JOC The Journal of Organic Chemistry

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Synthesis of 2-Aryl and 3-Aryl Benzo[*b*]furan Thioethers Using Aryl Sulfonyl Hydrazides as Sulfenylation Reagents

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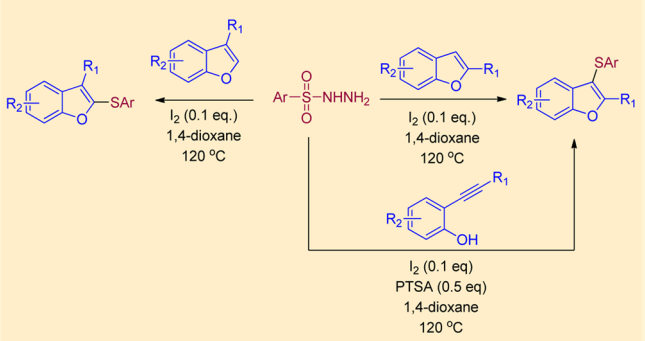
Supporting Information

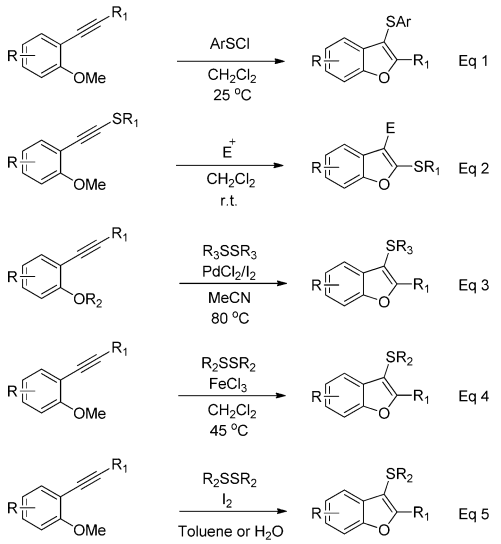
ABSTRACT: An efficient, metal-free protocol used to synthesize aryl benzo[*b*]furan thioethers based on the I_2-catalyzed cross-coupling of benzo[*b*]furans as well as the electrophilic cyclization of 2-alkynylphenol derivatives with aryl sulfonyl hydrazides was developed. Various 2-aryl and 3-aryl benzo[*b*]furan thioethers were obtained in moderate to good yields.



Benzofurans constitute basic units that frequently occur in natural products and represent the most important type of heterocycles in drug discovery,[1] as they have been reported to exhibit anticancer,[2] antiviral,[3] antifungal,[4] anti-inflammatory[5] and immunosuppressive activities.[6] Therefore, significant efforts have been put forth toward the efficient construction of benzofuran scaffolds. To the best of our knowledge, only a few methods have been reported to prepare 2-sulfenyl or 3-sulfenyl benzo[*b*]furans including (i) electrophilic cyclization of 2-(phenylethynyl)anisole with 4-nitrophenyl hypochlorothioite (Scheme 1, eq 1),[7] (ii) electrophilic cyclization of 2-sulfenylalkynylanisoles with electrophile sources such as I_2, ICl, Br_2 and PhSeBr (Scheme 1, eq 2),[8] (iii) $PdCl_2$-catalyzed annulation of 2-alkynylphenol derivatives with disulfides in the presence of 2 equiv of I_2 (Scheme 1, eq 3),[9] (iv) $FeCl_3$-promoted annulation of 2-alkynylanisoles with disulfides (Scheme 1, eq 4),[10] and (v) I_2-mediated cyclization of 2-alkynylanisoles with diaryl disulfides (Scheme 1, eq 5).[11] However, these methods require either expensive and air-sensitive metal catalysts or foul-smelling, toxic and unstable sulfur sources such as sulfenyl halides and disulfides. Hence, a direct and concise method to synthesize 2-sulfenyl or 3-sulfenyl benzo[*b*]furans using stable and environmentally friendly reagents remains a significant challenge for organic chemists.

In the past two years, sulfonyl hydrazides, which are readily accessible, nonodorous, and stable solids, have emerged as novel sulfenylation reagents. Specifically, they have been used in the sulfenylation of iodoles,[12] alkanes,[13] ethers,[13] naphthols and naphthylamines,[14] as well as in the oxysulfenylation of alkenes,[15] hydrothiolation of alkynes,[16] and in the synthesis of unsymmetrical sulfides.[17] Recently, we reported the I_2-catalyzed sulfenylation of pyrazolones with aryl sulfonyl hydrazides promoted by *p*-toluenesulfonic acid (PTSA).[18] Inspired by the aforementioned background and our interest in the chemistry of sulfonyl hydrazides, we envisaged that sulfenyl benzo[*b*]furans could be produced via the direct sulfenylation of benzofuran by sulfonyl hydrazides and electrophilic cyclization

Scheme 1. Synthesis 2- or 3-Sulfenyl Benzo[*b*]furans via Different Methods



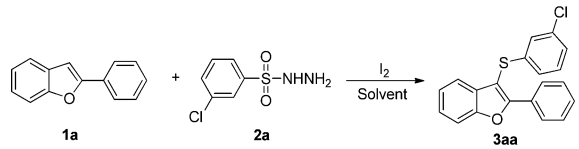
Received: January 20, 2015
Published: February 12, 2015

DOI: 10.1021/acs.joc.5b00146
J. Org. Chem. 2015, 80, 2918−2924

of 2-alkynylphenol derivatives with sulfonyl hydrazides. Herein, we disclose concise and convenient methods to synthesize 2-aryl and 3-aryl benzo[*b*]furan thioethers using aryl sulfonyl hydrazides as sulfenylation reagents via catalysis with iodine.

To begin our investigation, benzofuran was reacted with 3-chlorobenzenesulfonohydrazide **2a** using Tian's protocol (I_2 10 mol %, ethanol, 70 °C). Unfortunately, the sulfenylation reaction did not occur at all, and benzofuran decomposed at higher temperatures (120 °C). To circumvent this issue, a more stable benzofuran derivative, 2-phenylbenzofuran **1a**, was reacted with **2a** at 120 °C in ethanol (EtOH). To our delight, the desired sulfenylation product **3aa** was obtained in 75% yield in the presence of 0.1 equiv of I_2 as the catalyst at 120 °C (Table 1, entry 1). To identify the optimal reaction conditions,

Table 1. Optimization of I_2-Catalyzed Reaction of 1a with 2a[a]



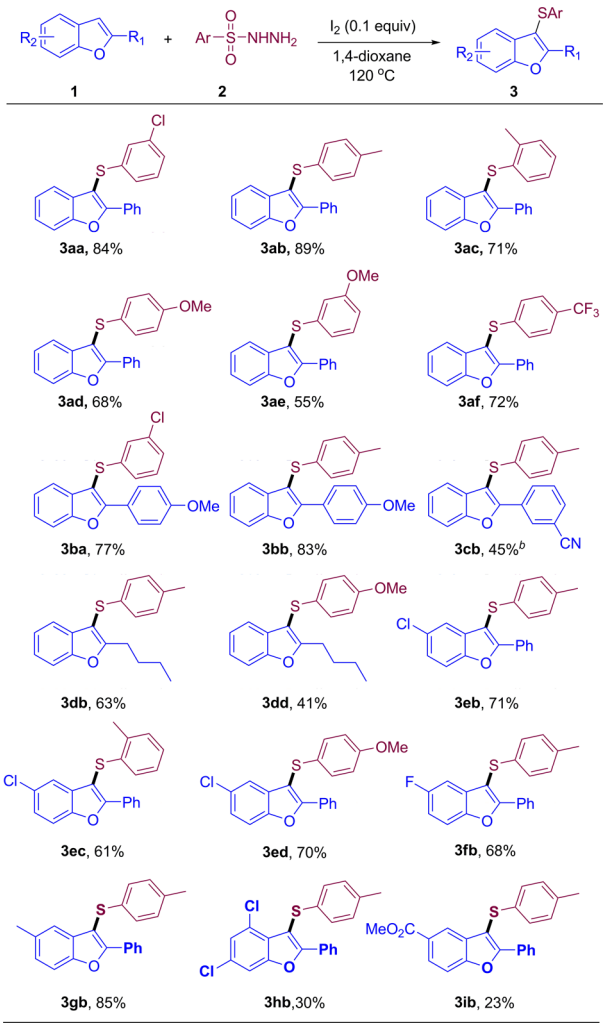
entry	I_2 (equiv)	t (h)	T (°C)	solvent	yield (%)
1	0.1	24	120	EtOH	75
2	0.1	24	120	H_2O	35
3	0.1	24	120	DCE	79
4	0.1	24	120	toluene	61
5	0.1	24	120	DMF	0
6	0.1	24	120	1,4-dioxane	83
7	0.1	24	130	1,4-dioxane	81
8	0.1	24	100	1,4-dioxane	71
9	0.1	24	80	1,4-dioxane	58
10	0.1	24	120	1,4-dioxane	72[b]
11	0.05	48	120	1,4-dioxane	69
12	0.01	48	120	1,4-dioxane	trace
13	0.1	24	120	1,4-dioxane	84[c]
14	0.1	24	120	1,4-dioxane	75[d]
15	0.1	24	120	1,4-dioxane	25[e]

[a]Reaction conditions: **1a** (1.0 mmol), **2a** (2.0 mmol), solvent (0.5 mL). [b]**1a** (1.0 mmol), **2a** (2.0 mmol), solvent (1.0 mL). [c]**1a** (1.0 mmol), **2a** (1.8 mmol), solvent (0.5 mL). [d]**1a** (1.0 mmol), **2a** (1.5 mmol), solvent (0.5 mL). [e]**1a** (1.0 mmol), **2a** (1.8 mmol), PTSA (1.0 mol), solvent (0.5 mL).

various solvents such as EtOH, 1,4-dioxane, toluene, 1,2-dichloroethane (DCE), *N*,*N*-dimethylformamide (DMF), and water were tested (Table 1, entry 2−6). 1,4-Dioxane gave the best result, in that 83% yield was obtained. Next, a few reaction temperatures and concentration were screened. Increasing the reaction temperature to 130 °C led to a slightly diminished yield (Table 1, entry 7). However, when the reaction was carried out at 100 and 80 °C, the yield decreased to 71 and 58%, respectively (Table 1, entries 8 and 9). It was noteworthy that decreasing the concentration led to a decrease of the yield (Table 1, entry 10). Finally, the effects of catalyst loading and equivalents of **2a** were investigated (Table 1, entry 11−14). The results suggested that 0.1 equiv of the I_2 catalyst was required to obtain a suitable product yield. When the catalyst loading was decreased to 1%, only a trace amount of the desired product was obtained (Table 1, entry 12). For sulfonyl hydrazide, 1.8 equiv of **2a** were sufficient to produce a suitable yield (Table 1, entry 13). Further decrease in the amount of **2a** led to a decrease in the yield (Table 1, entry 14). Notably, unlike in the sulfenylation of naphthols, naphthylamines, and pyrazolones, the addition of an acid did not facilitate the transformation.[14,18] In contrast, the presence of PTSA could accelerate the decomposition of 2-phenylbenzofuran (**1a**) which led to a diminished yield (Table 1, entry 15). Therefore, the optimized reaction conditions were determined to be as follows: **1a** (1.0 mmol), **2a** (1.8 mmol), I_2 (0.1 mmol), and 1,4-dioxane (0.5 mL), at 120 °C.

With the optimized reaction conditions in hand, the generality and substrate scope of 2-substituted benzofurans and sulfonyl hydrazides were examined in the sulfenylation reaction. The results are illustrated in Table 2. A variety of

Table 2. I_2-Catalyzed Cross Coupling with a Series of 2-Substituted Benzofurans and Aryl Sulfonyl Hydrazides[a]



[a]Reaction conditions **1a**−**i** (1.0 mmol), **2a**−**d** (1.8 mmol), I_2 (10 mol %), 1,4-dioxane (0.5 mL), 120 C, 24 h. [b]I_2 (20 mol %) was used

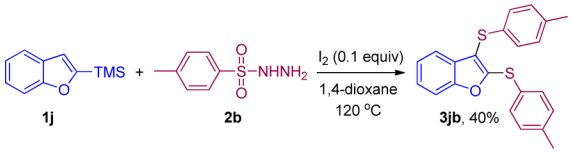
substituted aryl sulfonyl hydrazides could be coupled with various 2-substituted benzofurans to afford the corresponding benzofuran thioethers in moderate to excellent yields. However, when aliphatic sulfonyl hydrazides such as methanesulfonohydrazide and butane-1-sulfonohydrazide were employed as substrates, the desired coupling products were not detected under the optimized reaction conditions.

DOI: 10.1021/acs.joc.5b00146
J. Org. Chem. 2015, 80, 2918−2924

For aromatic sulfonyl hydrazides, both electron-withdrawing and electron-donating groups, as well as *meta*-, *ortho*-, and *para*-substitutions (**2a**–**2f**) were tolerated under the optimized conditions. Notably, the identity of the substituent on the benzofuran had a significant effect on the sulfenylation reaction. In regard to substituents in the 2-position, alkyl-substituted benzofuran (**1d**) resulted in lower yields compared with the corresponding phenyl substrate (**1a**) when using 4-methylbenzenesulfonohydrazide (**2b**) or 4-methoxybenzenesulfonohydrazide (**2d**) as the sulfenylation reagent. Moreover, electron-withdrawing groups in the 2-position of the aryl substituent (**1c**) and 5-position of benzofuran (**1f** and **1i**) resulted in lower yields as compared to that with substrates containing electron-donating groups.

Interestingly, when benzofuran-2-yltrimethylsilane (**1j**) was utilized as a substrate, the disulfenylation product (**3jb**) was obtained in 40% yield (Scheme 2).

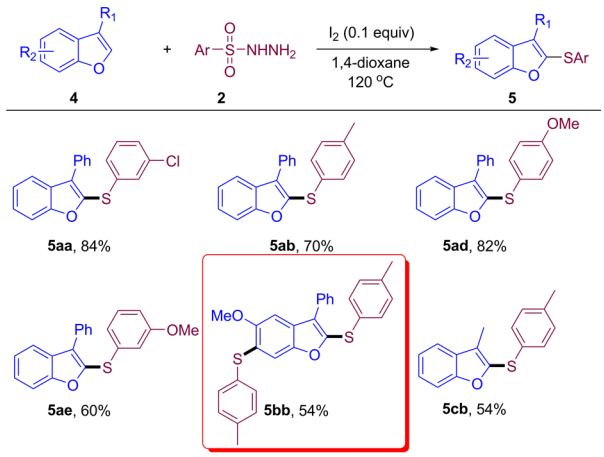
Scheme 2. Sulfenylation of Benzofuran-2-yltrimethylsilane



Notably, when 2-phenylbenzo[*b*]thiophene (**1k**) was coupled with 4-methylbenzenesulfonohydrazide (**2b**) under the optimized condition, the desired product 2-phenyl-3-(*p*-tolylthio)benzo[*b*]thiophene (**3kb**) was obtained in 24% yield.

In order to extend the scope of this transformation, 3-substituted benzofurans were tested under the optimized conditions. The results are summarized in Table 3. Both 3-

Table 3. I_2-Catalyzed Cross Coupling with a Series of 3-Substituted Benzofurans and Aryl Sulfonyl Hydrazides[a]

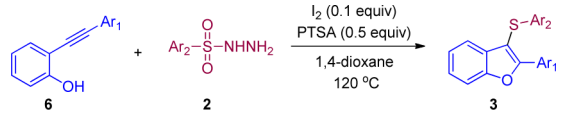


[a]Reaction conditions: **1a**–**i** (1.0 mmol), **2a**–**d** (1.8 mmol), I_2 (10 mol %), 1,4-dioxane (0.5 mL), 120 C, 24 h.

phenyl and 3-methyl substituted benzofurans reacted with various aryl sulfonyl hydrazides (**2b**, **2d**, and **2e**) smoothly and were converted to the sulfenylation products in moderate to good yields. Notably, when 5-methoxy-3-phenylbenzofuran (**4b**) was treated with 4-methylbenzenesulfonohydrazide (**2b**) under the catalysis of I_2, disulfenylation product (**5bb**) was obtained in 54% yield.

As mentioned previously, 2-sulfenyl or 3-sulfenyl benzo[*b*]furans can be synthesized by the annulation of 2-alkynylphenol derivatives.[7−11] Hence, 2-(phenylethynyl)phenol **6** was evaluated in the reaction with 4-methylbenzenesulfonohydrazide (**2b**). As expected, the desired product **3ab** was formed in 30% yield (Table 4, entry 1) under the standard conditions (I_2 10

Table 4. I_2-Catalyzed Electrophilic Cyclization of 2-Alkynylphenols with Aryl Sulfonyl Hydrazides[a]



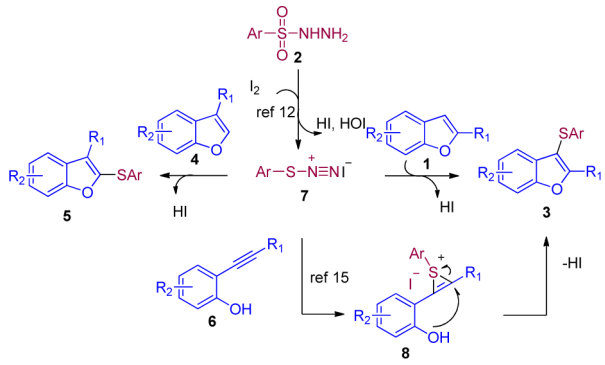
entry	**6**, Ar_1	**2**, Ar_2	yield (%)
1	**6a**, Ph	**2b**, *p*-MeC_6H_4	**3ab**, 30[b]
2	**6a**, Ph	**2b**, *p*-MeC_6H_4	**3ab**, 80
3	**6a**, Ph	**2c**, *o*-MeC_6H_4	**3ac**, 66
4	**6a**, Ph	**2d**, *p*-$MeOC_6H_4$	**3ad**, 35
5	**6a**, Ph	**2g**, *p*-BrC_6H_4	**3ag**, 39
6	**6b**, *p*-$MeOC_6H_4$	**2b**, *p*-MeC_6H_4	**3bb**, 78

[a]Reaction conditions: **6** (1.0 mmol), **2** (2.0 mmol), I_2 (0.1 mmol), PTSA (0.5 mmol), 1,4-dioxane (0.5 mL), 120 °C, 24 h. [b]PTSA was not added.

mol %, 1,4-dioxane, 120 °C). To improve the yield, various conditions were screened; addition of 0.5 equiv of PTSA greatly increased the yield (Table 4, entry 2). Other 2-alkynylphenol derivatives and aryl sulfonyl hydrazides were subjected to this tandem reaction, and fortunately provided the desired products in poor to good yields (Table 4, entry 3–6).

On the basis of the experimental and previously reported results,[12,15] a plausible mechanism for these transformations is proposed in Scheme 3. Initially, aryl sulfonyl hydrazide **2** is

Scheme 3. Possible Reaction Pathways



converted to thiodiazonium iodide **7**, which is attacked by benzofuran **1** and **4** to give sulfenylation products **3** and **5**, respectively. For the tandem reaction, electrophilic addition of thiodiazonium iodide **7** to alkyne **6** gives thiirenium ion **8**. Subsequently, intramolecular ring-opening of the thiirenium ion with the phenol moiety affords compound **3**.

In conclusion, we developed concise and efficient methods for the synthesis of 2-aryl and 3-aryl benzofuran thioethers by the I_2-catalyzed cross-coupling reaction of 3- and 2-substituted benzo[*b*]furans with aryl sulfonyl hydrazides via direct C–H functionalization, as well as the electrophilic cyclization of 2-alkynylphenol derivatives with aryl sulfonyl hydrazides. This study not only broadened the substrate scope of sulfonyl

DOI: 10.1021/acs.joc.5b00146
J. Org. Chem. 2015, 80, 2918–2924

hydrazides as novel and environmentally friendly reagents with sulfenylate electron-rich heterocycles, but also facilitated the synthesis of benzofuran thioethers via the oxysulfenylation of alkynes.

EXPERIMENTAL SECTION

General Experimental Methods. All solvents were distilled prior to use. Aryl benzo[*b*]furans were prepared according to the literature procedure.[19] 2-Alkynylphenol derivatives were prepared according to the literature procedure.[20] Unless otherwise noted, chemicals were used as received without further purification. For chromatography, 200−300 mesh silica gel was employed. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 400 and 100 MHz, respectively. Chemical shifts are reported in ppm using tetramethylsilane as internal standard. IR spectra were recorded in wave numbers (cm^{-1}) with a FT-IR spectrometer. HRMS was performed on an FTMS mass instrument. Melting points are reported as uncorrected.

General Procedure I. *I_2-Catalyzed Reactions between Aryl Benzo[b]furans **1a−i**, **4a−c** and Aryl Sulfonyl Hydrazides **2a−f** (Table 2 and Table 3).* Aryl benzo[*b*]furan (1.0 mmol), aryl sulfonyl hydrazide (1.8 mmol), I_2 (25.4 mg, 0.1 mmol) and 1,4-dioxane (0.5 mL) were mixed in a sealed tube. The mixture was stirred at 120 °C until the aryl benzo[*b*]furan disappeared detected by TLC. Then, the solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography to afford the pure product.

General Procedure II. *I_2-Catalyzed Reactions between 2-Alkynylphenol Derivatives **6a**, **6b** and Aryl Sulfonyl Hydrazides **2b**, **2c**, **2d**, **2g** (Table 4).* 2-Alkynylphenol derivative (1.0 mmol), aryl sulfonyl hydrazide (2.0 mmol), I_2 (25.4 mg, 0.1 mmol), 4-methylbenzenesulfonic acid (86 mg, 0.5 mmol) and 1,4-dioxane (0.5 mL) were mixed in a sealed tube. The mixture was stirred at 120 °C for 24 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography to afford the pure product.

*3-(3-Chlorophenylthio)-2-phenylbenzofuran (**3aa**).* The crude compound was prepared through the general procedure I. After purification by silica gel column chromatography (PE, PE = petroleum ether), compound **3aa** was isolated as a white solid (281 mg, 84%): mp (melting point) = 60−61 °C; R_f (PE) = 0.3; IR (film) 1576, 1460, 1442, 1086, 1069, 772, 744, 688 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.0 Hz, 1H), 7.34−7.49 (m, 5H), 7.24−7.27 (m, 1H), 7.17 (d, J = 1.6 Hz, 1H), 7.02−7.12 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.8, 153.9, 138.4, 134.9, 130.4, 130.0, 129.5, 129.4, 128.6, 127.3, 125.9, 125.6, 125.4, 124.3, 123.6, 120.1, 111.4, 103.5; HRMS (ESI, m/z) calcd for $C_{20}H_{14}ClOS$ [M + H]$^+$ 337.0448, found 337.0453.

*2-Phenyl-3-(p-tolylthio)benzofuran (**3ab**).*[9] The crude compound was prepared through the general procedure I or procedure II. After purification by silica gel column chromatography (PE), compound **3ab** was isolated as a pale yellow solid (281 mg, 89% for procedure I) (253 mg, 80% for procedure II): R_f (PE) = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.4 Hz, 1H), 7.44−7.49 (m, 3H), 7.38−7.41 (m, 1H), 7.31−7.35 (m, 1H), 7.20−7.24 (m, 1H), 7.11 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 2.26 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.1, 153.8, 135.3, 132.4, 130.8, 129.8, 129.2, 128.5, 127.3, 126.8, 125.1, 123.3, 120.4, 111.2, 105.2, 20.8.

*2-Phenyl-3-(o-tolylthio)benzofuran (**3ac**).* The crude compound was prepared through the general procedure I or procedure II. After purification by silica gel column chromatography (PE), compound **3ac** was isolated as a white solid (225 mg, 71% for procedure I), (209 mg, 66% for procedure II): mp (melting point) = 67−68 °C; R_f (PE) = 0.5; IR (film) 2932, 1590, 1453, 1442, 1067, 742, 689 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 7.2 Hz, 2H), 7.56 (d, J = 8.4 Hz, 1H), 7.38−7.45 (m, 4H), 7.32 (t, J = 7.2 Hz, 1H), 7.22 (d, J = 8.0 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.01 (t, J = 7.2 Hz, 1H), 6.92 (t, J = 7.2 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 2.50 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.5, 154.0, 135.2, 135.1, 130.8, 130.2, 129.8, 129.3, 128.5, 127.3, 126.6, 125.8, 125.3, 125.2, 123.4, 120.4, 111.3, 104.4, 20.0; HRMS (ESI, m/z) calcd for $C_{21}H_{17}OS$ [M + H]$^+$ 317.0995, found 317.0999.

*3-(4-Methoxyphenylthio)-2-phenylbenzofuran (**3ad**).*[9] The crude compound was prepared through the general procedure I or procedure II. After purification by silica gel column chromatography (PE:EA = 30:1, PE = petroleum ether, EA = ethyl acetate), compound **3ad** was isolated as a pale yellow oil (226 mg, 68% for procedure I), (116 mg, 35% for procedure II): R_f (PE:EA = 30:1) = 0.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.8 Hz, 2H), 7.53 (d, J = 8.0 Hz, 1H), 7.45−7.48 (m, 3H), 7.38−7.41 (m, 1H), 7.31 (t, J = 8.0 Hz, 1H), 7.18−7.24 (m, 3H), 6.76 (d, J = 8.8 Hz, 2H), 3.73 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.3, 156.6, 153.8, 130.8, 129.9, 129.24, 129.19, 128.5, 127.3, 126.4, 125.1, 123.3, 120.4, 114.7, 111.2, 106.4, 55.2.

*3-(3-Methoxyphenylthio)-2-phenylbenzofuran (**3ae**).* The crude compound was prepared through the general procedure I. After purification by silica gel column chromatography (PE:EA = 30:1), compound **3ae** was isolated as a pale yellow solid (183 mg, 55%): mp (melting point) = 83−84 °C; R_f (PE:EA = 30:1) = 0.5; IR (film) 2927, 1590, 1477, 1248, 1043, 768, 745, 687 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.38−7.48 (m, 3H), 7.34 (dt, J = 8.0 Hz, 1.2 Hz, 1H), 7.24 (t, J = 7.2 Hz, 1H), 7.12 (t, J = 8.0 Hz, 1H) 6.77 (d, J = 8.0 Hz, 1H), 6.75 (t, J = 2.0 Hz, 1H), 6.66 (dd, J = 8.0 Hz, 2.0 Hz, 1H) 3.68 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.0, 157.6, 153.9, 137.6, 130.8, 129.9, 129.7, 129.4, 128.5, 127.4, 125.3, 123.5, 120.4, 118.7, 112.1, 111.3, 111.0, 104.4, 55.1; HRMS (ESI, m/z) calcd for $C_{21}H_{17}O_2S$ [M + H]$^+$ 333.0944, found 333.0949.

*2-Phenyl-3-(4-(trifluoromethyl)phenylthio)benzofuran (**3af**).* The crude compound was prepared through the general procedure I. After purification by silica gel column chromatography (PE), compound **3af** was isolated as a white solid (265 mg, 72%): mp (melting point) = 77−79 °C; R_f (PE) = 0.6; IR (film) 1606, 1325, 1166, 1123, 1107, 1087, 1063, 1012, 827, 746, 689 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 1H), 7.41−7.47 (m, 6H), 7.35−7.39 (m, 1H), 7.23−7.26 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.2, 154.0, 141.5, 130.3, 129.7, 129.4, 128.7, 127.5 (q, J = 32 Hz, 1C), 127.4, 125.90 (q, J = 3.8 Hz, 1C), 125.85, 125.6, 124.1 (q, J = 270 Hz, 1C), 123.8, 120.1, 111.5, 102.9; HRMS (ESI, m/z) calcd for $C_{21}H_{13}F_3OS$ [M]$^+$ 370.0634, found 370.0632.

*3-(4-Bromophenylthio)-2-phenylbenzofuran (**3ag**).*[11b] The crude compound was prepared through the general procedure II. After purification by silica gel column chromatography (PE:EA = 50:1), compound **3ag** was isolated as a pale yellow oil (147 mg, 39%): R_f (PE:EA = 20:1) = 0.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 8.0 Hz, 1H), 7.41−7.49 (m, 4H), 7.29−7.38 (m, 3H), 7.25 (t, J = 7.2 Hz, 1H), 7.05 (d, J = 8.8 Hz,2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.7, 153.9, 135.4, 132.0, 130.4, 129.6, 129.5, 128.6, 127.9, 127.3, 125.4, 123.6, 120.2, 119.2, 111.4, 103.9.

*3-(3-Chlorophenylthio)-2-(4-methoxyphenyl)benzofuran (**3ba**).* The crude compound was prepared through the general procedure I. After purification by silica gel column chromatography (PE:EA = 40:1), compound **3ba** was isolated as a pale yellow solid (283 mg, 77%): mp (melting point) = 84−85 °C; R_f (PE:EA = 30:1) = 0.6; IR (film) 1609, 1576, 1499, 1460, 1452, 1256, 1177, 1081, 1033, 833, 774, 746 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13−8.17 (m, 2H), 7.55 (d, J = 8.4 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.33 (dt, J = 8.0 Hz, 1.2 Hz, 1H), 7.24 (t, J = 8.0 Hz, 1H), 7.16 (t, J = 1.6 Hz, 1H), 7.05−7.12 (m, 2H), 7.02 (dt, J = 7.6 Hz, 1.6 Hz, 1H), 6.95−6.99 (m, 2H), 3.84 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.7, 158.2, 153.7, 138.7, 134.9, 130.7, 130.1, 130.0, 125.8, 125.6, 125.0, 124.2, 123.6, 122.2, 119.8, 114.1, 111.3, 101.5, 55.3; HRMS (ESI, m/z) calcd for $C_{21}H_{16}ClO_2S$ [M + H]$^+$ 367.0554, found 367.0563.

*2-(4-Methoxyphenyl)-3-(p-tolylthio)benzofuran (**3bb**).* The crude compound was prepared through the general procedure I or procedure II. After purification by silica gel column chromatography (PE), compound **3bb** was isolated as a pale yellow solid (288 mg, 83% for procedure I), (269 mg, 78% for procedure II): mp (melting point) = 72−74 °C; R_f (PE) = 0.3; IR (film) 1609, 1499, 1451, 1255, 1177, 1079, 1034, 833, 804, 745 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19

DOI: 10.1021/acs.joc.5b00146
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(dd, J = 8.8 Hz, 2H), 7.52 (d, J = 8.4 Hz, 1H), 7.45−7.47 (m, 1H), 7.28−7.32 (m, 1H), 7.19−7.22 (m, 1H), 7.01 (d, J = 8.4 Hz, 2H), 6.96−7.02 (m, 4H), 3.85 (s, 3H), 2.26 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.4, 157.5, 153.7, 135.3, 132.7, 131.1, 129.8, 128.9, 126.7, 124.7, 123.3, 122.5, 120.1, 114.0, 103.2, 55.3, 20.9; HRMS (ESI, m/z) calcd for $C_{22}H_{19}O_2S$ $[M + H]^+$ 347.1100, found 347.1107.

*3-(3-(p-Tolylthio)benzofuran-2-yl)benzonitrile (**3cb**).* The crude compound was prepared through the general procedure I. After purification by silica gel column chromatography (PE:EA = 30:1), compound **3cb** was isolated as a pale yellow solid (153 mg, 45%): mp (melting point) = 116−118 °C; R_f (PE:EA = 30:1) = 0.3; IR (film) 2231, 1491, 1450, 1255, 1172, 1078, 1016, 865, 802, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.52 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.53−7.57 (m, 2H), 7.49 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 8.0 Hz, 1H), 7.25 (t, J = 8.0 Hz, 1H), 7.11 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 2.27 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 154.0, 153.9, 136.1, 132.1, 131.4, 131.2, 131.1, 130.6, 130.5, 130.0, 129.4, 127.3, 126.1, 123.8, 120.8, 118.5, 113.0, 111.5, 108.0, 20.9; HRMS (ESI, m/z) calcd for $C_{22}H_{16}NOS$ $[M + H]^+$ 342.0947, found 342.0952.

*2-Butyl-3-(p-tolylthio)benzofuran (**3db**).* The crude compound was prepared through the general procedure I. After purification by silica gel column chromatography (PE), compound **3db** was isolated as a pale yellow oil (186 mg, 63%): R_f (PE) = 0.3; IR (film) 2963, 2954, 1489, 1452, 1033, 1016, 803, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.22−7.26 (m, 1H), 7.15−7.19 (m, 1H), 7.03 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 2.94 (t, J = 7.6 Hz, 2H), 2.25 (s, 3H), 1,72 (dt, J = 7.6 Hz, 7.6 Hz, 2H), 1,37 (dt, J = 7.6 Hz, 7.4 Hz, 2H), 0.91 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.7, 154.3, 135.2, 132.2, 129.6, 128.5, 126.7, 124.0, 123.0, 119.7, 111.0, 104.9, 30.2, 26.3, 22.3, 20.9, 13.7; HRMS (ESI, m/z) calcd for $C_{19}H_{21}OS$ $[M + H]^+$ 297.1308, found 297.1312.

*2-Butyl-3-(4-methoxyphenylthio)benzofuran (**3dd**).* The crude compound was prepared through the general procedure I. After purification by silica gel column chromatography (PE:EA = 30:1), compound **3dd** was isolated as a pale yellow oil (128 mg, 41%): R_f (PE:EA = 30:1) = 0.3; IR (film) 2955, 2924, 1591, 1493, 1452, 1244, 1173, 1032, 822, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.0 Hz, 1H), 7.40 (dd, J = 8.0 Hz, 0.8 Hz, 1H), 7.22−7.26 (m, 1H), 7.18 (dd, J = 8.0 Hz, 0.8 Hz, 1H), 7.14 (d, J = 8.8 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H), 3.74 (s, 3H), 2.96 (t, J = 7.6 Hz, 2H), 1,72 (dt, J = 7.6 Hz, 7.6 Hz, 2H), 1,38 (dt, J = 7.6 Hz, 7.6 Hz, 2H), 0.93 (t, J = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.2, 158.1, 154.2, 129.6, 129.2, 127.2, 124.0, 123.0, 119.7, 114.6, 111.0, 106.0, 55.3, 30.2, 26.3, 22.3, 13.7; HRMS (ESI, m/z) calcd for $C_{19}H_{21}O_2S$ $[M + H]^+$ 313.1257, found 313.1263.

*5-Chloro-2-phenyl-3-(p-tolylthio)benzofuran (**3eb**).*[11a] The crude compound was prepared through the general procedure I. After purification by silica gel column chromatography (PE), compound **3eb** was isolated as a pale yellow solid (249 mg, 71%): R_f (PE) = 0.4; ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, J = 8.0 Hz, 1.2 Hz, 2H), 7.41−7.47 (m, 5H), 7.22 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 2.27 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.7, 152.2, 135.8, 132.5, 131.9, 130.0, 129.7, 129.4, 129.2, 128.6, 127.4, 126.9, 125.5, 120.0, 112.3, 105.0, 20.9.

*5-Chloro-2-phenyl-3-(o-tolylthio)benzofuran (**3ec**).* The crude compound was prepared through the general procedure I. After purification by silica gel column chromatography (PE), compound **3ec** was isolated as a pale yellow solid (213 mg, 61%): mp (melting point) = 119−120 °C; R_f (PE) = 0.4; IR (film) 1466, 1450, 1440, 1256, 1198, 1067, 804, 768, 744, 687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, J = 8.0 Hz, 1.2 Hz, 2H), 7.39−7.49 (m, 5H), 7.29 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.19 (d, J = 7.2 Hz, 1H), 7.03 (dt, J = 7.2 Hz, 1.2 Hz, 1H), 6.96 (t, 7.2 Hz, 1H), 6.82 (d, 7.6 Hz, 1H), 2.50 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.0, 152.3, 135.3, 134.6, 132.4, 130.4, 129.7, 129.3, 129.2, 128.6, 127.4, 126.7, 125.6, 125.5, 119.9, 112.3, 104.0, 20.4; HRMS (ESI, m/z) calcd for $C_{21}H_{15}ClOS$ $[M]^+$ 350.0527, found 350.0535.

*5-Chloro-3-(4-methoxyphenylthio)-2-phenylbenzofuran (**3ed**).* The crude compound was prepared through the general procedure I. After purification by silica gel column chromatography (PE:EA = 30:1), compound **3ed** was isolated as a pale yellow solid (255 mg, 70%): mp (melting point) = 99−101 °C; R_f (PE:EA = 30:1) = 0.5;IR (film)1596, 1493, 1450, 1440, 1246, 1067, 1032, 825, 804, 768, 717, 688 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.8 Hz, 2H), 7.43−7.50 (m, 5H), 7.27 (dd, J = 8.8 Hz, 2.0 Hz, 1H), 7.19 (dd, J = 6.8 Hz, 2.0 Hz, 2H), 6.79 (dd, J = 6.8 Hz, 2.0 Hz, 2H), 3.75 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 158.4, 158.1, 152.2, 132.4, 129.7, 129.4, 129.3, 129.1, 128.6, 127.4, 125.8, 125.4, 120.0, 114.9, 112.3, 106.0, 55.3; HRMS (ESI, m/z) calcd for $C_{21}H_{15}ClO_2S$ $[M]^+$ 366.0476, found 366.0481.

*5-Fluoro-2-phenyl-3-(p-tolylthio)benzofuran (**3fb**).* The crude compound was prepared through the general procedure I. After purification by silica gel column chromatography (PE), compound **3fb** was isolated as a pale yellow solid (228 mg, 68%): mp (melting point) = 81−82 °C; R_f (PE:EA = 50:1) = 0.5; IR (film) 1491, 1468, 1443, 1158, 1085, 1069, 947, 855, 802, 767, 689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.21−8.24 (m, 2H), 7.40−7.47 (m, 4H), 7.09−7.13 (m, 3H), 7.00−7.04 (m, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.6 (d, J = 238 Hz, 1C), 158.9, 150.0, 135.8, 132.1 (d, J = 11 Hz, 1C), 131.9, 129.9, 129.6, 129.5, 128.6, 127.3, 127.0, 112.9 (d, J = 26 Hz, 1C), 112.0 (d, J = 9.4 Hz, 1C), 106.0 (d, J = 25 Hz, 1C), 105.6 (d, J = 3.9 Hz, 1C), 20.9; HRMS (ESI, m/z) calcd for $C_{21}H_{16}FOS$ $[M + H]^+$ 335.0900, found 335.0908.

*5-Methyl-2-phenyl-3-(p-tolylthio)benzofuran (**3gb**).* The crude compound was prepared through the general procedure I. After purification by silica gel column chromatography (PE), compound **3gb** was isolated as a pale yellow solid (282 mg, 85%): mp (melting point) = 96−98 °C; R_f (PE:EA = 50:1) = 0.4; IR (film) 2921, 1491, 1473, 1444, 1202, 1085, 1068, 1016, 827, 801, 766, 689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.21−8.23 (m, 2H), 7.35−7.46 (m, 4H), 7.29 (s, 1H), 7.13 (dd, J = 7.6 Hz, 1.2 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H), 2.26 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 157.5, 152.3, 135.3, 133.0, 132.7, 131.0, 129.9, 129.8, 129.2, 128.5, 127.3, 126.5, 120.1, 110.8, 104.6, 21.4, 20.9; HRMS (ESI, m/z) calcd for $C_{22}H_{19}OS$ $[M + H]^+$ 331.1151, found 331.1156.

*4,6-Dichloro-2-phenyl-3-(p-tolylthio)benzofuran (**3hb**).* The crude compound was prepared through the general procedure I. After purification by silica gel column chromatography (PE), compound **3hb** was isolated as a white solid (116 mg, 30%): mp (melting point) = 147−148 °C; R_f (PE:EA = 50:1) = 0.4; IR (film) 2921, 2846, 1723, 1575, 1491, 1455, 1398, 1325, 1176, 1081, 1068, 965, 839, 799, 682 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.16−8.19 (m, 2H), 7.50 (d, J = 1.6 Hz, 1H), 7.44−7.47 (m, 3H), 7.23 (d, J = 1.6 Hz, 1H), 7.03−7.07 (m, 4H), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.9, 154.6, 135.4, 134.0, 130.8, 130.1, 129.9, 128.8, 128.6, 127.9, 127.5, 126.2, 126.0, 125.5, 110.8, 104.8, 20.9; HRMS (ESI, m/z) calcd for $C_{21}H_{15}Cl_2OS$ $[M + H]^+$ 385.0215, found 385.0219.

*Methyl 2-phenyl-3-(p-tolylthio)benzofuran-5-carboxylate (**3ib**).* The crude compound was prepared through the general procedure I. After purification by silica gel column chromatography (PE), compound **3ib** was isolated as a pale yellow solid (85 mg, 23%): mp (melting point) = 116−117 °C; R_f (PE:EA = 30:1) = 0.4; IR (film) 2918, 2847, 1721, 1491, 1441, 1232, 1095, 767, 746, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.23−8.26 (m, 3H); 8.07 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.40−7.49 (m, 3H), 7.10 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 3.90 (s, 3H), 2.27 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.0, 158.7, 156.4, 135.8, 132.1, 131.2, 129.9, 129.7, 129.3, 128.6, 127.4, 127.0, 126.9, 125.9, 122.7, 111.2, 105.9, 52.1, 20.9; HRMS (ESI, m/z) calcd for $C_{23}H_{19}O_3S$ $[M + H]^+$ 375.1049, found 375.1057, calcd for $C_{23}H_{18}NaO_3S$ $[M + Na]^+$ 397.0869, found 397.0875.

*2,3-Bis(p-tolylthio)benzofuran (**3jb**).* Benzofuran-2-yltrimethylsilane (190 mg, 1 mmol), 4-methylbenzenesulfonohydrazide (335 mg, 1.8 mmol), I_2 (23.0 mg, 0.09 mmol) and 1,4-dioxane (0.5 mL) were mixed in a sealed tube. The mixture was stirred at 120 °C for 24 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography (PE),

DOI: 10.1021/acs.joc.5b00146
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compound **3jb** was isolated as a pale yellow solid (130 mg, 40%): mp (melting point) = 60−61 °C; R_f (PE:EA = 50:1) = 0.4; IR (film) 2920, 1597, 1491, 1443, 1083, 1029, 1016, 803, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41−7.43 (m, 1H), 7.35−7.38 (m, 1H), 7.26−7.32 (m, 3H), 7.15−7.19 (m, 1H), 7.13 (dd, J = 6.4 Hz, 1.6 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 2.31 (s, 3H), 2.27 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.9, 153.1, 137.9, 136.1, 131.6, 131.1, 130.0, 129.7, 129.2, 129.0, 128.4, 125.5, 123.4, 120.4, 116.4, 111.5, 21.1, 20.9; HRMS (ESI, m/z) calcd for $C_{22}H_{19}OS_2$ $[M + H]^+$ 363.0872, found 363.0881.

*2-Phenyl-3-(p-tolylthio)benzo[b]thiophene (**3kb**).* 2-Phenylbenzo-[b]thiophene (210 mg, 1 mmol), 4-methylbenzenesulfonohydrazide (335 mg, 1.8 mmol), I_2 (23.0 mg, 0.09 mmol) and 1,4-dioxane (0.5 mL) were mixed in a sealed tube. The mixture was stirred at 120 °C for 24 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography (PE), compound **3kb** was isolated as a pale yellow solid (80 mg, 24%): mp (melting point) = 72−73 °C; R_f (PE) = 0.4; IR (film) 2949, 2918, 2846, 1738, 1491, 1430, 1082, 1015, 804, 752, 731, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80−7.87 (m, 2H), 7.87 (dd, J = 8.0 Hz, 1.6 Hz, 2H), 7.33−7.44 (m, 5H), 6.94−6.99 (m, 4H), 2.25 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 149.2, 141.0, 138.3, 135.0, 133.9, 133.4, 129.8, 129.7, 128.8, 128.4, 126.3, 125.1, 125.0, 123.9, 122.1, 111.8, 20.9; HRMS (ESI, m/z) calcd for $C_{21}H_{17}S_2$ $[M + H]^+$ 333.0766, found 333.0771.

*2-(3-Chlorophenylthio)-3-phenylbenzofuran (**5aa**).* The crude compound was prepared through the general procedure I. After purification by silica gel column chromatography (PE), compound **5aa** was isolated as a pale yellow oil (282 mg, 84%): R_f (PE) = 0.4; IR (film) 2990, 2900, 1576, 1460, 1445, 1264, 1092, 1079, 965, 773, 739, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.6 Hz, 1H), 7.60 (d, J = 7.6 Hz, 2H), 7.45−7.52 (m, 3H), 7.36−7.41(m, 2H), 7.29 (t, J = 7.6 Hz, 1H), 7.21 (s, 1H), 7.13−7.15 (m, 2H), 7.06−7.09 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 156.1, 142.1, 137.0, 135.0, 131.1, 130.2, 129.2, 129.0, 128.7, 128.2, 127.8, 127.6, 126.8, 126.1, 126.0, 123.3, 120.7, 111.6; HRMS (ESI, m/z) calcd for $C_{20}H_{14}ClOS$ $[M + H]^+$ 337.0448, found 337.0452.

*3-Phenyl-2-(p-tolylthio)benzofuran (**5ab**).* The crude compound was prepared through the general procedure I. After purification by silica gel column chromatography (PE), compound **5ab** was isolated as a pale yellow solid (221 mg, 70%): mp (melting point) = 54−56 °C; R_f (PE) = 0.3; IR (film) 1491, 1444, 1119, 1078, 964, 804, 770, 749, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.0 Hz, 1H), 7.62−7.64 (m, 2H), 7.45−7.49 (m, 3H), 7.32−7.40 (m, 2H), 7.27 (dt, J = 8.0 Hz, 0.8 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 156.0, 144.1, 136.9, 131.5, 130.1, 130.0, 129.3, 128.9, 128.6, 128.1, 127.9, 127.5, 125.6, 123.1, 120.5, 111.5, 21.0; HRMS (ESI, m/z) calcd for $C_{21}H_{17}OS$ $[M + H]^+$ 317.0995, found 317.1002.

*2-(4-Methoxyphenylthio)-3-phenylbenzofuran (**5ad**).* The crude compound was prepared through the general procedure I. After purification by silica gel column chromatography (PE:EA = 30:1), compound **5ad** was isolated as a pale yellow solid (274 mg, 82%): mp (melting point) = 55−57 °C; R_f (PE:EA = 30:1) = 0.4; IR (film) 1592, 1493, 1444, 1290, 1246, 1173, 1031, 964, 825, 770, 749, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63−7.66 (m, 3H), 7.46−7.51 (m, 3H), 7.41 (t, J = 7.2 Hz, 1H), 7.34 (dt, J = 8.0 Hz, 1.2 Hz, 1H), 7.27−7.31 (m, 2H), 7.24−7.26 (m, 1H), 6.81 (dd, J = 6.8 Hz, 2.0 Hz, 2H), 3.76 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.3, 155.8, 145.1, 131.9, 131.6, 129.4, 128.6, 128.1, 127.8, 126.3, 125.4, 124.4, 123.0, 120.4, 114.8, 111.4, 55.3; HRMS (ESI, m/z) calcd for $C_{21}H_{17}O_2S$ $[M + H]^+$ 333.0944, found 333.0952.

*2-(3-Methoxyphenylthio)-3-phenylbenzofuran (**5ae**).* The crude compound was prepared through the general procedure I. After purification by silica gel column chromatography (PE:EA = 30:1), compound **5ae** was isolated as a pale yellow solid (198 mg, 60%): mp (melting point) = 77−79 °C; R_f (PE:EA = 30:1) = 0.5; IR (film) 1590, 1477, 1444, 1248, 1232, 1041, 964, 770, 749, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.6 Hz, 2H), 7.45−7.52 (m, 3H), 7.40 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 7.15 (t, J = 8.0 Hz, 1H), 6.79−6.82 (m, 2H), 6.71 (dd, J = 8.8 Hz, 1.2 Hz, 1H), 3.70 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.1, 156.1, 143.1, 136.2, 131.4, 130.0, 129.3, 128.6, 128.5, 128.0, 127.9, 125.8, 123.2, 120.6, 120.3, 113.6, 112.3, 111.6, 55.2; HRMS (ESI, m/z) calcd for $C_{21}H_{17}O_2S$ $[M + H]^+$ 333.0944, found 333.0948.

*5-Methoxy-3-phenyl-2,6-bis(p-tolylthio)benzofuran (**5bb**).* 5-Methoxy-3-phenylbenzofuran (224 mg, 1 mmol), 4-methylbenzenesulfonohydrazide (558 mg, 3 mmol), I_2 (25.4 mg, 0.1 mmol) and 1,4-dioxane (0.5 mL) were mixed in a sealed tube. The mixture was stirred at 120 °C for 24 h. Then, the solvent was evaporated under reduced pressure and the residue was purified by silica gel column chromatography (PE:EA = 30:1), compound **5bb** was isolated as a pale yellow solid (252 mg, 54%): mp (melting point) = 120−122 °C; R_f (PE:EA = 30:1) = 0.3; IR (film) 1491, 1457, 1438, 1269, 1198, 1149, 955, 807, 765, 737, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.4 Hz, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.40−7.43 (m, 3H), 7.21 (d, J = 7.6 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 7.03−7.05 (m, 3H), 6.88 (s, 1H), 3.92 (s, 3H), 2.39 (s, 3H), 2.28 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.7, 151.1, 143.7, 138.8, 136.7, 134.3, 131.5, 131.0, 130.4, 129.9, 129.1, 128.63, 128.60, 128.3, 127.9, 127.7, 127.4, 125.9, 110.8, 100.5, 56.4, 21.2, 20.9; HRMS (ESI, m/z) calcd for $C_{29}H_{25}O_2S_2$ $[M]^+$ 469.1290, found 469.1279.

*5-Methoxy-3-phenyl-2-(p-tolylthio)benzofuran (**5cb**).* The crude compound was prepared through the general procedure I. After purification by silica gel column chromatography (PE), compound **5cb** was isolated as a pale yellow oil (137 mg, 54%): R_f (PE) = 0.3; IR (film) 1492, 1448, 1233, 1073, 803, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.6 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.30 (dt, J = 8.0 Hz, 1.2 Hz, 1H), 7.21- (t, J = 7.6 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 2.35 (s, 3H), 2.26 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 155.7, 143.8, 136.6, 131.4, 129.9, 129.3, 128.4, 125.3, 123.4, 122.5, 119.7, 111.3, 20.9, 9.3; HRMS (ESI, m/z) calcd for $C_{16}H_{15}OS$ $[M + H]^+$ 255.0838, found 255.0842.

■ ASSOCIATED CONTENT

Supporting Information

Spectroscopic for compounds **3aa**−**3kb** and **5aa**−**5cb**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors sincerely thank the financial support from National Science Foundation of China (Grants 21202119, 21202118).

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DOI: 10.1021/acs.joc.5b00146
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