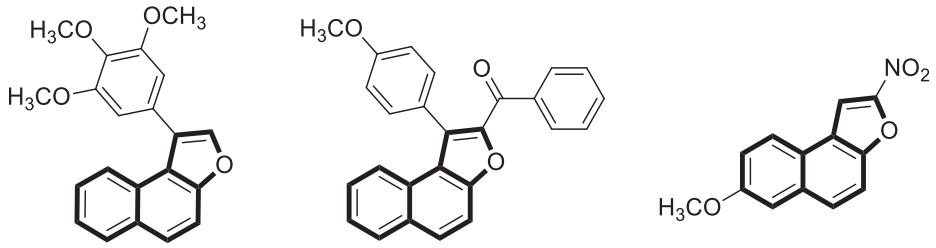


Figure 1. Biologically important molecules of naphtho[2,1-*b*]furan compounds

Considerable attention has been directed toward the synthesis of compounds with naphtho[2,1-*b*]furan framework because of their remarkable biological activities. In more recent years, a wider variety of efficient methods have been developed for the synthesis of naphtho[2,1-*b*]furan. Among which. the more approaches are *via* the cyclization reactions of allyl naphthols or allyl iodonaphthyl ethers promoted by metal catalysts such as Cu and Pd.[12] More recently, Rao and his co-workers also reported an efficient and simple strategy using sequential hydroarylation of naphthols and alkynes in the presence of $In(OTf)_3$ under microwave irradiation followed by one-pot Heck-oxyarylation of generated 1-substituted-α-hydroxystyrenes.[13] And Hajra also used $In(OTf)_3$ catalyst for the coupling of nitroalkenes with naphthols into naphthofurans.[14] In addition, there is another way to synthesis naphthofurans, that is using acid-catalyst.[15] It also can prepare naphthofurans in a high yield.

A number of methods have been developed for the synthesis of 2,3-diarylbenzofurans, but synthetic routes for naphthofurans are limited. Most of the existing methods suffer from certain liminations with respect to yield, substrate scope, or apparative requirements, and are not suitable for the preparation of compound libraries.[16] The synthesis of diversified naphthofurans still presents a major challenge in organic synthesis. Therefore, the development of a versatile method to synthesize substituted naphtho[2,1-*b*]furans is highly desired.

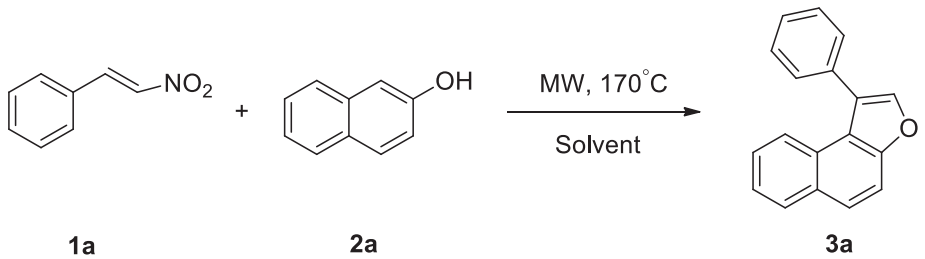
Our recent studies have been focusing on the development of new synthetic pathways for the preparation of heterocyclic compounds.[17] We report herein an environmentally benign and efficient method for the synthesis of naphtho[2,1-*b*]furans from naphthalen-2-ol and (*E*)-(2-nitrovinyl)benzene via tandem reaction through microwave-assisted technology. To the best of our knowledge, this is the first report of the synthesis of naphtho[2,1-*b*]furan derivatives under catalyst-free conditions in aqueous media.

Initially, we explored the tandem reaction of (*E*)-(2-nitrovinyl)benzene **1a** (29.8 mg, 0.2 mmol) and naphthalen-2-ol **2a** (57.6 mg, 0.4 mmol) in different solvents (5 mL) at 170 °C for 25 min under

microwave-assisted condition. As shown in Table 1, we attempted a range of solvents including dimethyl sulfoxide, dimethylformamide, acetonitrile, ethyl alcohol and water (Table 1, entries 1-9). It was pleased to find that the reaction using water-ethanol mixtures as the solvent gave the product **3a** in higher yields, and the yields increased with the increasing of proportion of water (Table 1, entries 5-8). And the corresponding product was obtained in 65% yield in the presence of pure water. Other mixed solvent such as *t*-butyl alcohol-water also yielded a lower result for this conversion (Table 1, entry 9). From the above results, the reaction showed a good reactivity in high polar solvent. In order to further improve the yield, saturated brine was tested for this reaction, the results showed that the yield of the reaction increased to 70% in the presence of 5 mL saturated brine (Table 1, entry 10). It may be assumed that brine has a high concentration and great polarity. When saturated brine was used as a solvent, the reaction temperature can increase stably and rapidly. And reaction temperature is higher than the pure water's boiling point. Meanwhile reactant molecule can vibrate at a high speed. So the reaction can complete in a short period of time. Further investigation reveals the reaction time also affects the addition result (Table 1, entries 11-13), meanwhile 25 min was found to be the most suitable time for the reaction. But when acids, such as TsOH, or weak bases, such as $NaHCO_3$ or K_2CO_3 were employed as promoter, the yields of products were moderate (Table 1, entries 15-17). From the economical and environmental point of view, saturated brine was chosen as the reaction medium for all further reactions.

To further explore the scope of this protocol, we decided to investigate the reaction of (*E*)-(2-nitrovinyl)benzene **1** and naphthalen-2-ol **2** in saturated brine as solvent under catalyst-free conditions (Table 2). The scope of the reaction was examined and the results are shown in Table 2.

Table 1. Optimization of reaction conditions[a]

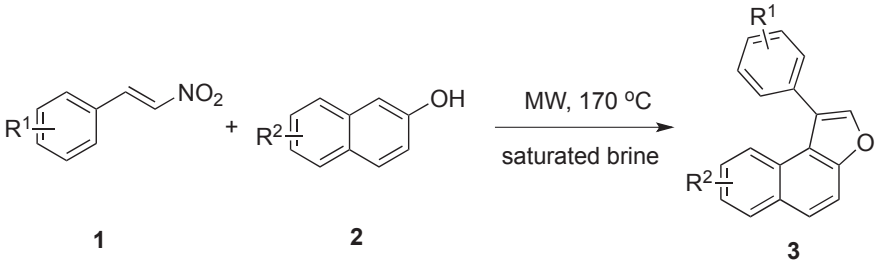


1a **2a** **3a**

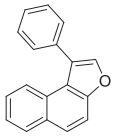
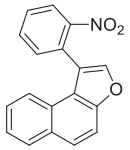
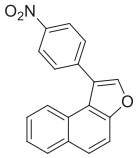
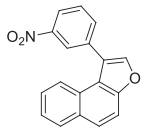
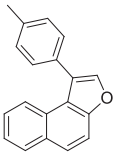
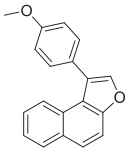
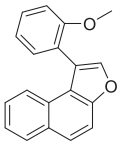
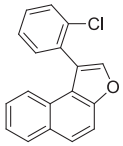
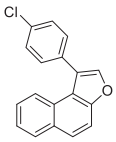
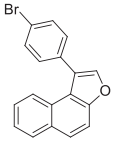
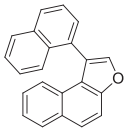
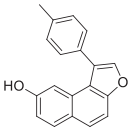
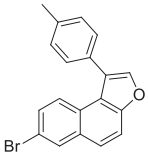
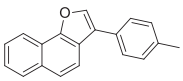
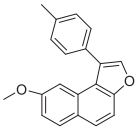
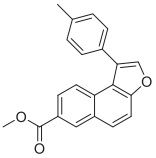
Entry	Solvent	Time	Yield (%)[b]
1	DMSO	25 min	21
2	DMF	25 min	25
3	MeCN	25 min	27
4	EtOH	25 min	37
5	EtOH:H_2O=1:5	25 min	49
6	EtOH:H_2O=1:10	25 min	55
7	EtOH:H_2O=1:20	25 min	60
8	H_2O	25 min	65
9	*t*-BuOH:H_2O=1:20	25 min	51
10	saturated brine	25 min	70
11	saturated brine	10 min	60
12	saturated brine	20 min	63
13	saturated brine	30 min	68
14[c]	saturated brine	10 h	46
15[d]	saturated brine	12 h	34
16[e]	saturated brine	12 h	59
17[f]	saturated brine	12 h	43

[a] A mixture of (*E*)-(2-nitrovinyl)benzene **1a** (29.8 mg, 0.2 mmol) and naphthalen-2-ol **2a** (57.6 mg, 0.4 mmol) without a catalyst in different solvents (5 mL) was placed into a sealed glass vessel together with a Teflon-coated magnetic stirring bar and heated in a microwave reactor for the time at the 170 °C. [b] Isolated yields. [c] The reaction was carried out under reflux conditions. [d] Under reflux conditions，not microwave irradiation conditions, TsOH as promoter. [e] Under reflux conditions， not microwave irradiation conditions, $NaHCO_3$ as promoter. [f] Under reflux conditions，not microwave irradiation conditions, K_2CO_3 as promoter.

Table 2. Reaction of substituted naphtho[2,1-*b*]furans under optimized conditions[a]



1 **2** **3**

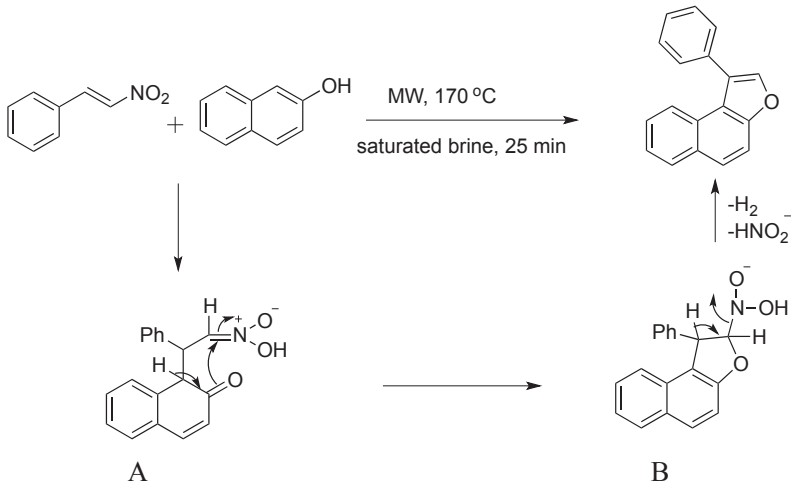
 **3a**, 63%	 **3b**, 88%	 **3c**, 76%	 **3d**, 72%
 **3e**, 70%	 **3f**, 54%	 **3g**, 59%	 **3h**, 64%
 **3i**, 52%	 **3j**, 53%	 **3k**, 60%	 **3l**, 80%
 **3m**, 64%	 **3n**, 77%	 **3o**, 62%	 **3p**, 0%

[a] Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol) were stirred in saturated brine in sealing microwave reaction tube. Isolated yields based on **1**. The average yields of 3 times reactions

Firstly, we investigated a variety of (*E*)-(2-nitrovinyl)benzenes under the similar reaction conditions. Most of products got moderate to good yields, especially when the nitro was touched to the ring of benzene (Table 2, **3b**-**3d**). However, substrates with electron-donating groups and halogen groups (chlorine and bromine) afforded lower yields (Table 2, **3f**-**3j**). In summary we added different group onto the benzene ring of the 2-naphthol or the (*E*)-(2-nitrovinyl)benzene, Obviously, those almost reacted well

(Table 2, **3k**-**3o**). It is a pity that methyl 1-(*p*-tolyl)naphtho[2,1-*b*]furan-7-carboxylate does not react with (*E*)-1-methyl-4-(2-nitrovinyl)benzene under the reaction conditions described above (Table 2, **3p**). For synthetic utility, (*E*)-1-methyl-4-(2-nitrovinyl)benzene (**1e**, 10 mmol) and (*E*)-1-bromo-4-(2-nitrovinyl)benzene (**1j**, 10 mmol) react with naphthalen-2-ol (20 mmol) on the condition to give the corresponding products in 49% and 31% yields, respectively.

Presumably, this process involves Michael addition of naphthols to unsaturated nitroalkenes followed by subsequent cyclization, thereby leading to the final product. We assumed that the formation of the final product need two steps (A and B), as shown in Scheme 1. We thought that the initial formation of Michael adduct (A) leads to the furan moiety after successive intramolecular cyclization followed by elimination of H_2 and nitroxyl (HNO_2^-) from the intermediate (B). Although it was so hard to detect for the detailed process, we deduced that the Michael adduct gave the final product in high yield at specific conditions. All in all, it is clear that the selected conditions enhanced the rate of formation of the final product.



Scheme 1. Proposed mechanism for the efficient reaction

We have developed an efficient, catalyst-free, step-economic, and eco-friendly method for the synthesis of naphtho[2,1-*b*]furan from (*E*)-(2-nitrovinyl)benzene and naphthalen-2-ol under microwave irradiation conditions in saturated brine media as a green reaction medium. The simple work-up, mild reaction conditions and high yields make this new strategy attractive for the preparation of a wide variety of biologically relevant naphtho[2,1-*b*]furan. The investigation of the applications and the design of new synthetic crafts for these products are ongoing in our laboratory.

EXPERIMENTAL

General. All anhydrous solvents were purified according to standard methods. All commercially available reagents were used without further purification. Reactions were monitored by thin-layer chromatography (TLC) on GF 254 plates. Column chromatography was conducted on silica gel (200-300 mesh) using compound-appropriate mixtures of petroleum ether and EtOAc as eluent. ^{1}H and ^{13}C NMR spectra were obtained on a 500 or 600 MH_Z NMR spectrometer.

Synthesis of 1-phenylnaphtho[2,1-*b*]furan derivatives. Compound **1** (0.2 mmol) and compound **2** (0.4 mmol) were stirred in saturated brine in sealing microwave reaction tube. Then the reaction irradiated in a microwave reactor for 25 min at the 170 ºC. After the completion of the reaction, the solution was extracted by EtOAc (3×10 mL). The organic solution removed under reduced pressure and the residue was purified by column chromatography to afford the desired products **3**.

1-Phenylnaphtho[2,1-*b*]furan (3a). (31 mg, 63%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 9.0 Hz, 1H), 7.78 (dd, *J* = 13.7, 7.5 Hz, 2H), 7.71 (dt, *J* = 3.4, 1.9 Hz, 2H), 7.63 – 7.51 (m, 4H), 7.46 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.28, 141.80, 133.23, 130.94, 129.98, 129.03, 128.70, 128.46, 127.97, 126.09, 126.07, 124.56, 124.47, 123.49, 120.84, 112.75. IR (KBr) ν (cm^{-1}): 3055, 2960, 1814, 1584, 1444, 1385, 1252, 1027, 948.

1-(2-Nitrophenyl)naphtho[2,1-*b*]furan (3b). (48 mg, 88%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.83 (dd, *J* = 9.1, 5.3 Hz, 1H), 7.78 – 7.68 (m, 3H), 7.64 (tdd, *J* = 9.0, 6.4, 2.7 Hz, 2H), 7.56 (dd, *J* = 9.6, 5.2 Hz, 1H), 7.47 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.38 (ddd, *J* = 10.6, 5.9, 2.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.96, 149.90, 141.53, 133.51, 132.97, 130.89, 129.53, 129.10, 128.12, 127.98, 126.47, 126.38, 124.68, 124.62, 122.46, 121.38, 119.45, 112.67. IR (KBr) ν (cm^{-1}): 3063, 2965, 1815, 1614, 1528, 1447, 1348, 1263, 1146, 996. HRMS (ESI) calcd for $[C_{18}H_{11}NO_3+Na]^+$: 312.0637, found: 312.0633.

1-(4-Nitrophenyl)naphtho[2,1-*b*]furan (3c). (44 mg, 76%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.6 Hz, 2H), 7.99 (t, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.87 – 7.71 (m, 5H), 7.50 (dd, *J* = 11.1, 3.9 Hz, 1H), 7.46 – 7.40 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.59, 147.59, 142.27, 140.33, 131.00, 130.50, 129.29, 127.88, 126.75, 126.43, 124.78, 123.92, 122.98, 122.82, 119.85, 112.67. IR (KBr) ν (cm^{-1}): 3070, 2960, 1886, 1601, 1516, 1443, 1344, 1251, 1059, 863.

1-(3-Nitrophenyl)naphtho[2,1-*b*]furan (3d). (40 mg, 72%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (t, *J* = 1.9 Hz, 1H), 8.43 – 8.33 (m, 1H), 8.03 – 7.94 (m, 2H), 7.89 – 7.81 (m, 2H), 7.78 – 7.69 (m, 3H), 7.53 –

7.46 (m, 1H), 7.42 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.46, 148.49, 142.29, 135.87, 135.11, 130.96, 129.61, 129.28, 127.91, 126.65, 126.43, 124.73, 124.54, 122.89, 122.79, 122.44, 119.99, 112.68. IR (KBr) ν (cm^{-1}): 3050, 2959, 1898, 1593, 1515, 1430, 1349, 1251, 1059, 867. HRMS (ESI) calcd for $[C_{18}H_{11}NO_3+Na]^+$: 312.0637, found: 312.0639.

1-(*p*-Tolyl)naphtho[2,1-*b*]furan (3e). (36 mg, 70%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.3 Hz, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.81 – 7.74 (m, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.53 (ddd, *J* = 9.3, 6.6, 2.6 Hz, 1H), 7.46 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 2H), 2.57 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.24, 141.71, 137.69, 130.91, 130.14, 129.84, 129.41, 128.99, 128.52, 126.02, 125.95, 124.46, 124.41, 123.53, 120.95, 112.74, 21.43. IR (KBr) ν (cm^{-1}): 3048, 2946, 1884, 1594, 1498, 1443, 1341, 1251, 1059, 861.

1-(4-Methoxyphenyl)naphtho[2,1-*b*]furan (3f). (30 mg, 54%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 – 8.13 (m, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.78 (dd, *J* = 7.3, 3.6 Hz, 1H), 7.74 (s, 1H), 7.63 – 7.59 (m, 2H), 7.53 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 1H), 7.47 (ddd, *J* = 10.4, 5.9, 2.4 Hz, 1H), 7.16 – 7.11 (m, 2H), 3.97 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.53, 153.20, 141.67, 131.10, 130.92, 129.01, 128.54, 126.06, 125.94, 125.29, 124.42, 124.12, 123.45, 121.08, 114.16, 112.75, 55.40. IR (KBr) ν (cm^{-1}): 3001, 2952, 1880, 1591, 1497, 1461, 1342, 1242, 1062, 947.

1-(2-Methoxyphenyl)naphtho[2,1-*b*]furan (3g). (32 mg, 59%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 1H), 7.89 – 7.77 (m, 4H), 7.60 – 7.48 (m, 3H), 7.46 – 7.41 (m, 1H), 7.21 – 7.13 (m, 2H), 3.77 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.01, 153.01, 142.00, 131.99, 130.80, 129.81, 128.90, 128.67, 125.85, 125.71, 124.25, 123.53, 122.15, 121.79, 120.76, 120.51, 112.78, 111.01, 55.49. IR (KBr) ν (cm^{-1}): 3055, 2933, 1906, 1626, 1510, 1462, 1343, 1239, 1061, 948. HRMS (ESI) calcd for $[C_{19}H_{14}O_2+Na]^+$: 297.0891, found: 297.0890.

1-(2-Chlorophenyl)naphtho[2,1-*b*]furan (3h). (36 mg, 64%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.82 (t, *J* = 7.3 Hz, 2H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.70 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.50 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.99, 142.22, 135.29, 132.52, 132.36, 130.87, 129.94, 129.80, 128.89, 128.49, 126.99, 126.37, 126.16, 124.59, 123.16, 121.39, 121.38, 112.76. IR (KBr) ν (cm^{-1}): 3059, 2926, 1925, 1670, 1526, 1468, 1342, 1226, 1079, 950. HRMS (ESI) calcd for $[C_{18}H_{11}OCl+Na]^+$: 301.0396, found: 301.0398.

1-(4-Chlorophenyl)naphtho[2,1-*b*]furan (3i). (29 mg, 52%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 11.8, 4.1 Hz, 2H), 7.82 (d, *J* = 9.0 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.70 (d, *J* = 6.2 Hz, 1H), 7.60 –

7.48 (m, 5H), 7.45 (ddd, *J* = 8.2, 7.0, 1.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.29, 141.79, 134.00, 131.66, 131.20, 130.91, 129.10, 128.91, 128.23, 126.24, 126.20, 124.55, 123.39, 123.22, 120.51, 112.69. IR (KBr) ν (cm^{-1}): 3065, 2924, 1900, 1621, 1521, 1482, 1381, 1226, 1058, 859.

1-(4-Bromophenyl)naphtho[2,1-*b*]furan (3j). (37 mg, 53%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 15.9, 8.1 Hz, 2H), 7.83 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 8.9 Hz, 1H), 7.70 (dd, *J* = 6.2, 4.3 Hz, 3H), 7.56 – 7.49 (m, 3H), 7.48 – 7.44 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.34, 141.77, 132.17, 131.88, 131.53, 130.94, 129.14, 128.25, 126.29, 126.25, 124.60, 123.43, 123.25, 122.16, 120.45, 112.71. IR (KBr) ν (cm^{-1}): 3062, 2955, 1902, 1621, 1550, 1479, 1381, 1178, 1098, 945. HRMS (ESI) calcd for $[C_{18}H_{11}OBr+Na]^+$: 344.9891, found: 344.9889.

1-(Naphthalen-1-yl)naphtho[2,1-*b*]furan (3k). (35 mg, 60%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 7.95 (m, 3H), 7.91 – 7.79 (m, 4H), 7.74 – 7.63 (m, 2H), 7.59 – 7.52 (m, 1H), 7.44 – 7.31 (m, 3H), 7.15 (ddd, *J* = 8.2, 7.0, 1.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.03, 142.54, 133.72, 133.06, 130.84, 130.57, 128.78, 128.70, 128.35, 128.34, 128.27, 126.55, 126.40, 126.23, 126.15, 126.08, 125.58, 124.37, 123.56, 122.24, 121.97, 112.73. IR (KBr) ν (cm^{-1}): 3055, 2926, 1928, 1624, 1554, 1449, 1382, 1187, 1059, 931.

1-(*p*-Tolyl)naphtho[2,1-*b*]furan-8-ol (3l). (44 mg, 80%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.65 (s, 1H), 7.57 (dd, *J* = 8.9, 3.9 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.35 (dt, *J* = 14.2, 6.9 Hz, 3H), 7.06 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.35 – 4.96 (m, 1H), 2.48 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.74, 153.66, 141.29, 137.68, 130.84, 130.01, 129.82, 129.64, 129.34, 125.91, 125.79, 124.19, 119.76, 115.47, 110.33, 106.42, 21.33. IR (KBr) ν (cm^{-1}): 3364, 3069, 2917, 1900, 1625, 1529, 1439, 1319, 1178, 1022, 864. HRMS (ESI) calcd for $[C_{19}H_{14}O_2+Na]^+$: 297.0891, found: 297.0892.

7-Bromo-1-(*p*-tolyl)naphtho[2,1-*b*]furan (3m). (45 mg, 64%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.77 – 7.70 (m, 2H), 7.68 (d, *J* = 9.0 Hz, 1H), 7.55 – 7.46 (m, 3H), 7.38 (d, *J* = 7.7 Hz, 2H), 2.54 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 153.16, 142.05, 137.88, 132.16, 130.86, 129.68, 129.64, 129.48, 129.14, 126.87, 125.12, 124.85, 124.22, 121.03, 118.10, 113.76, 21.42. IR (KBr) ν (cm^{-1}): 3052, 2941, 1893, 1562, 1452, 1467, 1301, 1089, 890.

3-(*p*-Tolyl)naphtho[1,2-*b*]furan (3n). (40 mg, 77%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.95 – 7.88 (m, 2H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.68 – 7.60 (m, 3H), 7.59 – 7.52 (m, 1H), 7.35 (d, *J* = 7.8 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.42, 140.28, 137.30, 131.51, 129.72, 129.25, 128.29, 127.58, 126.42, 125.32, 123.58, 123.44, 122.08, 121.66, 120.14,

118.85, 21.28. IR (KBr) ν (cm^{-1}): 3052, 2919, 1908, 1597, 1516, 1457, 1385, 1082, 1015, 808. HRMS (ESI) calcd for $[C_{19}H_{14}O+Na]^+$: 281.0942, found: 281.0943.

8-Methoxy-1-(*p*-tolyl)naphtho[2,1-b]furan (3o). (36 mg, 62%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.9 Hz, 1H), 7.78 – 7.68 (m, 2H), 7.59 (dd, *J* = 17.1, 8.3 Hz, 3H), 7.46 – 7.33 (m, 3H), 7.18 – 7.10 (m, 1H), 3.65 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.77, 153.69, 141.17, 137.63, 130.29, 130.10, 129.98, 129.61, 129.14, 125.77, 125.63, 124.21, 120.25, 116.24, 110.20, 103.17, 54.97, 21.35. IR (KBr) ν (cm^{-1}): 3019, 2952, 1907, 1628, 1522, 1471, 1378, 1228, 1022, 822. HRMS (ESI) calcd for $[C_{19}H_{14}O+Na]^+$: 311.1048, found: 311.1051.

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18. **3a**, **3c**, **3f**, **3i**, **3k** and **3m** are known compounds.