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Pd-Catalyzed Tandem Chemoselective Synthesis of 2-Arylbenzofurans using Threefold Arylating Triarylbismuth Reagents

Maddali L. N. Rao,*[a] Deepak N. Jadhav,[a] and Priyabrata Dasgupta[a]

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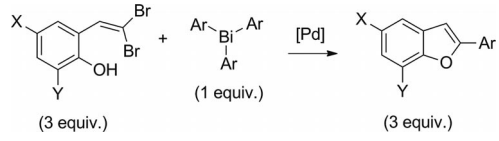
A tandem chemoselective synthesis of 2-arylbenzofurans was accomplished from *o*-hydroxy-*gem*-(dibromovinyl)benzenes and $BiAr_3$ reagents under palladium-catalyzed conditions. This unique and synthetically valuable strategy proceeds through three consecutive coupling reactions involving triarylbismuth reagents and provides 2-arylbenzofuran products in high yields.

Introduction

The benzofuran scaffold is present in many medicinally important compounds that show biological activity, including anticancer and anti-inflammatory activities.[1] These scaffolds are widely present in many natural products.[2] Recently, benzofuran derivatives labeled with ^{18}F and ^{99m}Tc tags were studied by positron emission tomography (PET) and single photon emission computed tomography (SPECT) imaging, respectively, for β-amyloid plaques in Alzheimer's disease.[3] Extended molecular frameworks of benzofurans are useful as bowl-shaped hosts in supramolecular chemistry.[4]

Tandem or domino couplings are highly sought after approaches for the construction of molecular skeletons in a facile manner.[5] Recently, Chelucci excellently reviewed the chemistry of 1,1-dihaloalkenes as novel molecular synthons in synthetic organic chemistry.[6] Metal-catalyzed reactions involving 1,1-dihaloalkenes provide well-defined core skeletons dictated by the choice of the substrates.[7,8] However, other metal-mediated approaches are also available for the synthesis benzofurans.[9] In particular, *o*-hydroxy-*gem*-(dibromovinyl)benzenes are of special interest, as they deliver substituted benzofurans in combination with organometallic reagents through intramolecular couplings. However, this known approach involving the use of palladium also employs boron and tin reagents in excess amounts.[8] Another serious drawback encountered in this reaction is the competitive formation of undesired bis-benzofurans. This can partly be circumvented by using organometallic reagents in excess amounts, which results in the formation of one equivalent of the 2-arylbenzofuran product.

However, the usefulness of triarylbismuth reagents as facile threefold arylating agents in coupling reactions[10] prompted us to address these issues and to enrich the process with additional chemoselective options under palladium conditions. The development of tandem annulations by using *o*-hydroxy-*gem*-(dibromovinyl)benzenes with triarylbismuths were planned as depicted in Scheme 1. This process was expected to deliver three equivalents of the 2-arylbenzofuran for every one equivalent of the triarylbismuth reagent employed and was believed to serve as a more advantageous process (vide supra). Herein, we describe these efforts under palladium-catalyzed conditions.



Scheme 1. Tandem synthesis by using $BiAr_3$ reagents.

Results and Discussion

To realize this tandem process, a systematic investigation was carried out (Table 1). For the coupling reaction, *o*-hydroxy-*gem*-(dibromovinyl)benzene (**1**) was treated with $BiPh_3$ in the presence of $[Pd(PPh_3)_4]$ with different bases in DMF under heating conditions (Table 1, entries 1 and 2). These reactions furnished tandem coupled 2-phenylbenzofuran (**1a**) in 54 and 66% yield with K_3PO_4 and Cs_2CO_3 as the base, respectively. Further investigation was carried out in different solvents to check their efficacy. For example, reactions in *N*,*N*-dimethylacetamide (DMA), *N*-methyl-2-pyrrolidone (NMP), and tetrahydrofuran (THF) provided the products in poor to moderate yields (Table 1, entries 3–5). So far, DMF with Cs_2CO_3 provided the desired tandem

[a] Department of Chemistry, Indian Institute of Technology Kanpur,
Kanpur 208016, India
Fax: +91-512-259-7532
E-mail: maddali@iitk.ac.in
Homepage: http://www.iitk.ac.in

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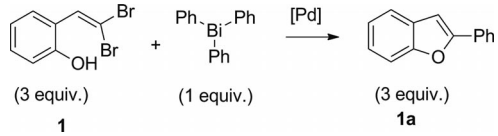
couplings in better yield. Additional screening was performed in DMF with different bases including K_2CO_3, KOAc, and NaOAc (Table 1, entries 6–8), but these bases were found to be less effective.

Table 1. Screening conditions.[a]



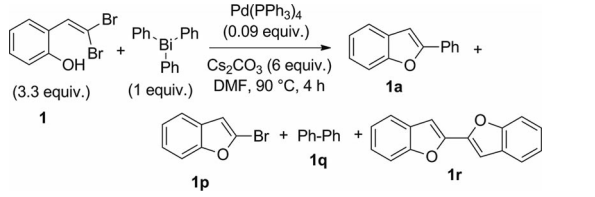
Entry	Catalyst	Base	Solvent	Time [h]	Yield[b] [%]
1	$[Pd(PPh_3)_4]$	K_3PO_4	DMF	2	54
2	$[Pd(PPh_3)_4]$	Cs_2CO_3	DMF	2	66
3	$[Pd(PPh_3)_4]$	Cs_2CO_3	DMA	2	54
4	$[Pd(PPh_3)_4]$	Cs_2CO_3	NMP	2	56
5	$[Pd(PPh_3)_4]$	Cs_2CO_3	THF	2	<1[c]
6	$[Pd(PPh_3)_4]$	K_2CO_3	DMF	2	52
7	$[Pd(PPh_3)_4]$	KOAc	DMF	2	32[c]
8	$[Pd(PPh_3)_4]$	NaOAc	DMF	2	21[c]
9	$[PdCl_2(PPh_3)_2]$	Cs_2CO_3	DMF	4	42
10	$[Pd(OAc)_2]$	Cs_2CO_3	DMF	4	38[d]
11	$[Pd_2(dba)_3]$	Cs_2CO_3	DMF	4	37[d]
12	$[Pd(PPh_3)_4]$	Cs_2CO_3	DMF	4	72
13	$[Pd(PPh_3)_4]$	Cs_2CO_3	DMF	2	58[e]
14	$[Pd(PPh_3)_4]$	Cs_2CO_3	DMF	4	75[f]
15	$[Pd(PPh_3)_4]$	Cs_2CO_3	DMF	4	53[g]
16	$[Pd(PPh_3)_4]$	Cs_2CO_3	DMF	4	64[h]
17	$[Pd(PPh_3)_4]$	Cs_2CO_3	DMF	4	56[i]
18	$[Pd(PPh_3)_4]$	Cs_2CO_3	DMF	2	46[j]

[a] Conditions: **1** (0.75 mmol, 3 equiv.), $BiPh_3$ (0.25 mmol, 1 equiv.), Pd catalyst (0.0225 mmol, 0.09 equiv.), base (1.5 mmol, 6 equiv.), solvent (3 mL), 90 °C. [b] Isolated yield. [c] Conversion based on GC. [d] With 0.18 equiv. of PPh_3. [e] With 0.50 mmol of $BiPh_3$. [f] With 3.3 equiv. of **1**. [g] At 60 °C. [h] At 80 °C. [i] At 100 °C. [j] With 3 equiv. of Cs_2CO_3.

Different catalyst precursors also produced poor yields (Table 1, entries 9–11). Encouragingly, the reaction with Cs_2CO_3 as the base in DMF furnished the product in 4 h in 72% yield (Table 1, entry 12). Further couplings with excess amounts of $BiPh_3$ did not improve the yield (Table 1, entry 13). However, coupling with 3.3 equiv. of **1** furnished the product in 4 h in 75% yield (Table 1, entry 14). The tandem process was then evaluated at different temperatures, but only moderate yields of the product were obtained (Table 1, entries 15–17). An attempt with 3 equiv. of Cs_2CO_3 furnished the product in lower yield (Table 1, entry 18). In all of these screenings, a minor amount of homocoupled biphenyl from $BiPh_3$ was formed, and this is inevitable under palladium catalysis.[11] However, the amount of homocoupled product formed can be minimized with high cross-coupling conversion. In some cases, the formation of trace amounts of homocoupled bis-benzofuran was observed. From this screening, the tandem coupling reaction was established to be effective with $[Pd(PPh_3)_4]$ as the catalyst in DMF with Cs_2CO_3 as the base to furnish **1a** in 75% yield (Table 1, entry 14). This protocol successfully delivered the desired tandem coupling product against the odds of competitive homocoupling in the presence of a palladium catalyst.[8]

To understand this tandem process, further investigation was carried out with control experiments (Table 2). For example, a reaction without the catalyst provided 2-bromobenzofuran (**1p**) in 80% yield (Table 2, entry 1). Couplings without base afforded a mixture of **1a**, **1p**, and **1q** in minor amounts (Table 2, entry 2). Additional control without a palladium catalyst or $BiPh_3$ also provided **1p** as the major product (Table 2, entry 3). In the presence of a palladium catalyst but without $BiPh_3$, **1p** and homocoupled **1r** were formed (Table 2, entry 4). This study clearly demonstrated the formation of 2-bromobenzofuran as a reaction intermediate during the course of the tandem reaction.

Table 2. Control experiments.[a]



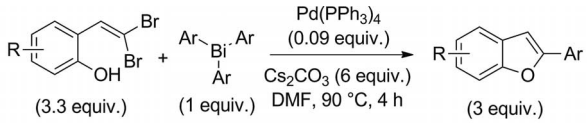
Entry	$BiPh_3$	[Pd]	Base	1	1a	1p	1q	1r
1	+	–	+	–	–	100 (80)	–	–
2	+	+	–	20	23	12	41	–
3	–	–	+	–	–	100	–	–
4	–	+	+	–	–	63	–	8

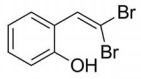
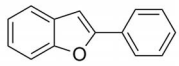
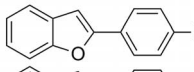
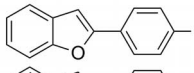
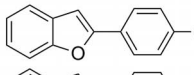
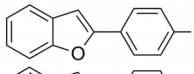
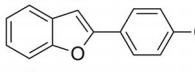
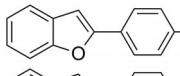
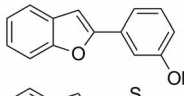
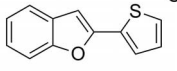
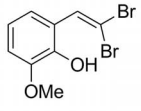
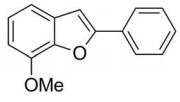
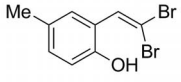
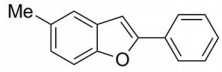
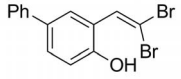
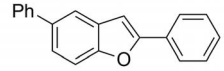
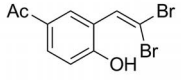
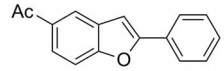
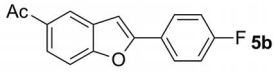
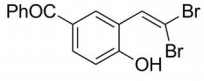
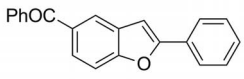
[a] Conditions: **1** (0.825 mmol, 3.3 equiv.), $BiAr_3$ (0.25 mmol, 1 equiv.), $[Pd(PPh_3)_4]$ (0.0225 mmol, 0.09 equiv.), Cs_2CO_3 (1.5 mmol, 6 equiv.), DMF (3 mL), 90 °C, 4 h. GC conversions are given, and isolated yields are given in parentheses.

Next, we sought to apply the established protocol condition (Table 1, entry 14) in the synthesis of various functionalized 2-arylbenzofurans (Table 3). Firstly, the reactivity of various electronically divergent $BiAr_3$ reagents with different dibromides was tested. $BiAr_3$ reagents substituted with *p*-methyl, *p*-methoxy, *p*-ethoxy, *p*-isopropoxy, *p*-fluoro, and *m*-methoxy groups furnished high yields of the corresponding 2-arylbenzofurans (Table 3, entries 2–5, 7, 8). The coupling reactions of 4-chloro-substituted triarylbismuth and tris-2-thienylbismuth provided moderate yields (Table 3, entries 6 and 9). Additionally, various functionalized *o*-hydroxy-*gem*-(dibromovinyl)benzenes provided moderate to high yields of the functionalized 2-arylbenzofuran products (Table 3, entries 10–15). In these couplings, the presence of acetyl and benzoyl groups in the *para* position to the hydroxy functionality did not affect the process, and the corresponding products were isolated in high yields (Table 3, entries 13–15). This investigation overall revealed the high reactivity of $BiAr_3$ as multicoupling organometallic nucleophiles that can act as threefold arylating reagents with a variety of functionalized *o*-hydroxy-*gem*-(dibromovinyl)benzenes. Moreover, the one-pot operation comprising three aryl couplings was complete in a reaction time of 4 h. This demonstrates the novel reactivity of $BiAr_3$ reagents, which furnished high yields of 2-arylbenzofurans, in comparison to the corresponding reactivity reported with the

use of excess amounts of aryl boron or tin reagents, even for only one C–C coupling.[8]

Table 3. Tandem synthesis of 2-arylbenzofurans.[a]

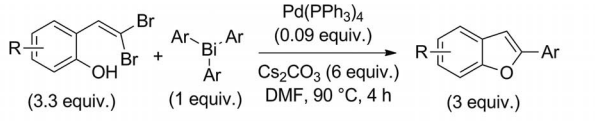


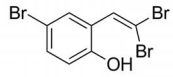
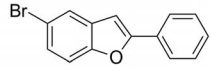
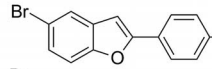
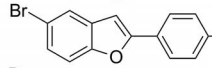
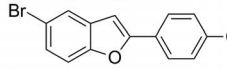
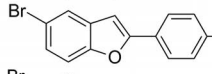
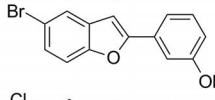
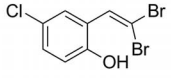
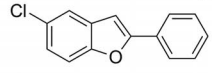
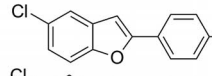
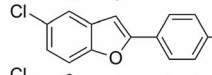
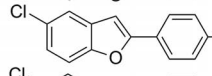
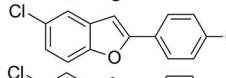
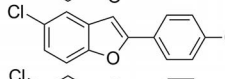
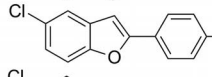
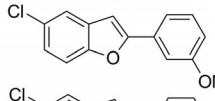
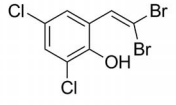
Entry	*gem*-Dibromide	2-Arylbenzofuran	Yield[b] [%]
1		 **1a**	75
2	"	 **1b**	81
3	"	 **1c**	72
4	"	 **1d**	73
5	"	 **1e**	82
6	"	 **1f**	61
7	"	 **1g**	78
8	"	 **1h**	70
9	"	 **1i**	51
10		 **2a**	58
11		 **3a**	52
12		 **4a**	59
13		 **5a**	72
14	"	 **5b**	76
15		 **6a**	71

[a] Conditions: *gem*-Dibromide (0.825 mmol, 3.3 equiv.), $BiAr_3$ (0.25 mmol, 1 equiv.), $[Pd(PPh_3)_4]$ (0.0225 mmol, 0.09 equiv.), Cs_2CO_3 (1.5 mmol, 6.0 equiv.), DMF (3 mL), 90 °C, 4 h. Biaryls from $BiAr_3$ were formed in minor amounts. [b] Isolated yield, and 0.75 mmol of product corresponds to 100% yield.

The tandem process was further studied in terms of a chemoselective synthesis, as this was not realized so far in these couplings.[8] The site-selective and/or chemoselective study is important from the viewpoint that these reactions

Table 4. Chemoselective tandem couplings.[a]



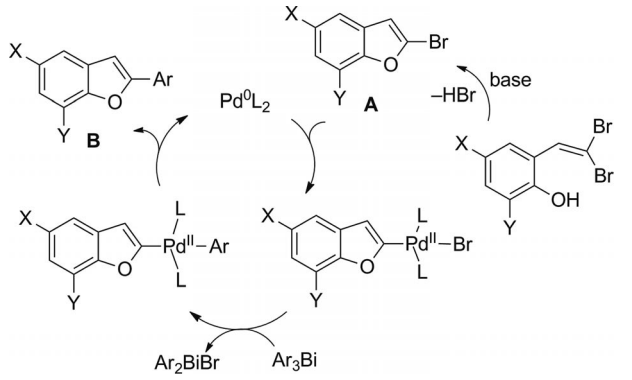
Entry	*gem*-Dibromide	2-Arylbenzofuran	Yield[b] [%]
1		 **7a**	70
2	"	 **7b**	80
3	"	 **7c**	72
4	"	 **7d**	77
5	"	 **7e**	75
6	"	 **7f**	76
7		 **8a**	78
8	"	 **8b**	74
9	"	 **8c**	71
10	"	 **8d**	76
11	"	 **8e**	78
12	"	 **8f**	72
13	"	 **8g**	73
14	"	 **8h**	74
15		**9a**	75
16	"	**9b**	79
17	"	**9c**	72
18	"	**9d**	78

[a] Conditions: *gem*-Dibromide (0.825 mmol, 3.3 equiv.), $BiAr_3$ (0.25 mmol, 1 equiv.), $[Pd(PPh_3)_4]$ (0.0225 mmol, 0.09 equiv.), Cs_2CO_3 (1.5 mmol, 6 equiv.), DMF (3 mL), 90 °C, 4 h. Biaryls from $BiAr_3$ were formed in minor amounts. [b] Isolated yield, and 0.75 mmol of product corresponds to 100% yield.

furnish molecular skeletons with reactive functionality[12] useful for further structural elaboration. This study was carried out with halogen-substituted dibromides. Under the established conditions, 5-bromo- and 5-chloro-substituted *o*-hydroxy-*gem*-(dibromovinyl)benzenes reacted in a chemoselective manner with the bismuth reagents to furnish the corresponding 5-bromo- and 5-chloro-functionalized 2-arylbenzofurans in excellent yields (Table 4, entries 1–14).

The coupling reactions of 3,5-dichloro-substituted *o*-hydroxy-*gem*-(dibromovinyl)benzenes also gave 5,7-dichloro-substituted 2-arylbenzofurans in high yields (Table 4, entries 15–18). This is a unique demonstration of site-selective and chemoselective tandem couplings in the synthesis of functionalized 2-arylbenzofurans.[8] Given the high reactivity of aryl halides to give cross-coupled biaryls, the present method is a notable chemoselective tandem coupling process involving polyhalogenated systems.[12] Thus, a series of diverse *o*-hydroxy-*gem*-(dibromovinyl)benzenes furnished facile tandem couplings and an array of functionalized 2-arylbenzofurans in a one-pot operation.

On the basis of the screening and control studies that were carried out (Tables 1 and 2), a plausible mechanism is depicted in Scheme 2. The base-mediated cyclization of *o*-hydroxy-*gem*-(dibromovinyl)benzene generates 2-bromobenzofuran **A**,[13a] and this species would be involved in the cross-coupling with the bismuth reagent to deliver 2-arylbenzofuran **B** under palladium-catalyzed conditions.[14]



Scheme 2. Proposed mechanism.

Exclusive formation of 2-bromobenzofuran without a metal catalyst is noteworthy.[13a] Formation of 2-bromobenzofuran and bis-benzofurans (in minor amounts) in control reactions is in favor of the proposed catalytic cycle.[8,13a] The possible involvement of in situ formed arylbismuth species in subsequent catalytic cycles successfully provides three aryl couplings from $BiAr_3$ in a one-pot operation.

Palladium-catalyzed coupling reactions are well established in the synthesis of heterocycles by cyclization and oxidative addition processes.[15] There are many approaches reported for the synthesis of benzofuran derivatives[16] in general and for 2-substituted benzofurans in particular.[17] Some of the methods known for the synthesis of 2-arylbenzofuran include [3,3] sigmatropic rearrangement of oxime ethers,[18a] intramolecular *o*-arylation of enolates under metal conditions,[18b,18c] McMurry couplings,[9b] cross-couplings of (*E*)-1,2-dichlorovinyl ethers with arylboronic acids,[18d] and intramolecular cyclization of *o*-alkynylphenols or their derivatives under metal catalysis.[19] Synthesis of 2-arylbenzofurans can also be accomplished through cross-coupling reactions of preformed 2-halobenzofurans with organometallic reagents.[20] Although useful, this approach requires the additional synthesis of 2-bromobenzofuran through a metal-catalyzed or tetrabutylammonium fluoride (TBAF)-mediated protocol,[13] and these couplings, in some cases, require high temperatures or reflux conditions and long reaction times. Further, couplings with preformed 2-benzofuranyl organometallic reagents, although suffering from stability related issues, can couple with aryl halides under palladium catalysis to give 2-arylbenzofurans.[21] From these counts, the present tandem process avoids the preformation of both 2-halobenzofuran and 2-benzofuranyl organometallic reagents as coupling partners, which simplifies the overall synthetic process. The tandem process described here is highly advantageous and utilizes in situ generated 2-bromobenzoufran and involves three consecutive arylations by using triarylbismuth reagents. It is of note that the 2-arylbenzofuran skeleton is ubiquitous in natural products such as moracin M., ailanthoidol, cicerfuran, and so forth.[22] Given the importance of this core skeleton, the present tandem strategy involving triarylbismuths as threefold arylating reagents would pave the way for the easy synthesis of various benzofuran analogs in a facile manner.

Conclusions

In summary, we have demonstrated a new, one-pot, chemoselective, tandem synthesis of functionalized 2-arylbenzofurans by using $BiAr_3$ as threefold arylating agents. This unique and synthetically valuable strategy proceeds through three consecutive coupling reactions involving triarylbismuth reagents and provides 2-arylbenzofuran products in high yields. This process obviates the use of preformed halobenzofurans or excess amounts of organometallic reagents in the synthesis of 2-arylbenzofurans. The chemoselective coupling of polyhalogenated systems at the *gem*-dibromide terminus is an additional highlight in the synthesis of halogenated 2-arylbenzofurans under palladium-catalyzed conditions. These products are highly useful for further core expansion under metal-catalyzed conditions.

Experimental Section

General: All coupling reactions were carried out under a N_2 atmosphere. Starting triarylbismuths[23] and 1,1-dibromides[24] were prepared by literature methods. GC analysis of the reaction mixtures was done with a Clarus 500 (Perkin–Elmer). NMR spectra were recorded with a JEOL (500 MHz) spectrometer, and HRMS measurements were recorded with a Waters HAB213 system.

Representative Cross-Coupling Procedure: A 50-mL, hot-oven-dried Schlenk tube was charged with Ph_3Bi (0.25 mmol, 110 mg,

1 equiv.), *o*-hydroxy-*gem*-(dibromovinyl)benzene (0.825 mmol, 229 mg, 3.3 equiv.), Cs_2CO_3 (1.5 mmol, 489 mg, 6 equiv.), Pd-$(PPh_3)_4$ (0.0225 mmol, 26 mg, 0.09 equiv.), and DMF (3 mL) under a N_2 atmosphere. The mixture was stirred in a preheated oil bath at 90 °C for 4 h. The contents were quenched with dilute HCl after cooling to room temperature and extracted with ethyl acetate. After usual workup, the crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate). Pure product **1a** and other products obtained by following this procedure were analyzed by evaluation of their spectroscopic data.

2-Phenylbenzofuran (1a):[19d] White solid (109 mg, 75%); m.p. 108–110 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.97 (d, J = 7.65 Hz, 2 H, CH_{Ar}), 7.31–7.69 (m, 7 H, CH_{Ar}), 7.12 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.8, 154.8, 130.4, 129.1, 128.7, 128.5, 124.9, 124.2, 122.9, 120.8, 111.1, 101.2 ppm. IR (KBr): $\tilde{\nu}$ = 3035, 2923, 1608, 1561, 1489, 1453, 1258, 1207, 1169, 1104, 1073, 1037, 1019, 917, 882, 806, 764, 744, 689 cm^{-1}. HRMS (EI): calcd. for $C_{14}H_{10}O$ $[M]^+$ 194.0732; found 194.0732.

2-(4-Methylphenyl)benzofuran (1b):[19d] White solid (126 mg, 81%); m.p. 116–118 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85 (d, J = 8.0 Hz, 2 H, CH_{Ar}), 7.66 (d, J = 7.45 Hz, 1 H, CH_{Ar}), 7.61 (d, J = 8.0 Hz, 1 H, CH_{Ar}), 7.30–7.38 (m, 4 H, CH_{Ar}), 7.06 (s, 1 H, CH_{Ar}), 2.49 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.1, 154.7, 138.5, 129.4, 129.3, 127.7, 124.8, 123.9, 122.8, 120.7, 111.0, 100.5, 21.3 ppm. IR (KBr): $\tilde{\nu}$ = 3029, 2914, 1587, 1502, 1350, 1302, 1256, 1205, 1168, 1108, 1032, 1011, 919, 884, 824, 801, 739 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{12}O$ $[M]^+$ 208.0888; found 208.0886.

2-(4-Methoxyphenyl)benzofuran (1c):[21a] White solid (122 mg, 72%); m.p. 136–138 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.78–7.80 (m, 2 H, CH_{Ar}), 7.48–7.55 (m, 2 H, CH_{Ar}), 7.19–7.26 (m, 2 H, CH_{Ar}), 6.97 (d, J = 8.8 Hz, 2 H, CH_{Ar}), 6.88 (s, 1 H, CH_{Ar}), 3.85 (s, 3 H, -OCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.9, 156.0, 154.6, 129.4, 126.3, 123.7, 123.3, 122.8, 120.5, 114.2,110.9, 99.6, 55.3 ppm. IR (KBr): $\tilde{\nu}$ = 2931, 1609, 1502, 1452, 1248, 1177, 1109, 1039, 1022, 800, 780, 746 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{12}O_2$ $[M]^+$ 224.0837; found 224.0839.

2-(4-Ethoxyphenyl)benzofuran (1d):[14] White solid (130 mg, 73%); m.p. 122–123 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77–7.79 (m, 2 H, CH_{Ar}), 7.54 (d, J = 7.65 Hz, 1 H, CH_{Ar}), 7.49 (d, J = 8.05 Hz, 1 H, CH_{Ar}), 7.19–7.26 (m, 2 H, CH_{Ar}), 6.95–6.96 (m, 2 H, CH_{Ar}), 6.87 (s, 1 H, CH_{Ar}), 4.07 (q, J = 6.8 Hz, 2 H, CH_2CH_3), 1.43 (t, J = 6.8 Hz, 3 H, CH_2CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.3, 156.1, 154.6, 129.4, 126.3, 123.6, 123.1, 122.7, 120.5, 114.7, 110.9, 99.5, 63.5, 14.7 ppm. IR (KBr): $\tilde{\nu}$ = 3059, 2980, 1610, 1503, 1474, 1451, 1252, 1177, 1115, 1046, 919, 837, 796, 747 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{14}O_2$ $[M]^+$ 238.0994; found 238.0997.

2-(4-Isopropoxyphenyl)benzofuran (1e): White solid (156 mg, 82%); m.p. 128–130 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.8 Hz, 2 H, CH_{Ar}), 7.54 (d, J = 7.65 Hz, 1 H, CH_{Ar}), 7.49 (d, J = 8.05 Hz, 1 H, CH_{Ar}), 7.19–7.26 (m, 2 H, CH_{Ar}), 6.95 (d, J = 8.8 Hz, 2 H, CH_{Ar}), 6.87 (s, 1 H, CH_{Ar}), 4.57–4.64 [m, 1 H, $CH(CH_3)_2$], 1.36 [d, J = 6.1 Hz, 6 H, $CH(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.3, 156.1, 154.6, 129.4, 126.4, 123.6, 123.0, 122.7, 120.5, 115.9, 110.9, 99.5, 69.9, 22.0 ppm. IR (KBr): $\tilde{\nu}$ = 2923, 1610, 1499, 1449, 1381, 1248, 1174, 1118, 1029, 950, 831, 801, 740 cm^{-1}. HRMS (EI):calcd. for $C_{17}H_{16}O_2$ $[M]^+$ 252.1150; found 252.1151.

2-(4-Chlorophenyl)benzofuran (1f):[14] White solid (104 mg, 61%); m.p. 145–147 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.3 Hz, 2 H, CH_{Ar}), 7.61 (d, J = 8.3 Hz, 1 H, CH_{Ar}), 7.55 (d, J = 8.0 Hz, 1 H, CH_{Ar}), 7.45 (d, J = 8.6 Hz, 2 H, CH_{Ar}), 7.31–7.34 (m, 1 H, CH_{Ar}), 7.28 (d, J = 7.75 Hz, 1 H, CH_{Ar}), 7.04 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.8, 154.7, 134.2, 129.0, 126.1, 124.5, 123.0, 120.9, 111.1, 101.7 ppm. IR (KBr): $\tilde{\nu}$ = 3057, 2924, 1601, 1485, 1448, 1403, 1255, 1168, 1093, 1030, 1009, 918, 883, 835, 804, 746 cm^{-1}. HRMS (EI): calcd. for $C_{14}H_9ClO$ $[M]^+$ 228.0342; found 228.0343.

2-(4-Fluorophenyl)benzofuran (1g):[14] White solid (124 mg, 78%); m.p. 115–117 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.80–7.85 (m, 2 H, CH_{Ar}), 7.56–7.58 (m, 1 H, CH_{Ar}), 7.50–7.51 (m, 1 H, CH_{Ar}), 7.11–7.29 (m, 4 H, CH_{Ar}), 6.95 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.8 (d, J = 246.8 Hz), 154.9, 154.8, 129.1, 126.7 (d, J = 8.33 Hz), 124.2, 123.0, 120.8, 115.8 (d, J = 21.46 Hz), 111.1, 100.9 ppm. IR (KBr): $\tilde{\nu}$ = 3065, 2922, 1601, 1570, 1451, 1410, 1350, 1233, 1156, 1098, 1030, 1009, 840, 802, 746 cm^{-1}. HRMS (EI): calcd. for $C_{14}H_9FO$ $[M]^+$ 212.0637; found 212.0637.

2-(3-Methoxyphenyl)benzofuran (1h):[25] Pale yellow solid (118 mg, 70%); m.p. 50–52 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.58 (d, J = 7.45 Hz, 1 H, CH_{Ar}), 7.52 (d, J = 7.45 Hz, 1 H, CH_{Ar}), 7.45 (d, J = 7.7 Hz, 1 H, CH_{Ar}), 7.41 (d, J = 1.7 Hz, 1 H, CH_{Ar}), 7.33–7.37 (m, 1 H, CH_{Ar}), 7.27–7.30 (m, 1 H, CH_{Ar}), 7.21–7.24 (m, 1 H, CH_{Ar}), 7.02 (s, 1 H, CH_{Ar}), 6.90 (d, J = 8.0 Hz, 1 H, CH_{Ar}), 3.89 (s, 3 H, -OCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.9, 155.7, 154.8, 131.7, 129.8, 129.1, 124.3, 122.9, 120.9, 117.4, 114.4, 111.1, 110.0, 101.6, 55.3 ppm. IR (KBr): $\tilde{\nu}$ = 3064, 2923, 1607, 1569, 1487, 1349, 1283, 1258, 1235, 1200, 1164, 1050, 1032, 934, 849, 779, 748, 687 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{12}O_2$ $[M]^+$ 224.0837; found 224.0836.

2-(Thiophen-2-yl)benzofuran (1i):[9b] White solid (77 mg, 51%); m.p. 89–92 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47–7.54 (m, 3 H, CH_{Ar}), 7.32–7.33 (m, 1 H, CH_{Ar}), 7.19–7.27 (m, 2 H, CH_{Ar}), 7.08–7.10 (m, 1 H, CH_{Ar}), 6.86 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.5, 151.2, 133.2, 129.0, 127.8, 125.7, 124.5, 124.2, 123.0, 120.7, 111.0, 101.0 ppm. IR (KBr): $\tilde{\nu}$ = 2924, 1585, 1502, 1449, 1419, 1361, 1250, 1224, 1045, 878, 848, 802, 748, 702 cm^{-1}. HRMS (EI): calcd. for $C_{12}H_8OS$ $[M]^+$ 200.0296; found 200.0294.

7-Methoxy-2-phenylbenzofuran (2a):[9b] White solid (98 mg, 58%); m.p. 78–80 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89–7.91 (m, 2 H, CH_{Ar}), 7.43–7.46 (m, 2 H, CH_{Ar}), 7.34–7.37 (m, 1 H, CH_{Ar}), 7.14–7.20 (m, 2 H, CH_{Ar}), 7.02 (s, 1 H, CH_{Ar}), 6.81 (dd, J = 1.15, 7.6 Hz, 1 H, CH_{Ar}), 4.06 (s, 3 H, OCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.0, 145.2, 144.0, 130.8, 130.2, 128.6, 128.5, 124.9, 123.5, 113.2, 106.6, 101.5, 56.0 ppm. IR (KBr): $\tilde{\nu}$ = 3032, 2961, 2842, 1620, 1588, 1498, 1450, 1326, 1270, 1176, 1098, 1021, 909, 852, 795, 768, 726, 682 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{12}O_2$ $[M]^+$ 224.0837; found 224.0835.

5-Methyl-2-phenylbenzofuran (3a):[9b] White solid (81 mg, 52%); m.p. 112–115 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.86 (d, J = 7.3 Hz, 2 H, CH_{Ar}), 7.33–7.46 (m, 5 H, CH_{Ar}), 7.07–7.11 (m, 1 H, CH_{Ar}), 6.96 (s, 1 H, CH_{Ar}), 2.45 (s, 1 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.9, 153.2, 132.3, 130.5, 129.2, 128.7, 128.3, 125.5, 124.8, 120.6, 110.6, 101.0, 21.3 ppm. IR (KBr): $\tilde{\nu}$ = 3058, 2918, 1610, 1465, 1444, 1329, 1265, 1197, 1072, 1039, 1020, 913, 803, 760, 741, 687 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{12}O$ $[M]^+$ 208.0888; found 208.0887.

2,5-Diphenylbenzofuran (4a):[9a] White solid (120 mg, 59%); m.p. 148–150 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.89 (d, J = 7.65 Hz, 2 H, CH_{Ar}), 7.78 (s, 1 H, CH_{Ar}), 7.64 (d, J = 7.6 Hz, 2 H, CH_{Ar}), 7.58 (d, J = 8.4 Hz, 1 H, CH_{Ar}), 7.52 (d, J = 8.4 Hz, 1 H, CH_{Ar}), 7.47 (t, J = 7.65 Hz, 4 H, CH_{Ar}), 7.34–7.39 (m, 2 H, CH_{Ar}), 7.07 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.5, 154.4, 141.6, 136.6, 130.3, 129.7, 128.8, 128.7, 128.6, 127.4, 126.8,

124.9, 123.9, 119.3, 111.2, 101.4 ppm. IR (KBr): $\tilde{\nu}$ = 3057, 2923, 1562, 1490, 1461, 1444, 1278, 1126, 1072, 1018, 905, 881, 806, 756, 686 cm^{-1}. HRMS (EI): calcd. for $C_{20}H_{14}O$ $[M]^+$ 270.1045; found 270.1046.

5-Acetyl-2-phenylbenzofuran (5a):[14] White solid (128 mg, 72%); m.p. 144–145 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.22 (s, 1 H, CH_{Ar}), 7.94 (d, J = 8.8 Hz, 1 H, CH_{Ar}), 7.86 (d, J = 8.0 Hz, 2 H, CH_{Ar}), 7.37–7.56 (m, 4 H, CH_{Ar}), 7.07 (s, 1 H, CH_{Ar}), 2.66 (s, 3 H, COCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.6, 157.5, 157.3, 132.8, 129.7, 129.2, 129.0, 128.8, 125.0, 122.1, 111.1, 101.5, 26.7 ppm. IR (KBr): $\tilde{\nu}$ = 2922, 1672, 1606, 1439, 1352, 1271, 1239, 1156, 1128, 1072, 1019, 908, 808, 761 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{12}O_2$ $[M]^+$ 236.0837; found 236.0833.

5-Acetyl-2-(4-fluorophenyl)benzofuran (5b):[14] White solid (145 mg, 76%); m.p. 135–137 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.22 (d, J = 1.55 Hz, 1 H, CH_{Ar}), 7.94–7.96 (m, 1 H, CH_{Ar}), 7.82–7.86 (m, 2 H, CH_{Ar}), 7.54 (d, J = 8.4 Hz, 1 H, CH_{Ar}), 7.13–7.18 (m, 2 H, CH_{Ar}), 7.01 (s, 1 H, CH_{Ar}), 2.67 (s, 3 H, COCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 197.6, 163.1 (d, J = 247.9 Hz), 157.3, 156.6, 132.9, 129.3, 126.9 (d, J = 8.35 Hz), 126.1, 125.0, 122.0, 116.0 (d, J = 22.65 Hz), 111.0, 101.3, 26.7 ppm. IR (KBr): $\tilde{\nu}$ = 2928, 1673, 1606, 1503, 1438, 1355, 1282, 1233, 1157, 1098, 1030, 975, 836, 804, 748 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{11}FO_2$ $[M]^+$ 254.0743; found 254.0743.

5-Benzoyl-2-phenylbenzofuran (6a):[26] White solid (158 mg, 71%); m.p. 115–117 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.06 (s, 1 H, CH_{Ar}), 7.88 (d, J = 8.0 Hz, 2 H, CH_{Ar}), 7.81–7.84 (m, 3 H, CH_{Ar}), 7.59–7.62 (m, 2 H, CH_{Ar}), 7.46–7.52 (m, 4 H, CH_{Ar}), 7.38–7.40 (m, 1 H, CH_{Ar}), 7.08 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.6, 157.6, 157.2, 138.3, 133.0, 132.2, 130.1, 129.1, 129.0, 128.3, 126.9, 125.1, 124.1, 111.1, 101.6 ppm. IR (KBr): $\tilde{\nu}$ = 3056, 3022, 2932, 1650, 1600, 1567, 1492, 1464, 1441, 1343, 1283, 1172, 1109, 1017, 976, 826, 764, 748 cm^{-1}. HRMS (EI): calcd. for $C_{21}H_{14}O_2$ $[M]^+$ 298. 0994; found 298.0995.

5-Bromo-2-phenylbenzofuran (7a):[14] White solid (143 mg, 70%); m.p. 140–141 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.85 (d, J = 7.45 Hz, 2 H, CH_{Ar}), 7.70 (s, 1 H, CH_{Ar}), 7.44–7.47 (m, 2 H, CH_{Ar}), 7.36–7.40 (m, 3 H, CH_{Ar}), 6.95 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.1, 153.5, 131.1, 129.8, 128.9, 128.8, 127.0, 125.0, 123.4, 115.9, 112.5, 100.5 ppm. IR (KBr): $\tilde{\nu}$ = 3075, 2996, 2919, 1678, 1598, 1400, 1360, 1262, 1005, 837, 764, 686, 593 cm^{-1}. HRMS (EI): calcd. for $C_{14}H_9BrO$ $[M]^+$ 271.9837 and $[M + 2]^+$ 273.9816; found 271.9837 and 273.9895.

5-Bromo-2-(4-methylphenyl)benzofuran (7b):[14] White solid (173 mg, 80%); m.p. 161–164 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72 (d, J = 8.3 Hz, 2 H, CH_{Ar}), 7.67 (d, J = 1.7 Hz, 1 H, CH_{Ar}), 7.32–7.37 (m, 2 H, CH_{Ar}), 7.24–7.26 (m, 2 H, CH_{Ar}), 6.88 (s, 1 H, CH_{Ar}), 2.39 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.4, 153.4, 139.1, 131.3, 129.5, 127.1, 126.7, 124.9, 123.2, 115.8, 112.4, 99.8, 21.4 ppm. IR (KBr): $\tilde{\nu}$ = 2915, 1606, 1578, 1502, 1441, 1376, 1322, 1262, 1205, 1115, 1048, 1015, 921, 875, 823, 796, 738, 670 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{11}BrO$ $[M]^+$ 285.9993 and $[M + 2]^+$ 287.9973; found 285.9991 and 288.0038.

5-Bromo-2-(4-ethoxyphenyl)benzofuran (7c):[14] White solid (171 mg, 72%); m.p. 173–175 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75 (d, J = 8.8 Hz, 2 H, CH_{Ar}), 7.65 (s, 1 H, CH_{Ar}), 7.31–7.36 (m, 2 H, CH_{Ar}), 6.96 (d, J = 8.8 Hz, 2 H, CH_{Ar}), 6.79 (s, 1 H, CH_{Ar}), 4.08 (q, J = 6.9 Hz, 2 H, CH_2CH$_3$), 1.44 (t, J = 6.9 Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.6, 157.4, 153.3, 131.5, 126.5, 126.4, 123.0, 122.4, 115.8, 114.7, 112.3, 98.8, 63.5, 14.7 ppm. IR (KBr): $\tilde{\nu}$ = 2975, 2928, 1609, 1501, 1442, 1393, 1251, 1176, 1116, 1044, 922, 872, 836, 794 cm^{-1}. HRMS (EI): calcd. for $C_{16}H_{13}BrO_2$ $[M]^+$ 316.0099 and $[M + 2]^+$ 318.0078; found 316.0096 and 318.0254.

5-Bromo-2-(4-isopropoxyphenyl)benzofuran (7d): White solid (192 mg, 77%); m.p. 142–144 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75 (d, J = 8.85 Hz, 2 H, CH_{Ar}), 7.66 (d, J = 2.0 Hz, 1 H, CH_{Ar}), 7.31–7.36 (m, 2 H, CH_{Ar}), 6.95 (d, J = 8.85 Hz, 2 H, CH_{Ar}), 6.80 (s, 1 H, CH_{Ar}), 4.59–4.64 [m, 1 H, CH(CH$_3$)$_2$], 1.37 [d, J = 6.0 Hz, 6 H, CH(CH_3)$_2$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.6, 157.4, 153.3, 131.5, 126.5, 126.4, 123.0, 122.3, 115.9, 115.8, 112.3, 98.8, 69.9, 21.9 ppm. IR (KBr): $\tilde{\nu}$ = 2976, 2925, 1608, 1501, 1442, 1378, 1321, 1303, 1255, 1179, 1034, 950, 894, 867, 835, 793 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{15}BrO_2$ $[M]^+$ 330.0255 and $[M + 2]^+$ 332.0235; found 330.0258 and 332.0334.

5-Bromo-2-(4-fluorophenyl)benzofuran (7e):[14] White solid (163 mg, 75%); m.p. 128–130 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.80–7.82 (m, 2 H, CH_{Ar}), 7.68 (s, 1 H, CH_{Ar}), 7.37 (s, 2 H, CH_{Ar}), 7.12–7.16 (m, 2 H, CH_{Ar}), 6.87 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.0 (d, J = 248 Hz), 156.2, 153.5, 131.1, 127.0, 126.9 (d, J = 8.35 Hz), 126.1, 123.4, 116.0 (d, J = 21.46 Hz), 112.5, 100.3 ppm. IR (KBr): $\tilde{\nu}$ = 2923, 1605, 1567, 1501, 1441, 1241, 1157, 1099, 1049, 1031, 922, 874, 842, 797, 738 cm^{-1}. HRMS (EI): calcd. for $C_{14}H_8BrFO$ $[M]^+$ 289.9743 and $[M + 2]^+$ 291.9722; found 289.9742 and 291.9752.

5-Bromo-2-(3-methoxyphenyl)benzofuran (7f): White solid (172 mg, 76%); m.p. 92–94 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.69 (s, 1 H, CH_{Ar}), 7.34–7.44 (m, 5 H, CH_{Ar}), 6.91–6.94 (m, 2 H, CH_{Ar}), 3.89 (s, 1 H, OCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.9, 156.9, 153.5, 131.1, 129.9, 127.1, 123.4, 117.5, 115.9, 114.8, 112.5, 110.2, 100.9, 55.3 ppm. IR (KBr): $\tilde{\nu}$ = 3001, 2964, 1612, 1571, 1489, 1454, 1435, 1285, 1221, 1159, 1056, 1036, 874, 856, 800, 774 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{11}BrO_2$ $[M]^+$ 301.9942 and $[M + 2]^+$ 303.9922; found 301.9940 and 303.9945.

5-Chloro-2-phenylbenzofuran (8a):[9b,27] White solid (133 mg, 78%); m.p. 133–134 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77–7.79 (m, 2 H, CH_{Ar}), 7.58 (d, J = 7.65 Hz, 1 H, CH_{Ar}), 7.51 (d, J = 8.05 Hz, 1 H, CH_{Ar}), 7.40–7.42 (m, 2 H, CH_{Ar}), 7.22–7.31 (m, 2 H, CH_{Ar}), 7.00 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.8, 154.7, 134.2, 129.0, 128.9, 126.0, 124.5, 123.0, 120.9, 111.1, 101.7 ppm. IR (KBr): $\tilde{\nu}$ = 3094, 2923, 1608, 1581, 1490, 1438, 1324, 1261, 1162, 1114, 1061, 1038, 1019, 903, 878, 807, 763, 738, 689 cm^{-1}. HRMS (EI): calcd. for $C_{14}H_9ClO$ $[M]^+$ 228.0342; found 228.0348.

5-Chloro-2-(4-methylphenyl)benzofuran (8b):[27] White solid (134 mg, 74%); m.p. 158–160 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.73 (d, J = 8.4 Hz, 2 H, CH_{Ar}), 7.51 (d, J = 2.3 Hz, 1 H, CH_{Ar}), 7.40 (d, J = 8.8 Hz, 1 H, CH_{Ar}), 7.19–7.26 (m, 3 H, CH_{Ar}), 6.89 (s, 1 H, CH_{Ar}), 2.39 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.6, 153.1, 139.1, 130.6, 129.5, 128.3, 127.2, 124.9, 124.0, 120.2, 111.9, 100.0, 21.4 ppm. IR (KBr): $\tilde{\nu}$ = 2918, 1609, 1583, 1503, 1443, 1263, 1162, 1059, 1034, 904, 876, 823, 796, 739 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{11}ClO$ $[M]^+$ 242.0498; found 242.0498.

5-Chloro-2-(4-methoxyphenyl)benzofuran (8c):[27] White solid (137 mg, 71%); m.p. 161–163 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.85 Hz, 2 H, CH_{Ar}), 7.50 (d, J = 2.0 Hz, 1 H, CH_{Ar}), 7.40 (d, J = 8.6 Hz, 1 H, CH_{Ar}), 7.18–7.20 (m, 1 H, CH_{Ar}), 6.97 (d, J = 8.9 Hz, 2 H, CH_{Ar}), 6.81 (s, 1 H, CH_{Ar}), 3.86 (s, 3 H, OCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.2, 157.5, 153.0, 130.8, 128.3, 126.5, 123.7, 122.7, 120.0, 114.3, 111.8, 99.1, 55.3 ppm. IR (KBr): $\tilde{\nu}$ = 2928, 1608, 1582, 1444, 1420, 1306, 1253,

1208, 1176, 1110, 1060, 1038, 904, 877, 831, 794, 739, 695 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{11}ClO_2$ [M]$^+$ 258.0448; found 258.0444.

5-Chloro-2-(4-ethoxyphenyl)benzofuran (8d): White solid (156 mg, 76%); m.p. 164–166 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.76 (d, J = 8.0 Hz, 2 H, CH_{Ar}), 7.50 (s, 1 H, CH_{Ar}), 7.39 (d, J = 8.4 Hz, 1 H, CH_{Ar}), 7.18–7.20 (m, 1 H, CH_{Ar}), 6.96 (d, J = 7.65 Hz, 2 H, CH_{Ar}), 6.80 (s, 1 H, CH_{Ar}), 4.08 (q, J = 6.9 Hz, 2 H, CH_2CH_3), 1.44 (t, J = 6.9 Hz, 3 H, CH_2CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.6, 157.6, 153.0, 130.8, 128.3, 126.5, 123.7, 122.5, 120.0, 114.8, 111.8, 99.0, 63.5, 14.7 ppm. IR (KBr): $\tilde{\nu}$ = 2977, 1609, 1502, 1445, 1394, 1306, 1250, 1176, 1116, 1045, 923, 874, 836, 794 cm^{-1}. HRMS (EI): calcd. for [M]$^+$ $C_{16}H_{13}ClO_2$ 272.0604; found 272.0605.

5-Chloro-2-(4-isopropoxyphenyl)benzofuran (8e): White solid (167 mg, 78%); m.p. 133–135 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75 (d, J = 8.8 Hz, 2 H, CH_{Ar}), 7.50 (d, J = 1.9 Hz, 1 H, CH_{Ar}), 7.39 (d, J = 8.4 Hz, 1 H, CH_{Ar}), 7.17–7.20 (m, 1 H, CH_{Ar}), 6.95 (d, J = 8.8 Hz, 2 H, CH_{Ar}), 6.80 (s, 1 H, CH_{Ar}), 4.57–4.65 [m, 1 H, $CH(CH_3)_2$], 1.37 [d, J = 6.15 Hz, 6 H, $CH(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.6, 157.6, 153.0, 130.9, 128.3, 126.5, 123.7, 122.4, 120.0, 116.0, 111.8, 99.0, 70.0, 22.0 ppm. IR (KBr): $\tilde{\nu}$ = 2978, 1607, 1501, 1444, 1382, 1303, 1255, 1120, 1034, 905, 865, 835, 793, 696 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{15}ClO_2$ [M]$^+$ 286.0761; found 286.0763.

5-Chloro-2-(4-chlorophenyl)benzofuran (8f): White solid (143 mg, 72%); m.p. 152–154 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.74–7.76 (m, 2 H, CH_{Ar}), 7.52 (s, 1 H, CH_{Ar}), 7.40–7.41 (m, 3 H, CH_{Ar}), 7.21–7.25 (m, 1 H, CH_{Ar}), 6.92 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.1, 153.2, 134.7, 130.3, 129.0, 128.6, 128.4, 126.2, 124.6, 120.4, 112.1, 101.1 ppm. IR (KBr): $\tilde{\nu}$ = 2922, 1599, 1580, 1484, 1441, 1402, 1323, 1259, 1204, 1162, 1091, 1059, 1032, 1009, 905, 873, 829, 800, 729, 697 cm^{-1}. HRMS (EI): calcd. for $C_{14}H_8Cl_2O$ [M]$^+$ 261.9952; found 261.9957.

5-Chloro-2-(4-fluorophenyl)benzofuran (8g): White solid (135 mg, 73%); m.p. 126–128 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.79–7.83 (m, 2 H, CH_{Ar}), 7.52 (d, J = 1.95 Hz, 1 H, CH_{Ar}), 7.41 (d, J = 8.4 Hz, 1 H, CH_{Ar}), 7.11–7.25 (m, 3 H, CH_{Ar}), 6.88 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.0 (d, J = 248 Hz), 156.4, 153.1, 130.5, 128.5, 126.9 (d, J = 8.35 Hz), 126.2, 124.4, 120.3, 115.9 (d, J = 21.46 Hz), 112.0, 100.4 ppm. IR (KBr): $\tilde{\nu}$ = 1603, 1569, 1500, 1442, 1323, 1240, 1157, 1098, 1031, 1011, 926, 904, 875, 843, 797, 739, 695 cm^{-1}. HRMS (EI): calcd. for $C_{14}H_8ClFO$ [M]$^+$ 246.0248; found 246.0246.

5-Chloro-2-(3-methoxyphenyl)benzofuran (8h): White solid (144 mg, 74%); m.p. 65–67 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, J = 1.9 Hz, 1 H, CH_{Ar}), 7.42–7.44 (m, 2 H, CH_{Ar}), 7.34–7.38 (m, 2 H, CH_{Ar}), 7.22–7.24 (m, 1 H, CH_{Ar}), 6.91–6.95 (m, 2 H, CH_{Ar}), 3.89 (s, 3 H, OCH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.9, 157.1, 153.1, 131.1, 130.4, 129.9, 128.4, 124.4, 120.4, 117.6, 114.8, 112.1, 110.2, 101.1, 55.3 ppm. IR (KBr): $\tilde{\nu}$ = 2940, 1613, 1567, 1489, 1454, 1326, 1285, 1220, 1157, 1056, 1036, 938, 908, 875, 856, 800, 773, 687 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{11}ClO_2$ [M]$^+$ 258.0448; found 258.0445.

5,7-Dichloro-2-phenylbenzofuran (9a):[19d] White solid (149 mg, 75%); m.p. 114–116 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.87 (d, J = 7.25 Hz, 2 H, CH_{Ar}), 7.38–7.48 (m, 4 H, CH_{Ar}), 7.27 (d, J = 1.9 Hz, 1 H, CH_{Ar}), 6.97 (s, 1 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.1, 149.2, 131.4, 129.4, 129.2, 128.8, 128.6, 125.2, 124.2, 119.0, 117.1, 101.1 ppm. IR (KBr): $\tilde{\nu}$ = 3086, 1607, 1577, 1488, 1454, 1436, 1326, 1234, 1172, 1076, 1037, 1019, 977, 908, 838, 797, 757, 732 cm^{-1}. HRMS (EI): calcd. for $C_{14}H_8Cl_2O$ [M]$^+$ 261.9952; found 261.9956.

5,7-Dichloro-2-(4-methylphenyl)benzofuran (9b):[14] White solid (164 mg, 79%); m.p. 106–108 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75 (d, J = 8.3 Hz, 2 H, CH_{Ar}), 7.40 (d, J = 2.0 Hz, 1 H, CH_{Ar}), 7.24–7.26 (m, 3 H, CH_{Ar}), 6.90 (s, 1 H, CH_{Ar}), 2.40 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.4, 149.1, 139.6, 131.6, 129.5, 128.5, 126.5, 125.1, 123.9, 118.8, 116.9, 100.4, 21.4 ppm. IR (KBr): $\tilde{\nu}$ = 2917, 1574, 1500, 1442, 1408, 1326, 1276, 1231, 1171, 1033, 976, 908, 866, 831, 791, 756, 732 cm^{-1}. HRMS (EI): calcd. for $C_{15}H_{10}Cl_2O$ [M]$^+$ 276.0109; found 276.0109.

5,7-Dichloro-2-(4-chlorophenyl)benzofuran (9c):[14] White solid (160 mg, 72%); m.p. 139–141 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, J = 5.7 Hz, 2 H, CH_{Ar}), 7.40–7.42 (m, 3 H, CH_{Ar}), 7.24–7.26 (m, 1 H, CH_{Ar}), 6.93 (d, J = 2.85 Hz, 1 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 156.9, 149.2, 135.3, 131.2, 129.1, 128.8, 127.7, 126.4, 124.5, 119.1, 117.1, 101.5 ppm. IR (KBr): $\tilde{\nu}$ = 2923, 1606, 1576, 1486, 1442, 1403, 1327, 1282, 1169, 1091, 1035, 1012, 985, 909, 862, 825, 758, 732 cm^{-1}. HRMS (EI): calcd. for $C_{14}H_7Cl_3O$ [M]$^+$ 295.9562; found 295.9565.

5,7-Dichloro-2-(4-fluorophenyl)benzofuran[l] (9d):[14] White solid (164 mg, 78%); m.p. 135–137 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.82–7.85 (m, 2 H, CH_{Ar}), 7.42 (s, 1 H, CH_{Ar}), 7.24–7.26 (m, 1 H, CH_{Ar}), 7.13–7.16 (m, 2 H, CH_{Ar}), 6.90 (d, J = 1.9 Hz, 1 H, CH_{Ar}) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.3 (d, J = 249.18 Hz), 157.1, 149.1, 131.4, 128.7, 127.1 (d, J = 8.35 Hz), 124.3, 119.0, 117.0, 116.0 (d, J = 21.46 Hz), 100.9 ppm. IR (KBr): $\tilde{\nu}$ = 2921, 1605, 1569, 1501, 1442, 1294, 1029, 868, 831, 792, 759, 732 cm^{-1}. HRMS (EI): calcd. for $C_{14}H_7Cl_2FO$ [M]$^+$ 279.9858; found 279.9853.

Supporting Information (see footnote on the first page of this article): NMR (proton and carbon), mass spectra and HPLC traces of products.

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