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Synthesis of Dibenzofurans via C−H Activation of *o*-Iodo Diaryl Ethers

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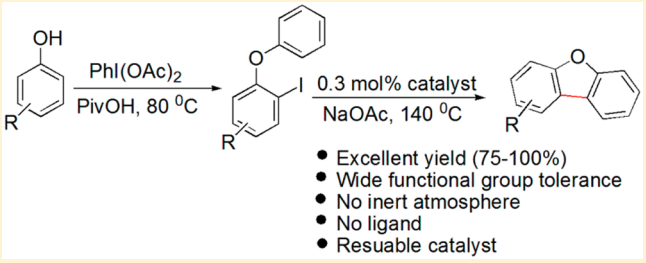
Supporting Information

ABSTRACT: An efficient method for the synthesis of dibenzofuran from *o*-iododiaryl ether using reusable Pd/C under ligand-free conditions has been developed. Synthesis of *o*-iododiaryl ether was achieved in one pot through sequential iodination and O-arylation of phenol under mild reaction conditions.



INTRODUCTION

The dibenzofuran nucleus is an omnipresent motif of numerous natural products and pharmaceutical candidates that exhibit anticancer, antibacterial, antiallergy, antimalarial, and anti-inflammatory activities.[1] Dibenzofurans are also endowed as a photolabile protecting group (caging group) in the biological process investigation.[2] In addition, fused benzofuran motifs are considered to be potential host material in blue phosphorescent organic light-emitting diodes (PhOLEDs).[3] The rising use of dibenzofurans has spurred considerable interest in developing new methods with enhanced scope, generality, and cost effectiveness for their synthesis. Of the reported methods, annulation of the *o*-arylphenol represents a classical synthetic methodology[4] to achieve dibenzofurans. Cyclization of the diaryl ether through oxidative aryl−aryl bond formation is another potential (may be more popular) approach. Evidently, the diaryl ethers required for the later cyclization are conventionally obtained by SN_{Ar} reaction or by transition-metal-catalyzed Ullman C−O coupling reactions,[5] which are often associated with limitations such as harsh reaction conditions, high temperature, limited substrate scope, and use of molar excess of catalyst.[6] In conjunction, several pioneering efforts have been made for the cyclization of diaryl ether derivatives (Scheme 1). For instance, photoinduced annulation of *o*-chloronaphthyl phenyl ether was reported by Henderson and Zweig.[7] The Pschorr reaction, which allows the intramolecular free-radical cyclization of diazotized *o*-(aryloxy)anilines in the presence of excess Cu catalyst, was successfully employed to afford dibenzofurans.[8] Because it is inexpensive and has good solubility, ferrous sulfate could also potentially be used to improve the yield of dibenzofuran.[9] Du et al. employed $Pd(OAc)_2$ for the cyclization of *o*-aryldiazonium tetrafluoroborate to afford dibenzofuran in moderate to good yield.[10] Intriguingly, a Pschorr-type radical cyclization process using organoboronic acids and trifluoroborates instead of hazardous diazonium salt in the presence of catalytic amount of silver nitrate and stoichiometric potassium persulfate was developed by Baran and co-workers.[11] Glorius et al. prepared dibenzofurans through decarboxylative C−C bond formation reaction using $Pd(OTf)_2/Ag_2CO_3$ catalyst.[12] Very recently, Ishida et al. exploited the oxidative coupling of two C−H bonds of diaryl ethers to enable dibenzofuran by ZrO_2-supported $Pd(OH)_2$ catalyst using molecular O_2 as a sole oxidant.[13] Fu and co-workers transformed the dibenzoxaborininols into dibenzofuran derivatives in good to excellent yield under palladium catalysis in the presence of iodine.[14] Beside these worthy developments, transition-metal-catalyzed oxidative cyclization of *o*-halodiaryl ether to dibenzofuran is relatively less explored.[7,15] Intriguingly, Liu and Larock reported a ligand-assisted Pd-catalyzed route (i.e., $Pd(OAc)_2/PCy_3$) for the coupling of *ortho*-iodophenol with the in situ generated benzyne intermediate to accomplish dibenzofuran.[15b] Fagnou and co-workers made an appealing effort by employing a similar catalytic system (e.g., $Pd(OAc)_2/PCy_3$) for the intramolecular cyclization of *o*-chlorodiaryl ether to produce dibenzofuran.[15c] However, they observed that the hydrodehalogenation was a competent reaction under similar reaction conditions. Notably, in order to inhibit the hydrodehalogenation, an equimolar amount of Ag_2CO_3 was employed along with the Pd catalyst. Later, the same group used Pearlman's catalyst ($Pd(OH)_2/C$) for the effective cyclization of *o*-iododiaryl ether at 140 °C.[15d] Although these methods are promising, the use of the expensive catalyst, ligand, and limited substrate scope often impedes their generality to achieve the dibenzofuran unit. Additionally, multistep access of *o*-halodiaryl ether garners further interest for the development of an efficient route to access such species from the readily available phenols and their

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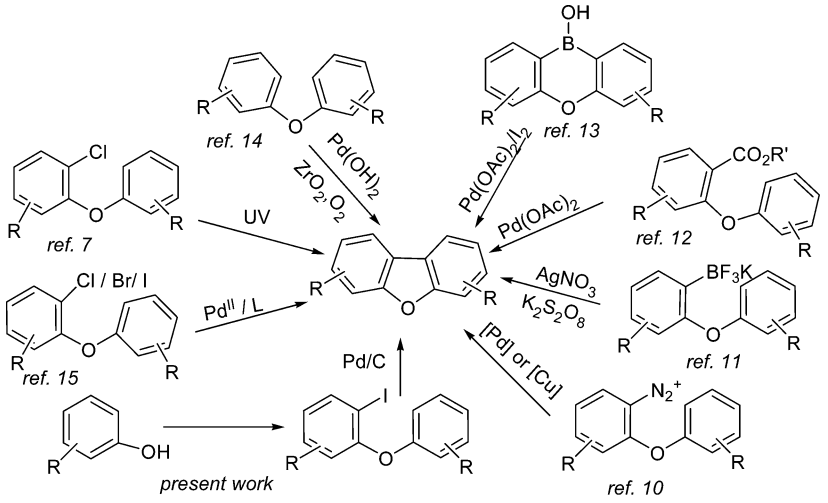
Scheme 1. Synthesis of Dibenzofuran from Functionalized Diaryl Ether



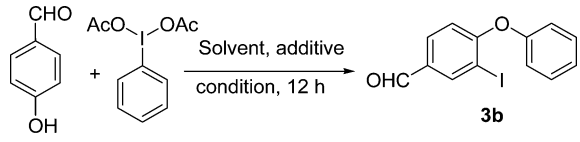
subsequent transformation to dibenzofuran derivatives. In continuation of our interest in the development of novel protocols for heterocycle synthesis,[16] here we report a practical and inexpensive method for the synthesis of *o*-iododiaryl ether from the readily available phenols. Subsequently, cyclization of the same by intramolecular aryl−aryl coupling to dibenzofuran derivatives was achieved by the use of less expensive, reusable Pd/C catalyst under ligand-free conditions.

RESULTS AND DISCUSSION

We initiated our work with a search for a suitable method for the synthesis of *o*-halodiaryl ether. Typically, transition-metal catalyzed O-arylation of *o*-halophenol is disconsolate. On the other hand, the pioneering work of Olofsson has emerged as a more companionable protocol for the selective O-arylation reaction[17] by diaryliodonium tetrafluoroborates/triflates. In contrast, use of precious diaryliodonium salt with the loss of an equimolar amount of expensive iodobenzene impedes its large-scale utility. Thus, development of an economical and efficient method for O-arylation with simultaneous *ortho*-halogenation is recognized to be important.

In continuing studies, we envisaged that hypervalent iodine(III)-promoted O-arylation reactions[18] could be employed to prepare *o*-iododiaryl ethers from the readily available phenols. In fact, utilizing 4-nitrophenol (**1a**) as the substrate in the presence of 1.5 equiv of phenyliodine diacetate (PIDA) in acetic acid under reflux leads to the formation of 1-(2-iodo-4-nitrophenoxy)benzene (**3a**) in quantitative yield. However, when 4-hydroxybenzaldehyde was treated with PIDA, under similar reaction conditions, 3-iodo-4-phenoxybenzaldehyde (**3b**) was obtained, albeit in poor yield (30%). In order to improve the yield, the reaction conditions were optimized by screening the additives and solvents (Table 1). We observed that when the reaction was carried out with PIDA in the presence of 5 equiv of acetic acid in dichloroethane at 80 °C, **3b** was obtained in 45% yield. Furthermore, upon changing the additive from acetic acid to pivalic acid, the yield of the reaction was further increased to 60%. Use of other acids (trifluoroacetic acid, triflic acid, *p*-toluene sulfonic acid, benzoic acid) and bases (K_2CO_3, Cs_2CO_3, ^tBuOk, NaOAc) as additives was found to be less efficient. Notably, other hypervalent iodines such as

Table 1. Optimization of Reaction Conditions[a]



entry	solvent	additive	conditions (°C)	yield (%)
1	CH_3COOH		reflux	30
2	CH_3CN	CH_3COOH	reflux	35
3	MeOH	CH_3COOH	reflux	23
4	DCE	CH_3COOH	reflux	45
5	DCE	CF_3COOH	reflux	7
6	DCE	CF_3SO_3H	reflux	5
7	DCE	CF_3SO_3H	reflux	10
8	toluene	CH_3COOH	80	46
9	DCE	PivOH	80	60
10	PivOH		80	20
11	DCE	CF_3COOH	80	7
12	CF_3COOH		reflux	13
13	DCE	base	reflux	0−5

[a]Reaction conditions: 4-hydroxybenzaldehyde (**1b**) (100 mg, 0.82 mmol), PIDA (1.5 equiv), additive (5 equiv) in 3 mL of solvent, heat, base: K_2CO_3/ Cs_2CO_3/^tBuOk/NaOAc.

$PhICl_2$ and $PhI(OCOCF_3)_2$ were found to be inefficient to produce **3b** (0−10% yield). Thus, the optimum yield of **3b** was obtained when 4-hydroxybenzaldehyde was treated with 1.5 equiv of PIDA and 5 equiv of pivalic acid in dichloroethane at 80 °C for 12 h. Unlike Steven's work[18a] when **1a** was treated with PIDA and acetic acid in dichloroethane at room temperature for 3 days, partial conversion occurs with the formation **3a** (40% yield) and no trace of iodinium ylide; i.e., phenyliodonio-4-nitrophenolate was identified (from the ^1H NMR of crude reaction mixture). Gratifyingly, the formation of analogous ether from the reaction of dimedone and PIDA was precedent in the literature. It has been reported that such reaction proceeds through the initial formation of iodinium ylide that undergoes subsequent phenyl migration to afford the desired ether. Notably, Nozaki et al. suggested a five-membered cyclic pathway for phenyl migration,[18b] whereas Moriarty proposed a ligand-coupling mechanism with four-membered cyclic

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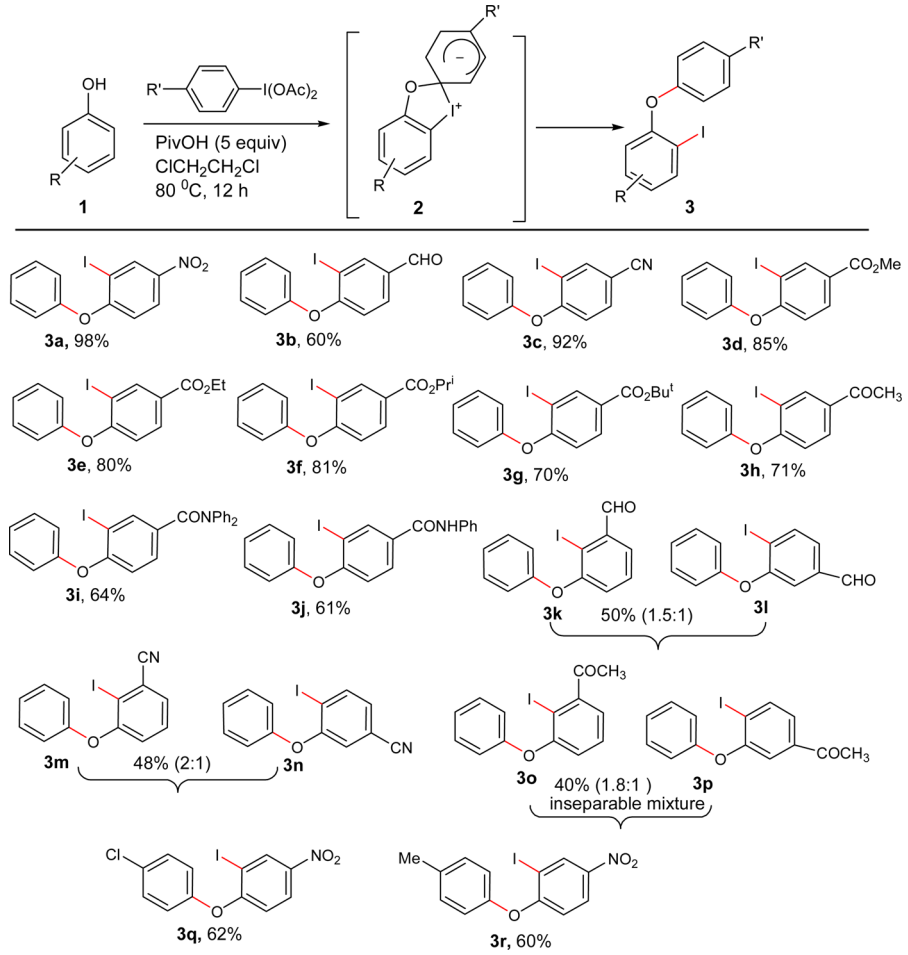
Scheme 2. Synthesis of *o*-Iodo Diaryl Ethers[a]



[a]Reaction conditions: phenol **1** (100 mg), $ArI(OAc)_2$ (1.5 equiv), PivOH (5 equiv) in 3 mL of dichloroethane, 80 °C.

intermediate.[18c] In contrary, from DFT study, Bakalbassis proved that the intramolecular thermal phenyl migration proceeds via a concerted mechanism through a five-membered cyclic transition-state (more resembles with Nozaki's pathway) without forming any intermediate.[18d] In line with the above precedence, it may be expected that our sequential iodination and arylation takes place via a transient intermediate **2** (Scheme 2).

Next, by using optimized reaction conditions, several *o*-iododiaryl ethers (**3a**−**p**) were prepared from the commercially available phenols bearing electron-withdrawing groups such as $-NO_2$, −CN, −CHO, $-COCH_3$, $-CONR_2$, −CONHR, $-CO_2R$, etc. in moderate to excellent yield (Scheme 2). Notably, 4-substituted phenols lead to the desired product in good yield whereas 3-substituted phenols lead to a mixture of iodo-derivatives in moderate yield. Nevertheless, the reaction of phenol, bearing an electron-donating or -neutral group (e.g., phenol, *p*-cresol, 4-hydroxy anisole), did not produce any 2-phenoxyaryl iodide. Thus, it may be revealed that the presence of electron-withdrawing groups in the aromatic ring that imparts a balance between the nucleophilicity of the phenol and the electron deficiency in the ring is responsible for the cascade iodination and O-arylation process. Eventually, differently aryl-substituted hypervalent iodine reagents were also found to be useful to produce *o*-iododiaryl ethers in good yield. Thus, when *p*-nitrophenol was treated with substituted aryl diacetates (Ar = 4-chlorophenyl and 4-methylphenyl) under optimized reaction conditions, the corresponding *o*-iododiaryl ethers **3q** and **3r** were produced in appreciable yield.

Having a series of *o*-iododiaryl ethers (**3**), next we sought to investigate the annulation reaction to produce dibenzofuran derivatives. For the initial screening, 3-iodo-4-phenoxybenzonitrile (**3c**) was taken as a model substrate and treated with various palladium catalysts and 3 equiv of potassium carbonate in *N*,*N*-dimethylacetamide (DMA) at 140 °C for 12 h. When 5 mol % of palladium acetate was used, the intramolecular cyclization as well as hydrodehalogenation occurs and a mixture of dibenzofuran (**6c**) and hydrodehalogenated product (**7**) was produced (9:1 mixture from ^1H NMR). Reducing the $Pd(OAc)_2$ concentration from 5 to 0.5 mol % also furnish the same result. We observed that $PdCl_2$ and $Pd(PPh_3)_4$ also produced the dibenzofuran **6c** in DMA in the presence of 3 equiv of K_2CO_3 (~90% yield) along with the inseparable byproduct **7** (from GC analysis). Change of catalyst to a heterogeneous catalyst such as 3 mol % of Pd (10 wt %) on activated charcoal support[19] also furnishes a similar result. It may be noted that both the dibenzofuran (**6c**) and hydrodehalogenated product (**7**) have same R_f value and are obtained as an inseparable mixture. In order to hinder the hydrodehalogenation reaction, several attempts have been made with the different combinations of

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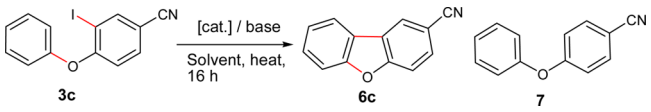
catalyst, base, and solvent at different temperatures (Table 2). Among the various tested bases, NaOAc was found to be more appropriate to produce only **6c** in the presence of Pd/C catalyst. Under controlled experimentation, when the reaction was carried out in the absence of the catalyst, the hydrodehalogenation product (e.g., **7**) was formed (Table 2, entry 16). Among the tested solvents, dimethylacetamide (DMA) affords the product **6c** in highest yield (95%), whereas other solvents like THF, EtOH, DMSO, DMF, etc. did not furnish **6c** in appreciable yield. It may be expected that DMA served as both solvent and chelating agent for the catalyst to produce **6c**. Nevertheless, lowering of temperature from 140 to 100 °C could not produce **6c** even after a prolonged period (36 h). In the absence of the base, about 30% conversion occurs even after 24 h. After several experimentations, we observed that 0.3 mol % of Pd/C is equally potent to produce **6c** quantitatively (95% yield) over a period of 16 h with excellent selectivity for arylation over hydrodehalogenation reaction.

Table 2. Optimization of the Reaction Conditions[a]



entry	catalyst	base	solvent	yield (%) (**6c**:**7**)
1	$Pd(OAc)_2$	K_2CO_3	DMA	90 (9:1)
2	$PdCl_2$	K_2CO_3	DMA	89 (9:1)
3	$Pd(PPh_3)_4$	K_2CO_3	DMA	90 (9:1)
4	Pd/C	K_2CO_3	DMA	90 (9:1)
5	$Pd(OAc)_2$	Cs_2CO_3	DMA	90 (8:2)
6	$Pd(OAc)_2$	$NaHCO_3$	DMA	90 (9:1)
7	Pd/C	$NaHCO_3$	DMA	92 (9:1)
8	Pd/C	Cs_2CO_3	DMA	95 (8:2)
9	Pd/C	NaOAc	DMA	95 (1:0)
10	Pd/C	NaOAc	DMF	35 (1:0)
11	Pd/C	NaOAc	DMSO	45 (1:0)
12[b]	Pd/C	NaOAc	DCE	n.r.
13[b]	Pd/C	NaOAc	THF	n.r.
14[b]	Pd/C	NaOAc	EtOH	n.r.
15[c]	Pd/C	NaOAc	DMA	95 (1:0)
16		^{t}BuOK	DMA	90 (0:1)

[a]Reaction conditions: 3-iodo-4-phenoxybenzonitrile (**3c**) (100 mg), catalyst (5 mol %), base (3 equiv) in 3 mL of solvent, 140 °C. [b]Reaction was carried out at reflux temperature. [c]Reaction was carried out at in the presence of 0.3 mol % of Pd/C for 16 h. n.r. = no reaction.

With the optimized reaction conditions, we observed that all of the synthesized *o*-iododiaryl ethers undergo cyclization smoothly to furnish the dibenzofurans in good to excellent yield. Functional groups such as $-NO_2$, $-CN$, $-CHO$, $-COCH_3$, $-CONR_2$, $-CONHR$, $-CO_2R$, etc. were found to be unaffected by the optimized reaction conditions (Table 3). Furthermore, this protocol is also proficient to produce dibenzofurans (**6s**) from the *o*-iododiphenyl ethers (e.g., **8**) in excellent yield without forming any hydrodehalogenated product.

It is noteworthy that the catalyst, i.e., Pd/C, used for the cyclization can be recovered and may possess enough catalytic activity for the subsequent coupling reactions. The activity of the used Pd/C was monitored by injecting 3-iodo-4-phenoxybenzonitrile (**5c**) after the completion of the reaction (after 16 h) along with 3 equiv of NaOAc (Table 4). We observed that the rate of transformation becomes slightly sluggish, but catalytic efficiency is almost unaltered even up to three consecutive cycles to produce **6c** in 92% yield (from GC analysis). It may be assumed that, the cyclization reaction proceed through the initial oxidative addition leading to the intermediate **I** (Scheme 3). Subsequent insertion of an *ortho* aromatic C−H bond to the Pd leads to the intermediate **II**. Reductive elimination from **II** finally affords the dibenzofuran with the regeneration of Pd(0) for the subsequent catalytic cycle.

CONCLUSIONS

In summary, a practical and efficient catalytic route for the intramolecular cyclization of *o*-iododiaryl ether to dibenzofuran using less expensive Pd (10 wt %) on charcoal support was developed. We observed that 0.3 mol % of the catalyst was effective enough for the aryl−aryl bond formation through C−H activation, with excellent selectivity over hydrodehalogenation reaction. Aryl iododiacetates were successfully used for one-pot sequential iodination and O-arylation of phenol to furnish the *o*-iododiaryl ethers under mild reaction conditions. This reaction can tolerate a wide variety of electron-withdrawing functional groups and is complementary to the previous methods for the synthesis of diaryl ether with the tandem incorporation of additional iodo functionality.

EXPERIMENTAL SECTION

General Procedure for the Synthesis of *o*-Iododiaryl Ethers 3a−r. A mixture of aryl alcohol **1** (100 mg), aryliodo diacetate ($ArI(OAc)_2$) (1.5 equiv), and pivalic acid (5 equiv) in 3 mL of dichloroethane was stirred at 80 °C. The progress of the reaction was monitored by TLC. After 12 h, the reaction mixture was quenched with water (20 mL) and then extracted with diethyl ether (3 × 15 mL). The combined organic layer was washed with dilute ammonia (10%) solution (2 × 10 mL). Then the solvent was removed under reduced pressure, and the crude reaction mixture was purified by column chromatography over silica gel (60−120 mesh) using mixture of ethyl acetate and petroleum ether as eluent.

General Procedure for the Pd/C-Catalyzed Synthesis of Dibenzofurans. To a mixture of *o*-iododiaryl ether (50 mg) and NaOAc (3 equiv) in DMA (3 mL) was added 3 mg (0.3 mol %) of Pd/C (10 wt %),[19] and the reaction mixture was heated at 140 °C for 16 h. After completion of the reaction (monitored by GC), it was cooled to room temperature and poured into water (10 mL). Then the product was extracted with ether (3 × 15 mL), and solvent was removed by rotary evaporator. The crude product was purified by column chromatography over silica gel (60−120 mesh) using a mixture of ethyl acetate and petroleum ether as eluent to afford the dibenzofuran **6** in 75−100% yield.

2-Iodo-4-nitro-1-phenoxy-benzene (***3a***): white low-melting solid (240 mg, 98% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, 1H, J = 2.8 Hz), 8.14−8.10 (m, 1H), 7.51−7.43 (m, 2H), 7.34−7.28 (m, 1H), 7.14−7.08 (m, 2H,), 6.75 (d, 1H, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 154.6, 142.9, 135.4, 130.4, 125.8, 125.3, 120.4, 115.2, 86.0; HRMS (Q-TOF ESI) m/z calcd for $C_{12}H_9INO_3^+$ $[M + H]^+$ 341.9627, found 341.9610.

3-Iodo-4-phenoxybenzaldehyde[18a] (***3b***): light yellow liquid (159 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 8.38 (d, 1H, J = 2.0 Hz), 7.79−7.72 (m, 1H), 7.47−7.39 (m, 2H), 7.30−7.22 (m, 1H), 7.12−7.05 (m, 2H), 6.82 (d, 1H, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 162.1, 155.0, 141.6, 132.7, 131.3, 130.2, 125.3, 120.2, 116.5, 87.5; HRMS (Q-TOF ESI) m/z calcd for $C_{13}H_{10}IO_2^+$ $[M + H]^+$ 324.9725, found 324.9728.

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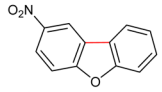
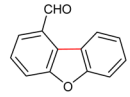
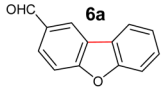
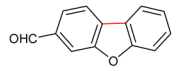
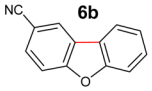
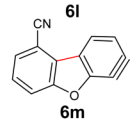
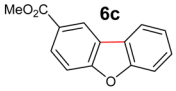
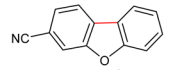
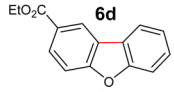
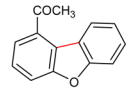
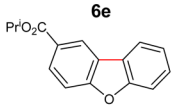
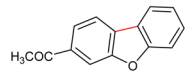
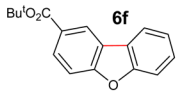
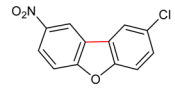
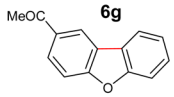
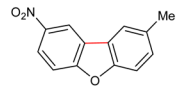
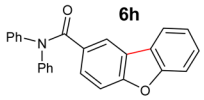
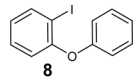
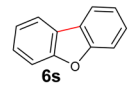
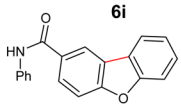
Table 3. Pd/C-Catalyzed Synthesis of Dibenzofurans[a]

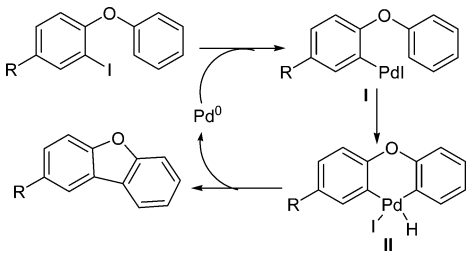
Entry	Substrate	Product	Yield (%)	Entry	Substrate	Product	Yield (%)
1	3a	 6a	100	11	3k	 6k	90
2	3b	 6b	90	12	3l	 6l	90
3	3c	 6c	95	13	3m	 6m	93
4	3d	 6d	94	14	3n	 6n	99
5	3e	 6e	98	15	3o	 6o	90
6	3f	 6f	97	16	3p	 6p	90
7	3g	 6g	75	17	3q	 6q	95
8	3h	 6h	90	18	3r	 6r	93
9	3i	 6i	84	19	 8	 6s	95
10	3j	 6j	82				

[a]Reaction conditions: *o*-iododiaryl ether (50 mg), Pd/C (10 wt %) (3 mg, 0.3 mol %), NaOAc (3 equiv) in 3 mL of DMA at 140 °C for 16 h.

Table 4. Reusability of Pd/C for Cyclization Reaction

cycle	reaction time (h)	% GC yield of **6c**
1	16	95
2	24	92
3	24	92

Scheme 3. Plausible Mechanism for the Dibenzofuran Synthesis



3-Iodo-4-phenoxybenzonitrile (***3c***)*:* white solid (248 mg, 92% yield); mp 80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, 1H, J = 2 Hz) 7.57−7.50 (m, 1H), 7.49−7.41 (m, 2H), 7.31−7.24 (m, 2H), 7.08 (d, 2H, J = 7.6 Hz), 6.76 (d, 1H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 154.7, 143.3, 133.6, 130.3, 125.4, 120.2, 117.1, 116.4, 107.8, 87.1; HRMS (Q-TOF ESI) m/z calcd for $C_{13}H_9INO^+$ $[M + H]^+$ 321.9729, found 321.9738.

3-Iodo-4-phenoxybenzoic acid methyl ester[18a] (***3d***)*:* white solid (198 mg, 85% yield); mp 59 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, 1H, J = 2 Hz), 7.93 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2 Hz), 7.46−7.38 (m, 2H), 7.27−7.19 (m, 1H), 7.07 (d, 2H, J = 7.6 Hz), 6.78 (d, 1H, J = 8.4 Hz), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 160.9, 155.4, 141.4, 137.4, 131.2, 130.2, 130.1, 126.2, 124.8, 119.8, 116.5, 86.9, 52.2; HRMS (Q-TOF ESI) m/z calcd for $C_{14}H_{12}IO_3^+$ $[M + H]^+$ 354.9831, found 354.9822.

3-Iodo-4-phenoxybenzoic acid ethyl ester (***3e***)*:* colorless liquid (177 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, 1H, J = 2 Hz), 7.93 (dd, 1H, J_1 = 8.6 Hz, J_2 = 2 Hz), 7.45−7.36 (m, 2H), 7.26−7.18 (m, 1H), 7.09−7.02 (m, 2H), 6.78 (d, 1H, J = 8.4 Hz), 4.38 (q, 2H, J = 7.2 Hz), 1.406 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7 (s), 160.7 (s), 155.5 (s), 141.3 (d), 131.2 (d), 130.1 (d), 126.6 (s), 124.7 (d), 119.7 (d), 116.6 (d), 87 (s), 61.2 (t), 14.3 (q); HRMS (Q-TOF ESI) m/z calcd for $C_{15}H_{14}IO_3^+$ $[M + H]^+$ 368.9989, found 368.9981.

Isopropyl 3-iodo-4-phenoxybenzoate (***3f***)*:* colorless liquid, (172 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, 1H, J = 2 Hz), 7.94 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2 Hz), 7.41 (t, 2H, J = 7.8 Hz), 7.22 (t, 1H, J = 7.4 Hz), 7.05 (d, 2H, J = 8 Hz), 6.78 (d,1H, J = 8.8 Hz), 5.30−5.20 (m, 1H), 1.38 (d, 6H, J = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 160.6, 155.6, 141.3, 131.2, 130.1, 127.1, 124.7, 119.6, 116.7, 87.0, 68.7, 21.6; HRMS (Q-TOF ESI) m/z calcd for $C_{16}H_{16}IO_3^+$ $[M + H]^+$ 383.0144, found 383.0133.

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*tert-Butyl 3-iodo-4-phenoxybenzoate (**3g**):* colorless liquid (143 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, 1H, J = 2 Hz), 7.90 (dd, 1H, J_1 = 8.6 Hz, J_2 = 1.8 Hz), 7.40 (t, 2H, J = 8.4 Hz), 7.21 (t, 1H, J = 7.6 Hz), 7.05 (d, 2H, J = 8 Hz), 6.78 (d, 1H, J = 8.8 Hz), 1.60 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 160.3, 155.7, 141.2, 131.1, 130.1, 128.3, 124.6, 119.6, 116.7, 87.0, 81.5, 28.2; HRMS (Q-TOF ESI) m/z calcd for $C_{13}H_{10}IO_3^+$ [M + 2H − ^{t}Bu]$^+$ 340.9675, found 340.9677.

*1-(3-Iodo-4-phenoxyphenyl)ethanone (**3h**):* colorless liquid (176 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, 1H, J = 1.6 Hz), 7.85 (d, 1H, J = 8.8 Hz), 7.46−7.38 (m, 2H), 7.27−7.19 (m, 1H), 7.07 (d, 2H, J = 8 Hz), 6.78 (d, 1H, J = 8.4 Hz), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 161.0, 155.3, 140.5,133.5, 130.1, 130.0, 124.9, 119.9, 116.5, 87.3, 26.4; GC MS (EI, +ve) m/z (relative intensity) 337.9 ([M]$^+$, 100). HRMS (Q-TOF ESI) m/z calcd for $C_{14}H_{12}IO_2^+$ [M + H]$^+$ 338.9882, found 338.9889.

*3-Iodo-4-phenoxy-N,N-diphenylbenzamide (**3i**):* white yellowish solid (109 mg, 64% yield); mp 138 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, 1H, J = 2 Hz), 7.41−7.29 (m, 7H), 7.23 (t, 2H, J = 7.4 Hz), 7.20−7.11 (m, 5H), 6.96 (d, 2H, J = 8 Hz), 6.60 (d, 1H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 158.3, 155.7, 143.6, 141.2, 137.4, 132.2, 130.8, 130.2, 130.0, 129.2, 127.4, 127.4, 126.6, 124.4, 119.3, 116.7, 87.0; HRMS (Q-TOF ESI) m/z calcd for $C_{25}H_{19}INO_2^+$ [M + H]$^+$ 492.0462, found 492.0455.

*3-Iodo-4-phenoxy-N-phenylbenzamide (**3j**):* yellowish solid (119 mg, 61% yield); mp 145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39−8.33 (m,1H), 8.35 (s, 1H), 7.78 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.4 Hz), 7.64 (d, 2H, J = 8 Hz), 7.46−7.34 (m, 4H), 7.25 (s, 1H), 7.25−7.14 (m, 1H), 7.06 (d, 2H, J = 8 Hz) 6.83 (d, 1H, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 159.9, 155.6, 138.7, 137.6, 131.1, 130.1, 129.1, 128.8, 124.8, 124.7, 120.3, 119.6, 117.2, 87.7; HRMS (Q-TOF ESI) m/z calcd for $C_{19}H_{15}INO_2^+$ [M + H]$^+$ 416.0147, found 416.0129.

*2-Iodo-3-phenoxybenzaldehyde (**3k**):* light yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.23 (d,1H, J = 0.8 Hz), 7.67 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.6 Hz), 7.44−7.34 (m, 3H), 7.21 (d, 1H, J = 0.8 Hz), 7.19−7.09 (m, 1H), 7.05−6.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 157.2, 156.5, 137.1, 130.0, 129.6, 125.2, 124.2, 124.1, 118.6, 115.3, 96.0; GC MS (EI, +ve) m/z (relative intensity) 323.9 ([M]$^+$, 10); HRMS (Q-TOF ESI) m/z calcd for $C_{13}H_{10}IO_2^+$ [M + H]$^+$ 324.9725, found 324.9712.

*4-Iodo-3-phenoxybenzaldehyde (**3l**):* pale yellow solid; mp 60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (s, 1H), 8.09 (d, 1H, J = 8 Hz), 7.72 (dd, 1H, J_1 = 8.4 Hz, J_2 = 1 Hz), 7.46−7.38 (m, 2H), 7.38−7.31 (m, 1H), 7.26−7.13 (m, 1H), 7.08−7.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 140.7, 137.8, 137.4, 130.2, 130.1, 127.4, 125.6, 124.6, 119.2, 117.2, 96.9; GC MS (EI, +ve) m/z (relative intensity) 323.9 ([M]$^+$, 100); HRMS (Q-TOF ESI) m/z calcd for $C_{13}H_{10}IO_2^+$ [M + H]$^+$ 324.9725, found 324.9729.

*2-Iodo-3-phenoxybenzonitrile (**3m**):* white solid; mp 110 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.35 (m, 4H), 7.22 (t, 1H, J = 7.4 Hz), 7.05−6.97 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 155.6, 130.2, 130.0, 129.0, 124.7, 122.6, 121.7, 119.2, 119.1, 93.1; GC MS (EI, +ve) m/z (relative intensity) 296.9 ([M + H]+, 100%); GC MS (EI, +ve) m/z (relative intensity) 320.9 ([M]$^+$, 99), 193.9 ([M + H − I]$^+$, 100); HRMS (Q-TOF ESI) m/z calcd for $C_{13}H_9INO^+$ [M + H]$^+$ 321.9729, found 321.9721.

*4-Iodo-3-phenoxybenzonitrile (**3n**):* colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, 1H, J = 8 Hz), 7.48−7.26 (m, 2H), 7.26 (t, 1H, J = 7.2 Hz), 7.10 (dd, 1H, J_1 = 8.2 Hz, J_2 = 2 Hz), 7.08−7.01 (m, 2H), 6.98 (d, 1H, J = 2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 155.1, 140.9, 130.3, 127.3, 125.1, 119.9, 119.6, 117.7, 113.2, 94.5; GC MS (EI, +ve) m/z (relative intensity) 320.9 ([M]$^+$, 99), 193.9 ([M + H − I]$^+$, 100); HRMS (Q-TOF ESI) m/z calcd for $C_{13}H_9INO^+$ [M + H]$^+$ 321.9729, found 321.9734.

*1-(2-Iodo-3-phenoxyphenyl)ethanone (**3o**)/1-(4-iodo-3-phenoxyphenyl)ethanone (**3p**):* inseparable mixture (136 mg, 40% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d,1H, J = 8.4 Hz), 7.46−7.29 (m, 9H), 7.21−6.99 (m, 9H), 6.92 (dd, 2H, J_1 = 8.4 Hz, J_2 = 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 196.7, 157.2, 157.1, 156.5, 156.2, 147.9, 140.2, 138.7, 130.1, 130.0, 129.7, 124.6, 124.1, 123.9, 122.4, 120.2, 118.7, 118.6, 117.7, 95.7, 85.9, 30.0, 26.6.

*1-(2-Iodo-4-nitrophenoxy)-4-chlorobenzene (**3q**):* white solid (82 mg, 61% yield); mp 100−102 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, 1H, J = 2.4 Hz), 8.15 (dd, 1H, J_1 = 7.6 Hz, J_2 = 2.8 Hz), 7.43 (d, 2H, J = 8.8 Hz), 7.05 (d, 2H, J = 8.8 Hz), 6.77 (d, 1H, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 153.3, 143.3, 135.6, 131.0, 130.4, 125.3, 121.5, 115.5, 86.2; HRMS (Q-TOF ESI) m/z calcd for $C_{12}H_8ClINO_3^+$ [M + H]$^+$ 375.9237, found 375.9231.

*1-(2-Iodo-4-nitrophenoxy)-4-methylbenzene (**3r**):* off-white gummy solid (76 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, 1H, J = 2.8 Hz), 8.18 (dd, 1H, J_1 = 7.6 Hz, J_2 = 2.8 Hz), 7.26 (d, 2H, J = 8.0 Hz), 6.95 (d, 2H, J = 8.4 Hz), 6.72 (d, 1H, J = 7.6 Hz), 2.40 (s,1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 153.2, 145.2, 135.3, 132.7, 130.8, 130.4, 120.3, 115.3, 90.6, 20.6; HRMS (Q-TOF ESI) m/z calcd for $C_{13}H_{11}INO_3^+$ [M + H]$^+$ 355.9784, found 355.9776.

*1-Iodo-2-phenoxybenzene[20] (**8**):* colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, 1H , J_1 = 8 Hz, J_2 = 1.6 Hz),7.45−7.34 (m, 2H), 7.36−7.30 (m, 1H), 7.23−7.15 (m, 1H), 7.09−7.02 (m, 2H), 7.00−6.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 156.5, 139.9, 128.9, 129.8, 125.4, 123.6, 119.5, 118.5; GC MS (EI, +ve) m/z (relative intensity) 296.9 ([M + H]$^+$, 100).

*2-Nitrodibenzofuran[21] (**6a**):* white solid (31 mg, 100% yield); mp 151−152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, 1H, J = 1.6 Hz), 8.46−8.39 (m, 1H), 8.06 (d, 2H, J_1 = 8.4 Hz), 7.71−7.67 (m, 2H), 7.64−7.56 (m, 1H), 7.51−7.43 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 157.4, 143.8, 128.9, 125.0, 123.9, 123.1, 123.0, 121.3, 117.1, 112.2, 112.0; HRMS (Q-TOF ESI) m/z calcd for $C_{12}H_7NNaO_3^+$ [M + Na]$^+$ 236.0324, found 236.0307.

*Dibenzofuran-2-carbaldehyde[22] (**6b**):* white crystalline solid (27 mg, 90% yield), mp 70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H) 8.47 (s, 1H), 8.01 (d, 2H, J = 8.0 Hz), 7.70−7.65 (m, 1H), 7.63−7.58 (m, 1H), 7.57−7.51 (m, 1H), 7.46−7.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.4, 159.7, 156.8, 131.9, 129.2, 128.2, 125.1, 123.6, 123.3, 123.0, 121.1, 112.3, 112.0; HRMS (Q-TOF ESI) m/z calcd for $C_{13}H_9O_2^+$ [M + H]$^+$ 197.0603, found 197.0597.

*Dibenzofuran-2-carbonitrile[22] (**6c**):* white solid (28 mg, 95% yield); mp 136 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s,1H) 7.97 (d, 1H, J = 8 Hz), 7.77−7.71 (m, 1H), 7.67−7.59 (m, 2H), 7.60−7.52 (m, 1H,), 7.43 (t, 1H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 156.7, 130.8, 128.7, 125.4, 125.2, 123.7, 122.5, 121.1, 119.2, 112.8, 112.1, 106.5; HRMS (Q-TOF ESI) m/z calcd for $C_{13}H_8NO^+$ [M + H]$^+$ 194.0606, found 194.0597.

*Dibenzofuran-2-carboxylic acid methyl ester[15b] (**6d**):* white solid (30 mg, 94% yield); mp 76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, 1H, J = 1.6 Hz), 8.20 (dd, 1H, J_1 = 8.4 Hz, J_2 = 1.6 Hz), 8.05−7.99 (m, 1H), 7.64−7.58 (m, 2H), 7.56−7.48 (m, 1H),7.45−7.37 (m, 1H), 4.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 158.8, 156.7, 128.9, 127.8, 124.9, 124.4, 123.7, 123.3, 122.9, 120.9, 111.9, 111.5, 52.2; HRMS (Q-TOF ESI) m/z calcd for $C_{14}H_{11}O_3^+$ [M + H]$^+$ 227.0708, found 227.0698.

*Dibenzofuran-2-carboxylic acid ethyl ester[23] (**6e**):* white solid (32 mg, 98% yield); mp 58 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d,1H, J = 1.2 Hz), 8.23−8.17 (m, 1H), 8.00 (d, 1H, J =7.6 Hz), 7.63−7.55 (m, 2H), 7.54−7.46 (m, 1H), 7.43−7.35 (m, 1H), 4.46 (q, 2H, J = 7.2 Hz), 1.47 (t, 3H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 158.8, 156.7, 128.9, 127.8, 125.3, 124.3, 123.7, 123.2, 122.8, 120.9, 111.8, 111.4, 61.1, 14.4; HRMS (Q-TOF ESI) m/z calcd for $C_{15}H_{13}O_3^+$ [M + H]$^+$ 241.0865, found 241.0859.

*Dibenzofuran-2-carboxylic acid isopropyl ester (**6f**):* white solid (32 mg, 97% yield); mp 68 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.20 (dd, 1H, J_1 = 8.4 Hz, J_2 = 1.2 Hz) 8.02 (d, 1H, J = 7.6 Hz), 7.64−7.56 (m, 2H), 7.51 (t, 1H, J = 7.8 Hz), 7.40 (t, 1H, J = 7.4 Hz), 5.39−5.29 (m, 1H), 1.45 (d, 6H, J = 6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 158.7, 156.7, 128.9, 127.8, 125.7, 124.3, 123.7, 123.2, 122.8, 121.0, 111.8, 111.3, 68.5, 22.0; HRMS (Q-TOF ESI) m/z calcd for $C_{16}H_{15}O_3^+$ [M + H]$^+$ 255.1021, found 255.1014.

*tert-Butyl dibenzofuran-2-carboxylate (**6g**):* colorless liquid (25 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, 1H, J = 1.2

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Hz), 8.16 (dd, 1H, J_1 = 8.8 Hz, J_2 = 1.6 Hz), 8.02 (d, 1H, J = 7.6 Hz), 7.60 (t, 2H, J = 8.8 Hz), 7.51 (t, 1H, J = 7.8 Hz), 7.40 (t, 1H, J = 7.6 Hz), 1.67 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 158.6, 156.7, 128.8, 127.7, 126.8, 124.2, 123.8, 123.2, 122.6, 120.9, 111.8, 111.2, 81.1, 28.3; HRMS (Q-TOF ESI) m/z calcd for $C_{13}H_9O_3^+$ [M + 2H − ^{t}Bu]$^+$ 213.0552, found 213.0542.

2-Acetyldibenzofuran[4e] ***(6h):*** white solid (28 mg, 90% yield); mp 203 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, 1H, J = 2 Hz), 8.13 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2 Hz), 8.02 (d, 1H, J = 7.6 Hz), 7.62 (d, 2H, J = 8.4 Hz), 7.57−7.49 (m, 1H),7.45−7.38 (m, 1H), 2.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3 (s), 158.9 (s), 156.8 (s), 132.5 (s), 128.0 (d), 124.5 (s), 123.7 (s), 123.4 (d), 121.6 (d), 120.9 (d), 111.9 (d), 111.6 (d), 26.8 (s); HRMS (Q-TOF ESI) m/z calcd for $C_{14}H_{11}O_2^+$ [M + H]$^+$ 211.0759, found 211.0751.

N,N-Diphenyldibenzofuran-2-carboxamide ***(6i):*** white solid (31 mg, 84% yield); mp 128 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21(d, 1H, J = 2 Hz), 7.89 (d, 1H, J = 8 Hz) 7.60−7.53 (m, 2H),7.52−7.44 (m, 1H) 7.40−7.26 (m, 6H), 7.25−7.17 (m, 6H);^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 156.9, 156.6, 144.1, 130.8, 129.2, 128.6, 127.6, 127.5, 126.4, 124.0, 123.7, 123.1, 122.6, 120.8, 111.8, 110.9; HRMS (Q-TOF ESI) m/z calcd for $C_{25}H_{18}$ NO_2^+ [M + H]$^+$ 364.1338, found 364.1333.

Dibenzofuran-2-carboxylic acid phenylamide ***(6j):*** white solid (28 mg, 82% yield); mp 180 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d,1H, J = 1.6 Hz), 8.17 (s, 1H), 7.98−7.91 (m, 2H), 7.72 (d, 2H, J = 7.6 Hz), 7.63−7.55 (m, 2H),7.56−7.47 (s, 1H), 7.44−7.34 (m, 3H),7.22−7.15(m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 158.0, 156.8, 138.0, 129.8, 129.1, 128.0, 126.1, 124.7, 124.6, 123.5, 123.3, 120.9, 120.3, 120.3, 111.9, 111.7; HRMS (Q-TOF ESI) m/z calcd for $C_{19}H_{14}NO_2^+$ [M + H]$^+$ 288.1025, found 288.1030.

Dibenzofuran-1-carbaldehyde[24] ***(6k):*** white solid (27 mg, 90% yield); mp 64 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.39 (s,1H), 8.96 (d, 1H, J = 7.6 Hz), 7.86 (t, 2H, J = 8 Hz), 7.68−7.55 (m, 3H), 7.48−7.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 157.0, 156.6, 132.0, 129.5, 128.9, 126.6, 126.4, 123.1, 123.1, 122.9, 117.4, 111.4; HRMS (Q-TOF ESI) m/z calcd for $C_{13}H_9O_2^+$ [M + H]$^+$ 197.0603, found 197.0609.

3-Dibenzofurancarboxaldehyde ***(6l).*** white solid (27 mg, 90% yield); mp 130 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 8.08 (d, 2H, J = 8 Hz) 8.02 (d, 1H, J = 8 Hz), 7.89 (dd, 1H, J_1 = 8 Hz, J_2 = 1.2 Hz), 7.63 (d, 1H, J = 8.4 Hz), 7.61−7.53 (m, 1H), 7.45−7.37 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6, 157.7, 155.9, 135.3, 130.0, 129.0, 124.7, 123.3, 123.1, 121.6, 121.0, 112.6, 112.1; HRMS (Q-TOF ESI) m/z calcd for $C_{13}H_9O_2^+$ [M + H]$^+$ 197.0603, found 197.0610.

1-Dibenzofurancarbonitrile[25] ***(6m):*** white solid (28 mg, 93% yield); mp 104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, 1H, J = 8 Hz), 7.80 (d, 1H, J = 8.4 Hz) 7.69−7.58 (m, 3H), 7.53 (t, 1H, J = 8 Hz) 7.47−7.43 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 155.6, 129.1, 127.2, 126.9, 125.8, 123.6, 121.9, 121.7, 117.4, 116.3, 111.9, 104.4; HRMS (Q-TOF ESI) m/z calcd for $C_{13}H_8NO^+$ [M + H]$^+$ 194.0606, found 194.0601.

3-Cyanodibenzofuran[26] ***(6n):*** white solid (30 mg, 99% yield); mp 124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07−7.99 (m, 2H), 7.66 (s, 1H) 7.65 (dd, 2H, J_1 = 8.2 Hz, J_2 = 1 Hz), 7.63−7.55 (m, 1H), 7.48−7.40 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 154.9, 129.3, 128.6, 126.6, 123.6, 122.7, 121.5, 121.4, 119.1, 115.7, 112.1, 109.7; HRMS (Q-TOF ESI) m/z calcd for $C_{13}H_8NO^+$ [M + H]$^+$ 194.0606, found 194.0599.

1-Acetyldibenzofuran ***(6o):*** colorless liquid (28 mg, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (d,1H, J = 8.4 Hz), 7.88 (d, 1H, J = 7.6 Hz) 7.81 (d, 1H, J = 8 Hz), 7.64−7.51 (m, 3H), 7.44−7.36 (m, 1H), 2.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 157.6, 155.9, 136.0, 128.7, 128.6, 123.3, 123.2, 123.1, 121.4, 120.4, 112.0, 111.8, 26.9; HRMS (Q-TOF ESI) m/z calcd for $C_{14}H_{11}O_2^+$ [M + H]$^+$ 211.0759, found 211.0753.

3-Acetyldibenzofuran[27] ***(6p):*** white solid (28 mg, 90% yield); mp 121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.07−7.97 (m, 3H) 7.64 (d, 1H, J = 8.4 Hz), 7.60−7.52(m, 1H), 7.45−7.41 (m, 1H), 2.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 157.0, 156.8, 133.6, 128.4, 126.4, 126.2, 125.1, 123.1, 122.9, 122.8, 116.1, 111.2, 28.6; HRMS (Q-TOF ESI) m/z calcd for $C_{14}H_{11}O_2^+$ [M + H]$^+$ 211.0759, found 211.0751.

8-Chloro-2-nitrodibenzofuran ***(6q):*** white crystalline solid (31 mg, 95%); mp 224 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (d, 1H, J = 2.4 Hz), 8.44 (dd, 1H, J_1 = 7.6 Hz, J_2 = 2.4 Hz), 8.01 (d, 1H, J = 2.4 Hz), 7.68 (d, 1H, J = 8.8 Hz), 7.61−7.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 155.7, 144.0, 129.6, 129.0, 124.4, 124.0, 123.6, 121.1, 117.3, 113.3, 112.3; HRMS (Q-TOF ESI) m/z calcd for $C_{12}H_7ClNO_3^+$ [M + H]$^+$ 248.0114, found 248.0108.

8-Methyl-2-nitrodibenzofuran[4f] ***(6r):*** white solid (30 mg, 93% yield); mp 146 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 1H), 8.37 (d, 1H, J = 8.8 Hz), 7.81 (s, 1H), 7.62 (d, 1H, J = 8.8 Hz), 7.52 (d, 1H, J = 8.4 Hz), 7.38 (d, 1H, J = 8.4 Hz), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 155.82, 143.7, 133.6, 130.0, 124.9, 123.0, 122.7, 121.1, 116.9, 111.8, 111.7, 21.3.

Dibenzofuran[15b] ***(6s):*** white solid (27 mg, 95% yield); mp 83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, 2H, J = 4.6 Hz), 7.61 (d, 2H, J = 8.4 Hz),7.53−7.45 (m, 2H),7.42−7.55 (m, 1H) 7.48−7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 127.1, 124.2, 122.7, 120.6, 118.4, 111.6; GC MS (EI, +ve) m/z (relative intensity) 167.9 ([M]$^+$, 100).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

NMR spectra of compounds **3a−r**, **8**, and **6a−s**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00634.

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Notes

The authors declare no competing financial interest.

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