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Graphical Abstract

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Acid-Promoted Furan Annulation and Aromatization: An Access to Benzo[*b*]furan Derivatives

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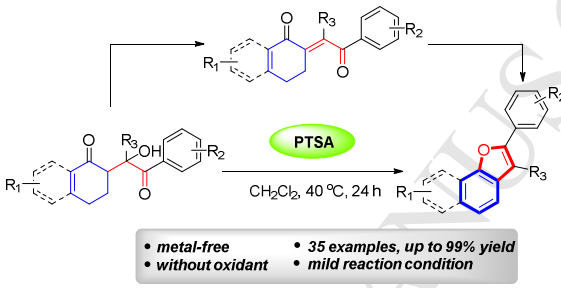
Jun Ao[a], Yidong Liu[a], Shiqi Jia[a], Lu Xue[a], Dongmei Li[a], Yu Tan[a], Wenling Qin[a]* and Hailong Yan[a]*

[a]*Chongqing Key Laboratory of Natural Product Synthesis and Drug Research, School of Pharmaceutical Sciences, Chongqing University, Chongqing 401331, P. R. China.*



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[a] *Chongqing Key Laboratory of Natural Product Synthesis and Drug Research, School of Pharmaceutical Sciences, Chongqing University, Chongqing 401331, P. R. China.*

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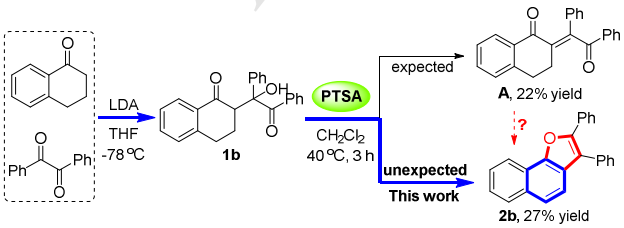
ABSTRACT

An unprecedented PTSA-promoted furan annulation and aromatization in one pot has been developed. This process offers a simple and efficient synthetic route for the construction of various highly substituted benzo[*b*]furan derivatives, which are widely used not only in drug active molecules but also organic semiconductor and organic light-emitting devices. The preliminary mechanism study indicated this transformation proceeded sequentially via furan annulation and aromatization.

1. Introduction

In an ongoing program by our research group, it is required to synthesize α,β-unsaturated 1,4 di-ketone **A** (Scheme 1). Theoretically, the required compound **A** can be easily obtained via an aldol type reaction between 3,4-dihydronaphthalen-1(*2H*)-one and benzil, subsequent dehydration under acidic reaction conditions.[1] However, under these reaction conditions, compound **A** was formed in a relatively low yield along with the formation of an unexpected benzo[*b*]furan derivative **2b**. To the best of our knowledge, such a reaction of substrate **1b** to form highly substituted benzo[*b*]furans under acidic conditions has not been reported. These types of substituted benzo[*b*]furans are privileged structures found in numerous natural products and biologically active compounds,[2] such as vignafuran, stemofuran E, fuliginosin A, and 1,3-dimethoxy-4,6-dimethylnaphthofuran et al. (Figure 1). As a result, there is considerable interest from the synthetic organic community to access benzo[*b*]furan motifs by efficient methodologies, and indeed, various synthetically viable strategies



Scheme 1. Unexpected formation of benzo[*b*]furan motif.

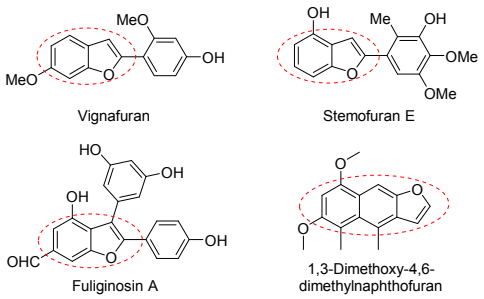
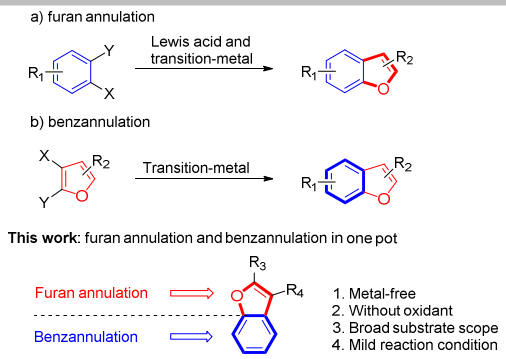


Figure 1. Representative benzo[*b*]furan-containing natural products.

have been devised for the construction of benzo[*b*]furan and its derivatives.[3] Some of the conceptually distinct synthetic strategies toward benzo[*b*]furans are shown in Scheme 2. There are two common ways for the construction of these bicyclic motifs. One of the most explored methods for this purpose is the annulation of the furan ring starting from poly-substituted benzene derivatives through Lewis acid-catalyzed condensation[4] or transition metal-catalyzed oxidative cyclization.[5] Another possible way, for constructing the benzene portion of benzo[*b*]furan via benzannulation of furan derivatives has been recently realized via Ru-catalyzed carbonylative benzannulation by Tang and co-workers.[6] Despite these achievements, the limitations of the preparation of benzo[*b*]furan derivatives still exist. For example, multicomponent catalyst systems, requirement of high temperature and a large excess of reagents et al. As inexpensive and metal-free alternatives, organocatalytic

* Corresponding author. Wenling Qin; e-mail: wenling.qin@cqu.edu.cn;
* Corresponding author. Hailong Yan; e-mail: yhl198151@cqu.edu.cn.

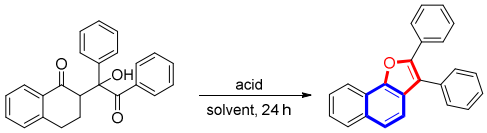


Scheme 2. Strategies toward benzo[*b*]furans.

methods[7] for the synthesis of furan derivatives have recently attracted great interest. Great achievements have been made in this field through phosphine-mediated reactions.[8] However; the synthetic potential of this strategy is limited to the synthesis of benzo[*b*]furan derivatives. Organocatalytic construction of benzo[*b*]furan and their derivatives via furan annulation and aromatization in one pot, to our surprise, has remained elusive

2. Results and discussion

Table 1. Optimization of the reaction conditions.[a]

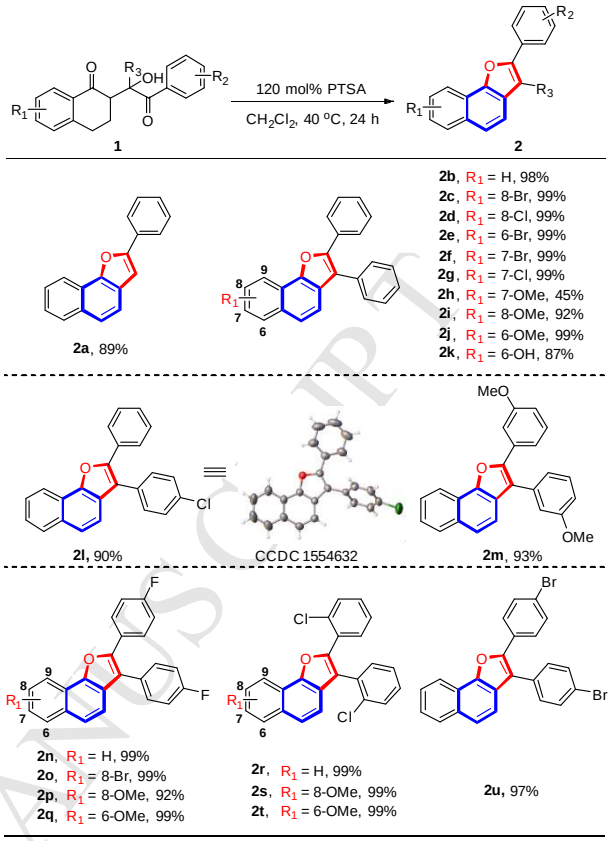


1b 2b

Entry	*T*(°C)	Solvent (1.5 mL)	Acid (mol%)	Yield (%)[b]
1	40	CH_2Cl_2	boric acid (120)	NR
2	40	CH_2Cl_2	citric acid (120)	NR
3	40	CH_2Cl_2	cinnamic acid (120)	NR
4	40	CH_2Cl_2	malonic acid (120)	NR
5	40	CH_2Cl_2	benzoic acid (120)	NR
6	40	CH_2Cl_2	formic acid (120)	NR
7	40	CH_2Cl_2	benzene sulfonic acid (120)	95
8	40	CH_2Cl_2	PTSA (120)	98
9	40	CH_2Cl_2	PTSA (100)	95
10	40	CH_2Cl_2	PTSA (50)	43
11	40	CH_2Cl_2	PTSA (10)	7
12	40	THF	PTSA (120)	21
13	40	toluene	PTSA (120)	73
14	40	$CHCl_3$	PTSA (120)	89
15	40	CCl_4	PTSA (120)	10
16	25	CH_2Cl_2	PTSA (120)	7
17	50	CH_2Cl_2	PTSA (120)	86

[a] Reaction conditions: **1b** (0.1 mmol) and acid in the solvent (1.5 mL) for 24 h. [b] Isolated yield. NR = no reaction.

Table 2. Substrate scope.[a]

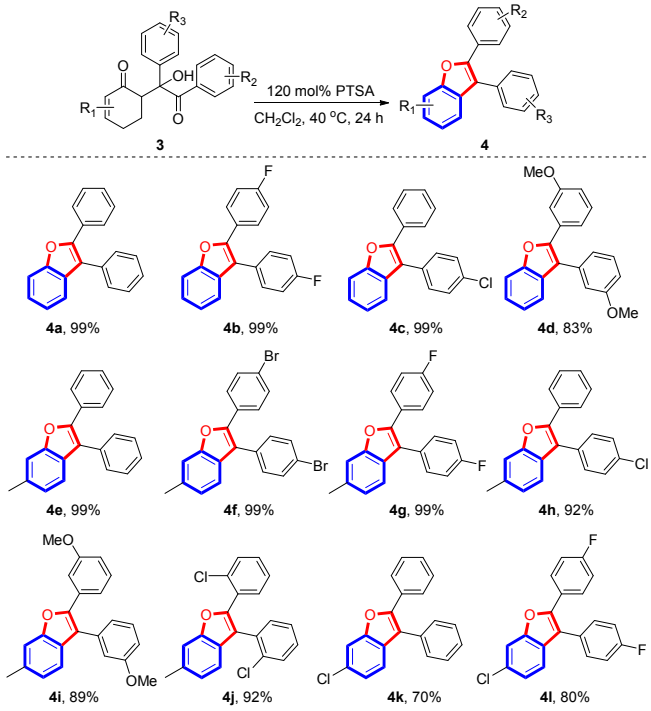


[a] Reaction conditions: **1** (0.1 mmol) and PTSA (120 mol%) in CH_2Cl_2 (1.5 mL) at 40 °C for 24 h. Isolated yield.

until now. We report herein our recent studies towards such process. Moreover, the synthetic process we report herein proceeds efficiently at mild conditions.

Considering the strategies applicable to our goal as well as atomic economy and operating simplicity, we prepared compound **1b** as the model substrate to optimize the reaction conditions. We envisaged that, in an acidic circumstance, **1b** could be dehydrated and then underwent a furan annulation and aromatization in one pot to form benzo[*b*]furan. In order to find the better reaction conditions, as shown in Table 1, firstly, the effect of organic acid on the reaction outcome was investigated with an acid loading of 120 mol% in CH_2Cl_2 (entries 1-8). Among these tested acids, benzene sulfonic acid and *p*-toluenesulfonic acid (PTSA) were found to be the best in term of yield (Table 1, entries 7 and 8) in this benzo[*b*]furan formation reaction. However other organic acids (Table 1, entries 1-6), such as boric acid, benzoic acid, and cinnamic acid did not work at all for this transformation. Although the benzene sulfonic acid and *p*-toluenesulfonic acid (PTSA) showed the almost similar performance, considering more facile commercial availability, PTSA was chosen as the best catalyst for the further condition optimization. The influence of the loading amount of PTSA (entries 9-11) was also studied. The yields of **2b** were gradually decreased with the decrease in the dosage of PTSA. When 10 mol% PTSA was used, only a trace amount of product could be detected. In further experiments, different solvents were examined (entries 12-15). CH_2Cl_2 was proved to be the optimal choice. Polar solvents such as THF was proved to be the much worse solvent for this reaction (entry 12). Finally, we performed

Table 3. Substrate scope.[a]

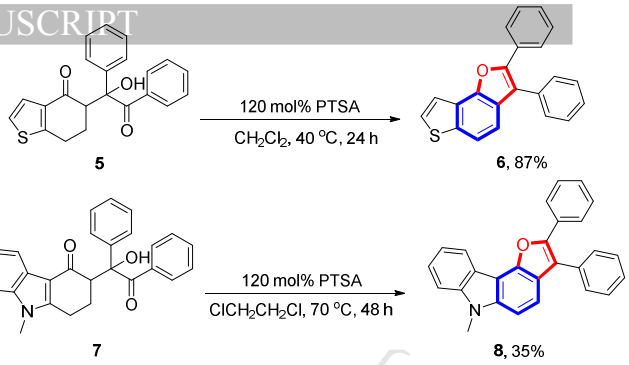


[a] Reaction conditions: **3** (0.1 mmol) and PTSA (120 mol%) in CH_2Cl_2 (1.5 mL) at 40 °C for 24 h. Isolated yield.

the reaction at different temperatures. Both the decrease and the increase in the reaction temperature affected the yield of the reaction, and 40 °C was demonstrated to be the most suitable reaction temperature.

With the optimized reaction condition in hand, we next turned our attention to the substrate scope of this transformation. First, product **2a** was successfully formed with good yield from substrate **1a**. Then, the scope of substitution on 3,4-dihydronaphthalen-1(*2H*)-one was investigated under the optimal conditions. Various substituents at different positions on the aryl rings were well tolerated. When R_1 were halogen substituents, products **2c**-**2g** were formed with high yields and different positions of halogen substituent did not influence the yield of the reaction. However, when R_1 was shifted to 7-methoxyl group, the yield decreased dramatically (**2h**). Surprisingly, when methoxyl group entered the *C*-8 or *C*-6 position, the yields respectively reached to 92% (**2i**) and 99% (**2j**), even with the hydroxyl group, the yield was still high (**2k**). Next, we turned our attention to examine the influence of the electricity nature and the regio effect of substitution groups R_2 and R_3. When R_3 group was *para*-chloro substitution, the reaction also gave the excellent yield (**2l**). The structure of **2l** was confirmed by X-ray analysis. When R_2 and R_3 were *meta*-methoxyl group, a perfect yield of the reaction was obtained (**2m**). When R_2 and R_3 groups were *para*-fluoro substitutions, a series of R_1 groups including 8-bromo (**2o**), 8-methoxyl (**2p**), and 6-methoxyl (**2q**) at different positions were investigated. All of these products were formed with excellent yields. This transformation was also enforceable in the substrates **1r**-**1u**. The nature or position of R_1 group on 3,4-dihydronaphthalen-1(*2H*)-one had no effect on the yield of the reaction. The corresponding products (**2r**-**2u**) were formed with excellent yields as well.

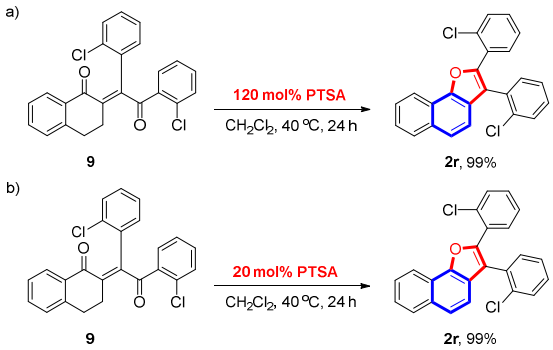
Encouraged by these results, we subsequently investigated the reaction by using 6-(1-hydroxy-2-oxo-1,2-diphenylethyl)cyclohex-2-en-1-one **3a** as substrate. Gratifyingly,



Scheme 3. Synthesis of polycyclic derivatives containing benzo[*b*]furan.

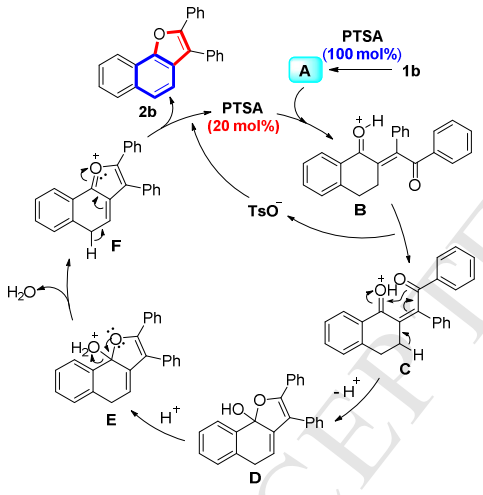
in the presence of PTSA, the reaction proceeded smoothly to afford 2,3-disubstituted benzo[*b*]furan **4a** in the unexceptionable yield under the same conditions. Based on this delighting result, we subsequently explored the scope of this transformation to produce a series of benzo[*b*]furans under this mild reaction conditions. First, we tested the influence of substitution group of R_2 and R_3. As shown in Table 3, di-*para*-fluoro substituted substrate was well tolerated to this transformation and gave product **4b** in the excellent yield. When R_3 was *para*-chloro (**4c**), the yield of the reaction was still perfect. Next, we evaluated di-*meta*- methoxyl substituted substrate, which leads to the product **4d** in wonderful yield as well. Finally, we turned our attention to test the effect of substitution group R_1. No matter what the substitution groups R_2 and R_3 were, when the substitution group at *C*-6 position was methyl group, the corresponding products **4e**-**4j** were formed smoothly with high yields. However, when the R_1 substitution group at *C*-6 position was chlorine, as shown in Table 3, products **4k** and **4l** were obtained in a slightly lower yield because the electron withdrawing nature of chlorine might lead to the electron deficiency in the formed benzo[*b*]furan ring system.

Besides the biological potential of benzo[*b*]furan derivatives, polycyclic derivatives containing benzo[*b*]furan were also widely used in photoelectricity chemistry. After determining the substrate scope of the reaction, we were interested in extending this transformation to photoelectricity area. Polycyclic dithiophenes containing a furan ring has the potential to be used as an organic semiconductor in organic electronic devices.[9] As shown in Scheme 3, product 2,3-diphenylthieno[2,3-*g*]benzofuran **6** has been formed arising from substrate **5** in the satisfied yield. Furthermore, as shown in Scheme 3, we also synthesized a fused heterocyclic ring compound **8** under the same reaction conditions with a slight modification (see Supporting Information). Compound **8** has showed the promising prospect in the field of Organic Light-Emitting Devices (OLED).[10]



Scheme 4. Mechanism study.

When monitoring the reaction with thin layer chromatography (TLC), we found that, at the early stage of the reaction, two new spotsappeared simultaneously. In the process of reaction, however, the signals on TLC showed a change in two different trends. The intermediate spot disappeared in pace with the increase in final product spot (for details please see Supplementary data). We envisage that this intermediate may be the dehydrated product of substrate **1** and can be isolated for structural identification. As shown in Scheme 4 a, intermediate **9** was isolated and treated under normal reaction conditions. Subsequently, product **2r** was successfully formed in a yield of 99%. Inspirit by this result, we performed a reaction with catalytic amount (20 mol%) of acid in the transformation of **9**, as shown in Scheme 4 b, the desired benzo[*b*]furan derivative was successfully formed with high yield. This result indicated that our reaction firstly proceeded via a dehydration process and then through a cascade furan annulation and aromatization to form benzo[*b*]furan derivatives in one pot. Based on the experimental results and phenomenon, simultaneously inspired by the previous reports,[11] a postulated reaction pathway for this transformation is depicted in Scheme 5. We assumed that substrate **1b** was converted into intermediate **A** through dehydration in the presence of PTSA. Then, intermediate **A** was protonated by PTSA, and the protonated **B** underwent an inner molecular aldol type reaction to form an acetal **D**, which was unstable under an acidic condition and subsequently converted into intermediate **E**. Next, intermediate **E** was then transformed to **F** through dehydration. Finally, intermediate **F** was deprotonated to formed final product **2b** through an aromatization process, meanwhile the catalytic acid was regenerated, thus close the catalytic cycle.



Scheme 5. Proposed mechanism.

3. Conclusion

In summary, we developed an efficient organocatalytic method to access benzo[*b*]furan derivatives via furan annulation and aromatization in one pot. According to this metal-free procedure, a range of highly substituted benzo[*b*]furan motifs were synthesized with excellent yields. Notably, we utilized this method to achieve the preparation of fused ring systems containing a benzo[*b*]furan motif which had shown their potential as photoelectric materials. Based on the experimental results, a plausible mechanism via furan annulation and aromatization has been proposed for this transformation. Further detailed mechanistic studies and applications of this reaction are currently in progress in our laboratory.

4. Experimental section

4.1 General methods

All reagents were obtained from Adamas, Aladin, Accela, or Acros and used without further purification unless otherwise noted. The products were purified by column chromatography with Huanghai Silica Gel 50-75 um, ultrapure silica gel. ^{1}H and ^{13}C NMR spectra were recorded on an Agilent 400MR DD2 (400 MHz) or Agilent 600MR DD2 (600 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and tetramethylsilane or the residual solvent peak was used as an internal reference. ^{1}H (tetramethylsilane δ 0.00), ^{13}C (chloroform δ 77.00). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. High resolution mass spectra (HRMS) were performed on Bruker solarix 7.0T. X-ray crystallography analysis of single crystals was performed on an Agilent SuperNova-CCD X-Ray diffractometer. Melting points were measured using SGWX-4A Microscopic melting point meter and are uncorrected. No melting points were reported for amorphous solids. All reactions were carried out under nitrogen atmosphere in oven-dried glassware with magnetic stirring. Unless otherwise stated, all solvents employed in the reactions were distilled from appropriate drying agents prior to use.

*4.2 Synthesis of 2-(1-hydroxy-2-oxo-1, 2-diphenylethyl) cyclohexan-1-ones (**1, 3, 5, 7**)*

A solution of i-Pr_2NH (1.3 mL, 9.1 mmol) and *n*-BuLi (4.9 mL, 1.6 M in hexane) in THF (15 mL) was stirred at 0 ºC for 1.5 h. To this solution was added ketone (5 mmol) in THF (3 mL) at 0 ºC. After stirring for 1 h, Benzil (6.5 mmol) in THF (5 mL) was added at –78 ºC dropwise via syringe over 0.5 h. After 12 h, the reaction was quenched with saturated NH_4Cl. Products were extracted with EtOAc. Combined organic layers were washed with brine, dried over Na_2SO4, and concentrated to give a crude mixture, which was purified by silica gel column chromatography (eluent: EtOAc / hexane = 1/20) to afford a white solid. The Characterization data of substrates **1, 3, 5, 7** can be found in Appendix A. Supplementary data.

4.3 General procedure for the acid-promoted reactions

A flame-dried Schlenk tube equipped with a magnetic stirring bar, was charged with **1**, **3**, **5**, **7** (0.1 mmol), *p*-toluenesulfonic acid (22.8 mg, 0.12 mmol). Dichloromethane (1.5 mL) was injected into the tube at 40 ºC. After stirring for 24 h, the mixture was filtered and purified by silica gel chromatography (PE / EtOAc = 10/1) to afford the product **2, 4, 6, 8**.

4.4 The Characterization data of products

2-phenylnaphtho[1,2-b]furan (**2a**)

Yellow oil (21.6 mg, yield: 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, *J* = 8.3 Hz, 1H), 7.95 (dd, *J* = 12.0, 8.2 Hz, 3H), 7.68 – 7.59 (m, 3H), 7.49 (q, *J* = 7.4 Hz, 3H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.15 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.31, 150.30, 131.48, 130.73, 128.80, 128.41, 128.21, 126.32, 125.01, 124.81, 124.65, 123.61, 121.35, 120.01, 119.53, 102.45. HRMS (ESI): m/z Calcd for $[C_{18}H_{12}NaO, M + Na]^+$: 267.07803, Found: 267.07792.

2,3-diphenylnaphtho[1,2-b]furan (**2b**)

White solid (31.4 mg, yield: 98%), m. p. 101–103 ºC**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 7.4 Hz, 2H), 7.65 – 7.57 (m, 2H), 7.54 (d, *J* = 6.7 Hz, 3H), 7.48 (t, *J* = 7.2 Hz, 3H), 7.44 – 7.38 (m, 1H),

7.37 – 7.24 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.98, 149.48, 132.94, 131.72, 130.90, 129.82, 128.97, 128.44, 128.38, 128.04, 127.63, 126.76, 126.36, 125.56, 125.20, 123.58, 121.22, 120.16, 118.79, 118.48. HRMS (ESI): m/z Calcd for $[C_{24}H_{16}NaO, M + Na]^+$: 343.10959, Found: 343.10934.

8-bromo-2,3-diphenylnaphtho[1,2-b]furan (**2c**)

White solid (39.4 mg, yield: 99%), m.p. 129–131 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (d, *J* = 1.8 Hz, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 6.7 Hz, 2H), 7.62 – 7.42 (m, 8H), 7.37 – 7.28 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.62, 148.28, 132.60, 130.56, 130.06, 129.98, 129.77, 129.03, 128.49, 128.45, 128.30, 127.78, 126.80, 126.48, 123.34, 122.56, 122.14, 120.50, 118.96, 118.72. HRMS (ESI): m/z Calcd for $[C_{24}H_{15}BrNaO, M + Na]^+$: 421.01985, Found: 421.01963.

8-chloro-2,3-diphenylnaphtho[1,2-b]furan (**2d**)

White solid (35.1 mg, yield: 99%), m.p. 130–132 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.71 (d, *J* = 7.0 Hz, 2H), 7.61 – 7.37 (m, 8H), 7.37 – 7.24 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.54, 148.43, 132.59, 132.28, 130.55, 129.97, 129.76, 129.02, 128.48, 128.28, 127.76, 126.78, 126.43, 125.92, 123.27, 121.68, 119.30, 118.76, 118.70.HRMS (ESI): m/z Calcd for $[C_{24}H_{15}ClNaO, M + Na]^+$: 377.07036, Found: 377.07017.

6-bromo-2,3-diphenylnaphtho[1,2-b]furan (**2e**)

White solid (39.6 mg, yield: 99%), m.p. 167–169 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, *J* = 8.2 Hz, 1H), 8.08 (d, *J* = 8.9 Hz, 1H), 7.80 (d, *J* = 7.4 Hz, 1H), 7.74 (d, *J* = 7.4 Hz, 2H), 7.66 (d, *J* = 8.9 Hz, 1H), 7.59 – 7.41 (m, 6H), 7.39 – 7.29 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.86, 149.23, 132.53, 130.61, 129.99, 129.76, 129.31, 129.06, 128.50, 128.33, 127.81, 126.86, 126.65, 126.26, 123.46, 122.70, 122.36, 119.97, 119.80, 118.66. HRMS (ESI): m/z Calcd for $[C_{24}H_{15}BrNaO, M + Na]^+$: 421.01985, Found: 421.01962.

7-bromo-2,3-diphenylnaphtho[1,2-b]furan (**2f**)

White solid (39.3 mg, yield: 99%), m.p. 144–146 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.7 Hz, 1H), 8.05 (s, 1H), 7.67 (dd, *J* = 19.0, 8.3 Hz, 3H), 7.57 – 7.38 (m, 7H), 7.35 – 7.24 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.40, 149.23, 132.74, 132.59, 130.62, 130.47, 129.76, 129.57, 129.02, 128.48, 128.24, 127.76, 126.77, 125.98, 122.62, 121.87, 119.75, 119.59, 118.99, 118.75. HRMS (ESI): m/z Calcd for $[C_{24}H_{15}BrNaO, M + Na]^+$: 421.02009, Found: 421.01984.

7-chloro-2,3-diphenylnaphtho[1,2-b]furan (**2g**)

White solid (35 mg, yield: 99%), m.p. 149–151 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, J = 8.8 Hz, 1H), 7.88 (s, 1H), 7.70 (d, J = 6.8 Hz, 2H), 7.59 – 7.38 (m, 8H), 7.36 – 7.26 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.36, 149.25, 132.64, 132.37, 130.89, 130.65, 129.77, 129.03, 128.48, 128.23, 127.77, 127.26, 127.11, 126.78, 125.89, 122.69, 121.80, 119.81, 119.42, 118.76. HRMS (ESI): m/z Calcd for $[C_{24}H_{15}ClNaO, M + Na]^+$: 377.07062, Found: 377.07036.

7-methoxy-2,3-diphenylnaphtho[1,2-b]furan (**2h**)

White solid (15.8 mg, yield: 45%), m.p. 142–144 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.6 Hz, 1H), 7.72 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 4H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.45 – 7.39 (m, 1H), 7.36 – 7.25 (m, 5H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.36, 149.89, 149.32, 133.13, 133.08, 131.01, 129.81, 128.95, 128.42, 127.86, 127.58, 126.63, 123.99, 122.61, 121.81, 119.12, 118.72, 118.52, 116.41, 107.24, 55.34. HRMS (ESI): m/z Calcd for $[C_{25}H_{18}NaO_2, M + Na]^+$: 373.12021, Found: 373.11990.

8-methoxy-2,3-diphenylnaphtho[1,2-b]furan (**2i**)

White solid (32.3 mg, yield: 92%), m.p. 145–147 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.9 Hz, 1H), 7.74 (d, *J* = 7.4 Hz, 2H), 7.68 (d, *J* = 1.9 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.44 – 7.37 (m, 2H), 7.37 – 7.25 (m, 3H), 7.14 (dd, *J* = 8.9, 2.3 Hz, 1H), 4.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.26, 150.00, 149.13, 132.99, 130.95, 130.04, 129.82, 128.95, 128.44, 128.06, 127.60, 127.00, 126.88, 126.00, 123.34, 122.09, 118.88, 117.56, 115.93, 98.88, 55.53. HRMS (ESI): m/z Calcd for $[C_{25}H_{18}NaO_2, M + Na]^+$: 373.11990, Found: 373.11935.

6-methoxy-2,3-diphenylnaphtho[1,2-b]furan (**2j**)

White solid (34.9 mg, yield: 99%), m.p. 155–157 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 7.1 Hz, 2H), 7.60 – 7.45 (m, 6H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.36 – 7.22 (m, 3H), 6.87 (d, *J* = 7.7 Hz, 1H), 4.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.00, 150.08, 149.48, 132.99, 130.92, 129.84, 128.97, 128.44, 128.05, 127.61, 126.82, 126.69, 126.08, 123.32, 122.18, 118.72, 117.55, 117.49, 112.59, 103.88, 55.56. HRMS (ESI): m/z Calcd for $[C_{25}H_{18}NaO_2, M + Na]^+$: 373.11987, Found: 373.11958.

2,3-diphenylnaphtho[1,2-b]furan-6-ol (**2k**)

White solid (29.2 mg, yield: 87%), m.p. 156–158 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (t, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 7.4 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 3H), 7.51 – 7.39 (m, 4H), 7.37 – 7.25 (m, 3H), 6.83 (d, *J* = 7.5 Hz, 1H), 5.32 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.99, 150.17, 149.47, 132.88, 130.84, 129.82, 128.98, 128.45, 128.10, 127.65, 126.81, 126.62, 126.09, 122.52, 122.05, 118.77, 117.76, 117.06, 113.05, 108.73. HRMS (ESI): m/z Calcd for $[C_{24}H_{16}NaO_2, M + Na]^+$: 359.10425, Found: 359.10381.

3-(4-chlorophenyl)-2-phenylnaphtho[1,2-b]furan (**2l**)

White solid (31.9 mg, yield: 90%), m.p. 138–140 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.75 – 7.56 (m, 4H), 7.55 – 7.38 (m, 6H), 7.37 – 7.25 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.19, 149.54, 133.56, 131.74, 131.44, 131.12, 130.59, 129.27, 128.55, 128.40, 128.28, 126.81, 126.47, 125.33, 125.16, 123.78, 121.18, 120.13, 118.08, 117.54. HRMS (ESI): m/z Calcd for $[C_{24}H_{15}ClNaO, M + Na]^+$: 377.07052, Found: 377.07036.

2,3-bis(3-methoxyphenyl)naphtho[1,2-b]furan (**2m**)

White solid (35.4 mg, yield: 93%), m.p. 89–91 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.66 – 7.53 (m, 3H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.38 (dd, *J* = 17.1, 8.7 Hz, 2H), 7.31 (s, 1H), 7.25 – 7.18 (m, 1H), 7.16 – 7.06 (m, 2H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.01, 159.48, 149.78, 149.36, 134.24, 132.01, 131.76, 129.99, 129.48, 128.38, 126.37, 125.53, 125.24, 123.63, 122.31, 121.17, 120.16, 119.23, 118.94, 118.49, 115.18, 114.24, 113.46, 111.73, 55.28, 55.09. HRMS (ESI): m/z Calcd for $[C_{26}H_{20}NaO_3, M + Na]^+$: 403.13047, Found: 403.12997.

2,3-bis(4-fluorophenyl)naphtho[1,2-b]furan (**2n**)

White solid (35.3 mg, yield: 99%), m.p. 114–116 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.57 (m, 4H), 7.52 – 7.43 (m, 4H), 7.21 – 7.13 (m, 2H), 7.03 (t, *J* = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ

163.74, 163.61, 161.26, 161.15, 149.38, 149.21, 131.72, 131.45, 131.37, 128.61, 128.53, 128.42, 126.94, 126.91, 126.50, 125.34, 123.81, 121.12, 120.06, 118.12, 117.46, 116.28, 116.06, 115.75, 115.54. HRMS (ESI): m/z Calcd for $[C_{24}H_{14}F_2NaO, M + Na]^+$: 379.09049, Found: 379.09011.

8-bromo-2,3-bis(4-fluorophenyl)naphtho[1,2-b]furan (**2o**)

White solid (43 mg, yield: 99%), m.p. 169–171 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.55 (dd, *J* = 14.9, 8.7 Hz, 2H), 7.48 – 7.42 (m, 3H), 7.18 (t, *J* = 8.1 Hz, 2H), 7.03 (t, *J* = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.92, 163.72, 161.44, 161.25, 149.87, 148.22, 131.45, 131.37, 130.10, 130.02, 128.70, 128.62, 128.32, 128.29, 126.63, 126.60, 126.27, 123.58, 122.50, 122.07, 120.66, 118.61, 117.43, 116.36, 116.15, 115.83, 115.62. HRMS (ESI): m/z Calcd for $[C_{24}H_{13}BrF_2NaO, M + Na]^+$: 457.00101, Found: 457.00079.

2,3-bis(4-fluorophenyl)-8-methoxynaphtho[1,2-b]furan (**2p**)

White solid (35.6 mg, yield: 92%), m.p. 148–150 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.9 Hz, 1H), 7.71 – 7.62 (m, 3H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.22 – 7.12 (m, 3H), 7.05 (t, *J* = 8.6 Hz, 2H), 4.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.80, 163.63, 161.32, 161.17, 158.38, 149.26, 149.06, 131.48, 131.40, 130.09, 128.76, 128.73, 128.68, 127.05, 127.00, 125.80, 123.58, 122.05, 117.68, 117.61, 116.25, 116.04, 115.75, 115.57, 115.53, 55.54. HRMS (ESI): m/z Calcd for $[C_{25}H_{16}F_2NaO_2, M + Na]^+$: 409.10106, Found: 409.10083.

2,3-bis(4-fluorophenyl)-6-methoxynaphtho[1,2-b]furan (**2q**)

White solid (38.2 mg, yield: 99%), m.p. 139–141 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.65 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.54 – 7.44 (m, 4H), 7.17 (t, *J* = 8.6 Hz, 2H), 7.03 (t, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 7.7 Hz, 1H), 4.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.76, 163.61, 161.29, 161.16, 155.99, 149.38, 149.30, 131.47, 131.39, 128.66, 128.58, 126.97, 126.94, 126.84, 125.84, 123.34, 122.09, 117.74, 117.39, 117.16, 116.25, 116.03, 115.72, 115.51, 112.45, 103.96, 55.55. HRMS (ESI): m/z Calcd for $[C_{25}H_{16}F_2NaO_2, M + Na]^+$: 409.10128, Found: 409.10106.

2,3-bis(2-chlorophenyl)naphtho[1,2-b]furan (**2r**)

White solid (38.5 mg, yield: 99%), m.p. 129–131 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.6 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.56 – 7.41 (m, 5H), 7.34 – 7.22 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.11, 149.59, 134.27, 134.01, 132.29, 132.20, 131.76, 131.63, 130.29, 130.17, 130.02, 129.97, 129.19, 128.36, 126.85, 126.54, 126.45, 125.42, 124.30, 123.51, 121.43, 120.19, 119.30, 119.23. HRMS (ESI): m/z Calcd for $[C_{24}H_{14}Cl_2NaO, M + Na]^+$: 411.03139, Found: 411.03112.

2,3-bis(2-chlorophenyl)-8-methoxynaphtho[1,2-b]furan (**2s**)

White solid (41.5 mg, yield: 99%), m.p. 203–205 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.9 Hz, 1H), 7.68 (s, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.53 – 7.42 (m, 3H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.34 – 7.22 (m, 5H), 7.19 – 7.14 (m, 1H), 3.99 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.33, 149.72, 149.53, 134.24, 134.05, 132.28, 132.26, 131.62, 130.24, 130.22, 130.00, 129.15, 126.99, 126.82, 126.55, 124.74, 123.24, 122.28, 119.30, 117.78, 116.72, 98.90, 55.54. HRMS (ESI): m/z Calcd for $[C_{25}H_{16}Cl_2NaO_2, M + Na]^+$: 441.04196, Found: 441.04163.

2,3-bis(2-chlorophenyl)-6-methoxynaphtho[1,2-b]furan (**2t**)

White solid (41.7 mg, yield: 99%), m.p. 123–125 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.8 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.35 (m, 5H), 7.32 – 7.15 (m, 5H), 6.84 (d, *J* = 7.7 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.95, 150.05, 149.64, 134.19, 133.91, 132.24, 132.16, 131.60, 130.24, 130.13, 129.98, 129.93, 129.13, 126.80, 126.51, 124.76, 123.31, 122.32, 119.10, 118.31, 117.42, 112.52, 104.06, 55.53. HRMS (ESI): m/z Calcd for $[C_{25}H_{16}Cl_2NaO_2, M + Na]^+$: 441.04213, Found: 441.04196.

2,3-bis(4-bromophenyl)naphtho[1,2-b]furan (**2u**)

White solid (46.3 mg, yield: 97%), m.p. 152–154 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.56 (m, 4H), 7.55 – 7.40 (m, 6H), 7.35 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.62, 148.99, 132.35, 131.86, 131.76, 131.56, 131.30, 129.44, 128.43, 128.14, 126.57, 125.53, 124.99, 124.00, 122.37, 121.98, 121.09, 120.10, 118.12, 117.99. HRMS (ESI): m/z Calcd for $[C_{24}H_{14}Br_2NaO, M + Na]^+$: 498.93036, Found: 498.93019.

2,3-diphenylbenzofuran (**4a**)

White solid (26.7 mg, yield: 99%), m.p. 121–123 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 – 7.62 (m, 2H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.43 (m, 5H), 7.43 – 7.37 (m, 1H), 7.32 (dd, *J* = 14.0, 7.2 Hz, 4H), 7.23 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.98, 150.51, 132.84, 130.65, 130.23, 129.75, 128.95, 128.40, 128.33, 127.61, 127.01, 124.66, 122.89, 120.01, 117.49, 111.09. HRMS (ESI): m/z Calcd for $[C_{20}H_{14}NaO, M + Na]^+$: 293.09369, Found: 293.09328.

2,3-bis(4-fluorophenyl)benzofuran (**4b**)

White solid (30 mg, yield: 99%), m.p. 96–98 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.44 (dd, *J* = 8.1, 5.4 Hz, 3H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.23 (d, *J* = 7.1 Hz, 1H), 7.16 (t, *J* = 8.5 Hz, 2H), 7.01 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.92, 163.60, 161.44, 161.14, 153.87, 149.77, 131.41, 131.33, 130.03, 128.90, 128.82, 128.55, 128.52, 126.71, 126.67, 124.83, 123.09, 119.77, 116.26, 116.20, 116.05, 115.73, 115.52, 111.13. HRMS (ESI): m/z Calcd for $[C_{20}H_{12}F_2NaO, M + Na]^+$: 329.07484, Found: 329.07469.

3-(4-chlorophenyl)-2-phenylbenzofuran (**4c**)

White solid (30 mg, yield: 99%), m.p. 102–104 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.47 – 7.39 (m, 5H), 7.36 – 7.27 (m, 4H), 7.23 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.98, 150.77, 133.52, 131.35, 131.05, 130.34, 129.83, 129.25, 128.56, 128.51, 127.05, 124.83, 123.05, 119.72, 116.25, 111.19. HRMS (ESI): m/z Calcd for $[C_{20}H_{13}ClNaO, M + Na]^+$: 327.05471, Found: 327.05453.

2,3-bis(3-methoxyphenyl)benzofuran (**4d**)

Pale yellow oil (27.4 mg, yield: 83%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 8.1 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.20 (m, 3H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.05 (s, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 3.80 (s, 3H), 3.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.99, 159.44, 153.84, 150.30, 134.15, 131.74, 130.19, 129.96, 129.42, 124.74, 122.92, 122.24, 120.06, 119.47, 117.63, 115.06, 114.78, 113.47, 111.75, 111.07, 55.26, 55.08. HRMS (ESI): m/z Calcd for $[C_{22}H_{18}NaO_3, M + Na]^+$: 353.11482, Found: 353.11449.

6-methyl-2,3-diphenylbenzofuran (**4e**)

White solid (28.1 mg, yield: 99%), m.p. 89–91 ºC.. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.4 Hz, 2H), 7.51 – 7.40 (m, 4H), 7.40 – 7.32 (m, 3H), 7.32 – 7.21 (m, 3H), 7.04 (d, *J* = 7.9 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.39, 149.89, 134.99, 133.03, 130.84, 129.70, 128.89, 128.35, 128.08, 127.79, 127.50, 126.85, 124.30, 119.50, 117.40, 111.30, 21.72. HRMS (ESI): m/z Calcd for $[C_{21}H_{16}NaO, M + Na]^+$: 307.10934, Found: 307.10902.

2,3-bis(4-bromophenyl)-6-methylbenzofuran (**4f**)

White solid (43.6 mg, yield: 99%), m.p. 157–159 ºC.. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 6.6 Hz, 2H), 7.49 – 7.38 (m, 4H), 7.36 – 7.25 (m, 4H), 7.06 (d, *J* = 7.9 Hz, 1H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.40, 148.96, 135.60, 132.28, 131.69, 131.20, 129.41, 128.26, 127.19, 124.66, 122.45, 121.82, 119.29, 116.78, 111.41, 21.74. HRMS (ESI): m/z Calcd for $[C_{21}H_{14}Br_2NaO, M + Na]^+$: 462.93036, Found: 462.93019.

2,3-bis(4-fluorophenyl)-6-methylbenzofuran (**4g**)

White solid (31.7 mg, yield: 99%), m.p. 130–132 ºC.. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (dd, *J* = 8.1, 5.8 Hz, 2H), 7.43 (dd, *J* = 7.9, 5.8 Hz, 2H), 7.36 – 7.29 (m, 2H), 7.15 (t, *J* = 8.6 Hz, 2H), 7.07 (d, *J* = 7.9 Hz, 1H), 7.00 (t, *J* = 8.6 Hz, 2H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.78, 163.54, 161.31, 161.09, 154.29, 149.16, 135.22, 131.35, 131.27, 128.73, 128.65, 127.58, 126.90, 126.87, 124.49, 119.26, 116.20, 116.12, 115.98, 115.67, 115.45, 111.34, 21.72. HRMS (ESI): m/z Calcd for $[C_{21}H_{14}F_2NaO, M + Na]^+$: 343.09049, Found: 343.09015.

3-(4-chlorophenyl)-6-methyl-2-phenylbenzofuran (**4h**)

White solid (29.3 mg, yield: 92%), m.p. 123–125 ºC.. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 – 7.58 (m, 2H), 7.42 (d, *J* = 1.1 Hz, 4H), 7.36 – 7.26 (m, 5H), 7.06 (d, *J* = 8.0 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.40, 150.16, 135.22, 133.40, 131.55, 131.01, 130.54, 129.20, 128.48, 128.34, 127.40, 126.91, 124.47, 119.22, 116.17, 111.41, 21.72.HRMS (ESI): m/z Calcd for $[C_{21}H_{15}ClNaO, M + Na]^+$: 341.07036, Found: 341.07011.

2,3-bis(3-methoxyphenyl)-6-methylbenzofuran (**4i**)

Pale yellow oil (30.6 mg, yield: 89%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (dd, *J* = 10.1, 6.2 Hz, 3H), 7.26 – 7.20 (m, 3H), 7.07 (dd, *J* = 18.0, 8.8 Hz, 3H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 3.80 (s, 3H), 3.70 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.96, 159.42, 154.27, 149.71, 135.10, 134.36, 131.95, 129.91, 129.38, 127.77, 124.34, 122.22, 119.56, 119.33, 117.56, 115.03, 114.55, 113.40, 111.62, 111.29, 55.26, 55.08, 21.72. HRMS (ESI): m/z Calcd for $[C_{23}H_{20}NaO_3, M + Na]^+$: 367.13047, Found: 367.13031.

2,3-bis(2-chlorophenyl)-6-methylbenzofuran (**4j**)

White solid (32.4 mg, yield: 92%), m.p. 100–102 ºC.. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.8 Hz, 1H), 7.43 – 7.30 (m, 4H), 7.30 – 7.16 (m, 5H), 7.10 (d, *J* = 8.0 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.78, 149.74, 135.20, 134.18, 133.97, 132.19, 132.09, 131.60, 130.19, 130.16, 129.94, 129.04, 126.75, 126.48, 126.18, 124.29, 120.45, 117.95, 111.62, 21.73. HRMS (ESI): m/z Calcd for $[C_{21}H_{14}Cl_2NaO, M + Na]^+$: 375.03139, Found: 375.03130.

6-chloro-2,3-diphenylbenzofuran (**4k**)

White solid (21.3 mg, yield: 70%), m.p. 133–135 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 4.8 Hz, 2H), 7.55 (s, 1H), 7.46 (d, *J* = 4.1 Hz, 4H), 7.42 (dd, *J* = 8.2, 4.1 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 5.1 Hz, 3H), 7.21 (t, *J* = 8.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.01, 151.23, 132.26, 130.41, 130.22, 129.66, 129.06, 128.99, 128.60, 128.47, 127.87, 126.96, 123.65, 120.56, 117.28, 111.63. HRMS (ESI): m/z Calcd for $[C_{20}H_{13}ClNaO, M + Na]^+$: 327.05485, Found: 327.05471.

6-chloro-2,3-bis(4-fluorophenyl)benzofuran (**4l**)

white solid (27.2 mg, yield: 80%), m.p. 117–119 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.52 (m, 3H), 7.45 – 7.38 (m, 2H), 7.34 (dd, *J* = 8.3, 3.6 Hz, 1H), 7.25 – 7.14 (m, 3H), 7.06 – 6.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.04, 163.71, 161.55, 161.25, 153.86, 150.45, 131.33, 131.25, 130.57, 128.86, 128.78, 128.75, 127.95, 127.91, 126.25, 126.22, 123.83, 120.29, 116.39, 116.17, 115.97, 115.82, 115.60, 111.66. HRMS (ESI): m/z Calcd for $[C_{20}H_{11}ClF_2NaO, M + Na]^+$: 363.03587, Found: 363.03571.

2,3-diphenylthieno[2,3-g]benzofuran (**6**)

white solid (28.4 mg, yield: 87%), m.p. 111–113 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 5.5 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 3H), 7.54 (d, *J* = 5.9 Hz, 3H), 7.51 – 7.40 (m, 4H), 7.36 – 7.27 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.23, 148.69, 137.87, 133.01, 130.81, 129.83, 128.99, 128.43, 128.06, 127.66, 126.84, 126.82, 125.94, 125.29, 118.96, 118.34, 117.44, 116.69. HRMS (ESI): m/z Calcd for $[C_{22}H_{14}NaOS, M + Na]^+$: 349.06576, Found: 349.06546.

6-methyl-2,3-diphenyl-6H-furo[3,2-c]carbazole (**8**)

brown oil (13.1 mg, yield: 35%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 7.7 Hz, 2H), 7.56 – 7.42 (m, 6H), 7.39 – 7.27 (m, 5H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.87, 148.63, 140.41, 140.21, 133.49, 131.29, 129.94, 128.95, 128.41, 127.62, 127.53, 126.52, 125.19, 122.55, 122.51, 120.37, 119.41, 118.26, 117.46, 108.51, 107.61, 104.88, 29.68. HRMS (ESI): m/z Calcd for $[C_{27}H_{19}NNaO, M + Na]^+$: 396.13589, Found: 396.13578.

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Appendix A. Supplementary data

Supplementary data related to this article can be found as a separated file.

References and notes

[1] Saga, Y.; Motoki, R.; Makino, S.; Shimizu, Y.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2010**, *132*, 7905.

[2] (a) Preston, N. W.; Chamberlain, K.; Skipp, R. A. *Phytochem.* **1975**, *14*, 1843. (b) Pacher, T.; Seger, C.; Engelmeier, D.; Vajrodaya, S.; Hofer, O.; Greger, H. *J. Nat. Prod.* **2002**, *65*, 820. (c) Liu, Q.; Shen, L.; Wang, T.-T.; Chen, C.-J.; Qi, W.-Y.; Gao, K. *Food Chem.* **2010**, *122*, 55. (d) Brkljača, R.; White, J. M.; Urban, S. *J. Nat. Prod.* **2015**, *78*, 1600.

[3] For selected reviews, see: (a) Horton, D. A.; Bourne, G. T.; Smythe, M. L. *Chem. Rev.* **2003**, *103*, 893. (b) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079. (c) Zeni, G.; Larock, R. C. *Chem. Rev.* **2006**, *106*, 4644. (d) Chinchilla, R.; Nájera, C. *Chem. Rev.* **2007**, *107*, 874. (e) Patil, N. T.; Yamamoto, Y. *Chem. Rev.* **2008**, *108*, 3395. (f) Godoi, B.; Schumacher, R. F.; Zeni, G. *Chem. Rev.* **2011**, *111*, 2937. (g) Wu, X.-F.; Neumann, H.; Beller, M. *Chem. Rev.* **2013**, *113*, 1. (h) Keylor, M. H.; Matsuura, B. S.; Stephenson, C. R. J. *Chem. Rev.* **2015**, *115*, 8976

[4] For selected examples, see: (a) Morrison, B. J.; Musgrave, O. C. *Tetrahedron* **2002**, *58*, 4255. (b) Kumar, M. P.; Liu, R.-S. *J. Org. Chem.* **2006**, *71*, 4951. (c) Bonnamour, J.; Piedrafita, M.; Bolm, C.

Adv. Synth. Catal. **2010**, *352*, 1577. (d) Matsuda, N.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2012**, *77*, 617. (e) Zeng, W.; Wu, W.; Jiang, H.; Huang, L.; Sun, Y.; Chen, Z.; Li, X. *Chem. Commun.* **2013**, *49*, 6611. (f) Konishi, A.; Yasunaga, R.; Chiba, K.; Yasuda, M. *Chem. Commun.* **2016**, *52*, 3348. (g) Sreenivasulu, C.; Reddy, A. G. K.; Satyanarayana, G. *Org. Chem. Front.* **2017**, *4*, 972. (h) Warner, A. J.; Churn, A.; McGough, J. S.; Ingleson, M. J. *Angew. Chem. Int. Ed.* **2017**, *56*, 354.

[5] For selected examples, see: (a) Lu, B.; Wang, B.; Zhang, Y.; Ma, D. *J. Org. Chem.* **2007**, *72*, 5337. (b) Tsuchikama, K.; Hashimoto, Y.-k.; Endo, K.; Shibata, T. *Adv. Synth. Catal.* **2009**, *351*, 2850. (c) Martínez, C.; Álvarez, R.; Aurrecoechea, J. M. *Org. Lett.* **2009**, *11*, 1083. (d) Komine, Y.; Kamisawa, A.; Tanaka, K. *Org. Lett.* **2009**, *11*, 2361. (e) Wang, R.; Mo, S.; Lu, Y.; Shen, Z. *Adv. Synth. Catal.* **2011**, *353*, 713. (f) Kuram, M. R.; Bhanuchandra, M.; Sahoo, A. K. *Angew. Chem. Int. Ed.* **2013**, *52*, 4607. (g) Zhu, R.; Wei, J.; Shi, Z. *Chem. Sci.* **2013**, *4*, 3706. (h) Zhao, Y.; Li, S.; Zheng, X.; Tang, J.; She, Z.; Gao, G.; You, J. *Angew. Chem. Int. Ed.* **2017**, *56*, 4286. (i) Mai, S.; Song, Q. *Angew. Chem. Int. Ed.* **2017**, *56*, 7952.

[6] Liu,J.-t.; Simmons, C. J.; Xie, H.; Yang, F.; Zhao, X.-l.; Tang, Y.; Tang, W. *Adv. Synth. Catal.* **2017**, *359*, 693.

[7] For selected examples, see: (a) Shen, Z.; Dong, V. M. Angew. Chem. Int. Ed. **2009**, 48, 784. (b) Meng, L.; Zhang, G.; Liu, C.; Wu, K.; Lei, A. Angew. Chem. Int. Ed. **2013**, 52, 10195. (c) Hu, M.; Song, R.-J.; Li, J.-H. Angew. Chem. Int. Ed. **2015**, 54, 608. (d)Tharra, P.; Baire, B. Chem. Commun. **2016**, 52, 14290.

[8] For selected examples, see: (a) Syu, S.-e.; Lee, Y.-T.; Jang, Y.-J.; Lin, W. *Org. Lett.* **2011**, *13*, 2970. (b) Lee, Y.-T.; Jang, Y.-J.; Syu, S.-e.; Chou, S.-C.; Lee, C.-J.; Lin, W. *Chem. Commun.* **2012**, *48*, 8135. (c) Tsai, Y.-L.; Das, U.; Syu, S.-e.; Lee, C.-J.; Lin, W. *Eur. J. Org. Chem.* **2013**, 4634. (d) Fan, Y.-S.; Das, U.; Hsiao, M.-Y.; Liu, M.-H.; Lin, W. *J. Org. Chem.* **2014**, *79*, 11567. (e) Lee, C.-J.; Tsai, C.-C.; Hong, S.-H.; Chang, G.-H.; Yang, M.-C.; Möhlmann, L.; Lin, W. *Angew. Chem. Int. Ed.* **2015**, *54*, 8502. (f) Liang, L.; Dong, X.; Huang, Y. *Chem. Eur. J.* **2017**, *23*, 7882. (g) Naveen, T.; Deb, A.; Maiti, D. *Angew. Chem. Int. Ed.* **2017**, *56*, 1111.

[9] Welker, M.; Turbiez, M. G. R.; Chebotareva, N.; Kirner, H. J.; Schaefer, T.; Dithienobenzofuran polymers and small molecules for electronic application, WO 2014016219.

[10] Kim, H.; Kim, B.; Kim, Y.; Kim, C.; Shin, C.; Lee, S.; Yu, E.; Choi, B.; Hwang, K.; Condensed cyclic compound and organic light-emitting device including the same, EP 2894157.

[11] (a) Zhao, Y.; Li, J.; Li, C.; Yin, K.; Ye, D.; Jia, X. Green Chem. **2010**, 12, 1370. (b) Buyck, T.; Wang, Q.; Zhu, J. J. Am. Chem. Soc. **2014**, 136, 11524. (c) Melis, N.; Secci, F.; Boddaert, T.; Aitken, D. J.; Frongia, A. Chem. Commun. **2015**, 51, 15272. (d) Jin, S.; Hunt, A. J.; Clark, J. H.; McElroy, C. R.` Green Chem. **2016**, 18, 5839.

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