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TfOH-SiO_2 AS AN EFFICIENT AND RECYCLABLE CATALYST FOR SYNTHESIS OF 3-ARYLBENZOFURANS

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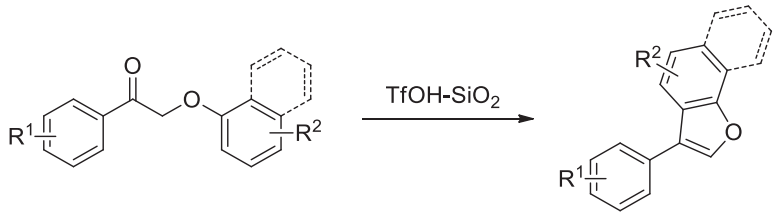
Abstract – A convenient process for the synthesis of 3-arylbenzofurans and their derivatives by 2-phenoxy-1-phenylethanones *via* TfOH-SiO_2 catalyzed is developed. This method provides several advantages such as simple work-up procedure, simple post-treatment process, high yields, broad applicability, practicability, and recycling of the catalyst.

Following the principles of "green chemistry", the search for more environmentally friendly forms of catalysis has gained extensive attentions due to economic and environmental considerations, and one of the leading contenders for environmentally acceptable alternatives is solid-supported catalysis.[1] In the past several years, some Brønsted acids, such as H_2SO_4,[2] $HClO_4$,[3] *etc*.[4] have been successfully supported onto silica gel and applied as solid acids in various catalytic reactions. TfOH supported on functionalized silica also had immerged as a powerful catalyst in organic transformations, but the study of TfOH supported on unmodified chromatographic silica gel is still very rare.[5]

Benzofurans are ubiquitous structural motifs in both natural products and synthetic pharmaceuticals.[6] Numerous natural products containing the benzofuran framework have been reported to display significant biological activities such as antitumor,[7] antiviral,[8] antioxidative,[9] and antifungal properties.[10] Their broad range of biological activities and significant pharmacological potentials have led to the development of many methods for their synthesis. Many methods such as palladium-catalyzed cross-coupling cyclization reaction from alkynes and *o*-halophenols, palladium-catalyzed enolate arylation, cyclofragmentation of oxiranes have been developed to synthesize benzofurans.[11] These processes often required tedious work-up and led to large amount of catalysts waste in Lewis acid catalysis system; And a part of transition metal catalysts were often highly expensive and provided hard separation of the products. Therefore, the development of a simple, fast and flexible method to generate

libraries of such compounds was desirable.

Our recent studies have been focusing on the development of new synthetic pathways for the preparation of heterocyclic compounds.[12] In this paper, we would like to describe an efficient route to benzofurans via TfOH-SiO_2 catalyzed intramolecular Friedel-Crafts reaction of 2-phenoxy-1-phenylethanones (Scheme 1). It can obtain target products 3-arylbenzofurans in a high yields and no by-products 2-arylbenzofurans. To the best of our knowledge, there are no reports for the immobilized Brønsted acid-mediated reaction of 2-phenoxy-1-arylethanones.

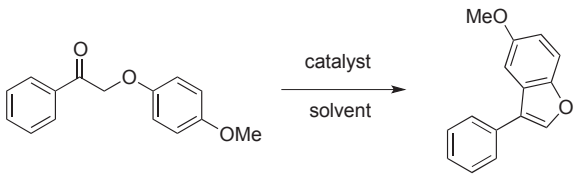


Scheme 1. Synthesis of 3-phenylbenzofuran derivatives

Initially, we started to optimize the reaction conditions by using 2-(4-methoxyphenoxy)-1-phenylethanone[13] **1a** as a model substrate (Table 1). Firstly, we chose 1,2-dichloroethane as reaction solvent, the process was investigated in different immobilized catalysts including $HClO_4$-SiO_2, H_2SO_4-SiO_2, TfOH-SiO_2 under reflux (Table 1, entries 1-3), the product was obtained in 22-45% yields, and we observed that the reaction took place smoothly to give the corresponding product **2a** in the best yield in TfOH-SiO_2 system.

In order to further improve the efficiency of this procedure, different solvents, including water, methanol, ethanol, acetonitrile, tetrahydrofuran, dichloromethane, acetone and toluene were used (Table 1, entries 4-10). Results show that the yield of the reaction increased to 77% in the presence of toluene (Table 1, entry 11). Meanwhile the catalyst loading have a major influence on the yield, when 40 mol% catalysts resulted in higher reaction yield (Table 1, entry 12). Consequently, the optimum reaction conditions were determined to be TfOH-SiO_2 (40 mol%) in toluene under reflux conditions.

Table 1. Optimization of the reaction conditions[a]



1a **2a**

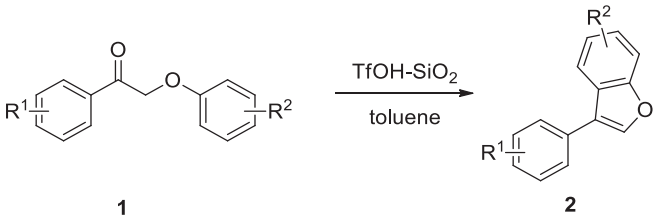
Entry	Catalyst (eq.)	Solvent	Yield (%)[b]
1	$HClO_4$-SiO_2 (0.2 eq.)	$ClCH_2CH_2Cl$	27

2	H_2SO_4-SiO_2 (0.2 eq.)	$ClCH_2CH_2Cl$	22
3	TfOH-SiO_2 (0.2 eq.)	$ClCH_2CH_2Cl$	45
4	TfOH-SiO_2 (0.2 eq.)	H_2O	<10
5	TfOH-SiO_2 (0.2 eq.)	MeOH	<10
6	TfOH-SiO_2 (0.2 eq.)	EtOH	<10
7	TfOH-SiO_2 0.2 eq.)	MeCN	<10
8	TfOH-SiO_2 (0.2 eq.)	THF	<10
9	TfOH-SiO_2 (0.2 eq.)	CH_2Cl_2	43
10	TfOH-SiO_2 (0.2 eq.)	acetone	49
11	TfOH-SiO_2 (0.2 eq.)	toluene	77
12	TfOH-SiO_2 (0.4 eq.)	toluene	94

[a] Reaction condition: Different catalysts were added to a stirred solution of the 2-(4-methoxyphenoxy)-1-phenylethanone (242 mg, 1 mmol) in different solvents (5 mL). The mixture was refluxed for 6 h. Then the crude product was purified by column chromatography give product **2a**. [b] Isolated yields.

To explore the substrate scope of this protocol, the optimized reaction conditions were applied to synthesis a series of 3-arylbenzofuran compounds. 2-Phenoxy-1-phenylethanone compounds **1** were synthesized by using phenols and bromoacetophenones as materials (Table 2). Firstly, the scope of the substrates with different groups on phenoxy ring was explored. It was pleased to find that the reactions proceed well. A wide range of functional groups including F, Cl, Br, Me, 4-*tert*-butyl, 3,4-dimethyl could be well tolerated, leading to the products in moderate to good yields (Table 2, entries 1-8). Then, a range of 2-Phenoxy-1-phenylethanone with electronically different substituents on phenylethanone ring were investigated (Table 2, entries 11-18). The results showed that 2-phenoxy-1-phenylethanone bearing different groups such as Me, Cl, Br, OMe, also afforded the corresponding 3-phenylbenzofurans **2i-2p** in good to high yields.

Table 2. The reaction of various substrates for the synthesis of 3-phenylbenzofuran derivatives[a]



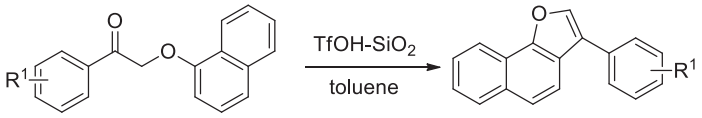
1 2

Entry	R^1	R^2	Yield (%)[b]
1	H	4-OMe	94 **(2a)**
2	H	H	84 **(2b)**
3	H	4-F	73 **(2c)**
4	H	4-Cl	88 **(2d)**
5	H	4-Br	86 **(2e)**
6	H	4-Me	85 **(2f)**
7	H	4-*tert*-butyl	93 **(2g)**
8	H	3,4-dimethyl	86 **(2h)**
9	2-Cl	4-OMe	82 **(2i)**
10	4-Cl	4-OMe	85 **(2j)**
11	4-Br	4-OMe	81 **(2k)**
12	2-Me	4-OMe	88 **(2l)**
13	3-Me	4-OMe	84 **(2m)**
14	4-Me	4-OMe	92 **(2n)**
15	4-*tert*-butyl	4-OMe	74 **(2o)**
16	4-OMe	4-OMe	86 **(2p)**

[a] Reaction condition: TfOH-SiO_2 (0.4 eq.) was added to a stirred solution of the 2-phenoxy-1-phenylethanone derivatives (1 mmol) in toluene (5 mL). The mixture was refluxed for 8 h. Then the crude product was purified by column chromatography to give corresponding product. [b] Isolated yields.

Extension of these results into a bicyclic series gave the expected product naphtho[2,1-*b*]furan by cyclize the 2-naphthoxy-1-phenylethanone. The cyclization of both methyl substituted and halogen substituted 2-naphthoxy-1-phenylethanone proceeded smoothly to afford the corresponding naphthofuran in moderate to good yields (Table 3).

Table 3. The synthesis of 3-phenylnaphthofuran derivatives[a]

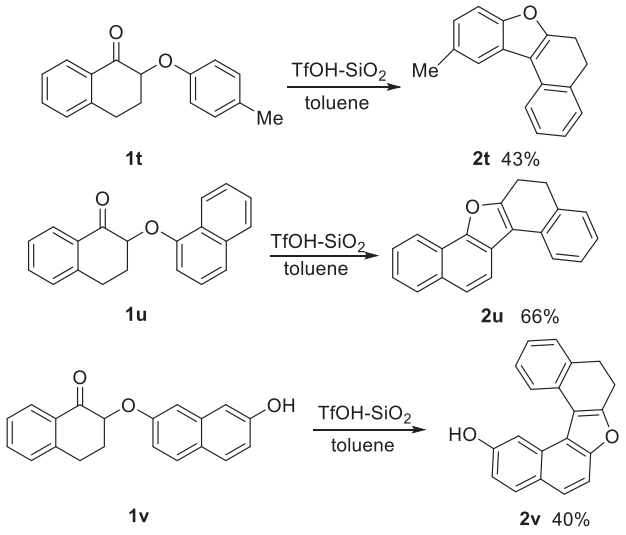


Entry	R^1	Yield (%)[b]
1	H	86 **(2q)**

2	2-Br	**72 (2r)**
3	3-Me	**70 (2s)**

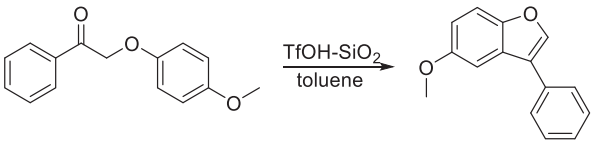
[a] Reaction condition: TfOH-SiO_2 (0.4 eq.) was added to a stirred solution of the 2-naphthoxy-1-phenylethanone derivatives (1 mmol) in toluene (5 mL). The mixture was refluxed for 12 h. Then the crude product was purified by column chromatography to give corresponding product. [b] Isolated yields.

Series of benzofuran derivatives having been readily obtained, we decided to evaluate the scope of this reaction further. Polycyclic compounds **2t-2v** were also obtained under the optimum conditions (Scheme 2), it was found that the ring closing reaction proceeded perfectly to generate the product.



Scheme 2. Synthesis of polycyclic compounds

Table 4. The recycling of 0.5 mmol/g of TfOH-SiO_2



Entry	Times	Yield (%)[a]
1	2	92
2	3	88
3	4	87
4	5	87

5	6	85

[a] Isolated yields. Reaction time was 6 h.

Next, we investigated the reusability and recycling of TfOH-SiO_2. 2-(4-methoxyphenoxy)-1-phenylethanone was selected as a model reaction under the optimized conditions. When the reaction was completed, the catalyst was separated by simple filtration and recovered. TfOH-SiO_2 was reused in subsequent reactions without significant decrease in activity even after six runs (Table 4).

In conclusion, a series of 3-arylbenzofuran derivatives have been synthesized with the catalysis of an efficient and recyclable solid acid catalyst through direct absorption of TfOH onto very cheap chromatographic silica gel. TfOH-SiO_2 has been applied as the catalyst for intramolecular Friedel-Crafts reaction of various 2-phenoxy-1-phenylethanones and gave the products in moderate to excellent yields. The catalyst TfOH-SiO_2 can readily be recovered and reused with almost stable reactivity and yields in 6 runs. In comparison with the homogeneous reactions catalyzed by TfOH, the reaction provides a mildness of the conversion, simple experimental procedure which possesses the potential for application in industry. Further investigations and the design of new synthetic crafts to expand the usage of this TfOH-SiO_2 catalyst to more catalytic organic reactions 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 400 or 500 MH_Z NMR spectrometer.

Preparation for catalyst TfOH-SiO_2. TfOH (3.06 g, 20 mmol) was added to a stirred Et_2O (100 mL) of silica gel (40.0 g, 200-300 mesh). The mixture was stirred for 60 min at rt. Then, Et_2O was removed in vacuo and the residue was dried at 110 °C for 2 h to afford TfOH-SiO_2 (0.5 mmol $\cdot$ g^{-1}) as a white powder.

Synthesis of 3-phenylbenzofuran. 1 was dissolved in 5 mL toluene, 40 mol% TfOH-SiO_2 was added and the mixture refluxed for 6-12 h. The reaction was monitored by TLC, the mixture was collected by filtration after the reaction was finished. The filtrate was purified by column chromatography using EtOAc/ petroleum ether to give corresponding product 3-arylbenzofuran **2**.

5-Methoxy-3-phenylbenzofuran (2a). Yellow oil (211 mg, 94%): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 1H), 7.71 – 7.67 (m, 2H), 7.57 – 7.48 (m, 3H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 2.6 Hz, 1H), 7.03 (dd, *J* = 8.9, 2.6 Hz, 1H), 3.92 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 156.4, 150.9, 142.2, 132.2, 129.0, 127.5, 127.4, 127.1, 122.4, 113.4, 112.2, 103.0, 56.0. HRMS (ESI) calcd for $[C_{15}H_{12}O_2+Na]^+$: 247.0730, found: 247.0732.

3-Phenylbenzofuran (2b). Yellow oil (163 mg, 84%): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.03 – 8.00 (m, 1H), 7.92 (s, 1H), 7.82 – 7.79 (m, 2H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.64 – 7.60 (m, 2H), 7.54 – 7.49 (m, 2H), 7.48 – 7.45 (m, 1H); ^{13}C-NMR (100MHz, $CDCl_3$): δ 156.0, 141.5, 132.2, 129.1, 127.7, 127.6, 126.6, 124.7, 123.2, 122.4, 120.6, 111.9. HRMS (ESI) calcd for $[C_{14}H_{10}O+Na]^+$: 217.0624, found: 217.0626.

5-Fluoro-3-phenylbenzofuran (2c). Yellow oil (155 mg, 73%): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.71 (d, *J* = 7.3 Hz, 2H), 7.66 – 7.55 (m, 4H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.21 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 160.8, 158.5, 152.1, 143.1, 131.7, 129.2, 127.8, 127.4, 122.7, 112.6, 112.5, 106.3. HRMS (ESI) calcd for $[C_{14}H_9OF+Na]^+$: 235.0530, found: 235.0532.

5-Chloro-3-phenylbenzofuran (2d). Yellow oil (201 mg, 88%): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 2.0 Hz, 1H), 7.82 (s, 1H), 7.66 – 7.62 (m, 2H), 7.56 – 7.49 (m, 3H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.36 (dd, *J* = 8.7, 2.1 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 154.2, 142.5, 131.3, 129.1, 128.8, 127.9, 127.8, 127.5, 124.9, 122.1, 120.1, 112.8. HRMS (ESI) calcd for $[C_{14}H_9OCl+Na]^+$: 251.0234, found: 251.0237.

5-Bromo-3-phenylbenzofuran (2e). Yellow solid (234 mg, 86%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 1.8 Hz, 1H), 7.81 (s, 1H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.55 – 7.49 (m, 2H, 7.49 – 7.41 (m, 3H); ^{13}C-NMR (100MHz, $CDCl_3$): δ 154.5, 142.4, 131.3, 129.1, 128.5, 127.8, 127.6, 127.5, 123.2, 122.0, 116.3, 113.3. HRMS (ESI) calcd for $[C_{14}H_9OBr+Na]^+$: 271.9837, found: 271.9838.

5-Methyl-3-phenylbenzofuran (2f). Pale yellow solid (177 mg, 85%): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 1H), 7.82 – 7.77 (m, 3H), 7.65 – 7.56 (m, 3H), 7.55 – 7.47 (m, 1H), 7.34 – 7.28 (m, 1H), 2.63 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 154.4, 141.6, 132.6, 132.4, 129.1, 127.6, 127.5, 126.7, 126.0, 122.1, 120.3, 111.4, 21.6. HRMS (ESI) calcd for $[C_{15}H_{12}O+Na]^+$: 231.0780, found: 231.0782.

5-(*tert*-Butyl)-3-phenylbenzofuran (2g). White solid (233 mg, 93%): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.88 (d, *J* = 1.9 Hz, 1H), 7.83 – 7.76 (m, 2H), 7.67 – 7.60 (m, 3H), 7.59 – 7.47 (m, 2H), 1.55 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 154.2, 146.2, 141.7, 132.5, 129.1, 127.7, 127.6, 127.5, 126.2, 122.7, 122.6, 116.4, 111.2, 35.0, 32.1. HRMS (ESI) calcd for $[C_{18}H_{18}O+Na]^+$: 273.1250, found: 273.1252.

5,6-Dimethyl-3-phenylbenzofuran (2h). Yellow oil (191 mg, 86%): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 1.7 Hz, 1H), 7.86 – 7.80 (m, 2H), 7.70 – 7.61 (m, 3H), 7.58 – 7.51 (m, 1H), 7.16 (s, 1H), 2.70 (d, *J* = 23.6 Hz, 3H), 2.64 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 153.5, 141.4, 132.7, 129.1, 127.7, 127.4, 127.0, 126.2, 122.4, 121.6, 117.8, 21.6, 15.2. HRMS (ESI) calcd for $[C_{16}H_{14}O+Na]^+$: 245.0937,

found: 245.0938.

3-(2-Chlorophenyl)-5-methoxybenzofuran (2i). Yellow oil (212 mg, 82%): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.61 – 7.55 (m, 2H), 7.51 (d, *J* = 5.9 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.08 (d, *J* = 1.7 Hz, 1H), 7.02 (dd, *J* = 5.9, 1.7 Hz, 1H), 3.87 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 156.2, 150.1, 144.3, 133.5, 131.5, 130.8, 130.3, 128.9, 127.6, 127.0, 119.5, 113.5, 112.2, 103.2, 56.0. HRMS (ESI) calcd for $[C_{15}H_{11}O_2Cl+Na]^+$: 281.0340, found: 281.0340.

3-(4-Chlorophenyl)-5-methoxybenzofuran (2j). Yellow oil (219 mg, 85%): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.59 – 7.55 (m, 2H), 7.50 – 7.45 (m, 3H), 7.24 (d, *J* = 2.6 Hz, 1H), 7.00 (dd, *J* = 9.0, 2.6 Hz, 1H), 3.89 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 156.4, 150.8, 142.3, 133.2, 130.6, 129.2, 128.6, 126.7, 121.4, 113.4, 112.3, 102.7, 56.0. HRMS (ESI) calcd for $[C_{15}H_{11}O_2Cl+Na]^+$: 281.0340, found: 281.0342.

3-(4-Bromophenyl)-5-methoxybenzofuran (2k). Yellow oil (245 mg, 81%): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.64 – 7.61 (m, 2H), 7.52 – 7.46 (m, 3H), 7.24 (d, *J* = 2.6 Hz, 1H), 7.01 (dd, *J* = 9.0, 2.6 Hz, 1H), 3.89 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 156.4, 150.8, 142.3, 132.2, 131.1, 128.9, 126.6, 121.4, 121.3, 113.4, 112.3, 102.7, 56.0. HRMS (ESI) calcd for $[C_{15}H_{11}O_2Br+Na]^+$: 324.9835, found: 324.9836.

5-Methoxy-3-(*o*-tolyl)benzofuran (2l). White solid (210 mg, 88%): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.60 – 7.50 (m, 2H), 7.50 – 7.38 (m, 3H), 7.12 – 7.02 (m, 2H), 3.90 (s, 3H), 2.46 (s, 3H); ^{13}C-NMR (100MHz, $CDCl_3$): δ 156.3, 150.2, 143.2, 137.1, 131.1, 130.7, 130.5, 128.5, 128.0, 126.0, 121.7, 113.5, 112.2, 102.9, 56.0, 20.6. HRMS (ESI) calcd for $[C_{16}H_{14}O_2+Na]^+$: 261.0886, found: 261.0885.

5-Methoxy-3-(*m*-tolyl)benzofuran (2m). White solid (200 mg, 84%): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.86 – 7.81 (m, 1H), 7.59 – 7.52 (m, 3H), 7.52 – 7.45 (m, 1H), 7.45 – 7.39 (m, 1H), 7.30 (d, *J* = 9.9 Hz, 1H), 7.12 – 7.05 (m, 1H), 3.97 (s, 3H), 2.56 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 156.3, 150.9, 142.3, 138.7, 132.2, 129.0, 128.3, 128.2, 127.2, 124.6, 122.5, 113.2, 112.2, 103.2, 56.0, 21.6. HRMS (ESI) calcd for $[C_{16}H_{14}O_2+Na]^+$: 261.0886, found: 261.0884.

5-Methoxy-3-(*p*-tolyl)benzofuran (2n). Yellow oil (219 mg, 92%): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.9 Hz, 1H), 7.42 (d, *J* = 2.9 Hz, 2H), 7.40 (s, 1H), 7.10 (dd, *J* = 8.9, 2.6 Hz, 1H), 3.97 (s, 3H), 2.54 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 156.4, 150.9, 142.1, 137.3, 129.8, 129.3, 127.4, 127.3, 122.4, 113.3, 112.2, 103.1, 56.0, 21.3. HRMS (ESI) calcd for $[C_{16}H_{14}O_2+Na]^+$: 261.0886, found: 261.0888.

3-(4-(*tert*-Butyl)phenyl)-5-methoxybenzofuran (2o). White solid (207 mg, 74%): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 1H), 7.69 – 7.64 (m, 2H), 7.60 (dd, *J* = 8.1, 1.2 Hz, 2H), 7.54 – 7.50 (m, 1H), 7.39 (s, 1H), 7.08 – 7.03 (m, 1H), 3.94 (s, 3H), 1.48 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 156.3, 150.9, 150.5,

142.1, 129.3, 127.2, 126.6, 122.3, 113.4, 112.2, 103.0, 56.0, 34.7, 31.4. HRMS (ESI) calcd for $[C_{19}H_{20}O_2+Na]^+$: 303.1356, found: 303.1356.

5-Methoxy-3-(4-methoxyphenyl)benzofuran (2p). White solid (218 mg, 86%): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.60 – 7.57 (m, 2H), 7.47 (d, *J* = 5.9 Hz, 1H), 7.28 (d, *J* = 1.7 Hz, 1H), 7.08 – 7.04 (m, 2H), 7.01 – 6.96 (m, 1H), 3.90 (s, 3H), 3.90 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.1, 156.2, 150.7, 141.6, 128.6, 127.3, 126.4, 124.5, 122.0, 114.5, 114.2, 113.2, 112.2, 102.8, 56.0, 55.9, 55.4. HRMS (ESI) calcd for $[C_{16}H_{14}O_3+Na]^+$: 277.0835, found: 277.0836.

3-Penylnaphtho[1,2-*b*]furan (2q). White solid (210 mg, 86%): ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.45 – 8.42 (m, 1H), 8.22 – 8.17 (m, 1H), 7.99 (d, *J* = 0.8 Hz, 2H), 7.92 (s, 1H), 7.91 – 7.87 (m, 2H), 7.78 – 7.64 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 153.5, 142.0, 133.5, 131.2, 130.2, 129.3, 128.9, 128.7, 128.2, 126.4, 124.8, 124.7, 123.8, 121.1, 113.0. HRMS (ESI) calcd for $[C_{18}H_{12}O+Na]^+$: 267.0780, found: 267.0782.

3-(2-Bromophenyl)naphtho[1,2-*b*]furan (2r). Yellow oil (232 mg, 72%): ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.46 (d, *J* = 8.2 Hz, 1H), 8.02 (t, *J* = 4.1 Hz, 2H), 7.83 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.59 (ddd, *J* = 8.0, 4.2, 1.8 Hz, 2H), 7.47 (m, *J* = 7.5, 0.9 Hz, 1H), 7.32 (m, *J* = 7.8, 1.7 Hz, 1H).^{13}C NMR (126 MHz, $CDCl_3$): δ 150.72, 142.41, 133.56, 132.93, 131.97, 131.65, 129.34, 128.42, 127.54, 126.56, 125.46, 123.93, 123.60, 122.80, 122.37, 121.69, 120.16, 119.34. HRMS (ESI) calcd for $[C_{18}H_{11}BrO+Na]^+$: 321.9991, found: 321.9993. IR (KBr) ν (cm^{-1}): 3138, 3060, 2962, 2962, 2925, 2850, 1952, 1921, 1811, 1749, 1601, 1563, 1522, 1465, 1431, 1384, 1219, 1154, 1112, 1050, 755, 726.

3-(*m*-Tolyl)naphtho[1,2-*b*]furan (2s). Yellow oil (180 mg, 70%): ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.46 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.99 (t, *J* = 4.3 Hz, 1H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.74 – 7.67 (m, 1H), 7.61 (dd, *J* = 11.0, 4.0 Hz, 1H), 7.52 – 7.45 (m, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 2.55 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 151.52, 140.56, 138.73, 132.20, 131.60, 128.99, 128.45, 128.36, 128.35, 126.49, 125.40, 124.86, 123.68, 123.66, 122.08, 121.73, 120.21, 118.93, 21.64. HRMS (ESI) calcd for $[C_{19}H_{14}O+Na]^+$: 258.1043, found: 258.1045. IR (KBr) ν (cm^{-1}): 3133, 3058, 2922, 2854, 1943, 1811, 1744, 1610, 1520, 1456, 1383, 1255, 1113, 1035, 775, 746.

10-Methyl-5,6-dihydronaphtho[2,1-*b*]benzofuran (2t). Yellow oil (101 mg, 43%): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 – 7.76 (m, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.30 (dd, *J* = 10.2, 3.4 Hz, 1H), 7.22 (m, *J* = 7.4, 1.2 Hz, 1H), 7.15 (dd, *J* = 8.3, 1.2 Hz, 1H), 3.20 (t, *J* = 7.9 Hz, 1H), 3.08 (dd, *J* = 12.0, 4.6 Hz, 1H), 2.57 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.83, 153.65, 133.54, 132.55, 131.86, 128.10, 126.91, 125.82, 124.54, 122.74, 119.99, 113.26, 110.90, 29.38, 22.42, 21.61. HRMS (ESI) calcd for $[C_{17}H_{14}O+Na]^+$: 234.1047, found: 234.1045. IR (KBr) ν (cm^{-1}): 3056, 3019, 2925, 2851, 1948, 1907, 1862, 1739, 1619, 1500, 1465, 1378, 1340, 1230, 1151, 1020, 765, 745, 732.

5,6-Dihydrodinaphtho[1,2-*b*:1',2'-*d*]furan (2u). Yellow oil (178 mg, 66%): ^{1}H NMR (500 MHz,

$CDCl_3$): δ 8.50 (d, *J* = 8.2 Hz, 1H), 8.14 (d, *J* = 8.6 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 7.7 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.80 – 7.73 (m, 1H), 7.68 – 7.61 (m, 1H), 7.50 (td, *J* = 7.4, 1.1 Hz, 1H), 7.40 (d, *J* = 6.9 Hz, 1H), 7.35 (td, *J* = 7.4, 1.0 Hz, 1H), 3.31 – 3.26 (m, 2H), 3.26 – 3.20 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 155.77, 150.55, 133.85, 131.95, 131.02, 128.50, 128.35, 127.13, 126.53, 126.16, 124.96, 123.78, 122.97, 121.63, 121.22, 120.02, 118.99, 114.89, 29.66, 22.58. HRMS (ESI) calcd for $[C_{20}H_{14}O+Na]^+$: 270.1046, found: 270.1045. IR (KBr) ν (cm^{-1}): 3053, 2933, 2904, 2840, 1941, 1797, 1695, 1617, 1570, 1524, 1449, 1374, 1341, 1235, 1075, 760, 742, 727.

8,9-Dihydrodinaphtho[2,1-*b*:1',2'-*d*]furan-2-ol (2v). Yellow oil (115 mg, 40%): ^1H NMR (400 MHz, $CDCl_3$): δ 8.08 (dd, *J* = 10.4, 4.7 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 6.8 Hz, 1H), 7.14 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.01 (s, 1H), 3.12 (d, *J* = 7.5 Hz, 1H), 3.01 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.36, 153.55, 153.52, 134.94, 132.19, 130.98, 129.18, 128.29, 126.84, 126.28, 125.88, 125.06, 124.84, 119.04, 116.19, 115.60, 110.08, 108.14, 30.29, 22.78. HRMS (ESI) calcd for $[C_{20}H_{14}O_2+Na]^+$: 286.0995, found: 286.0994. IR (KBr) ν (cm^{-1}): 3503, 3459, 3046, 2942, 2888, 2827, 1906, 1770, 1710, 1620, 1529, 1462, 1355, 1284, 1177, 1027, 762, 740.

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14. The products **2a**, **2b**, **2d**, **2e**, **2f**, **2g**, **2j**, **2n**, **2p** and **2q** are known compounds.