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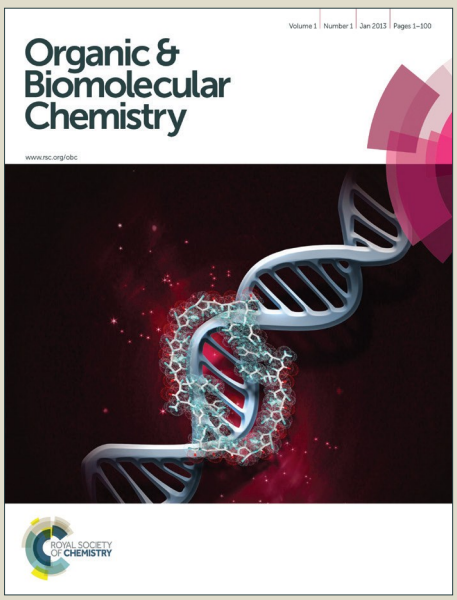

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A facile one-pot synthesis of 2,3-diarylated benzo[*b*]furans via relay NHC and palladium catalysis

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An efficient one-pot synthesis of 2,3-diarylated benzo[*b*]furans was realized through the relay catalysis of N-Heterocyclic Carbene (NHC) and palladium from substituted 2'-bromodiphenylbromomethanes and aryl aldehydes. The easy availability of the starting materials, good compatibility of catalysts, convergent assembly and concomitant modification of target scaffold, and potential utilization value of the products make this strategy attractive in organic synthesis.

Introduction

The wide distribution of benzo[*b*]furan skeleton in natural products[1] (**Figure 1**) and synthetic chemical entities with biological relevance has drawn much attention to its rapid construction and facile modification, e.g., arylation due to the diverse bioactivity[2] and electroluminescent property of arylated benzo[*b*]furans[3]. To date, several strategies have been developed to successfully construct benzo[*b*]furan scaffold from acyclic precursors including aryloxyketones[4], *o*-hydroxybenzophenones[5], *o*-halogenated phenols[6], *o*-alkynylphenols[7], substituted benzylic alcohols[8], O-aryl ketoximes[9], and diazo compounds[10] (**Scheme 1**, (a)~(h)). In addition, the effective introduction of an aryl group at C-2 or C-3 position of benzo[*b*]furan could also be achieved by transition-metal-catalyzed coupling reactions using unsubstituted benzo[*b*]furan as starting materials (**Scheme 1**, (i) and (j))[11]. However, the harsh conditions, long reaction time, complexity of feedstocks and intricacy of operation associated with these protocols necessitate the development of new alternative for the convenient fabrication and decoration of benzo[*b*]furan framework.

Recently, N-Heterocyclic Carbenes (NHCs) have been proved to be versatile catalysts for many organic transformations[12]. Apart from the traditional umpolung reaction of aldehydes (e.g., Benzoin condensation[13] and Stetter reaction[14]), numerous organic conversions including Michael addition[15], transesterification[16] and ring-opening polymerization[17] could be promoted by NHCs efficiently. In addition, the potential of NHCs as ligands for transition metals has been pioneered[18]. Interestingly, the compatibility of NHC catalysts with a transition-metal catalyst has also been demonstrated in some coupling reactions[19]. A recent report disclosed by Glorius et al showed that the NHC-catalyzed cross-coupling of aromatic aldehydes with activated alkyl halides delivered the aryl ketones readily (**Scheme 2**, (a))[20], thus we envisioned that the cross-coupling of 2'-bromodiphenylbromomethanes with aryl aldehydes and the subsequent annulation catalysed by palladium may proceed in a one-pot manner without the isolation of the intermediates, which could pave a new avenue to benzo[*b*]furans (**Scheme 2** (b)). To continue our work on NHCs-catalyzed cascade synthesis of heterocycles[21], we shall herein report our recent work on sequential synthesis of benzo[*b*]furans through the relay catalysis of NHC/palladium.

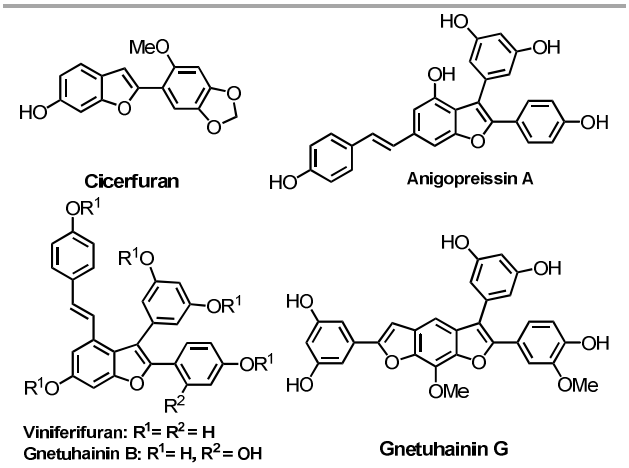

Figure 1. Representatives of natural products containing benzo[*b*]furan core

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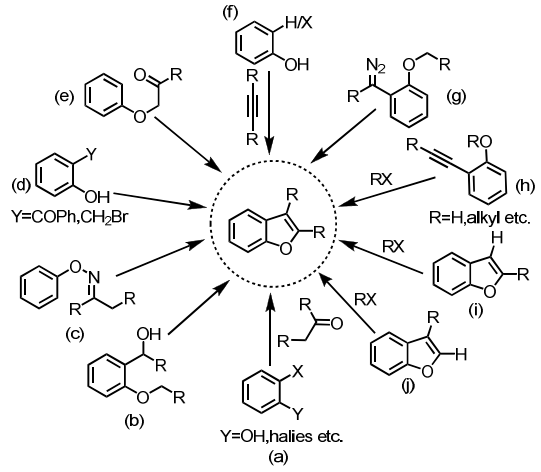
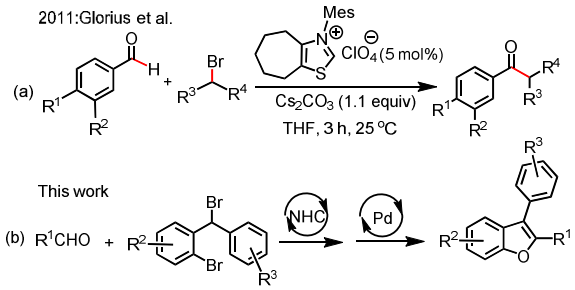


Scheme 1. Methods for the synthesis of diarylated benzo[*b*]furans

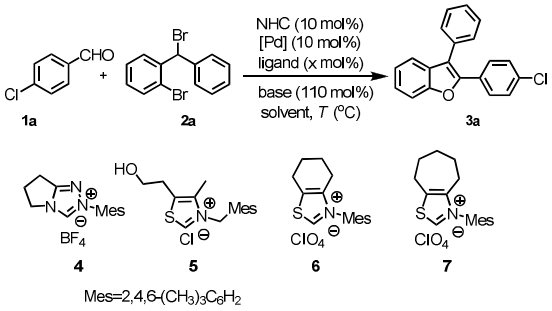


Scheme 2. Previous work and this work

Results and discussion

According to the hypothesis described above, we chose 4-chlorobenzaldehyde **1a** and 1-bromo-2-(bromo(phenyl)methyl)benzene **2a** as model substrates to optimize reaction conditions (Table 1). Initially, the formation of desired product **3a** was not detected when the reaction was conducted at room temperature presented by $Pd(OAc)_2$ and PPh_3 in DMF. To our delight, product **3a** was obtained in 46% yield in the presence of **7** when the reaction temperature was elevated to 90 °C (Table 1, entries 1-4). Then assessment of palladium salts and ligands demonstrated that the combination of $Pd(OAc)_2$ and PPh_3 should be favourable (Table 1, entries 5-12 and entry 4) and the ratio of PPh_3 to $Pd(OAc)_2$ should be 5:1 (Table 1, entries 13-14 and entry 4). Next the optimization of solvents showed that the DMF was superior to other counterparts (Table 1, entries 15-17 and entry 13). The following investigation of the effect of base on this process illuminated that Cs_2CO_3 was better than K_2CO_3, *t*BuOK, DBU, Et_3N, K_3PO_4 (Table 1, entries 18-22 and entry 13). Finally, the screening of temperature showed that 95 °C should be preferable (Table 1, entries 23-24 and entry 13).

Table 1. Optimization of the reaction conditions

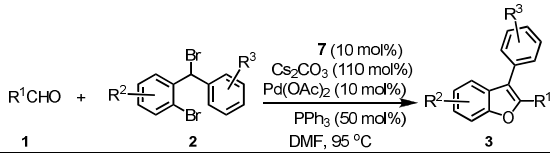


Entry	NHC/ [Pd]	Ligand (x mol%)	Base	Solvent	*T* (°C)	Yield (%)[a]
1	**4**/$Pd(OAc)_2$	PPh_3 (40)	Cs_2CO_3	DMF	90	--
2	**5**/$Pd(OAc)_2$	PPh_3 (40)	Cs_2CO_3	DMF	90	--
3	**6**/$Pd(OAc)_2$	PPh_3 (40)	Cs_2CO_3	DMF	90	Trace
4	**7**/$Pd(OAc)_2$	PPh_3 (40)	Cs_2CO_3	DMF	90	46
5	**7**/$Pd(PPh_3)_4$	--	Cs_2CO_3	DMF	90	10
6	**7**/$Pd(PPh_3)_2Cl_2$	--	Cs_2CO_3	DMF	90	Trace
7	**7**/$Pd_2(dba)_3$	--	Cs_2CO_3	DMF	90	Trace
8	**7**/$PdCl_2$	PPh_3 (40)	Cs_2CO_3	DMF	90	--
9	**7**/$Pd(OAc)_2$	P(*m*-tol)$_3$ (40)[b]	Cs_2CO_3	DMF	90	--
10	**7**/$Pd(OAc)_2$	dppf (40)[b]	Cs_2CO_3	DMF	90	Trace
11	**7**/$Pd(OAc)_2$	dppe (40)[b]	Cs_2CO_3	DMF	90	--
12	**7**/$Pd(OAc)_2$	dppb (40)[b]	Cs_2CO_3	DMF	90	--
13	**7**/$Pd(OAc)_2$	PPh_3 (50)	Cs_2CO_3	DMF	90	78
14	**7**/$Pd(OAc)_2$	PPh_3 (60)	Cs_2CO_3	DMF	90	53
15	**7**/$Pd(OAc)_2$	PPh_3 (50)	Cs_2CO_3	THF	Ref.	--[c]
16	**7**/$Pd(OAc)_2$	PPh_3 (50)	Cs_2CO_3	DMSO	90	19
17	**7**/$Pd(OAc)_2$	PPh_3 (50)	Cs_2CO_3	dioxane	Ref.	--[c]
18	**7**/$Pd(OAc)_2$	PPh_3 (50)	K_2CO_3	DMF	90	--
19	**7**/$Pd(OAc)_2$	PPh_3 (50)	*t*BuOK	DMF	90	--
20	**7**/$Pd(OAc)_2$	PPh_3 (50)	DBU	DMF	90	--
21	**7**/$Pd(OAc)_2$	PPh_3 (50)	Et_3N	DMF	90	--
22	**7**/$Pd(OAc)_2$	PPh_3 (50)	K_3PO_4	DMF	90	--
23	**7/Pd(OAc)$_2$**	**PPh_3 (50)**	**Cs_2CO_3**	**DMF**	**95**	**81**
24	**7**/$Pd(OAc)_2$	PPh_3 (50)	Cs_2CO_3	DMF	100	75

[a]. Isolated yield [b]. P(*m*-tol)$_3$ = Tri(m-tolyl)phosphine; dppf = 1,1'-bis(diphenyphosphino)ferrocene; dppe = 1,2-Bis(diphenylphosphino)ethane; dppb = 1,4-bis(diphenylphosphino)butane [c]. Intermediate **3aa** (2-(2-bromophenyl)-1-(4-chlorophenyl)-2-phenylethanone) was isolated (See SI).

With the optimized reaction conditions in hand, a concise exploration of the substrate scope of this one-pot protocol was carried out. As shown in Table 2, the aryl aldehydes bearing the electron-donating or electron-withdrawing groups could participate in the reaction and gave the desired products in moderate to good yields (52-85 %, Table 2, entries 1-8), thus the electronic nature of the substituents had no obvious effect on this protocol. Besides, the heterocyclic aryl aldehydes were also tolerated and the expected products were isolated in satisfactory yields (78 and 75 %, Table 2, entries 9-10). To expand the substrate scope further, substituted 2'-bromodiphenylbromomethane was subject to this procedure and the corresponding benzo[*b*]furans (**3k**-**3n**) could be acquired in moderate yields under standard conditions (53-63 %, Table 2, entries 11-14). These results highlighted the wide application range of this method. All of the products were characterized by IR, NMR and HRMS and they were in good agreement with the reported data.

Table 2. Synthesis of benzo[*b*]furans

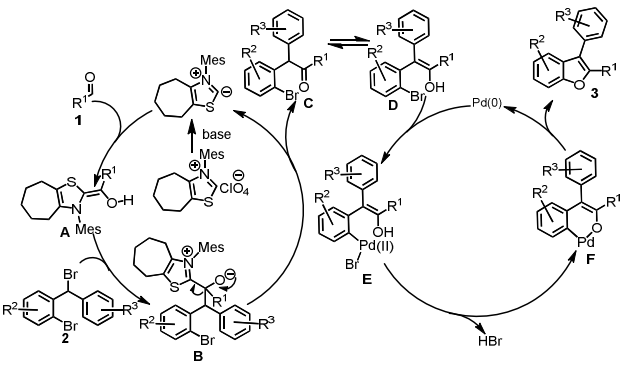


1 2 3

Entry	R^1	R^2	R^3	Time (h)	Product	Yield (%)[a]
1	4-ClC_6H_4	H	H	15	**3a**	81
2	4-FC_6H_4	H	H	16	**3b**	75
3	C_6H_5	H	H	18	**3c**	85
4	4-BrC_6H_4	H	H	16	**3d**	52
5	4-$CH_3C_6H_4$	H	H	24	**3e**	77
6	3-ClC_6H_4	H	H	16	**3f**	64
7	3-$CH_3C_6H_4$	H	H	16	**3g**	55
8	3,4-$Cl_2C_6H_3$	H	H	16	**3h**	72
9	Thiophen-2-yl	H	H	16	**3i**	78
10	Furan-2-yl	H	H	16	**3j**	75
11	4-ClC_6H_4	H	4-CH_3	17	**3k**	62
12	4-ClC_6H_4	5-Cl	H	17	**3l**	53
13	Thiophen-2-yl	5-Cl	H	16	**3m**	63
14	C_6H_5	5-Cl	H	16	**3n**	60

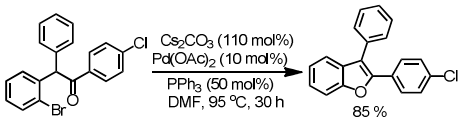
[a]. Isolated yield

A mechanism to rationalize the formation of benzo[*b*]furans was presented in **Scheme 3**. The nucleophilic attack of Breslow intermediate **A**, generated from aldehydes **1** and NHC, on 2'-bromodiphenylbromomethanes **2** provided intermediate **B**. The subsequent collapse of **B** afforded the key intermediate **C** and regenerated NHC catalyst[12,20,21]. The following keto-enol tautomerization and intramolecular C-O bond formation assisted by palladium gave rise to the ultimate product **3**[19].



Scheme 3. Plausible catalytic cycle

To shed some light on the reaction mechanism, a control experiment was carried out (**Scheme 4** and see SI). Intermediate **3aa** could undergo further intramolecular cyclization to furnish product **3a** under the catalysis of Pd. Thus, **3aa** should play a pivotal role in this one-pot synthesis of benzo[*b*]furan.



3aa 3a

Scheme 4. Pd-catalyzed cyclization of intermediate **3aa**

Conclusions

In summary, we have developed an efficient alternative approach to 2,3-diarylated benzo[*b*]furans by virtue of sequential catalysis of NHC and palladium from substituted 2'-bromodiphenylbromomethanes and aryl aldehydes. This protocol featured operational simplicity, easy accessibility of the raw materials, good tolerance of catalysts, and straightforward assembly with simultaneous modification of target scaffold. Other study aimed at the expansion of the application of the relay catalytic system consisting of NHC and metal is underway in our lab.

Experimental

Typical procedure for synthesis of benzo[*b*]furans. An oven-dried 25-mL flask equipped with a magnetic stir bar was charged with the thiazolium salt **7** (18.5 mg, 0.05 mmol), Cs_2CO_3 (179.2 mg, 0.55 mmol), freshly distilled DMF (5 mL), aromatic aldehydes **1** (0.5

mmol), 2'-bromodiphenylbromomethanes **2** (0.5 mmol), $Pd(OAc)_2$ (11.2 mg, 0.05 mmol) and PPh_3 (65.6 mg, 0.25 mmol). The mixture was stirred at 95 °C until completion (monitored by TLC). Deionized water (5 mL) was added and the mixture then extracted with EtOAc. The organic layer was dried over $MgSO_4$. The desired products **3** were obtained through filtration, concentration in vacuo and purification by column chromatography (silica gel, petroleum).

2-(4-chlorophenyl)-3-phenylbenzofuran (3a). 123 mg, 81 % yield; white solid; M.P.: 90 - 92 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 - 7.57 (m, 2H, ArH), 7.55 (d, J = 8.0 Hz, 1H, ArH), 7.50 - 7.40 (m, 6H, ArH), 7.36 - 7.32 (m, 1H, ArH), 7.30 - 7.22 (m, 3H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 149.3, 134.2, 132.5, 130.1, 129.7, 129.1, 129.1, 128.7, 128.2, 127.8, 124.9, 123.1, 120.1, 118.0, 111.1; IR (potassium bromide) (ν, cm^{-1}): 1618, 1608, 1582, 1560, 1483, 1449, 1402, 1253, 1201, 1089, 1064, 1014, 962, 840, 749, 695; HRMS (APCI) m/z: Calcd. for $[M+H]^+$ $C_{20}H_{14}ClO$: 305.0733, found: 305.0723.

2-(4-fluorophenyl)-3-phenylbenzofuran (3b). 108 mg, 75 % yield; white solid; M.P.: 87 - 88 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 - 7.60 (m, 2H, ArH), 7.55 (d, J = 8.0 Hz, 1H, ArH), 7.50 - 7.39 (m, 6H, ArH), 7.35 - 7.31 (m, 1H, ArH), 7.26 - 7.22 (m, 1H, ArH) 7.04 - 6.98 (m, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7 (J_{CF} = 250.0 Hz), 153.9, 149.6, 132.6, 130.1, 129.7, 129.0, 128.9 (J_{CF} = 10.0 Hz), 127.7, 126.9 (J_{CF} = 10.0 Hz), 124.7, 123.0, 120.0, 117.2 (J_{CF} = 1.0 Hz), 115.5 (J_{CF} = 20.0 Hz), 111.1; IR (potassium bromide) (ν, cm^{-1}): 1621, 1602, 1510, 1450, 1407, 1373, 1253, 1219, 1203, 1164, 1065, 963, 840, 797, 751, 696; HRMS (APCI) m/z: Calcd. for $[M+H]^+$ $C_{20}H_{14}FO$: 289.1023, found: 289.1023.

2,3-diphenylbenzofuan (3c). 114 mg, 85 % yield; white solid, M.P.: 115 - 116 °C (reported 122-123 °C)[22a]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 8.0 Hz, 2H, ArH), 7.57 - 7.39 (m, 7H, ArH), 7.35 - 7.29 (m, 4H, ArH), 7.25 - 7.22 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 150.5, 132.8, 130.7, 130.2, 129.8, 129.0, 128.4, 128.3, 127.6, 127.0, 124.7, 122.9, 120.0, 117.5, 111.1; IR (potassium bromide) (ν, cm^{-1}): 1601, 1568, 1496, 1455, 1440, 1368, 1339, 1203, 1187, 1109, 1062, 1027, 960, 827, 747, 693; HRMS (APCI) m/z: Calcd. for $[M+H]^+$ $C_{20}H_{15}O$: 271.1174, found: 271.1174.

2-(4-bromophenyl)-3-phenylbenzofuran (3d). 90 mg, 52 % yield; white solid; M.P.: 89 - 91 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 - 7.40 (m, 11H, ArH), 7.37 - 7.33(m, 1H, ArH), 7.23 (d, J = 7.6 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 149.4, 132.5, 131.6, 130.1, 129.7, 129.6, 129.1, 128.4, 127.9, 125.0, 123.1, 122.5, 120.1, 118.1, 111.1; IR (potassium bromide) (ν, cm^{-1}): 1603, 1577, 1497, 1482, 1451, 1396, 1253, 1076, 1006, 962, 894, 825, 772, 747, 703; HRMS (APCI) m/z: Calcd. for $[M+H]^+$ $C_{20}H_{14}BrO$: 349.0228, found: 349.0227.

3-phenyl-2-p-tolylbenzofuran (3e). 109 mg, 77 % yield; white solid; M.P.: 83 - 85 °C (reported 96 - 97 °C)[22b]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.0 Hz, 3H, ArH), 7.52 - 7.44 (m, 5H, ArH), 7.42 - 7.38 (m, 1H, ArH), 7.34 - 7.30 (m, 1H, ArH), 7.25 - 7.21 (m, 1H, ArH), 7.13 (d, J = 8.0 Hz, 2H, ArH), 2.35 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 150.8, 138.4, 133.0, 130.3, 129.8, 129.1, 128.9, 127.8, 127.5, 127.0, 124.4, 122.8, 119.9, 116.8, 111.0, 100.0, 21.4; IR (potassium bromide) (ν, cm^{-1}): 2916, 1604, 1512, 1453, 1442, 1369, 1255, 1202, 1181, 1110, 1076, 1065, 962, 817, 770, 739, 702; HRMS (APCI) m/z: Calcd. for $[M+H]^+$ $C_{21}H_{17}O$: 285.1279, found: 285.1278.

2-(3-chlorophenyl)-3-phenylbenzofuran (3f). 194 mg, 64 % yield; white solid; M.P.: 74 - 76 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H, ArH), 7.53 (d, J = 8.0 Hz, 1H, ArH), 7.48 -7.40 (m, 7H, ArH), 7.32 (t, J = 7.4 Hz, 1H, ArH), 7.24 - 7.19 (m, 2H, ArH), 7.16 (t, J = 7.8 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 148.8, 134.4, 132.3, 132.3, 130.0, 129.6, 129.6, 129.1, 128.2, 127.9, 126.7, 125.1, 124.9, 123.1, 120.2, 118.6, 111.1; IR (potassium bromide) (ν, cm^{-1}): 1598, 1560, 1497, 1476, 1452, 1370, 1257, 1207, 1114, 1080, 1062, 965, 843, 742, 699; HRMS (APCI) m/z: Calcd. for $[M+H]^+$ $C_{20}H_{14}ClO$: 305.0733, found: 305.0733.

3-phenyl-2-m-tolylbenzofuran (3g). 78 mg, 55 % yield; white solid; M.P.: 68 - 70 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.0 Hz, 2H, ArH), 7.51 - 7.49 (m, 3H, ArH), 7.47 - 7.43 (m, 2H, ArH), 7.41 - 7.36 (m, 2H, ArH), 7.34 - 7.30 (m, 1H, ArH), 7.23 - 7.21 (m, 1H, ArH), 7.16 (t, J = 7.8 Hz, 1H, ArH), 7.09 (d, J = 7.6 Hz, 1H, ArH), 2.31 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 150.7, 138.1, 132.9, 130.5, 130.2, 129.7, 129.1, 128.9, 128.2, 127.6, 127.6, 124.6, 124.3, 122.9, 120.0, 117.4, 111.1, 21.4; IR (potassium bromide) (ν, cm^{-1}): 2922, 1605, 1497, 1453, 1372, 1340, 1260, 1221, 1183, 1064, 1010, 965, 869, 769, 746, 699; HRMS (APCI) m/z: Calcd. for $[M+H]^+$ $C_{21}H_{17}O$: 285.1279, found: 285.1273.

2-(3,4-dichlorophenyl)-3-phenylbenzofuran (3h). 122 mg, 72 % yield; white solid; M.P.: 116 - 118 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 2.0 Hz, 1H, ArH), 7.56 (d, J = 8.0 Hz, 1H, ArH), 7.52 - 7.42 (m, 7H, ArH), 7.40 - 7.38 (m, 1H, ArH), 7.35 (t, J = 8.4 Hz, 2H, ArH), 7.28 - 7.24 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 147.9, 132.8, 132.2, 132.1, 130.6, 130.4, 130.0, 129.6, 129.2, 128.4, 128.1, 125.9, 125.4, 123.2, 120.3, 119.0, 111.2; IR (potassium bromide) (ν, cm^{-1}): 1595, 1548, 1449, 1369, 1274, 1261, 1206, 1133, 1071, 1028, 964, 887, 817, 768, 743, 698; HRMS (APCI) m/z: Calcd. for $[M+H]^+$ $C_{20}H_{13}Cl_2O$: 339.0343, found: 339.0333.

3-phenyl-2-(thiophen-2-yl)benzofuran (3i). 108 mg, 78 % yield; white solid; M.P.: 139 - 140 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 - 7.49 (m, 5H, ArH), 7.46 - 7.42 (m, 2H, ArH), 7.34 - 7.30 (m, 2H, ArH), 7.25 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1 H, ArH), 7.24 - 7.20 (m, 1H, ArH), 6.99 (dd, J_1 = 5.2 Hz, J_2 = 3.6 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 146.6, 132.7, 132.0, 130.2, 130.0, 128.9, 128.0, 127.4, 126.0, 125.7, 124.7, 123.1, 119.8, 116.8, 111.0; IR (potassium bromide) (ν, cm^{-1}): 1604, 1452, 1374, 1337, 1220, 1196, 1177, 1109, 1080, 957, 931, 851, 831, 798, 771, 748, 707, 698; HRMS (APCI) m/z: Calcd. for $[M+H]^+$ $C_{18}H_{13}OS$: 277.0687, found: 277.0684.

2-(furan-2-yl)-3-phenylbenzofuran (3j). 97 mg, 75 % yield; white solid; M.P.: 82 - 84 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 8.0 Hz, 2H, ArH), 7.56 - 7.48 (m, 4H, ArH), 7.44 - 7.40 (m, 2H, ArH), 7.34 (t, J = 7.8 Hz, 1H, ArH), 7.25 - 7.20 (m, 1H, ArH), 6.66 (d, J = 3.6 Hz,

1H, ArH), 6.45- 6.44 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 146.3, 145.9, 144.3, 142.9, 131.7, 129.7, 128.6, 127.7, 124.9, 123.2, 120.1, 111.5, 111.2, 109.2; IR (potassium bromide) (ν, cm^{-1}): 1734, 1718, 1701, 1654, 1647, 1636, 1559, 1541, 1458, 1442, 1091, 1012, 740, 700; HRMS (APCI) m/z: Calcd. for $[M+H]^+$ $C_{18}H_{13}O_2$: 261.0916, found: 261.0915.

2-(4-chlorophenyl)-3-p-tolylbenzofuran (3k). 92 mg, 62 % yield; white solid; M.P.: 110 - 112 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 - 7.58 (m, 2H, ArH), 7.53 (d, J = 8.0 Hz, 1H, ArH), 7.49 - 7.47 (m, 1H, ArH), 7.37 - 7.34 (m, 2H, ArH), 7.33 - 7.31 (m, 1H, ArH), 7.29 - 7.26 (m, 4H, ArH), 7.23 - 7.21 (m, 1H, ArH), 2.44 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 149.2, 137.6, 134.0, 130.2, 129.8, 129.5, 129.4, 129.3, 128.7, 128.1, 124.9, 123.0, 120.2, 118.0, 111.1, 21.4; IR (potassium bromide) (ν, cm^{-1}): 2919, 1514, 1487, 1450, 1254, 1201, 1108, 1085, 1065, 1012, 965, 898, 831, 748; HRMS (APCI) m/z: Calcd. for $[M+H]^+$ $C_{21}H_{16}ClO$: 319.0890, found: 319.0890.

5-chloro-2-(4-chlorophenyl)-3-phenylbenzofuran (3l). 89 mg, 53 % yield; white solid; M.P.: 79 - 81 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 - 7.57 (m, 1H, ArH), 7.56 - 7.55 (m, 1H, ArH), 7.49 - 7.47 (m, 2H, ArH), 7.45 - 7.44 (m, 5H, ArH), 7.30 - 7.29 (m, 2H, ArH), 7.28 - 7.27 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 150.8, 134.6, 131.8, 131.5, 129.6, 129.2, 128.8, 128.6, 128.2, 128.2, 125.1, 119.7, 117.6, 112.1; IR (potassium bromide) (ν, cm^{-1}): 1610, 1558, 1541, 1507, 1498, 1486, 1447, 1402, 1367, 1258, 1206, 1087, 1058, 1014, 967, 833, 798; HRMS (APCI) m/z: Calcd. for $[M+H]^+$ $C_{20}H_{13}Cl_2O$: 339.0338, found: 339.0326.

5-chloro-3-phenyl-2-(thiophen-2-yl)benzofuran (3m). 68 mg, 63 % yield; white solid; M.P.: 98 - 100 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 - 7.52 (m, 4H, ArH), 7.44 (d, J = 8.4 Hz, 1H, ArH), 7.38 (d, J = 2.0 Hz, 1H, ArH), 7.34 (dd, J_1 = 3.8 Hz, J_2 = 1.0 Hz, 1H, ArH), 7.30 - 7.27 (m, 2H, ArH), 7.25 (d, J = 2.4 Hz, 1H, ArH), 7.00 (dd, J_1 = 5.2 Hz, J_2 = 3.6 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 148.0, 132.1, 131.6, 131.3, 129.9, 129.1, 128.8, 128.3, 127.5, 126.6, 126.2, 124.8, 119.4, 116.3, 112.0; IR (potassium bromide) (ν, cm^{-1}): 1616, 1577, 1507, 1473, 1448, 1327, 1256, 1218, 1202, 1058, 1019, 966, 870, 804, 716, 693; HRMS (APCI) m/z: Calcd. for $[M+H]^+$ $C_{18}H_{11}ClOS$: 311.0297, found: 311.0298.

5-chloro-2,3-diphenylbenzofuran (3n). 91 mg, 63 % yield; white solid; M.P.: 101 - 102 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 - 7.63 (m, 2H, ArH), 7.48 - 7.45 (m, 6H, ArH), 7.33 - 7.29 (m, 4H, ArH), 7.27 (d, J = 2.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 151.9, 132.1, 131.7, 130.2, 129.6, 129.1, 128.7, 128.6, 128.5, 127.9, 127.0, 124.8, 119.6, 117.1, 112.1; IR (potassium bromide) (ν, cm^{-1}): 1603, 1505, 1450, 1439, 1321, 1257, 1206, 1081, 1066, 1057, 1026, 966, 915, 803, 764; HRMS (APCI) m/z: Calcd. for $[M+H]^+$ $C_{20}H_{14}ClO$: 305.0733, found: 305.0736.

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