Month 2014

Synthesis of Arylated Benzofurans by Regioselective Suzuki–Miyaura Cross-Coupling Reactions of 2,3-Dibromobenzofurans- and 2,3,5-Tribromobenzofurans

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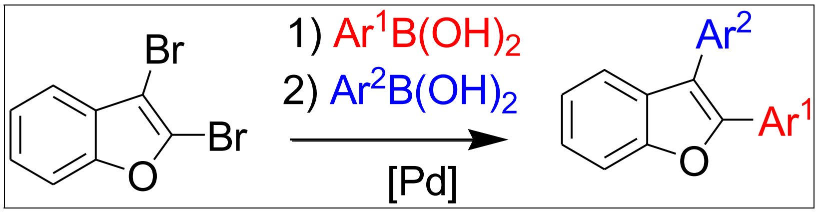
Received May 23, 2013
DOI 10.1002/jhet.2083



Arylated benzofurans were prepared by regioselective Suzuki–Miyaura cross-coupling reactions of 2,3-dibromobenzofuran. The reactions proceeded with very good site-selectivity in favor of the more electron deficient position 2. The Suzuki–Miyaura reactions of 2,3,5-tribromobenzofuran also proceeded in favor of position 2.

J. Heterocyclic Chem., **00,** 00 (2014).

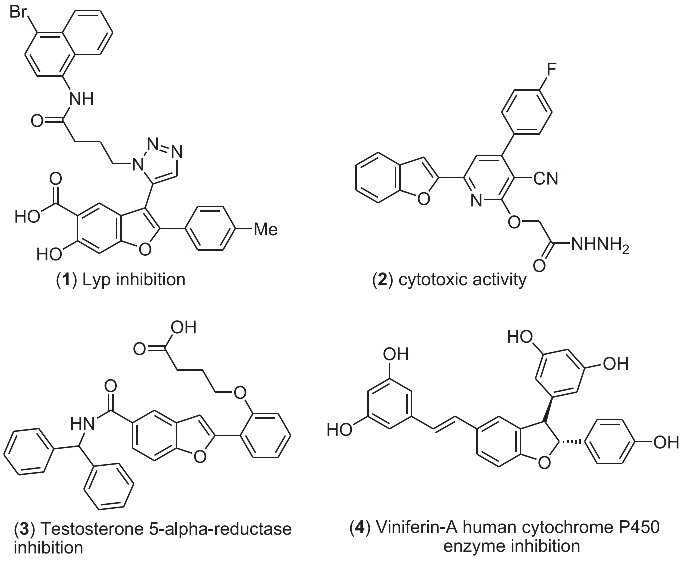
INTRODUCTION

The benzofuran scaffold has been identified as a privileged structure in medicinal chemistry. Benzofuran derivatives show various biological activities, such as antifungal and antimicrobial activity. They are also antagonists of the H_3 receptor and of angiotensin II [1]. Synthetic amiodarone represents a potent antiarrhythmic and antianginal drug [2]. Some 2-pyridinone derivatives of benzo[*b*]furans have been identified as selective and powerful inhibitors of HIV-1 reverse transcriptase. 7-Alkanoylbenzofurans and 7-alkanoyl-2,3-dihydrobenzofurans occur as natural products. Examples include longicaudatin [3], flemistrictin E, tovophenone C, vismiaguianone C, piperaduncin B, and the sessiliflorols A and B [3a,4]. Arylated benzofurans, such as compounds **1–4**, also possess a wide range of pharmacological activities (Figure 1) [5].

Polyhalogenated heterocycles can be site-selectively functionalized in palladium(0)-catalyzed cross-coupling reactions by selective activation of a single carbon atom. The site-selectivity is controlled by electronic and steric parameters [6]. Recently, we have reported the synthesis of aryl-substituted thiophenes [7], pyrroles [8], selenophenes [9], pyrimidines [10], and furans [11] based on site-selective Suzuki reactions of polyhalogenated heterocycles. In recent years, site-selective Sonogashira [12], Negishi [12], and Stille [13] coupling reactions of 2,3-dibromobenzofuran and 2,6-dibromobenzofuran have been studied. The first attack generally occurs at carbon atom C-2. Site-selective Negishi and Kumada cross-coupling reactions of 2,3,5-tribromobenzofuran have also been reported [14]. 3-Substituted benzofurans are difficult to obtain as the aryl group can rearrange from the 3-position to the 2-position [15]. Multi-step syntheses of 3-substituted benzofurans in low overall yields have been reported [16]. Recently, we have reported site-selective Suzuki–Miyaura reactions of 2,3-dibromobenzofuran [17]. Herein, we report full details of these studies.

RESULTS AND DISCUSSION

The Suzuki–Miyaura reaction of 2,3-dibromobenzofuran (**5**) with various arylboronic acids **6a–n** (2.0 equiv.) afforded 2,3-diarylbenzofurans **7a–n** (Scheme 1, Table 1). High yields were obtained for products derived from both electron-rich and electron-poor arylboronic acids. The syntheses of products **7** and **8** were carried out using Pd $(PPh_3)_4$ (5 mol-%) as the catalyst. The employment of Pd $(OAc)_2$ in the presence of XPhos [18] or SPhos [18] resulted in a decrease of the yield. All reactions were carried out at 80°C. An aqueous solution of K_2CO_3 (2 M) was used as the base. The employment of K_3PO_4 gave equally good results. 1,4-Dioxane was used as the solvent. In some cases, we observed the formation of 2-arylbenzofurans, containing a hydrogen atom located at carbon C-3, as by-products.



(**1**) Lyp inhibition

(**2**) cytotoxic activity

(**3**) Testosterone 5-alpha-reductase inhibition

(**4**) Viniferin-A human cytochrome P450 enzyme inhibition

Figure 1. Arylated benzofurans and 2,3-dihydrobenzofurans and their bioactivities.

Scheme 1. Synthesis of **7a–n**. Reagents and conditions: (*i*) **6a–n** (2.0 equiv.), Pd(PPh$_3$)$_4$ (5 mol-%), aq. K$_2$CO$_3$ (2 M), dioxane, 80°C, 8 h.

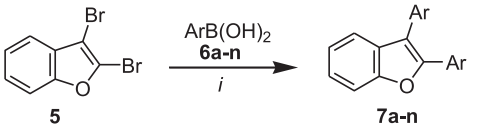


Table 1

Synthesis of 2,3-diarylbenzofurans **7a–n**.

6,7	Ar	% (7) [a]
a	C$_6$H$_5$	93[b]
b	4-MeC$_6$H$_4$	92
c	2-MeC$_6$H$_4$	81[c]
d	4-EtC$_6$H$_4$	86
e	4-*t*BuC$_6$H$_4$	88
f	2-ClC$_6$H$_4$	87
g	3-ClC$_6$H$_4$	78
h	4-ClC$_6$H$_4$	83
i	4-FC$_6$H$_4$	81
j	4-(CF$_3$)C$_6$H$_4$	73
k	2-(MeO)C$_6$H$_4$	82
l	4-(MeO)C$_6$H$_4$	75
m	2,5-(MeO)$_2$C$_6$H$_3$	85[d]
n	3,5-Me$_2$C$_6$H$_3$	79

[a] Yields of isolated products.
[b] Product **9a** was isolated as by-product (4%); for structures of products **9**, see Scheme 2 and Table 2.
[c] Product **9c** was isolated as by-product (9%).
[d] Product **9m** was isolated as by-product (8%).

The structures of **7e, 7h**, and **7i** were independently confirmed by X-ray crystal structure analysis (Figures 2–4) [9].

The Suzuki–Miyaura reaction of **5** with 1.0 equiv. of arylboronic acids **6b,d,g,h,k,n–r** afforded the 2-aryl-3-bromobenzofurans **8a–k** in good yields (Scheme 2, Table 2).

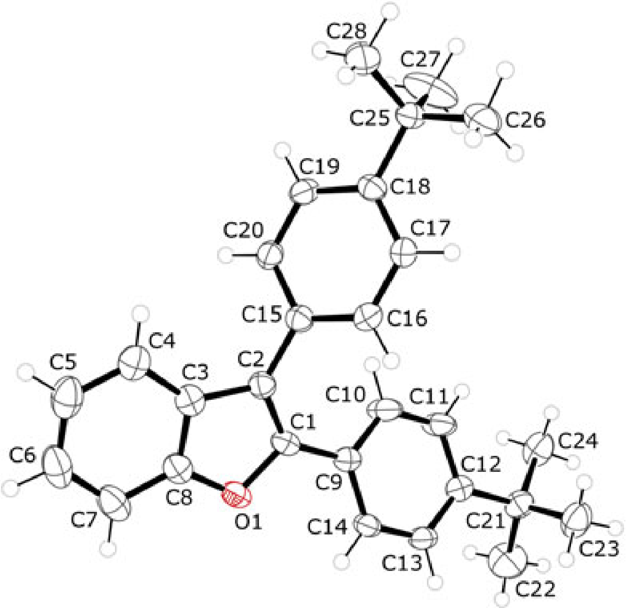


Figure 2. Crystal structure of **7e**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Both electron rich and poor arylboronic acids were successfully employed. The site-selectivity of the Suzuki–Miyaura reaction can be explained by the assumption that the oxidative addition of (nucleophilic) Pd(0) occurs more rapidly at the more electron-deficient carbon atom C-2. During the optimization, it proved to be important to carry out the reactions at 70°C instead of 80°C to avoid the formation of products **7**. However, in some cases, the hydrogenated by-products **9b,p,q,r** were isolated. In some cases, the products were formed (tlc control) but could not be isolated in pure form. Reduction

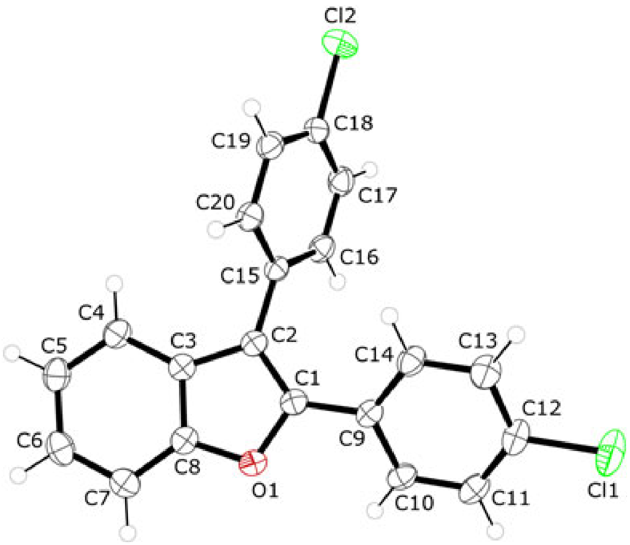


Figure 3. Crystal structure of **7h**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

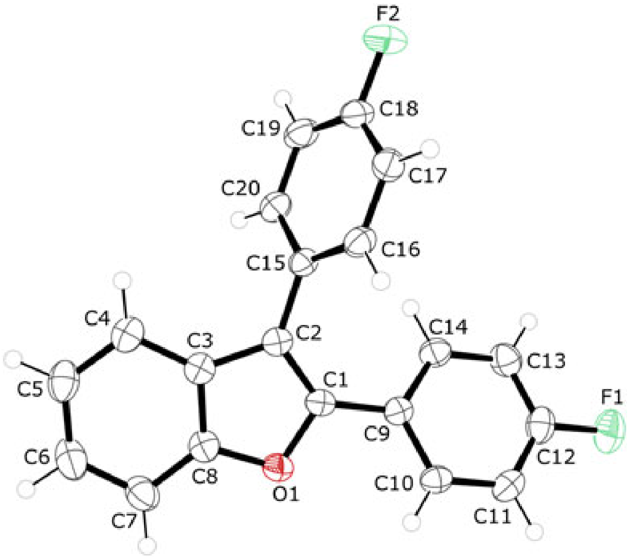
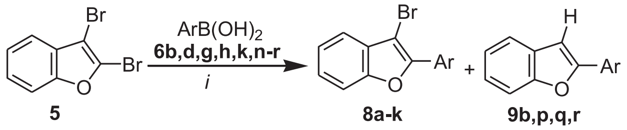


Figure 4. Crystal structure of **7i**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scheme 2. Synthesis of **8a–k**. Reagents and conditions: (*i*) **6b,d,g,h,k,n-r** (1.0 equiv.), Pd(PPh_3)$_4$ (5 mol-%), aq. K_2CO_3 (2 M), dioxane, 70°C, 6 h.



at C-3 was probably the reason for the fact that products **8j** and **8k** could be isolated only in moderate yields.

The structure of compound **8a** was unambiguously established by NOESY and HMBC experiments (Figure 5).

Table 2

Synthesis of 2-aryl-3-bromobenzofuran **8a-k**.

8,9	**6**	Ar	% (**8**) [a]	% (**9**) [a]
a	**b**	4-MeC_6H_4	93	4
b	**d**	4-EtC_6H_4	86	0
c	**g**	3-ClC_6H_4	73	0
d	**h**	4-ClC_6H_4	90	0
e	**j**	4-(CF_3)C_6H_4	79	0
f	**k**	2-(MeO)C_6H_4	87	0
g	**o**	4-(MeO)C_6H_4	70	0
h	**p**	2,6-(MeO)$_2C_6H_3$	89	0
i	**n**	3,5-$Me_2C_6H_3$	79	0
j	**q**	3-PhC_6H_4	67	23
k	**r**	2-Thienyl	63	15

[a] Yields of isolated products.

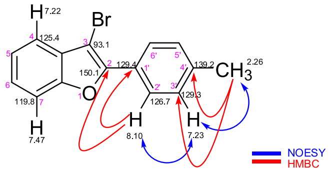


Figure 5. NOESY and HMBC correlations of compound **8a** (single headed arrow, HMBC; double headed arrow, NOESY). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scheme 3. Synthesis of **10a,b**. Reagents and conditions: (*i*) 1) **6b** (1.0 equiv.), Pd(PPh_3)$_4$ (5 mol-%), aq. K_2CO_3 (2 M), dioxane, 70°C, 6 h; 2) **6i,s** (1.0 equiv.), 80°C, 6 h.

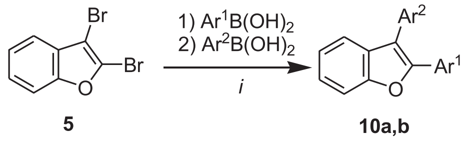


Table 3

One-pot and two-step syntheses of 2,3-diarylbenzofuran **10a,b**.

10	Ar^1	Ar^2	% (**10**) [a]
a	4-MeC_6H_4	3-(MeO)C_6H_4	76
b	4-MeC_6H_4	4-FC_6H_4	82

[a] Yields of isolated products.

The sequential addition of two different arylboronic acids in a one-pot procedure allowed for the direct synthesis of 2,3-diarylbenzofurans **10a,b** containing two different aryl groups (Scheme 3, Table 3). The yields of the products were significantly higher when the reactions were carried out following the one-pot procedure without isolation of the monoarylated product. The structure of **10b** was previously confirmed by X-ray crystal structure analysis [17].

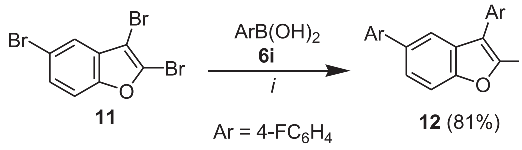
The Suzuki reaction of 2,3,5-tribromobenzofuran (**11**) with 3.0 equivalents of 4-fluorophenylboronic acid (**6i**) provided the triarylbenzofuran **12** in 81% yield (Scheme 4).

The reaction of **11** with one equivalent of 4-tolylboronic acid afforded 3,5-dibromo-2-arylbenzofuran **13** in 79% yield and with very good site-selectivity (Scheme 5). Attempts to prepare diarylbenzofurans by reaction of **11** with 2.0 equiv. of arylboronic acids resulted in the formation of complex mixtures under various conditions. This result suggests that the reactivity of carbon atoms C-3 and C-5 is similar under the reaction conditions studied.

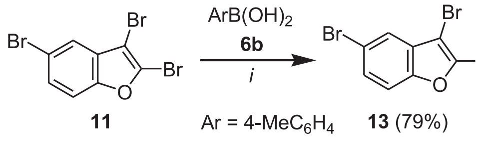
The structure of **13** was confirmed by 2D NMR. The aromatic protons H-2'/H-6' resonating at δ_H 7.96 (d, $J = 8.6$ Hz) showed clear HMBC correlations with C-2 resonating at δ_C 151.8. Furthermore, H-2'/H-6' did not show HMBC correlation with C-3. No NOESY correlation was observed with H-4 resonating at δ_H 7.20. All these facts revealed that the tolyl moiety is connected with C-2 (Figure 6).

In conclusion, 2,3-diarylbenzofurans were prepared by Suzuki–Miyaura reactions of 2,3-dibromobenzofuran with two equivalents of boronic acids. The reaction with one equivalent of arylboronic acids resulted in site-selective formation of 2-aryl-3-bromobenzofurans. 2,3-Diarylbenzofurans containing two different aryl groups were prepared from 2,3-dibromobenzofuran in a one-pot protocol by sequential addition of two different boronic acids. Hydrogenated products were also isolated, which can explain the drop of yields in specific cases. A 2,3,5-triarylbenzofuran and a 2-aryl-3,5-dibromobenzofuran were prepared from 2,3,5-tribromobenzofuran.

Scheme 4. Synthesis of **12**. Reagents and conditions: (*i*) **6i** (3.0 equiv.), $Pd(PPh_3)_4$ (5 mol-%), aq. K_2CO_3 (2 M), dioxane, 90°C, 8 h.



Scheme 5. Synthesis of **13**. Reagents and conditions: (*i*) **6b** (1.0 equiv.), $Pd(PPh_3)_4$ (5 mol-%), aq. K_2CO_3 (2 M), dioxane, 70°C, 4 h.



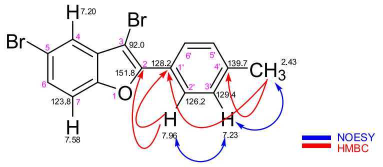


Figure 6. NOESY and HMBC correlations of compound **13** (single headed arrow, HMBC; double headed arrow, NOESY). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EXPERIMENTAL

General procedure for the synthesis of 7a–n, 8a–k, 10a–b, 12, and 13. The reaction was carried out in a pressure tube. To a dioxane suspension (5 mL) of **5** or **11** (1.0 mmol), Pd $(PPh_3)_4$ (58 mg, 5 mol-%, 0.05 mmol), and the arylboronic acid (**6**) (1.0 mmol per coupling) was added an aqueous solution of K_2CO_3 (2 M, 1 mL). The mixture was heated at the indicated temperature (70–80°C) under an argon atmosphere for the indicated period of time (6–8 h). The reaction mixture was diluted with water and extracted with CH_2Cl_2 (3×25 mL). The combined organic layers were dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography (silica gel, EtOAc/heptanes).

2,3-Diphenylbenzofuran (7a). Compound **7a** was prepared from **5** (276 mg 1.0 mmol) and phenylboronic acid (244 mg, 2.0 mmol) as a white solid (251 mg, 93%). Reaction temperature: 80°C, mp 84–85°C. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.13$–7.49 (m, 12H, ArH), 7.57–7.60 (m, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 111.1$ (CH), 117.5 (C), 120.0, 122.9, 134.7, 127.0, 127.6, 128.3, 128.4, 129.0, 129.8 (CH), 130.2, 130.7, 132.9, 150.5, 154.0 (C). IR (KBr): $\nu = 3062$, 3027, 2921, 2852, 1602, 1568, 1558, 1498, 1487, 1472 (w), 1455, 1441 (m), 1369, 1340, 1315, 1291 (w), 1255, 1203, 1188, 1110, 1079, 1062, 1022, 1008, 960, 917, 891, 836, 828 (m), 764, 746, 700, 692, 676 (s), 621 (m), 608 (s), 582, 561 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 270 ($[M]^+$, 100), 269 (19), 255 (10), 241 (21), 239 (22), 134 (9), 120 (9). HRMS (EI, 70 eV): calcd for $C_{20}H_{14}O$ $[M]^+$: 270.10392; found: 270.10393.

2,3-Di-p-tolylbenzofuran (7b). Compound **7b** was prepared from **5** (276 mg, 1.0 mmol) and *p*-tolylboronic acid (272 mg, 2.0 mmol) as a colorless highly viscous oil (274 mg, 92%). Reaction temperature: 80°C. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.27$ (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 7.05 (d, 2H, $J = 8.5$ Hz, ArH), 7.12–7.26 (m, 4H, ArH), 7.32 (d, 2H, $J = 8.1$ Hz, ArH), 7.40–7.51 (m, 4H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 21.4$ ($2CH_3$), 111.0 (CH), 116.8 (C), 120.0, 122.8, 124.4, 127.0 (CH), 128.0 (C), 129.1, 129.6, 129.7 (CH), 129.9, 130.5, 137.2, 138.3, 150.7, 153.9 (C). IR (KBr): $\nu = 3025$ (w), 2919, 2853 (m), 2731 (w), 1906, 1770, 1611 (w), 1519, 1500 (m), 1451 (s), 1371, 1289 (m), 1255 (s), 1205, 1178, 1109 (m), 1065 (s), 1019, 986 (m), 964 (s), 898, 838 (m), 816 (s), 785, 760 (m), 743, 719 (s), 649, 636 (m), 600 (s), 566 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 298 ($[M]^+$, 100), 268 (9), 255 (9). HRMS (EI, 70 eV): calcd for $C_{22}H_{18}O$ $[M]^+$: 298.13522; found: 298.13549.

2,3-Di-o-tolylbenzofuran (7c). Compound **7c** was prepared from **5** (276 mg, 1.0 mmol) and 2-methylphenylboronic acid (272 mg, 2.0 mmol) as a colorless highly viscous oil (241 mg, 81%). Reaction temperature: 80°C. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.13$ (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 7.12–7.20 (m, 1H, ArH), 7.28–7.49 (m, 10H, ArH), 7.64 (brd, 1H, $J = 8.7$ Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 20.1$, 20.6 (CH_3), 111.3 (CH), 118.4 (C), 120.5, 122.8, 124.3, 125.6, 126.0, 127.8, 129.0 (CH), 129.7 (C), 130.5, 130.6, 130.8, 131.0 (CH), 131.9, 137.2, 137.5, 152.6, 154.4 (C). IR (KBr): $\nu = 3058$, 3017, 2953, 2923, 2859 (w), 1479 (m), 1450 (s), 1379, 1364, 1294, 1280 (m), 1252 (s), 1207, 1196, 1114, 1066, 1055, 1036, 1008 (m), 961 (s), 945, 928, 899, 835 (m), 761, 743, 723 (s), 683, 666 (m), 616 (s), 590, 576, 549 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 298 ($[M]^+$, 100), 268 (9), 255 (9). HRMS (EI, 70 eV): calcd for $C_{22}H_{18}O$ $[M]^+$: 298.13522; found: 298.13515.

2,3-Bis(4-ethylphenyl)benzofuran (7d). Compound **7d** was prepared from **5** (276 mg, 1.0 mmol) and 4-ethylphenylboronic acid (300 mg, 2.0 mmol) as a colorless highly viscous oil (280 mg, 86%). Reaction temperature: 80°C. ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 1.30$ (t, 3H, $J = 7.4$ Hz, CH$_3$), 1.38 (t, 3H, $J = 7.4$ Hz, CH$_3$), 2.69 (q, 2H, $J = 7.8$ Hz, CH$_2$), 2.81 (q, 2H, $J = 7.8$ Hz, CH$_2$), 7.19–7.40 (m, 6H, ArH), 7.48–7.69 (m, 6H, ArH). ^{13}C NMR (62.9 MHz, CDCl$_3$): $\delta = 15.3$, 15.4 (CH$_3$), 28.7 (2CH$_2$), 111.0 (CH), 116.9 (C), 120.0 (CH), 120.8 (C), 122.8, 124.4, 127.0, 128.0, 128.3, 129.7 (CH), 130.2, 130.6, 143.5, 144.6, 150.7, 154.0 (C). IR (KBr): $\nu = 3025$ (w), 2962 (m), 2929, 2871, 1909, 1667, 1592 (w), 1519, 1499 (m), 1451 (s), 1413, 1372, 1337, 1289, 1256, 1207, 1177, 1109 (m), 1067 (s), 1048, 1018, 1008 (m), 963 (s), 928, 899 (m), 834 (s), 761 (m), 743(s), 691, 660, 647, 633 (m), 603 (s), 582, 557 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 326 ([M]$^+$, 100), 311 (34), 148 (9). HRMS (EI, 70 eV): calcd for C$_{24}$H$_{22}$O [M]$^+$: 326.16652; found: 326.16642.

2,3-Bis(4-tert-butylphenyl)benzofuran (7e). Compound **7e** was prepared from **5** (276 mg, 1.0 mmol) and 4-*tert*-butylphenylboronic acid (356 mg, 2.0 mmol) as a white crystalline solid (336 mg, 88%). Reaction temperature: 80°C, mp 121-122°C. ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 1.37$ (s, 9H, 3CH$_3$), 1.46 (s, 9H, 3CH$_3$), 7.23–7.35(m, 2H, ArH), 7.39 (d, 2H, $J = 8.7$ Hz, ArH), 7.51–7.60 (m, 6H, ArH), 7.71 (d, 2H, $J = 8.7$ Hz, ArH). ^{13}C NMR (62.9 MHz, CDCl$_3$): $\delta = 31.3$, 31.5 (3CH$_3$), 34.7, 34.8 (C), 111.0 (CH), 116.9 (C), 120.1, 122.7, 124.4, 125.4, 125.8, 126.6 (CH), 128.1 (C), 129.4, (CH), 129.9, 130.7, 150.4, 150.5, 151.4, 153.9 (C). IR (KBr): $\nu = 3035$ (w), 2960 (m), 2902, 2866, 1589 (w), 1520, 1497, 1472 (m), 1452 (s), 1408, 1393, 1362, 1267 (m), 1257 (s), 1209 (m), 1106 (s), 1064, 1015 (m), 965 (s), 907, 901 (m), 836 (s), 821 (m), 746, 739 (s), 625, 596, 582 (m), 547 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 382 ([M]$^+$, 100), 368 (26), 367 (89), 176 (14), 148 (23), 57 (12). HRMS (EI, 70 eV): calcd for C$_{28}$H$_{30}$O [M]$^+$: 382.22912; found: 382.22904.

2,3-Bis(2-chlorophenyl)benzofuran (7f). Compound **7f** was prepared from **5** (276 mg 1.0 mmol) and 2-chlorophenylboronic acid (312 mg, 2.0 mmol) as a white solid (294 mg, 87%). Reaction temperature: 80°C, mp 104–105°C. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.06$–7.19 (m, 6H, ArH), 7.23–7.38 (m, 5H, ArH), 7.48 (dt, $J = 0.7$, 8.1 Hz, 1H, ArH). ^{13}C NMR (62.9 MHz, CDCl$_3$): $\delta = 111.5$ (CH), 118.1 (C), 121.0, 123.0, 124.9, 126.6, 126.9 (CH), 128.7 (C), 129.2 (CH), 129.9 (C), 130.1, 130.3, 130.4 (CH), 131.4 (C), 132.2, 132.3 (CH), 134.1, 134.3, 150.4, 154.5 (C). IR (KBr): $\nu = 3056$, 1631, 1581, 1564, 1537, 1513 (w), 1486, 1448, 1438, 1369, 1295, 1271, 1245, 1204, 1161, 1111, 1088, 1061, 1041, 1030, 1008, 966, 949, 905, 829 (m), 760, 748, 736, 724, 713 (s), 697, 664, 658, 613, 570 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 342 ([M, 2Cl^{37}]$^+$, 02), 340 ([M, Cl^{37}, Cl^{35}]$^+$, 63), 338 ([M, 2Cl^{35}]$^+$, 94), 302 (11), 275 (11), 269 (22), 268 (100), 240 (11), 239 (47), 237 (16), 134 (32), 120 (27), 119 (20). HRMS (EI, 70 eV): calcd for C$_{20}$H$_{12}$Cl$_2$O [M]$^+$: 338.02597; found: 338.02554.

2,3-Bis(3-chlorophenyl)benzofuran (7g). Compound **7g** was prepared from **5** (276 mg 1.0 mmol) and 2-chlorophenylboronic acid (312 mg, 2.0 mmol) as a white solid (263 mg, 78%). Reaction temperature: 80°C, mp 76–78°C. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.14-7.19 (m, 4H, ArH), 7.24–7.47 (m, 2H, ArH), 7.55–7.75 (m, 4H, ArH), 8.08–8.13 (m, 2H, ArH). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ 102.4, 111.3 (CH), 121.1 (C), 122.9, 123.1, 124.8, 124.9, 126.9, 128.9, 129.8, 130.0, 132.0 (CH), 132.2 (C), 134.9 (CH), 138.3, 149.3, 153.7, 154.0, 154.3, 155.0 (C). IR (KBr) $\nu = 2994$, 2976, 2933 (w), 1600, 1451 (s), 1353, 1296, 1145 (m), 1147, 1064 (s), 997, 884 (m), 798, 712 (s), 626, 549 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = ([M, 2Cl^{37}]$^+$, 03), 340 ([M, Cl^{37}, Cl^{35}]$^+$, 61), 338 ([M]$^+$, 100), 254 (17), 209 (18). HRMS (EI, 70 eV): calcd for C$_{20}$H$_{12}$Cl$_2$O [M]$^+$: 338.02597; found: 338.02545.

2,3-Bis(4-chlorophenyl)benzofuran (7h). Compound **7h** was prepared from **5** (276 mg, 1.0 mmol) and 4-chlorophenylboronic acid (312 mg, 2.0 mmol) as a white crystalline solid (281 mg, 83%). Reaction temperature: 80°C, mp 102–103°C. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.15$–7.39 (m, 9H, ArH), 7.45–7.51 (m, 3H, ArH). ^{13}C NMR (75.5 MHz, CDCl$_3$): $\delta = 111.3$ (CH), 101.8, 116.8 (C), 119.9, 123.3, 125.2, 128.2, 128.5, 129.2 (CH), 129.8, 133.8, 134.5, 149.7, 154.0 (C), 131.0 (CH). IR (KBr): $\nu = 3078$, 3054, 3037, 2923, 2852 (w), 1581 (m), 1558 (w), 1497, 1484 (m), 1449 (s), 1401, 1373, 1289 (w), 1253, 1201, 1174 (m), 1089, 1066, 1011, 963 (s), 945, 930, 919, 899 (m), 832, 821, 811 (s), 760 (m), 749, 742, 720 (s), 682, 646, 631, 624, 616, 582 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = ([M, 2Cl^{37}]$^+$, 04), 340 ([M, Cl^{37}, Cl^{35}]$^+$, 64), 338 ([M]$^+$, 100), 302 (11), 268 (27), 239 (29), 134 (20), 120 (20), 119 (12). HRMS (EI, 70 eV): calcd for C$_{20}$H$_{12}$Cl$_2$O [M]$^+$: 338.02597; found: 338.02559.

2,3-Bis(4-fluorophenyl)benzofuran (7i). Compound **7i** was prepared from **5** (276 mg, 1.0 mmol) and 4-fluorophenylboronic acid (280 mg, 2.0 mmol) as a white crystalline solid (248 mg, 81%). Reaction temperature: 80°C, mp 80–81°C. ^{1}H NMR (250 MHz, CDCl$_3$): $\delta = 6.88$–6.95 (m, 2H, ArH), 7.03–7.27 (m, 4H, ArH), 7.31–7.64 (m, 6H, ArH). ^{19}F NMR (282.2 MHz, CDCl$_3$): $\delta = -115.3$, -113.1. ^{13}C NMR (62.9 MHz, CDCl$_3$): $\delta = 111.2$ (CH), 115.6 (d, $J_{\mathrm{F,C}} = 21.2$ Hz, CH), 116.2 (d, $J_{\mathrm{F,C}} = 21.6$ Hz, CH), 119.8, 123.1, 124.9 (CH), 127.7 (d, $J_{\mathrm{F,C}} = 3.3$ Hz, C), 128.6 (d, $J_{\mathrm{F,C}} = 3.5$ Hz, C), 128.8 (d, $J_{\mathrm{F,C}} = 8.2$ Hz, CH), 130.1 (C), 131.4 (d, $J_{\mathrm{F,C}} = 8.0$ Hz, CH), 149.8, 153.9 (C), 162.4 (d, $J_{\mathrm{F,C}} = 247.2$ Hz, CF), 162.5 (d, $J_{\mathrm{F,C}} = 249.5$ Hz, CF). IR (KBr): $\nu = 3067$, 3045, 3016, 2925, 2852 (w), 1594, 1582, 1515 (m), 1498, 1450 (s), 1409, 1374, 1338, 1302, 1254 (m), 1223 (s), 1205, 1161, 1155, 1109, 1099, 1088, 1068, 1014, 1009, 965, 934 (m), 836, 821, 814 (s), 802, 794 (m), 749 (s), 720, 686, 665, 627 (m), 598 (s), 580 (m), 564, 536 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 306 ([M]$^+$, 100), 305 (9), 277 (18), 275 (13). HRMS (EI, 70 eV): calcd for C$_{20}$H$_{12}$F$_2$O [M]$^+$: 306.08507; found: 306.08454.

2,3-Bis(4-(trifluoromethyl)phenyl)benzofuran (7j). Compound **7j** was prepared from **5** (276 mg, 1.0 mmol) and 4-(trifluoromethyl)phenylboronic acid (380 mg, 2.0 mmol) as a white crystalline solid (296 mg, 73%). Reaction temperature: 80°C, mp 166–168°C. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.07$–7.24 (m, 4H, ArH), 7.24–7.50 (m, 2H, ArH), 7.57-7.81 (m, 4H, ArH), 8.04–8.24 (m, 2H, ArH). ^{19}F NMR (282.2 MHz, CDCl$_3$): $\delta = -62.8$, -63.0. ^{13}C NMR (75.5 MHz, CDCl$_3$): $\delta = 112.2$, 112.5, 115.9 (CH), 118.1 (C), 118.2, 120.6 (CH), 121.3(q, $J_{F,C} = 3.7$ Hz, CH), 123.9 (q, $J_{F,C} = 3.6$ Hz, CH), 124.3 (q, $J_{F,C} = 271.5$ Hz, CF$_3$), 124.9 (q, $J_{F,C} = 272.1$ Hz, CF$_3$), 126.8 (CH), 128.2 (q, $J_{F,C} = 31.5$ Hz, C-CF$_3$), 128.7 (C), 128.8 (q, $J_{F,C} = 32.0$ Hz, C-CF$_3$), 130.4, 151.7, 155.3, 158.9 (C). IR (KBr): $\nu = 3001$, 2955 (w), 1672 (w), 1609, 1580 (m), 1460, 1402 (s), 1387, 1250 (w), 1213, 1194 (s), 1110, 1026, 963 (m), 860, 774 (w), 751 (s), 667, 524 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 406 ([M]$^+$, 100), 290 (09), 185 (18). HRMS (EI, 70 eV): calcd for C$_{22}$H$_{12}$F$_6$O [M]$^+$: 406.07293; found: 406.07288.

2,3-Bis(2-methoxyphenyl)benzofuran (7k). Compound **7k** was prepared from **5** (276 mg 1.0 mmol) and 2-methoxyphenylboronic acid (304 mg, 2.0 mmol) as a white solid (270 mg, 82%). Reaction temperature: 80°C, mp 78–79°C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.48$ (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 6.90 (d, 1H, $J = 8.3$ Hz, ArH), 6.97–7.06 (m, 3H, ArH), 7.26–7.40 (m, 5H, ArH), 7.56–7.64 (m, 3H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 55.0$, 55.2 (OCH_3), 111.0, 111.1, 111.2 (CH), 115.9 (C), 120.4, 120.5 (CH), 120.9 (C), 121.0, 122.4 (CH), 123.0 (C), 124.0, 128.5 (CH), 129.7 (C), 130.1, 130.7, 130.9 (CH), 149.9, 154.5, 157.0, 157.1 (C). IR (KBr): $\nu = 3062$, 2998, 2934 (w), 2833 (m), 1600, 1586, 1499, 1486 (m), 1459, 1447, 1433 (s), 1368 (w),1289 (m), 1242 (s), 1203, 1194, 1178, 1161, 1115, 1054, 1041 (m), 1024, 962 (s), 907, 899, 793, 785 (m), 743 (s), 696, 666, 647, 602, 615, 591, 570, 559, 536 (m) cm^{-1} GC-MS (EI, 70 eV): m/z (%) = 330 ([M]$^+$, 100), 271 (9), 255 (14), 121 (12). HRMS (EI, 70 eV): calcd for $C_{22}H_{18}O_3$ [M]$^+$: 330.12505; found: 330.12479.

2,3-Bis(4-methoxyphenyl)benzofuran (7l). Compound **7l** was prepared from **5** (276 mg 1.0 mmol) and 4-methoxyphenylboronic acid (304 mg, 2.0 mmol) as a white solid (247 mg, 75%). Reaction temperature: 80°C, mp 157–158°C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.75$–3.77 (s, 6H, 2OCH_3), 6.91–6.80 (m, 2H, ArH), 7.17–7.15 (m, 2H, ArH), 7.48–7.38 (m, 4H, ArH), 7.72 (d, 2H, $J = 7.5$ Hz, ArH), 8.04 (d, 2H, $J = 7.4$ Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): = 54.3, 54.4 (CH_3O), 111.0, 113.2, 114.1, 114.2 (CH), 114.3 (C), 120.6 (CH), 122.8, 123.7 (C), 126.4 (CH), 127.7 (C), 128.3, 132.5 (CH), 153.7, 155.0, 157.7, 159.0 (C). IR (KBr): $\nu = 3003$, 2957, 2912 (w), 1604, 1496, 1451 (s), 1353, 1296 (m), 1243, 1175, 1039 (s), 997, 919, 884 (m), 822, 798, 742 (s), 710, 660 (w), 626, 549 (m) cm^{-1}. GCMS (EI, 70 eV): m/z (%) = 330 ([M]$^+$, 100), 315 (21). HRMS (EI, 70 eV): calcd for $C_{22}H_{18}O_3$: [M]$^+$: 330.12505; found 330.124903.

2,3-Bis(2,5-dimethoxyphenyl)benzofuran (7m). Compound **7m** was prepared from **5** (276 mg 1.0 mmol) and 2,5-dimethoxyphenylboronic acid (364 mg, 2.0 mmol) as a light brown solid (331 mg, 85%). Reaction temperature: 80°C, mp 79–80°C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.46$ (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 6.82–6.96 (m, 5H, ArH), 7.18–7.38 (m, 3H, ArH), 7.56–7.63 (m, 2H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 55.7$, 55.8, 55.9 (OCH_3), 111.2, 112.3, 112.7, 113.5, 115.6, 115.8 (CH), 115.9 (C), 116.6, 121.0 (CH), 121.3 (C), 122.5 (CH), 123.8 (C), 124.1 (CH), 129.5, 149.8, 151.4, 151.5, 153.4, 153.6, 154.4 (C). IR (KBr): $\nu = 3057$, 2995, 2934, 2903 (w), 2831 (m), 1606, 1581 (w), 1492, 1453 (s), 1421 (m), 1359 (w), 1306, 1293, 1270, 1245 (m), 1216, 1175 (s), 1160 (m), 1042, 1022 (s), 991, 927, 909, 873, 861, 849, 799, 768 (m), 730 (s), 691, 647, 626, 611, 573, 556 (m) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 390 ([M]$^+$, 100), 345 (15), 344 (47), 301 (14), 172 (9). HRMS (EI, 70 eV): calcd for $C_{24}H_{22}O_5$ [M]$^+$: 390.14618; found: 390.14603.

2,3-Bis(3,5-dimethylphenyl)benzofuran (7n). Compound **7n** was prepared from **5** (276 mg 1.0 mmol) and 3,5-dimethylphenylboronic acid (302 mg, 2.0 mmol) as a white solid (258 mg, 79%). Reaction temperature: 80°C, mp 106–107°C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.18$ (s, 6H, 2CH_3), 2.27 (s, 6H, 2CH_3), 6.85 (s, 1H, ArH), 6.85 (s, 1H, ArH), 6.02 (s, 2H, ArH), 7.11–7.20 (m, 4H, ArH), 7.41–7.47 (m, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 21.3$, 21.4 (2CH_3), 111.0 (CH), 117.5 (C), 120.1, 120.7, 124.4, 124.7, 127.4, 129.2, 130.0 (CH), 130.4, 130.6, 132.7, 167.8, 168.3, 150.6, 153.9 (C). IR (KBr): $\nu = 3011$, 2913, 2855, 2730, 2142 (w), 1600, 1582 (m), 1566, 1503 (w), 1454, 1377, 1338, 1259, 1234, 1192, 1182, 1169, 1159, 1097, 1054, 1037, 1009 (m), 976, 947 (w), 924, 896 885, 873 (m), 856, 845 (s), 811, 757 (m), 738, 703, 680 (s), 628 (m), 591, 541, 534 (w) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 326 ([M]$^+$, 100), 296 (5), 252 (4). HRMS (EI, 70 eV): calcd for $C_{24}H_{22}O$ [M]$^+$: 326.16652; found: 326.16664.

Synthesis of 2-aryl-3-bromobenzofurans 8a–k

3-Bromo-2-p-tolylbenzofuran (8a). Compound **8a** was prepared from **5** (276 mg, 1.0 mmol) and *p*-tolylboronic acid (136 mg, 1.0 mmol) as a white solid (266 mg, 93%). Reaction temperature: 70°C, mp 81–82°C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.26$ (s, 3H, CH_3), 7.03–7.26 (m, 4H, ArH), 7.51–7.60 (m, 2H, ArH), 8.10 (d, 2H, $J = 8.3$ Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 21.5$ (CH_3), 93.1 (C), 111.2, 119.8, 123.4, 125.4, 126.7, 129.3 (CH), 129.4, 139.2, 150.6, 153.1 (C). IR (KBr): $\nu = 3030$, 2967, 2917, 2858 (w), 1502 (m), 1450 (s), 1412, 1342, 1325, 1303, 1271, 1252, 1203, 1189, 1175, 1107 (m), 1073 (s), 1018, 1007 (m), 985 (s), 932, 889, 830 (m), 816 (s), 785 (m), 739 (s), 712, 653, 632, 574, 537 (m) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 288 ([M, ^{81}Br]$^+$, 99), 286 ([M, ^{79}Br]$^+$, 100), 207 (10), 179 (30), 178 (33), 152 (10), 89 (11), 76 (9), 237 (16), 134 (32), 120 (27), 119 (20). HRMS (EI, 70 eV): calcd for $C_{15}H_{11}$Br O [M, ^{79}Br]$^+$: 285.99878; found: 285.99869.

3-Bromo-2-(4-ethylphenyl)benzofuran (8b). Compound **8b** was prepared from **5** (276 mg 1.0 mmol) and 4-ethylphenylboronic acid (150 mg, 1.0 mmol) as a white solid (258 mg, 86%). Reaction temperature: 70°C, mp 89–90°C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.19$ (t, 1H, $J = 7.6$ Hz, CH_3), 2.62 (q, 2H, $J = 7.6$ Hz, CH_2), 7.18-7.28 (m, 4H, ArH), 7.38-7.48 (m, 2H, ArH), 8.00 (d, 2H, $J = 8.4$ Hz, CH_3). ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 15.4$ (CH_3), 28.8 (CH_2), 93.1 (C), 111.2, 119.7, 123.4, 125.3, 126.8 (CH), 127.0 (C), 128.1 (CH), 129.7, 145.5, 150.6, 153.1 (C). IR (KBr): $\nu = 3028$ (w), 2962, 2927 (m), 2871, 2422, 1907, 1771, 1714, 1666, 1612, 1590 (w), 1502 (m), 1449 (s), 1416, 1345, 1319, 1297, 1272, 1254, 1205, 1185, 1108 (m), 1073 (s), 1049, 1018, 1006 (m), 985 (s), 926, 890 (m), 831, 738 (s), 659, 642, 631, 579, 552 (m) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 302 ([M]$^+$, ^{81}Br, 04), 300 ([M, ^{79}Br]$^+$, 05), 298 (100), 255 (11), 178 (9). HRMS (EI, 70 eV): calcd for $C_{16}H_{13}$BrO [M, ^{79}B]$^+$: 300.015065; found: 300.015364.

3-Bromo-2-(3-chlorophenyl)benzofuran (8c). Compound **8c** was prepared from **5** (276 mg 1.0 mmol) and 3-chlorophenylboronic acid (156 mg, 1.0 mmol) as a white solid (224 mg, 73%). Reaction temperature: 70°C, mp 200–202°C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.30$–7.11 (m, 2H, ArH), 7.75–7.42 (m, 4H, ArH), 8.05-8.04 (m, 2H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 99.0$ (C), 111.2, 119.7, 123.6, 125.9, 128.9, 130.5, 131.7, 134.2 (CH), 139.8, 149.2, 153.0, 153.5, 152.4 (C). IR (KBr) $\nu = 2987$, 2971, 2903 (w), 1601, 1448 (s), 1347, 1277, 1174 (m), 1147, 1064 (s), 990, 891 (m), 798, (s), 666, 524 (m) cm^{-1}. GC-MS (EI, 70 eV): m/z (%) = 310 ([M, ^{81}Br, ^{37}Cl]$^+$, 12), 308 ([M, ^{37}Cl ^{79}Br or ^{35}Cl^{81}Br]$^+$, 100), 306 ([M, ^{79}Br, ^{35}Cl]$^+$, 73), 267 (21). HRMS (EI, 70 eV): calcd for $C_{14}H_8$BrClO [M, ^{79}Br]$^+$: 305.094416; found: 305.094221.

3-Bromo-2-(4-chlorophenyl)benzofuran (8d). Compound **8d** was prepared from **5** (276 mg, 1.0 mmol) and 4-chlorophenylboronic acid (156 mg, 1.0 mmol) as a white solid (276 mg, 90%). Reaction temperature: 70°C, mp 114–115°C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.33$–7.60 (m, 6H, ArH), 8.14 (d, 2H, $J = 8.9$ Hz, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 94.3$ (C), 111.3, 120.0, 123.6, 125.9, 127.9 (CH), 128.0 (C), 128.9

(CH), 134.9, 149.2, 153.1 129.4 (C). IR (KBr) $v = 3066$ (w), 1889, 1769, 1714, 1594, 1556 (w), 1485, 1474 (m), 1449 (s), 1416, 1403, 1342, 1320, 1300, 1268, 1249, 1201 (m), 1177, 1111 (w), 1093, 1068 (s), 1011 (m), 986 (s), 928, 903, 889 (m), 822 (s), 814 (m), 737, 721 (s), 758, 648, 625, 600, 573 (m) cm^{-1}. GC-MS (EI, 70 eV) *m/z* (%) = 310 ([M, ^{81}Br, ^{37}Cl]$^+$, 11), 308 ([M, ^{37}Cl ^{79}Br or ^{35}Cl^{81}Br]$^+$, 100), 306 ([M, ^{79}Br, ^{35}Cl]$^+$, 77), 201 (12), 199 (36), 164 (15), 163 (27), 99 (10), 82 (9). HRMS (EI, 70 eV): calcd for $C_{14}H_8BrClO$ [M, ^{79}Br, ^{35}Cl]$^+$: 305.94416; found: 305.94395.

3-Bromo-2-(4-(trifluoromethyl)phenyl)benzofuran (8e). Compound **8e** was prepared from **5** (276 mg, 1.0 mmol) and 4-(trifluoromethyl)phenylboronic acid (190 mg, 1.0 mmol) as a white solid (269 mg, 79%). Reaction temperature: 70°C, mp 140-142°C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.90$–6.91 (m, 1H, ArH), 7.03–7.07 (m, 2H, ArH), 7.16–7.18 (m, 3H, ArH), 7.84–7.90 (m, 2H, ArH). ^{19}F NMR (282.2 MHz, $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 91.7$ (C), 112.5 (CH), 115.8 (C), 116.2, 124.3 (CH), 124.3 (q, $J_{F,C} = 272.9$ Hz, CF_3), 125.9 (CH), 126.0 (q, $J_{F,C} = 3.8$ Hz, CH), 128.37 (q, $J_{F,C} = 32.3.0$ Hz, C-CF_3), 128.5 (CH), 153.8, 154.3, 158.6 (C). IR (KBr) $v = 3077$, 2921, 2850 (w), 1609, 1580 (m), 1482, 1452 (s), 1392, 1255 (w), 1213 (s), 1154, 1108, 1048, 963 (m), 862, 790 (w), 749 (s), 667, 550 (w) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 341 ([M, ^{81}Br]$^+$, 99), 339 ([M, ^{79}Br]$^+$, 100), 227 (34), 213 (10), 132 (10), 123 (41), 95 (20). HRMS (EI, 70 eV): calcd for $C_{15}H_8BrF_3O$ [M, ^{79}Br]$^+$: 339.97106; found: 339.97133.

3-Bromo-2-(2-methoxyphenyl)benzofuran (8f). Compound **8f** was prepared from **5** (276 mg, 1.0 mmol) and 2-methoxyphenylboronic acid (152 mg, 1.0 mmol) as white solid (263 mg, 87%). Reaction temperature: 70°C, mp 86–87°C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.77$ (s, 3H, OCH_3), 6.91–7.00 (m, 2H, ArH), 7.19–7.24 (m, 2H, ArH), 7.24–7.28 (m, 2H, ArH), 7.31–7.33 (m, 2H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 55.7$ (OCH_3), 96.7 (C), 111.5, 111.6 (CH), 118.3 (C), 119.8, 120.5, 123.3, 125.2 (CH), 129.0 (C), 131.4, 131.7 (CH), 150.5, 153.9, 157.7 (C). IR (KBr): $v = 3062$, 3037, 3003, 2959, 2934, 2835 (w), 1610, 1586 (m), 1485 (s), 1461 (m), 1446, 1433 (s), 1313, 1296 (m), 1255, 1243 (s), 1200, 1180, 1162, 1120, 1107, 1073 (m), 1057, 1043, 1023, 984 (s), 932, 891, 827, 781 (m), 739 (s), 667, 636, 588, 554 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 304 ([M, ^{81}Br]$^+$, 84), 302 ([M, ^{79}Br]$^+$, 86), 223 (22), 209 (28), 208 (100), 167 (12), 165 (24), 152 (30), 151 (17). HRMS (EI, 70 eV): calcd for $C_{15}H_{11}BrO_2$ [M, ^{79}Br]$^+$: 301.99369; found: 301.99370.

3-Bromo-2-(4-methoxy phenyl)benzofuran (8g). Compound **8g** was prepared from **5** (276 mg, 1.0 mmol) and 4-methoxyphenylboronic acid (152 mg, 1.0 mmol) as a colorless viscous oil (212 mg, 70%). Reaction temperature: 70°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.80 (s, 3H, OCH_3), 6.94 (d, 2H, $J = 7.5$ Hz, ArH), 7.22–7.24 (m, 1H, ArH), 7.26–7.28 (m, 1H, ArH), 7.31–7.33 (m, 1H, ArH), 7.39–7.47 (m, 1H, ArH), 8.04 (d, 2H, $J = 7.5$ Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 55.4$ (OCH_3), 99.0 (C), 111.1, 114.2 (CH), 119.6 (C), 122.2 (CH), 123.4 (C), 125.1, 126.8, 128.3 (CH), 150.5, 153.0, 160.2 (C). IR (KBr): $v = 2998$, 2946, 2929 (w), 1607 (m), 1500 (s), 1449, 1439, 1306, 1273 (m), 1247, 1175 (s), 1070, 983 (m), 927, 889 (w), 828, 739 (s), 633, 548 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 304 ([M, ^{81}Br]$^+$, 99), 302 ([M, ^{79}Br]$^+$, 100), 207 (39), 134 (08). HRMS (EI, 70 eV): calcd for $C_{15}H_{11}BrO_2$: (M^+, [^{81}Br]): 303.99369; found 303.991943, calcd for (M^+, [^{79}Br]): 301.99369; found 301. 993881.

3-Bromo-2-(2,6-dimethoxyphenyl)benzofuran (8h). Compound **8h** was prepared from **5** (276 mg, 1.0 mmol) and 2,6-dimethoxyphenylboronic acid (182 mg, 1.0 mmol) as a white solid (295 mg, 89%). Reaction temperature: 70°C, mp 79–80°C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.72$ (s, 6H, $2OCH_3$), 6.57 (d, $J = 8.5$, 2H, ArH), 7.11–7.53 (m, 5H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 56.2$ ($2OCH_3$), 98.8 (C), 104.0, 111.6, 119.5 (CH), 120.7 (C), 122.9, 124.7 (CH), 128.7 (C), 132.2 (CH), 154.3, 159.2, 159.7 (C). IR (KBr): $v = 3056$, 3003, 2961, 2936, 2837 (w), 1619, 1587 (m), 1473 (s), 1448 (m), 1431 (s), 1297 (m), 1247 (s), 1202, 1134 (m), 1106 (s), 1050, 1031, 1012, 986, 919, 906 890, 820, 781, 748 (m), 728 (s), 693, 637, 591, 556 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 334 ([M, ^{81}Br]$^+$, 98), 332 ([M, ^{79}Br]$^+$, 100), 238 (29), 237 (16), 223 (78), 165 (9), 152 (11), 147 (42), 139 (16), 131 (20). HRMS (EI, 70 eV): calcd for $C_{16}H_{13}BrO_3$ [M, ^{79}Br]$^+$: 332.00426; found: 332.00332.

3-Bromo-2-(3,5-dimethylphenyl)benzofuran (8i). Compound **8i** was prepared from **5** (276 mg, 1.0 mmol) and 3,5-dimethylphenylboronic acid (150 mg, 1.0 mmol) as a white solid (237 mg, 79%). Reaction temperature: 70°C, mp 95–96°C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.45$ (s, 6H, $2CH_3$), 7.08 (s, 1H, ArH), 7.31–7.41 (m, 2H, ArH), 7.51–7.60 (m, 2H, ArH), 7.82 (s, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 21.5$ ($2CH_3$), 93.6 (C), 111.2, 119.8, 123.4, 124.6, 125.4 (CH), 129.4, 129.7 (C), 130.9 (CH), 138.2, 150.7, 153.1 (C). IR (KBr): $v = 3063$, 3037, 2947 (w), 2916 (m), 2855, 2724, 1925, 1888, 1767, 1740 (w), 1602, 1558 (m), 1451 (s), 1419, 1371, 1343, 1319, 1302, 1263, 1229, 1190, 1176, 1148, 1115, 1099 (m), 1019 (s), 1006, 980, 949, 926, 894, 872, 862 (m), 848 (s), 755 (m), 740, 692 (s), 662, 639, 592, 539, 531 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 302 ([M, ^{81}Br]$^+$, 99), 300 ([M, ^{79}Br]$^+$, 100), 193 (17), 178 (19). HRMS (EI, 70 eV): calcd for $C_{16}H_{13}BrO$ [M, ^{79}Br]$^+$: 300.01443; found: 300.01422.

2-(3-Phenylphenyl)-3-bromobenzofuran (8j). Compound **8j** was prepared from **5** (276 mg, 1.0 mmol) and 3-phenylphenylboronic acid (198 mg, 1.0 mmol) as a white solid (233 mg, 67%). Reaction temperature: 70°C, mp 78–79°C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.22$–7.62 (m, 11H, ArH), 8.08 (dt, 1H, $J = 1.5$, 7.7 Hz, ArH), 8.33 (t, 1H, $J = 1.4$ Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 94.16$ (C), 111.3, 120.0, 123.6, 125.5, 125.6, 125.7, 127.3, 127.7, 127.8, 128.9, 129.1 (CH), 129.6, 130.0, 140.7, 141.7, 150.3, 153.2 (C). IR (KBr): $v = 3053$, 3031 (m), 2918, 2849, 2790, 2682, 2351, 1953, 1894, 1811, 1705, 1674 (w), 1593, 1573, 1472 (m), 1453 (s), 1401, 1341, 1299, 1265, 1198, 1173, 1113 (m), 1071 (s), 1051, 1024, 1007 (m), 988 (s), 893, 843, 810 (m), 757, 741, 690, 671 (s), 640, 613, 577, 569 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 350 ([M, ^{81}Br]$^+$, 99), 348 ([M, ^{79}Br]$^+$, 100), 241 (21), 239 (36), 119 (10). HRMS (EI, 70 eV): calcd for $C_{20}H_{13}BrO$ [M, ^{79}Br]$^+$: 348.01443; found: 348.01420.

3-Bromo-2-(thiophen-2-yl)benzofuran (8k). Compound **8k** was prepared from **5** (276 mg, 1.0 mmol) and thien-2-ylboronic acid (128 mg, 1.0 mmol) as a white solid (175 mg, 63%). Reaction temperature: 70°C, mp 194–195°C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 6.98$–7.02 (m, 1H, ArH), 7.08–7.21 (m, 2H, ArH), 7.27–7.37 (m, 3H, ArH), 7.69 (dd, 1H, $J = 0.8$, 3.7 Hz, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 93.0$ (C), 111.2, 119.6, 123.7, 125.6, 126.6, 127.0, 127.7 (CH), 129.3, 131.3, 147.5, 153.1 (C). IR (KBr): $v = 3097$, 3071, 3034, 3016, 1932, 1895, 1779, 1667, 1551 (w), 1586 (m), 1494, 1471 (w), 1448 (s), 1420, 1362, 1341, 1303, 1270, 1254, 1223, 1206, 1194, 1171, 1148, 1082 (m), 1064, 1031 (s), 1004, 970, 887, 877, 848, 824, 791 (m), 741, 694 (s), 657, 634, 574, 547 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 280 ([M, $^{81}Br]^+$, 100), 278 ([M, $^{79}Br]^+$, 98), 171 (59), 139 (9), 127 (14), 85 (18). HRMS (EI, 70 eV): calcd for $C_{12}H_7BrOS$ [M, $^{79}Br]^+$: 277.93955; found: 277.93989.

2-Phenylbenzofuran (9a). Compound **9a** was obtained as a by-product of **7a** (8 mg, 4%). ^1H NMR (300 MHz, $CDCl_3$): δ = 6.95 (d, *J* = 0.8 Hz, 1H, ArH), 7.12–7.31 (m, 3H, ArH), 7.35–7.53 (m, 4H, ArH), 7.78–7.81 (m, 2H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 101.3, 111.2, 120.9, 122.9, 124.3, 125.0 (CH), 127.5 (C), 128.6, 128.8 (CH), 130.5, 154.9, 154.9 (C). GC-MS (EI, 70 eV): *m/z* (%) = 194 ($[M]^+$, 100), 176 (08). HRMS (EI, 70 eV): calcd for $C_{14}H_{10}O$ $[M]^+$: 194.07361; found: 194.07321.

2-p-Tolylbenzofuran (9b). Compound **9b** was obtained as a by-product of **8b** (9 mg, 4%). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.32 (s, 3H, CH_3), 7.11–7.21 (m, 5H, ArH), 7.41–7.50 (m, 2H, ArH), 7.66–7.70 (m, 2H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.8 (CH_3), 100.0, 110.5, 120.1, 122.2, 123.4, 124.3 (CH), 127.2, 128.7 (C), 128.9 (CH), 138.0, 154.2, 155.6 (C). IR (KBr): ν = 3060, 2953, 2928, 2865, 1923, 1847, 1809, 1771, 1667, 1604, 1575 (w), 1488, 1473 (m), 1449 (s), 1379, 1356, 1311, 1285 (w), 1254 (s), 11207, 1170, 1119, 1107 (m), 1054, 1034 (w), 1017 (s), 920, 885, 803 (m), 760, 744, 737, 718 (s), 662, 614, 572, 555, 530 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 208 ($[M]^+$, 100), 207 (74), 189 (16), 179 (18), 178 (27), 165 (12), 115 (10), 89 (14). HRMS (EI, 70 eV): calcd for $C_{15}H_{12}O$ $[M]^+$: 208.08827; found: 208.088577.

2-o-Tolylbenzofuran (9c). Compound **9c** was obtained as a by-product of **7c** (19 mg, 9%). ^1H NMR (250 MHz, $CDCl_3$): δ = 2.61 (s, 3H, CH_3), 6.92 (s, 1H, ArH), 7.23–7.37 (m, 5H, ArH), 7.53–7.65 (m, 2H, ArH), 7.85–7.89 (m, 1H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.9 (CH_3), 105.1, 111.1, 120.9, 122.8, 124.2, 126.1, 128.2, 128.5 (CH), 129.2, 129.9 (C), 131.3 (CH), 135.8, 154.4, 155.7 (C). IR (KBr): ν = 3060, 2953, 2928, 2865, 1923, 1847, 1809, 1771, 1667, 1604, 1575 (w), 1488, 1473 (m), 1449 (s), 1379, 1356, 1311, 1285 (w), 1254 (s), 11207, 1170, 1119, 1107 (m), 1054, 1034 (w), 1017 (s), 920, 885, 803 (m), 760, 744, 737, 718 (s), 662, 614, 572, 555, 530 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 208 ($[M]^+$, 100), 189 (16), 178 (27), 165 (12), 115 (10), 89 (14). HRMS (EI, 70 eV): calcd for $C_{15}H_{12}O$ $[M]^+$: 208.08827; found: 208.08861.

2-(2,5-Dimethoxyphenyl)benzofuran (9m). Compound **9m** was obtained as a by-product of **7m** (20 mg, 8%). ^1H NMR (250 MHz, $CDCl_3$): δ = 3.80 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 6.77–6.88 (m, 2H, ArH), 7.10–7.25 (m, 2H, ArH), 7.30 (d, *J* = 0.8 Hz, 1H, ArH), 7.42–7.56 (m, 3H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 54.9 (OCH_3), 55.0 (OCH_3), 105.6, 109.8, 110.9, 111.4, 113.8 (CH), 118.9 (C), 120.1, 121.7, 123.2 (CH), 127.5, 150.0, 150.1 152.7, 152.8 (C). IR (KBr): ν = 3060, 2996, 2946, 2931, 2904, 2831, 2495, 2349, 2068, 1613, 1584 (w), 1567 (m), 1500, 1453 (s), 1438 (m), 1347, 1322 (w), 1301 (m), 1273, 1259, 1242 (m), 1219, 1197 (s), 1180, 1160, 1132, 1122, 1108 (m), 1045, 1024 (s), 940, 868 (m), 809, 733 (s), 695, 666, 614, 540 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 254 ($[M]^+$, 100), 240 (16), 239 (96), 211 (16), 196 (13), 168 (18), 142 (14), 127 (9). HRMS (EI, 70 eV): calcd for $C_{16}H_{14}O_3$ $[M]^+$: 254.09429; found: 254.09411.

2-(Biphenyl-3-yl)benzofuran (9q). Compound **9q** was obtained as a by-product of **8j** (62 mg, 23%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.01 (s, 1H, ArH), 7.13–7.61 (m, 11H, ArH), 7.77 (dt, *J* = 1.6, 7.5 Hz, 1H, ArH), 8.02 (t, *J* = 1.7 Hz, 1H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 101.6, 111.2, 121.0, 123.0, 123.7, 123.8, 124.4, 127.2, 127.4, 127.6, 128.9 (CH), 129.2 (C), 129.3 (CH) 131.0, 140.9, 141.9, 155.0, 155.9 (C). IR (KBr): ν = 3119, 3053, 3026 (w), 1598, 1556, 1471, 1453, 1421 (m), 1391 (w), 1347, 1305, 1253, 1200, 1167 (m), 1144, 1107, 1095, 1074, 1056 (w), 1036 (m), 1018, 1004, 967 (w), 925, 892, 882, 820, 809 (m), 795, 760, 748, 740, 693, 675 (s), 617, 609, 578, 560, 537 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 270 ($[M]^+$, 100), 241 (9), 239 (14), 135 (10). HRMS (EI, 70 eV): calcd for $C_{20}H_{14}O$ $[M]^+$: 270.10392; found: 270.10402.

2-(Thiophen-2-yl)benzofuran (9r). Compound **9r** was obtained as a by-product of **8k** (30 mg, 15%). ^1H NMR (250 MHz, $CDCl_3$): δ = 6.88 (d, *J* = 0.8 Hz, 1H, ArH), 7.12 (dd, *J* = 3.7, 5.1 Hz, 1H, ArH), 7.20–7.36 (m, 3H, ArH), 7.49–7.58 (m, 3H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 101.1, 111.1, 120.8, 123.1, 124.3, 124.6, 125.8, 127.9 (CH), 129.1, 133.3, 151.3, 154.6 (C). GC-MS (EI, 70 eV): *m/z* (%) = 200 ($[M]^+$, 100), 185 (18). HRMS (EI, 70 eV): calcd for $C_{12}H_8OS$ $[M]^+$: 200.02959; found: 200.02977.

Procedure for the synthesis of 10a,b. The reaction was carried out in a pressure tube. To a dioxane suspension (10 mL) of **5** (546 mg, 2.0 mmol), Pd(PPh3)4 (116 mg, 5 mol %, 0.10 mmol), and Ar^1B(OH)2 (2.0 mmol) was added an aqueous solution of K_2CO_3 (2 M, 2 mL). The mixture was heated at 70°C under an argon atmosphere for 6 h. The mixture was cooled to 20°C and divided into two equal portions, and Ar^2B(OH)2 (1.0 mmol) was added to each portion. The reaction mixtures were heated under Argon atmosphere for 6 h at 80°C. Each reaction mixture was diluted with water and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried (Na_2SO_4) and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography (silica gel, EtOAc/heptanes). Products **10a** (238 mg, 76%) and **10b** (248 mg, 82%) were isolated as colorless oils.

3-(3-Methoxyphenyl)-2-p-tolylbenzofuran (10a). mp 73–74°C. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 3H, CH_3), 3.69 (s, 3H, OCH_3), 6.82–6.86 (m, 1H, ArH), 6.95–7.12 (m, 4H), ArH), 7.14–7.25 (m, 3H, ArH), 7.39–7.50 (m, 4H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.4 (CH_3), 55.3 (OCH_3), 111.1, 113.4, 115.1 (CH), 116.7 (C), 120.0, 122.3, 122.9, 124.5, 127.0 (CH), 127.8 (C), 129.2, 130.0 (CH), 130.3, 134.4, 138.5, 150.9, 153.9, 160.1 (C). IR (KBr): ν = 3031, 2997, 2917, 2832 (w), 1607, 1592, 1574, 1512, 1484 (m), 1451 (s), 1427, 1369, 1314, 1282 (m), 1246, 1234 (s), 1205, 1184, 1156, 1064 (m), 1042 (s), 1019, 1009, 987, 876, 838 (m), 819 (s), 779 (m), 742, 701 (s), 618, 610, 587, 563, 537 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 314 ($[M]^+$, 100), 271 (9), 255 (14), 121 (12). HRMS (EI, 70 eV): calcd for $C_{22}H_{18}O_2$ $[M]^+$: 314.13068; found: 314.12999.

3-(4-Fluorophenyl)-2-p-tolylbenzofuran (10b). mp 103–104°C. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 3H, CH_3), 7.17–7.31 (m, 5H, ArH), 7.35–7.40 (m, 1H, ArH), 7.50–7.54 (m, 3H, ArH), 7.57–7.61 (m, 3H, ArH). ^{19}F NMR (282.2 MHz, $CDCl_3$): δ = −114.35. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 21.4 (CH_3), 111.1 (CH), 115.8 (C), 116.1 (d, $J_{F,C}$ = 21.0 Hz, CH), 119.6, 123.0, 124.6, 127.0 (CH), 127.7 (C), 128.9 (d, $J_{F,}$

$_{C}=3.3$ Hz, C), 129.2 (CH), 130.2 (C), 131.4 (d, $J_{F,C}=8.1$ Hz, CH), 136.6, 151.1, 153.9 (C), 162.3 (d, $J_{F,C}=246.7$ Hz, C). IR (KBr): $\nu=3066$, 3036, 2918, 2853, 2790, 1613, 1601, 1557 (w), 1515, 1495 (m), 1452 (s), 1432, 1371, 1337, 1292 (3), 1254, 1230, 1216, 1205, 1196, 1182, 1156, 1091, 1066 (s), 1037, 1020, 1008, 964, 930, 897 (m), 842, 817, 811, 744 (s), 718, 716, 663, 598, 564 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 302 ($[M]^+$, 100), 286 (10), 259 (9), 257 (10). HRMS (EI, 70 eV): calcd for $C_{21}H_{15}FO$ $[M]^+$: 302.11014; found: 302.11031.

2,3,5-Tris(4-fluorophenyl)benzofuran (12). Compound **12** was prepared from **11** (177 mg, 0.5 mmol) and 4-fluorophenylboronic acid (210 mg, 1.5 mmol), according to the procedure given for the synthesis of products **7**, as a colorless highly viscous oil (162 mg, 81%). Reaction temperature: 90°C. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=6.42$–6.67 (m, 6H, ArH), 6.86–7.06 (m, 9H, ArH). ^{19}F NMR (282.2 MHz, $CDCl_3$): $\delta=-116.8$, -114.3, -112.3. ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta=111.2$ (CH), 115.6 (d, $J_{F,C}=21.2$ Hz, CH), 115.4 (d, $J_{F,C}=21.1$ Hz, CH), 116.2 (d, $J_{F,C}=21.6$ Hz, CH), 119.8, 123.1, 124.9 (CH), 127.6, 127.7 (d, $J_{F,C}=3.3$ Hz, C), 128.6 (d, $J_{F,C}=3.5$ Hz, C), 128.8 (d, $J_{F,C}=8.2$ Hz, CH), 130.1, 130.2 (C), 130.4 (d, $J_{F,C}=8.3$ Hz, CH), 131.4 (d, $J_{F,C}=8.0$ Hz, CH), 149.8, 153.9 (C), 1162.3 (d, $J_{F,C}=247.0$ Hz, CF), 1162.4 (d, $J_{F,C}=247.2$ Hz, CF), 1162.5 (d, $J_{F,C}=249.5$ Hz, CF). IR (KBr): $\nu=3067$, 3045, 3016, 2925, 2852 (w), 1594, 1582, 1515 (m), 1498, 1450 (s), 1409, 1374, 1338, 1302, 1254 (m), 1223 (s), 1205, 1161, 1155, 1589, 1099, 1088, 1068, 1014, 1009, 965, 934 (m), 836, 821, 814 (s), 802, 794 (m), 749 (s), 720, 686, 665, 627 (m), 598 (s), 580 (m), 564, 536 (s) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 400 ($[M]^+$, 100), 371 (7), 275 (8). HRMS (EI, 70 eV): calcd for $C_{26}H_{15}F_3O$ $[M]^+$: 400.10695; found: 400.10681.

3,5-Dibromo-2-p-tolylbenzofuran (13). Compound **13** was prepared from **11** (177 mg, 0.5 mmol), *p*-tolylboronic acid (68 mg, 0.5 mmol), according to the procedure given for the synthesis of products **7**, as a white solid (144 mg, 79%). Reaction temperature: 70°C, mp 114–115°C. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta=2.43$ (s, 3H, CH_3), 7.16–7.37 (m, 4H, ArH), 7.58–7.70 (m, 1H, ArH), 7.91–7.98 (m, 2H, ArH). ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta=21.5$ (CH_3), 92.0 (C), 112.7 (CH), 116.3 (C) 122.5 (CH), 123.8, 126.2 (C), 126.8, 128.2, 129.4 (CH), 131.6, 139.7, 151.8 (C). IR (KBr): $\nu=3086$, 3027, 2917, 2853, 2723, 1907, 1855, 1714, 1608, 1575 (w), 1500, 1461 (m), 1450, 1435 (s), 1409, 1390, 1325, 1298, 1257, 1203, 1191, 1186, 1133, 1112 (m), 1071 (s), 1050, 1017 (m), 986 (s), 902 (m), 858 (s), 833 (m), 813, 794 (s), 735, 710, 683 (m), 655 (s), 640, 593, 580, 551, 532 (m) cm^{-1}. GC-MS (EI, 70 eV): *m/z* (%) = 368 ($[M, {}^{81}Br, {}^{81}Br]^+$, 49), 366 ($[M, {}^{81}Br, {}^{79}Br]^+$, 100), 364 ($[M, {}^{79}Br, {}^{79}Br]^+$, 52), 259 (13), 257 (14), 177 (10), 176 (12). HRMS (EI, 70 eV): calcd for $C_{15}H_{10}OBr$ $[M, {}^{79}Br, {}^{79}Br]^+$: 363.90929; found: 363.90898.

Acknowledgments. Financial support by the State of Pakistan (HEC scholarships for M.H., N.A., and I.M.), by the DAAD (scholarships for I.M. and N.T.H.), by the State of Vietnam (MOET scholarship for N.T.H.), and by the State of Mecklenburg-Vorpommern (scholarships for M.H., R.A.K., and I.M.) is gratefully acknowledged. The work was supported by the European Union (EFRE program) and by the TÁMOP-4.2.1/B-09/KONV-2010-007 project. The project is implemented through the New Hungary Development Plan, co-financed by the European Social Fund and the European Regional Development Fund.

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