



Acid-promoted furan annulation and aromatization: An access to benzo[*b*]furan derivatives



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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.

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1. Introduction

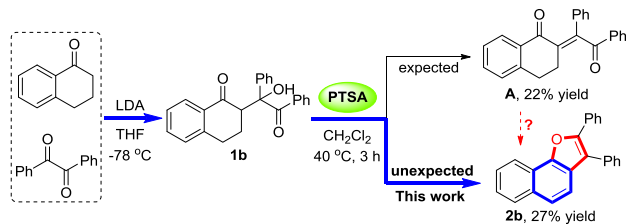
In an ongoing program by our research group, it is required to synthesize α,β -unsaturated 1,4 di-ketone **A** (Scheme 1). Theoretically, the required compound **A** can be easily obtained via an aldol type reaction between 3,4-dihydronaphthalen-1(2*H*)-one and benzil, subsequent dehydration under acidic 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. (Fig. 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 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 condensation⁴ 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 methods⁷ 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 until now. We report herein our recent studies towards such process under a mild condition with high efficiency.

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

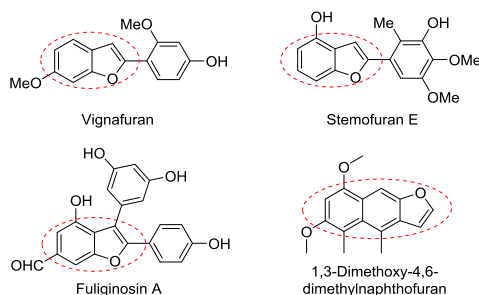
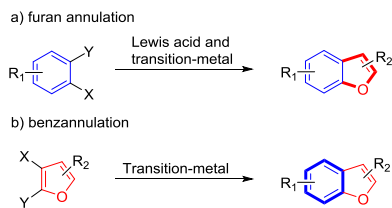
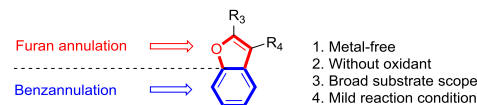


Fig. 1. Representative benzo[*b*]furan-containing natural products.

Previous work:



This work: furan annulation and benzannulation in one pot

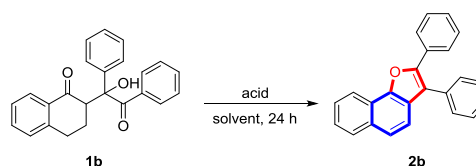


Scheme 2. Strategies toward benzo[*b*]furans.

2. Results and discussion

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 CH₂Cl₂ (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%

Table 1
Optimization of the reaction conditions.^a



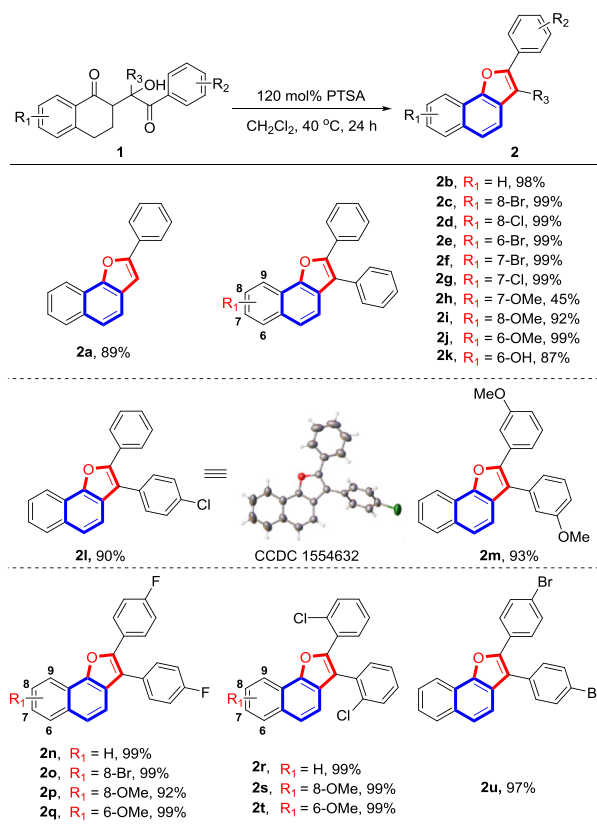
Entry	T(°C)	Solvent (1.5 mL)	Acid (mol%)	Yield (%) ^b
1	40	CH ₂ Cl ₂	boric acid (120)	NR
2	40	CH ₂ Cl ₂	citric acid (120)	NR
3	40	CH ₂ Cl ₂	cinnamic acid (120)	NR
4	40	CH ₂ Cl ₂	malonic acid (120)	NR
5	40	CH ₂ Cl ₂	benzoic acid (120)	NR
6	40	CH ₂ Cl ₂	formic acid (120)	NR
7	40	CH ₂ Cl ₂	benzene sulfonic acid (120)	95
8	40	CH ₂ Cl ₂	PTSA (120)	98
9	40	CH ₂ Cl ₂	PTSA (100)	95
10	40	CH ₂ Cl ₂	PTSA (50)	43
11	40	CH ₂ Cl 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 ₂ Cl ₂	PTSA (120)	7
17	50	CH ₂ Cl 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.

PTSA was used, only a trace amount of product could be detected. In further experiments, different solvents were examined (entries 12–15). CH₂Cl₂ 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 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 (see Table 2). First, product **2a** was successfully formed with good yield from substrate **1a**. Then, the scope of substitution on 3,4-dihydronaphthalen-1(2*H*)-one was investigated under the optimal conditions. Various substituents at different positions on the aryl rings were well tolerated. When R₁ 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 R₁ was shifted to 7-methoxy 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 R₂ and R₃. When R₃ group was *para*-chloro substitution, the reaction also gave the excellent yield (**2l**). The structure of **2l** was confirmed by X-ray analysis. When R₂ and R₃ were *meta*-methoxyl group, a perfect yield of the reaction was obtained (**2m**). When R₂ and R₃ groups were *para*-fluoro substitutions, a series of R₁ 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 R₁ group on 3,4-dihydronaphthalen-1(2*H*)-one had no effect on the yield of the reaction. The corresponding products (**2r–2u**) were formed with excellent yields as well.

Table 2
Substrate scope.^a

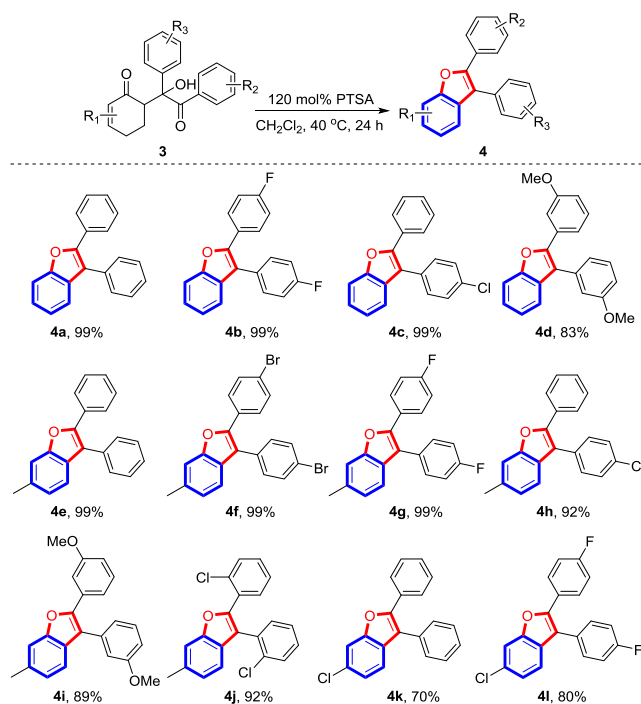
^a Reaction conditions: **1** (0.1 mmol) and PTSA (120 mol%) in CH₂Cl₂ (1.5 mL) at 40 °C for 24 h. Isolated yield.

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, 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 R₂ and R₃. 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 R₃ 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 R₁. No matter what the substitution groups R₂ and R₃ 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 R₁ 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.

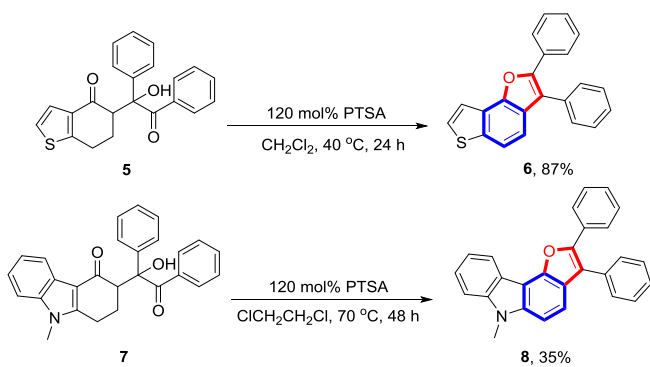
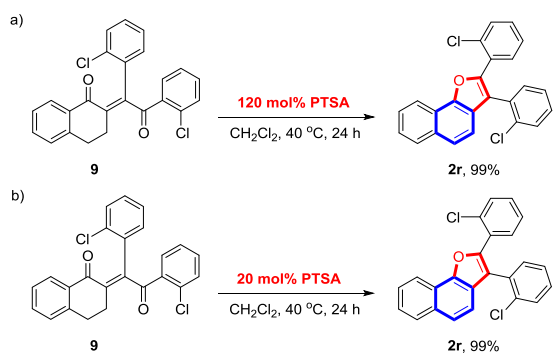
Besides the biological potential of benzo[*b*]furan derivatives, polycyclic derivatives containing benzo[*b*]furan were also widely used in photoelectricity chemistry. After determining the substrate scope of the reaction, we were interested in extending this transformation to photoelectricity area. 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

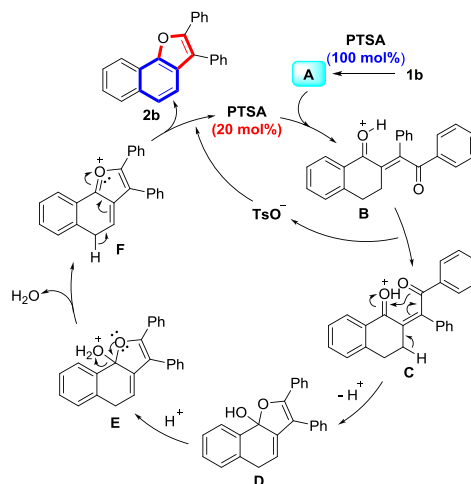
When monitoring the reaction with thin layer chromatography (TLC), we found that, at the early stage of the reaction, two new spots appeared simultaneously. In the process of reaction, however, the signals on TLC showed a change in two different trends. The intermediate spot disappeared in pace with 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 4a, intermediate **9** was isolated and treated under normal reaction conditions. Subsequently, product **2r** was successfully formed in a yield of 99%. Inspired by this result, we performed a reaction with catalytic amount (20 mol%) of acid in the transformation of **9**, as shown in Scheme 4b, 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

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.

**Scheme 3.** Synthesis of polycyclic derivatives containing benzo[*b*]furan.**Scheme 4.** Mechanism study.

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 form 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 μm , ultrapure silica gel. ^1H 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. ^1H (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 7.0 T. 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*-Pr₂NH (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 °C for 1.5 h. To this solution was added ketone (5 mmol) in THF (3 mL) at 0 °C. After stirring for 1 h, Benzil (6.5 mmol) in THF (5 mL) was added at –78 °C dropwise via syringe over 0.5 h. After 12 h, the reaction was quenched with saturated NH₄Cl. Products were extracted with EtOAc. Combined organic layers were washed with brine, dried over Na₂SO₄, 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 °C. 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

4.4.1. 2-phenylnaphtho[1,2-*b*]furan (**2a**)

Yellow oil (21.6 mg, yield: 89%). ^1H NMR (400 MHz, CDCl₃): 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, CDCl₃): 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 [C₁₈H₁₂NaO, M + Na]⁺: 267.07803, Found: 267.07792.

4.4.2. 2,3-diphenylnaphtho[1,2-*b*]furan (**2b**)

White solid (31.4 mg, yield: 98%), m. p. 101–103 °C. ^1H NMR (400 MHz, CDCl₃): 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, CDCl₃): 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 [C₂₄H₁₆NaO, M + Na]⁺: 343.10959, Found: 343.10934.

4.4.3. 8-Bromo-2,3-diphenylnaphtho[1,2-*b*]furan (**2c**)

White solid (39.4 mg, yield: 99%), m. p. 129–131 °C. ^1H NMR (400 MHz, CDCl₃): 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, CDCl₃): 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 [C₂₄H₁₅BrNaO, M + Na]⁺: 421.01985, Found: 421.01963.

4.4.4. 8-Chloro-2,3-diphenylnaphtho[1,2-*b*]furan (**2d**)

White solid (35.1 mg, yield: 99%), m. p. 130–132 °C. ^1H NMR (400 MHz, CDCl₃): 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, CDCl₃): 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 [C₂₄H₁₅ClNaO, M + Na]⁺: 377.07036, Found: 377.07017.

4.4.5. 6-Bromo-2,3-diphenylnaphtho[1,2-*b*]furan (**2e**)

White solid (39.6 mg, yield: 99%), m. p. 167–169 °C. ^1H NMR (400 MHz, CDCl₃): 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, CDCl₃): 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 [C₂₄H₁₅BrNaO, M + Na]⁺: 421.01985, Found: 421.01962.

4.4.6. 7-Bromo-2,3-diphenylnaphtho[1,2-*b*]furan (**2f**)

White solid (39.3 mg, yield: 99%), m. p. 144–146 °C. ^1H NMR (400 MHz, CDCl₃): 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, CDCl₃): 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 [C₂₄H₁₅BrNaO, M + Na]⁺: 421.02009, Found: 421.01984.

4.4.7. 7-Chloro-2,3-diphenylnaphtho[1,2-*b*]furan (**2g**)

White solid (35 mg, yield: 99%), m. p. 149–151 °C. ^1H NMR (400 MHz, CDCl₃): 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, CDCl₃): 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.

4.4.8. 7-Methoxy-2,3-diphenylnaphtho[1,2-*b*]furan (**2h**)

White solid (15.8 mg, yield: 45%), m. p. 142–144 °C. 1H 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.

4.4.9. 8-Methoxy-2,3-diphenylnaphtho[1,2-*b*]furan (**2i**)

White solid (32.3 mg, yield: 92%), m. p. 145–147 °C. 1H 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.

4.4.10. 6-Methoxy-2,3-diphenylnaphtho[1,2-*b*]furan (**2j**)

White solid (34.9 mg, yield: 99%), m. p. 155–157 °C. 1H 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.

4.4.11. 2,3-diphenylnaphtho[1,2-*b*]furan-6-ol (**2k**)

White solid (29.2 mg, yield: 87%), m. p. 156–158 °C. 1H 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.

4.4.12. 3-(4-chlorophenyl)-2-phenylnaphtho[1,2-*b*]furan (**2l**)

White solid (31.9 mg, yield: 90%), m. p. 138–140 °C. 1H 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.

4.4.13. 2,3-bis(3-methoxyphenyl)naphtho[1,2-*b*]furan (**2m**)

White solid (35.4 mg, yield: 93%), m. p. 89–91 °C. 1H 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.

4.4.14. 2,3-bis(4-fluorophenyl)naphtho[1,2-*b*]furan (**2n**)

White solid (35.3 mg, yield: 99%), m. p. 114–116 °C. 1H 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.

4.4.15. 8-Bromo-2,3-bis(4-fluorophenyl)naphtho[1,2-*b*]furan (**2o**)

White solid (43 mg, yield: 99%), m. p. 169–171 °C. 1H 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.

4.4.16. 2,3-bis(4-fluorophenyl)-8-methoxynaphtho[1,2-*b*]furan (**2p**)

White solid (35.6 mg, yield: 92%), m. p. 148–150 °C. 1H 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.

4.4.17. 2,3-bis(4-fluorophenyl)-6-methoxynaphtho[1,2-*b*]furan (**2q**)

White solid (38.2 mg, yield: 99%), m. p. 139–141 °C. 1H 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.

4.4.18. 2,3-bis(2-chlorophenyl)naphtho[1,2-*b*]furan (**2r**)

White solid (38.5 mg, yield: 99%), m. p. 129–131 °C. 1H 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.

4.4.19. 2,3-bis(2-chlorophenyl)-8-methoxynaphtho[1,2-*b*]furan (**2s**)

White solid (41.5 mg, yield: 99%), m. p. 203–205 °C. 1H 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.

4.4.20. 2,3-bis(2-chlorophenyl)-6-methoxynaphtho[1,2-b]furan (**2t**)

White solid (41.7 mg, yield: 99%), m. p. 123–125 °C. ^1H 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 $[\text{C}_{25}\text{H}_{16}\text{Cl}_2\text{NaO}_2, \text{M} + \text{Na}]^+$: 441.04213, Found: 441.04196.

4.4.21. 2,3-bis(4-bromophenyl)naphtho[1,2-b]furan (**2u**)

White solid (46.3 mg, yield: 97%), m. p. 152–154 °C. ^1H 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 $[\text{C}_{24}\text{H}_{14}\text{Br}_2\text{NaO}, \text{M} + \text{Na}]^+$: 498.93036, Found: 498.93019.

4.4.22. 2,3-Diphenylbenzofuran (**4a**)

White solid (26.7 mg, yield: 99%), m. p. 121–123 °C. ^1H 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 $[\text{C}_{20}\text{H}_{14}\text{NaO}, \text{M} + \text{Na}]^+$: 293.09369, Found: 293.09328.

4.4.23. 2,3-bis(4-fluorophenyl)benzofuran (**4b**)

White solid (30 mg, yield: 99%), m. p. 96–98 °C. ^1H 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 $[\text{C}_{20}\text{H}_{12}\text{F}_2\text{NaO}, \text{M} + \text{Na}]^+$: 329.07484, Found: 329.07469.

4.4.24. 3-(4-chlorophenyl)-2-phenylbenzofuran (**4c**)

White solid (30 mg, yield: 99%), m. p. 102–104 °C. ^1H 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 $[\text{C}_{20}\text{H}_{13}\text{ClNaO}, \text{M} + \text{Na}]^+$: 327.05471, Found: 327.05453.

4.4.25. 2,3-bis(3-methoxyphenyl)benzofuran (**4d**)

Pale yellow oil (27.4 mg, yield: 83%). ^1H 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 $[\text{C}_{22}\text{H}_{18}\text{NaO}_3, \text{M} + \text{Na}]^+$: 353.11482, Found: 353.11449.

4.4.26. 6-Methyl-2,3-diphenylbenzofuran (**4e**)

White solid (28.1 mg, yield: 99%), m. p. 89–91 °C. ^1H 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 $[\text{C}_{21}\text{H}_{16}\text{NaO}, \text{M} + \text{Na}]^+$: 307.10934, Found: 307.10902.

4.4.27. 2,3-bis(4-bromophenyl)-6-methylbenzofuran (**4f**)

White solid (43.6 mg, yield: 99%), m. p. 157–159 °C. ^1H 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 $[\text{C}_{21}\text{H}_{14}\text{Br}_2\text{NaO}, \text{M} + \text{Na}]^+$: 462.93036, Found: 462.93019.

4.4.28. 2,3-bis(4-fluorophenyl)-6-methylbenzofuran (**4g**)

White solid (31.7 mg, yield: 99%), m. p. 130–132 °C. ^1H 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 $[\text{C}_{21}\text{H}_{14}\text{F}_2\text{NaO}, \text{M} + \text{Na}]^+$: 343.09049, Found: 343.09015.

4.4.29. 3-(4-chlorophenyl)-6-methyl-2-phenylbenzofuran (**4h**)

White solid (29.3 mg, yield: 92%), m. p. 123–125 °C. ^1H 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 $[\text{C}_{21}\text{H}_{15}\text{ClNaO}, \text{M} + \text{Na}]^+$: 341.07036, Found: 341.07011.

4.4.30. 2,3-bis(3-methoxyphenyl)-6-methylbenzofuran (**4i**)

Pale yellow oil (30.6 mg, yield: 89%). ^1H 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 $[\text{C}_{23}\text{H}_{20}\text{NaO}_3, \text{M} + \text{Na}]^+$: 367.13047, Found: 367.13031.

4.4.31. 2,3-bis(2-chlorophenyl)-6-methylbenzofuran (**4j**)

White solid (32.4 mg, yield: 92%), m. p. 100–102 °C. ^1H 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 $[\text{C}_{21}\text{H}_{14}\text{Cl}_2\text{NaO}, \text{M} + \text{Na}]^+$: 375.03139, Found: 375.03130.

4.4.32. 6-Chloro-2,3-diphenylbenzofuran (**4k**)

White solid (21.3 mg, yield: 70%), m. p. 133–135 °C. ^1H 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 $[\text{C}_{20}\text{H}_{13}\text{ClNaO}, \text{M} + \text{Na}]^+$: 327.05485, Found: 327.05471.

4.4.33. 6-Chloro-2,3-bis(4-fluorophenyl)benzofuran (**4l**)

White solid (27.2 mg, yield: 80%), m. p. 117–119 °C. ^1H 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 $[\text{C}_{20}\text{H}_{11}\text{ClF}_2\text{NaO}, \text{M} + \text{Na}]^+$: 363.03587, Found: 363.03571.

4.4.34. 2,3-diphenylthieno[2,3-g]benzofuran (**6**)

White solid (28.4 mg, yield: 87%), m. p. 111–113 °C. ^1H 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 $[\text{C}_{22}\text{H}_{14}\text{NaOS}, \text{M} + \text{Na}]^+$: 349.06576, Found: 349.06546.

4.4.35. 6-Methyl-2,3-diphenyl-6H-furo[3,2-c]carbazole (**8**)

Brown oil (13.1 mg, yield: 35%). ^1H 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 $[\text{C}_{27}\text{H}_{19}\text{NNaO}, \text{M} + \text{Na}]^+$: 396.13589, Found: 396.13578.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at <https://doi.org/10.1016/j.tet.2017.11.049>. These data include MOL files and InChIKeys of the most important compounds described in this article.

References

- Saga Y, Motoki R, Makino S, Shimizu Y, Kanai M, Shibasaki M. *J Am Chem Soc.* 2010;132:7905.
- (a) Preston NW, Chamberlain K, Skipp RA. *Phytochemistry.* 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 JM, Urban S. *J Nat Prod.* 2015;78:1600.
- (For selected reviews, see:) (a) Horton DA, Bourne GT, Smythe ML. *Chem Rev.* 2003;103:893; (b) Alonso F, Beletskaya IP, Yus M. *Chem Rev.* 2004;104:3079; (c) Zeni G, Larock RC. *Chem Rev.* 2006;106:4644; (d) Chinchilla R, Nájera C. *Chem Rev.* 2007;107:874; (e) Patil NT, Yamamoto Y. *Chem Rev.* 2008;108:3395; (f) Godoi B, Schumacher RF, Zeni G. *Chem Rev.* 2011;111:2937; (g) Wu X-F, Neumann H, Beller M. *Chem Rev.* 2013;113:1; (h) Keylor MH, Matsuura BS, Stephenson CRJ. *Chem Rev.* 2015;115:8976.
- (For selected examples, see:) (a) Morrison BJ, Musgrave OC. *Tetrahedron.* 2002;58:4255; (b) Kumar MP, Liu R-S. *J Org Chem.* 2006;71:4951; (c) Bonnamour J, Piedrafitra 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, et al. *Chem Commun.* 2013;49:6611; (f) Konishi A, Yasunaga R, Chiba K, Yasuda M. *Chem Commun.* 2016;52:3348; (g) Sreenivasulu C, Reddy AGK, Satyanarayana G. *Org Chem Front.* 2017;4:972; (h) Warner AJ, Churn A, McGough JS, Ingleson MJ. *Angew Chem Int Ed.* 2017;56:354.
- (For selected examples, see:) (a) Lu B, Wang B, Zhang Y, Ma DJ. *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, Aurrecochea JM. *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 MR, Bhanuchandra M, Sahoo AK. *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, et al. *Angew Chem Int Ed.* 2017;56:4286; (i) Mai S, Song Q. *Angew Chem Int Ed.* 2017;56:7952.
- Liu J-t, Simmons CJ, Xie H, et al. *Adv Synth Catal.* 2017;359:693.
- (For selected examples, see:) (a) Shen Z, Dong VM. *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.
- (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, et al. *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.
- Welker M, Turbiez MGR, Chebotareva N, Kirner HJ, Schaefer T. Dithienobenzofuran polymers and small molecules for electronic application. WO 2014016219.
- 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.
- (a) Zhao Y, Li J, Li C, Yin K, Ye D, Jia X. *Green Chem.* 2010;12:1370; (b) Buyck T, Wang Q, Zhu JJ. *Am Chem Soc.* 2014;136, 11524; (c) Melis N, Secci F, Boddart T, Aitken DJ, Frongia A. *Chem Commun.* 2015;51, 15272; (d) Jin S, Hunt AJ, Clark JH, McElroy C. R. *Green Chem.* 2016;18:5839.