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## RHODIUM-CATALYZED SYNTHESIS OF BENZOFURANS BY THE REACTION OF KETONES AND *O*-DIFLUOROBENZENES

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**Abstract** – In the presence of catalytic amounts of  $\text{RhH}(\text{PPh}_3)_4$  and 1,2-bis(diphenylphosphino)ethane (dppe), ketones reacted with *o*-difluorobenzenes giving benzofurans in high yields. The  $\alpha$ -arylation of ketones and furan cyclization proceeded without using a base. Benzofuran cyclization was applied to substituted pentafluorobenzenes to give 6-substituted-4,5,7-trifluorobenzofuranes.

Dedicated to Professor Ei-ichi Negishi (Purdue University) on the occasion of his 77<sup>th</sup> birthday

### INTRODUCTION

Benzofurans are an important class of heterocyclic compounds exhibiting biological activities.<sup>1</sup> Among their various synthetic methods, a one-pot approach using the reaction of ketones and *o*-dihalobenzenes is attractive. The transformation is generally conducted in the presence of a transition-metal catalyst and a stoichiometric amount of base using *o*-dibromobenzenes and *o*-bromoiodobenzenes.<sup>2</sup> The use of *o*-difluorobenzene has not been reported, with the exception of the reaction of hexafluorobenzene with ketones in the presence of a stoichiometric amount of NaH without a metal catalyst.<sup>3</sup>

It was thus considered interesting to explore a transition-metal-catalyzed method of obtaining benzofurans from *o*-difluorobenzenes, particularly in the absence of a base. Such a method has potential for synthesizing novel benzofurans under mild conditions. Described in this study is the rhodium-catalyzed benzofuran cyclization of ketones and *o*-difluorobenzenes, which proceeds without using a base.<sup>4,5</sup> Another advantage of this method is that polyfluorinated benzofurans can be obtained by reacting various readily available polyfluorinated benzenes. Conventional methods of synthesizing

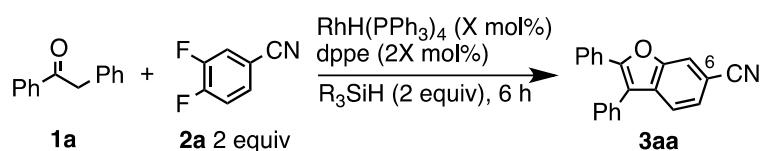
polyfluorobenzofurans employ stepwise cyclization, and a palladium-catalyzed reaction of dibromodifluorobenzene.<sup>6</sup> Our method allows the synthesis of various polyfluorinated benzofurans from polyfluorobenzenes.

This furan cyclization involves a *C*-arylation reaction of ketone enolates with aryl fluorides. The palladium-catalyzed *C*-arylation of ketone enolates using aryl triflates, iodides, bromides, and chlorides in the presence of a stoichiometric amount of base has been reported.<sup>7</sup> The present method entails ketone *C*-arylation using aryl fluoride in the absence of base, which was also briefly examined.

## RESULTS AND DISCUSSION

When a mixture of 1,2-diphenyl-1-ethanone **1a** and 3,4-difluorobenzonitrile **2a** (2 equiv) in chlorobenzene was heated at reflux for 6 h under argon in the presence of RhH(PPh<sub>3</sub>)<sub>4</sub> (5 mol%), 1,2-bis(diphenylphosphino)ethane (dppe, 10 mol%), and tributylsilane (2 equiv), 6-cyano-2,3-diphenylbenzofuran **3aa** (90%) was obtained (Table 1, entry 1). X-Ray analysis of the product **3aa** confirmed the structure (Figure 1).<sup>8</sup> The rhodium complex and dppe were both essential for the reaction, and no reaction occurred in the absence of either substance. Tributylsilane was converted into tributylsilyl fluoride by trapping the fluoride atom of hydrogen fluoride. Using triphenylsilane in place of tributylsilane, **3aa** was obtained in 77% yield (entry 2). The removal of hydrogen fluoride promoted the formation of benzofurans, and in the presence of RhH(PPh<sub>3</sub>)<sub>4</sub> (20 mol%) and dppe (40 mol%) the reaction proceeded in 80% yield without the silane reagent in refluxing *o*-dichlorobenzene (180 °C) under nitrogen bubbling (entry 3). The yield decreased to 48% at 150 °C (entry 4). Without nitrogen bubbling, the yield decreased to 38% in refluxing *o*-dichlorobenzene (entry 5). The reaction temperature could be markedly reduced from 180 °C for the *o*-dichlorobenzene reflux to 132 °C for the chlorobenzene reflux in the presence of the silane reagent, although the reagent itself is not essential for this reaction.

**Table 1.** Reaction of 1,2-diphenylethanone **1a** and 3,4-difluorobenzonitrile **2a**.



Entry	X	R	Reaction Temp.	Yield of <b>3aa</b> / %
1	5	Bu	PhCl reflux (132 °C)	90
2	5	Ph	PhCl reflux (132 °C)	77
3	20	-	<i>o</i> -Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub> reflux (180 °C), N <sub>2</sub> bubble	80
4	20	-	<i>o</i> -Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub> 150 °C, N <sub>2</sub> bubble	48
5	20	-	<i>o</i> -Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub> reflux (180 °C)	38

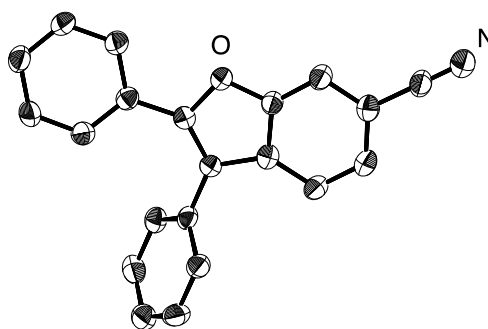
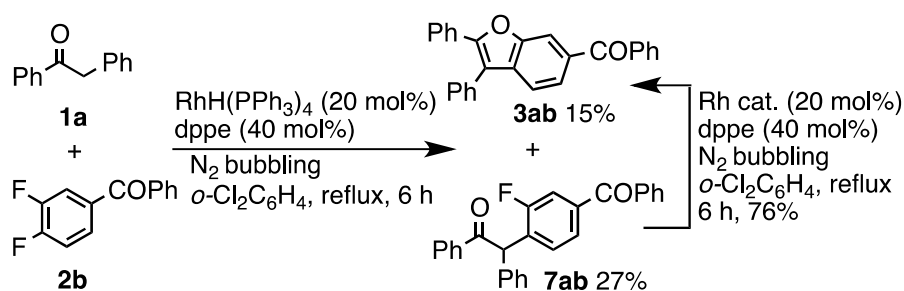


Figure 1. ORTEP view of **3aa**.

The formation of 6-cyanobenzofuran in this synthesis indicated that *C*-arylation occurred at the *p*-position of **2a** followed by *O*-arylation at the *m*-position. Rhodium enolate was formed by the  $\alpha$ -activation of the ketones, which was followed by *C*-arylation with difluorobenzenes giving  $\alpha$ -aryl ketones. Then, the intramolecular *O*-arylation of another rhodium enolate gave the product. In this reaction, rhodium enolates were formed twice without using a base. The mechanism was supported by the following experiment. When a mixture of **1a** and **2b** was heated in the presence of  $\text{RhH}(\text{PPh}_3)_4$  (20mol%) and dppe (40 mol%) in refluxing *o*-dichlorobenzene with nitrogen bubbling for 6 h, fluoroarylated ketone **7ab** (27%) and benzofuran **3ab** (15%) were obtained. The compound **7ab** could be converted into **3ab** in 76% yield under the same rhodium-catalyzed conditions (Scheme 1). The rhodium complex was essential for the second *O*-arylation step.

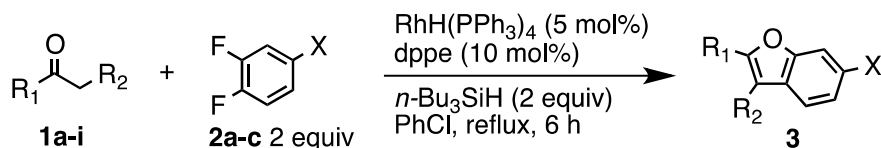


Scheme 1

Various ketones reacted with *o*-difluorobenzenes giving benzofurans (Table 2). Benzyl phenyl ketones possessing either *p*-electron-donating or *p*-electron-withdrawing groups on their aroyl moiety reacted with **2a** smoothly (entries 1-4 and 7). Difluorobenzenes with cyano-, benzoyl-, and nitro-groups at the 4-position also reacted in high yields (entries 4-6). No reaction, however, occurred with 1,2-difluoro-4-methylbenzene. 1-Phenyl-2-butanone and **2a** gave the corresponding benzofuran **3fa** in 81% yield (entry 8). Dibenzyl ketone gave **3ga** (38%) and its arylated product **4ga** (38%) (entry 9). The

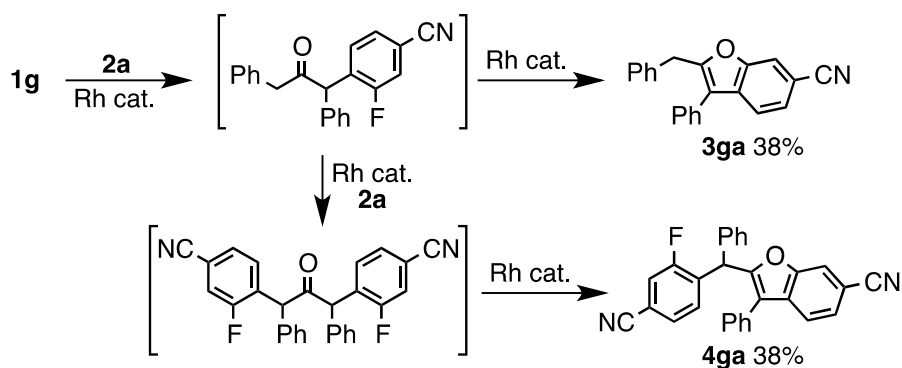
latter compound **4ga** was formed by the diarylation of **1g** at two benzyl positions followed by cyclization (Scheme 2). The reaction could be applied to 1,3-diketones (entries 10 and 11). An acetophenone derivative, 4-acetylbenzonitrile **1j**, also reacted to give the product **4ja**, which was formed by the diarylation of **1j** at the  $\alpha$ -methyl protons followed by cyclization (Scheme 3).

**Table 2.** Synthesis of 2,3-diarylbenzofurans.

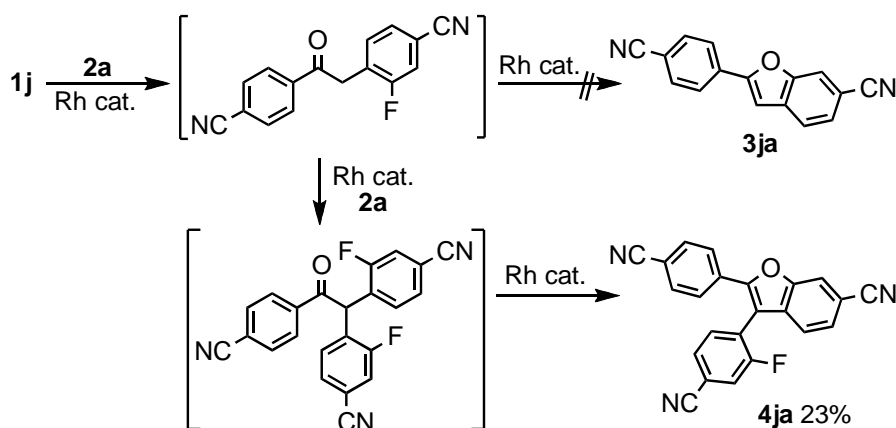


Entry	R <sub>1</sub>	R <sub>2</sub>	X	Yield of <b>3</b> / %
1	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> ( <b>1b</b> )	CN	89 ( <b>3ba</b> )
2	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	Ph ( <b>1c</b> )	CN	86 ( <b>3ca</b> )
3	Ph	Ph ( <b>1a</b> )	CN	90 ( <b>3aa</b> )
4	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	Ph ( <b>1d</b> )	CN	87 ( <b>3da</b> )
5	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	Ph ( <b>1d</b> )	PhCO ( <b>2b</b> )	67 ( <b>3db</b> )
6	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	Ph ( <b>1d</b> )	NO <sub>2</sub> ( <b>2c</b> )	58 ( <b>3dc</b> )
7	<i>p</i> -NCC <sub>6</sub> H <sub>4</sub>	Ph ( <b>1e</b> )	CN	90 ( <b>3ea</b> )
8	Et	Ph ( <b>1f</b> )	CN	81 ( <b>3fa</b> )
9	PhCH <sub>2</sub>	Ph ( <b>1g</b> )	CN	38 ( <b>3ga</b> ) + 38 ( <b>4ga</b> )
10	Me	MeCO ( <b>1h</b> )	CN	32 ( <b>3ha</b> )
11	Ph	PhCO ( <b>1i</b> )	CN	28 ( <b>3ia</b> ), 46 <sup>a</sup>
12	<i>p</i> -NC C <sub>6</sub> H <sub>4</sub>	H ( <b>1j</b> )	CN	23 ( <b>4ja</b> )

a) Rh cat. (20 mol%) and dppe (40 mol%) were used with nitrogen bubbling in refluxing *o*-dichlorobenzene.



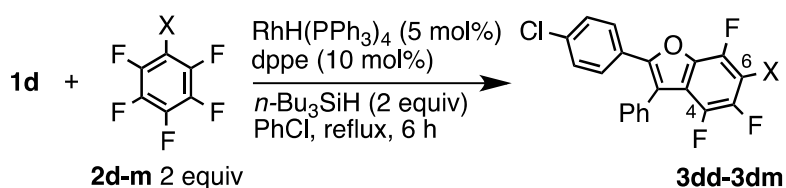
**Scheme 2**



Scheme 3

The reaction was then applied to polyfluorobenzenes, which gave novel polyfluorinated benzofurans not available by conventional methods. When (diphenylamino)pentafluorobenzene **2e** (2 equiv) was reacted with aryl benzyl ketone **1d** in the presence of  $\text{RhH}(\text{PPh}_3)_4$  (5 mol%), dppe (10 mol%), and tributylsilane (2 equiv) in refluxing chlorobenzene for 6 h, 6-diphenylamino-4,5,7-trifluorobenzofuran **3de** was obtained in 83% yield (Table 3, entry 2). An X-ray analysis of **3de** confirmed the structure (Figure 2).<sup>8</sup> Various monosubstituted pentafluorobenzenes reacted smoothly, and the structures of 6-substituted benzofurans were in all cases determined by  $^{19}\text{F}$ -NMR,  $\delta$  -151--154 for 4-fluorine (entries 1-8). X-Ray analysis was conducted for **3dd** and **3di** (entries 1 and 6, Figure 2).<sup>8</sup>

Table 3. Synthesis of 6-substituted-2,3-diaryl-4,5,7-trifluorobenzofurans.



Entry	X	Yield of <b>3</b> / %
1	$\text{Me}_2\text{N}$ ( <b>2d</b> )	46 ( <b>3dd</b> )
2	$\text{Ph}_2\text{N}$ ( <b>2e</b> )	83 ( <b>3de</b> )
3	$n\text{-C}_4\text{H}_9\text{S}$ ( <b>2f</b> )	73 ( <b>3df</b> )
4	$p\text{-TolS}$ ( <b>2g</b> )	74 ( <b>3dg</b> )
5	Me ( <b>2h</b> )	61 ( <b>3dh</b> )
6	H ( <b>2i</b> )	52 ( <b>3di</b> )
7	F ( <b>2j</b> )	65 ( <b>3dj</b> ) + 5 ( <b>4dj</b> )
8	$\text{PhCO}$ ( <b>2k</b> )	33 ( <b>3dk</b> )

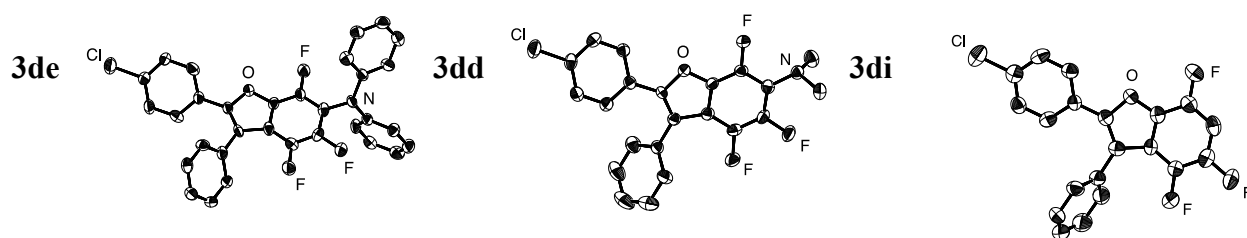
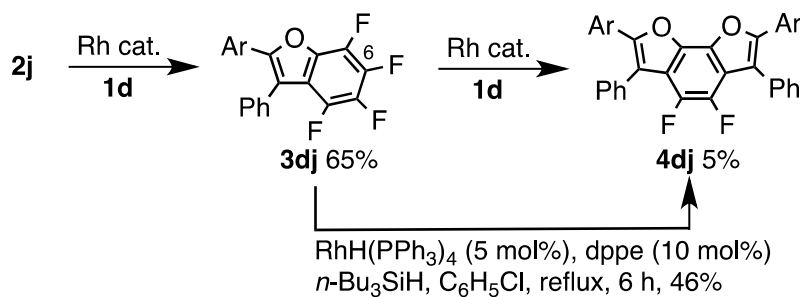


Figure 2. ORTEP view of **3de**, **3dd**, and **3di**.

When hexafluorobenzene was subjected to the reaction, benzofuran **3dj** (65%) was formed along with benzo[2,1-*b*:3,4-*b'*]difuran **4dj** (5%) (entry 7). The compound **4dj** was formed by two cyclizations (Scheme 4). X-Ray analysis of the product **4dj** confirmed the structure,<sup>8</sup> in which two oxygen atoms occupy the *o*-position (Figure 3). It was also observed that the reaction of **3dj** and **1d** gave **4dj** in 46% yield under the same conditions (Scheme 4). The results indicated that **1d** reacted with **3dj** at the 6-position.

The reaction of substituted pentafluorobenzenes gave 6-substituted-4,5,7-trifluorobenzofurans with either electron-donating groups such as diphenylamino, butylthio, *p*-tolylthio, and methyl groups or electron-withdrawing groups such as fluoro and benzoyl groups in high yields (Table 3, entries 1-8). The arylation generally proceeded at the *p*-position of the substituent in pentafluorobenzenes.



Scheme 4

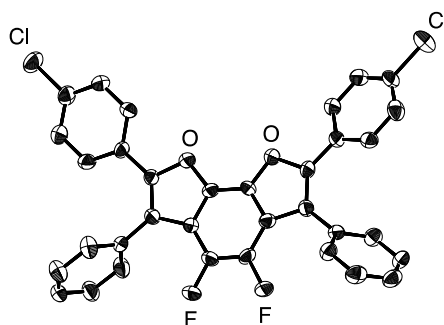
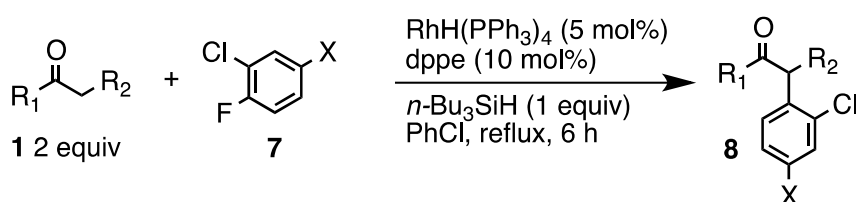


Figure 3. ORTEP view of **4dj**.

This synthesis includes the  $\alpha$ -arylation of rhodium enolate. The rhodium-catalyzed  $\alpha$ -arylation reaction of benzyl ketones was briefly examined. When a mixture of **1d** (2 equiv) and 3-chloro-4-fluorobenzonitrile **7a** in chlorobenzene was heated at reflux for 6 h in the presence of RhH(PPh<sub>3</sub>)<sub>4</sub> (5 mol%), dppe (10 mol%), and tributylsilane (1 equiv), the arylated ketone **8da** was obtained in 60% yield (Table 4, entry 1). Several other substituted benzyl phenyl ketones reacted smoothly. No reaction occurred in the absence of the rhodium complex or dppe. The rhodium-catalyzed enolate arylation proceeded using a fluorobenzene **7** without using a base.

**Table 4.**  $\alpha$ -Arylation of benzyl phenyl ketones using fluorobenzenes.



Entry	R <sub>1</sub>	R <sub>2</sub>	X	Yield of <b>8</b> / %
1	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	Ph ( <b>1d</b> )	CN ( <b>7a</b> )	60 ( <b>8da</b> )
2	Ph	Ph ( <b>1a</b> )	CN ( <b>7a</b> )	53 ( <b>8aa</b> )
3	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> ( <b>1b</b> )	CN ( <b>7a</b> )	54 ( <b>8ba</b> )
4	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	Ph ( <b>1d</b> )	NO <sub>2</sub> ( <b>7b</b> )	57 ( <b>8db</b> )

In summary, the benzofuran cyclization of ketones and *o*-difluorobenzenes proceeded in the presence of a catalytic amount of rhodium complex without using a base. Polyfluorinated benzofurans were also synthesized using monosubstituted pentafluorobenzenes. It should be emphasized that rhodium catalysis could be used for the activation of ketones and *o*-difluorobenzenes.

## EXPERIMENTAL

*General:* <sup>1</sup>H-, <sup>13</sup>C-, <sup>19</sup>F-NMR spectra were recorded on a Varian Mercury (400 MHz). Tetramethylsilane and trifluoroacetic acid were used as standard. IR spectra were measured on a JASCO FT/IR-410 spectrophotometer. Melting points were determined with a Yanaco micro melting point apparatus without correction. High- and low-resolution mass spectra were measured on a JEOL JMS-DX-303, a JEOL JMS-700, or a JMS-T100GC. Merck silica gel 60 (63-200 μm) was employed for flash column chromatography.

**6-Cyano-2,3-diphenylbenzofuran (3aa):** In a two-necked flask equipped with a reflux condenser were placed 1,2-diphenylethanone **1a** (0.25 mmol, 49 mg), 3,4-difluorobenzonitrile **2a** (0.5 mmol, 69.5 mg),

RhH(PPh<sub>3</sub>)<sub>4</sub> (5 mol%, 14.4 mg), 1,2-bis(diphenylphosphino)ethane (10 mol%, 10.0 mg), and tributylsilane (0.5 mmol, 129 μL) in chlorobenzene (1 mL) under an argon atmosphere, and solution was stirred under reflux for 6 h. Then, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving **3aa** (66.3 mg, 90%) as colorless crystals. Mp 143-144 °C (Hexane : EtOAc = 2 : 1). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33-7.37 (3H, m), 7.43-7.52 (5H, m), 7.56 (1H, dd, *J* = 8.0, 0.8 Hz), 7.66-7.68 (2H, m), 7.86 (1H, dd, *J* = 1.2, 0.8 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 107.2, 115.2, 117.5, 119.5, 120.8, 126.6, 127.2, 128.2, 128.6, 129.2, 129.4, 129.6, 131.4, 134.4, 152.6, 154.0. IR (KBr) 3055, 2220, 1479, 1425, 1269, 1063, 764, 692 cm<sup>-1</sup>. MS (EI) *m/z* 295 (M<sup>+</sup>, 100%). HRMS Calcd for C<sub>21</sub>H<sub>13</sub>ON: 295.0997. Found: 295.0995. One carbon peak of aromatic region was piled up in <sup>13</sup>C-NMR. CCDC 879726 contains the supplementary crystallographic data for compound **3aa**.

**2-(*p*-Benzoyl-*o*-fluorophenyl)-1,2-diphenyl-1-ethanone (7ab):** In a two-necked flask equipped with a reflux condenser were placed **1a** (0.25 mmol, 49 mg), 3,4-difluorobenzophenone **2b** (0.5 mmol, 54.5 mg), RhH(PPh<sub>3</sub>)<sub>4</sub> (20 mol%, 57.6 mg), and dppe (40 mol%, 39.8 mg) in *o*-dichlorobenzene (5 mL) under an argon atmosphere, and solution was stirred under reflux with nitrogen bubbling for 6 h. Then, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving 6-benzoyl-2,3-diphenylbenzofuran **3ab** (14.2 mg, 15%) and **7ab** (26.9 mg, 27%) as colorless crystals. **3ab**: Mp 134-135 °C (Hexane : EtOAc = 2 : 1). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33-7.35 (3H, m), 7.43-7.53 (7H, m), 7.57 (1H, d, *J* = 8.0 Hz), 7.61 (1H, t, *J* = 8.0 Hz), 7.67-7.70 (2H, m), 7.77 (1H, dd, *J* = 8.0, 1.6 Hz), 7.84 (2H, d, *J* = 7.6 Hz), 8.03 (1H, d, *J* = 1.2 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 113.6, 117.7, 119.6, 125.3, 127.2, 128.0, 128.3, 128.5, 129.1, 129.1, 129.7, 130.0, 130.0, 132.1, 132.1, 134.0, 134.2, 138.2, 153.2, 153.7, 196.3. IR (KBr) 3064, 1655, 1296, 715, 696 cm<sup>-1</sup>. MS (EI) *m/z* 374 (M<sup>+</sup>, 100%), 297 (M<sup>+</sup>-C<sub>6</sub>H<sub>5</sub>, 43%). HRMS Calcd for C<sub>27</sub>H<sub>18</sub>O<sub>2</sub>: 374.1307. Found: 374.1301. **7ab**: Mp 123-124 °C (Hexane : EtOAc = 2 : 1). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 6.36 (1H, s), 7.18 (1H, t, *J* = 7.6 Hz), 7.3-7.6 (13H, m), 7.79 (2H, d, *J* = 7.2 Hz), 8.02 (2H, d, *J* = 7.2 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 52.2 (d, *J* = 2.2 Hz), 116.5 (d, *J* = 23.5 Hz), 125.9 (d, *J* = 3.7 Hz), 127.8, 128.4, 128.7, 129.0, 129.2, 129.4, 130.0, 130.7 (d, *J* = 3.0 Hz), 131.7 (d, *J* = 15.2 Hz), 132.7, 133.4, 136.1, 136.3, 137.0, 138.3 (d, *J* = 6.8 Hz), 159.8 (d, *J* = 246.3 Hz), 194.9, 196.6. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -118.4. IR (KBr) 3063, 1683, 1641, 1285, 1263, 1211, 703 cm<sup>-1</sup>. MS (EI) *m/z* 394 (M<sup>+</sup>, 11%), 105 (M<sup>+</sup>-COC<sub>6</sub>H<sub>5</sub>, 100%). HRMS Calcd for C<sub>27</sub>H<sub>19</sub>O<sub>2</sub>F: 394.1368. Found: 394.1386.

**6-Cyano-2,3-bis(*p*-methoxyphenyl)benzofuran (3ba):** Colorless crystals. Mp 157-158 °C (Hexane : EtOAc = 2 : 1). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 3.83 (3H, s), 3.89 (3H, s), 6.87 (2H, d, *J* = 8.4 Hz), 7.02

(2H, d,  $J = 8.8$  Hz), 7.37 (2H, d,  $J = 8.8$  Hz), 7.47 (1H, d,  $J = 8.0$  Hz), 7.49 (1H, d,  $J = 8.8$  Hz), 7.61 (2H, d,  $J = 9.6$  Hz), 7.80 (1H, s).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  55.3, 55.3, 106.5, 114.1, 114.7, 114.9, 115.7, 119.7, 120.4, 122.2, 123.7, 126.6, 128.7, 130.8, 134.9, 152.5, 154.1, 159.4, 160.4. IR (KBr) 3059, 2962, 2225, 1606, 1500, 1254, 1026  $\text{cm}^{-1}$ . MS (EI)  $m/z$  355 ( $\text{M}^+$ , 100%), 340 ( $\text{M}^+ - \text{CH}_3$ , 16%). HRMS Calcd for  $\text{C}_{23}\text{H}_{17}\text{O}_3\text{N}$ : 355.1208. Found: 355.1220.

**6-Cyano-2-(*p*-methoxyphenyl)-3-phenylbenzofuran (3ca):** Colorless crystals. Mp 131.5-132.5 °C ( $\text{Et}_2\text{O}$ ).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.82 (3H, s), 6.86 (2H, d,  $J = 8.8$  Hz), 7.43-7.52 (7H, m), 7.60 (2H, d,  $J = 8.8$  Hz), 7.81 (1H, s).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  55.3, 106.6, 114.1, 115.0, 116.0, 119.6, 120.4, 122.0, 126.6, 128.1, 128.8, 129.2, 129.6, 131.7, 134.7, 152.5, 154.3, 160.5. IR (KBr) 3072, 2951, 2835, 2223, 1608, 1512, 1252, 1030  $\text{cm}^{-1}$ . MS (EI)  $m/z$  325 ( $\text{M}^+$ , 100%), 310 ( $\text{M}^+ - \text{CH}_3$ , 17%). HRMS Calcd for  $\text{C}_{22}\text{H}_{15}\text{O}_2\text{N}$ : 325.1103. Found: 325.1088.

**2-(*p*-Chlorophenyl)-6-cyano-3-phenylbenzofuran (3da):** Colorless crystals. Mp 163-164 °C ( $\text{Et}_2\text{O}$ ).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 (2H, d,  $J = 8.8$  Hz), 7.43-7.56 (7H, m), 7.60 (2H, d,  $J = 8.8$  Hz), 7.85 (1H, s).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  107.5, 115.3, 118.0, 119.4, 120.9, 126.8, 127.9, 128.4, 128.5, 129.4, 129.5, 131.1, 134.3, 135.4, 152.6, 152.9. IR (KBr) 3054, 2223, 1480, 1427, 1092, 833, 826  $\text{cm}^{-1}$ . MS (EI)  $m/z$  329 ( $\text{M}^+$ , 100%). HRMS Calcd for  $\text{C}_{21}\text{H}_{12}\text{ONCl}$ : 329.0607. Found: 329.0589.

**6-Benzoyl-2-(*p*-chlorophenyl)-3-phenylbenzofuran (3db):** Colorless crystals. Mp 159-160 °C (Hexane : EtOAc = 2 : 1).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (2H, d,  $J = 8.8$  Hz), 7.43-7.52 (7H, m), 7.55 (1H, d,  $J = 8.4$  Hz), 7.58- 7.62 (3H, m), 7.76 (1H, dd,  $J = 1.2, 8.0$  Hz), 7.83 (2H, d,  $J = 6.8$  Hz), 8.01 (1H, d,  $J = 0.8$  Hz).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  113.5, 118.1, 119.7, 125.4, 128.2, 128.3, 128.3, 128.4, 128.8, 129.2, 129.6, 129.9, 131.7, 132.2, 134.0, 134.2, 134.9, 138.1, 152.5, 153.2, 196.1. IR (KBr) 3051, 1658, 1288, 1093  $\text{cm}^{-1}$ . MS (EI)  $m/z$  408 ( $\text{M}^+$ , 100%), 331 ( $\text{M}^+ - \text{C}_6\text{H}_5$ , 36%). HRMS Calcd for  $\text{C}_{27}\text{H}_{17}\text{O}_2\text{Cl}$ : 408.0917. Found: 408.0901.

**2-(*p*-Chlorophenyl)-6-nitro-3-phenylbenzofuran (3dc):** Yellow crystals. Mp 169-170 °C ( $\text{Et}_2\text{O}$ ).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (2H, d,  $J = 8.4$  Hz), 7.45-7.56 (6H, m), 7.61 (2H, d,  $J = 8.8$  Hz), 8.18 (1H, dd,  $J = 2.0, 8.4$  Hz), 8.45 (1H, d,  $J = 1.6$  Hz).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  107.6, 118.1, 119.0, 119.9, 127.8, 128.5, 128.6, 129.0, 129.4, 129.5, 131.0, 135.7, 135.9, 145.2, 152.5, 154.6. IR (KBr) 3101, 1512, 1344, 1095, 825  $\text{cm}^{-1}$ . MS (EI)  $m/z$  349 ( $\text{M}^+$ , 100%), 303 ( $\text{M}^+ - \text{NO}_2$ , 17%). HRMS Calcd for  $\text{C}_{20}\text{H}_{12}\text{O}_3\text{NCl}$ : 349.0506. Found: 349.0494.

**6-Cyano-2-(*p*-cyanophenyl)-3-phenylbenzofuran (3ea):** Colorless crystals. Mp >220 °C (EtOAc : Hexane = 2 : 1). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 (2H, dd, *J* = 1.6, 8.0 Hz), 7.49-7.58 (5H, m), 7.62 (2H, d, *J* = 8.8 Hz), 7.77 (2H, d, *J* = 8.0 Hz), 7.88 (1H, s). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 108.5, 112.5, 115.5, 118.3, 119.0, 120.4, 121.4, 126.9, 127.3, 128.9, 129.4, 129.5, 130.5, 132.3, 133.6, 134.0, 151.4, 152.8. IR (KBr) 3060, 2225, 1606, 845, 820, 702 cm<sup>-1</sup>. MS (EI) *m/z* 320 (M<sup>+</sup>, 100%). HRMS Calcd for C<sub>22</sub>H<sub>12</sub>ON<sub>2</sub>: 320.0950. Found: 320.0940.

**6-Cyano-2-ethyl-3-phenylbenzofuran (3fa):** Colorless crystals. Mp 112 °C (Hexane : EtOAc = 2 : 1). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 1.37 (3H, t, *J* = 8.0 Hz), 2.92 (2H, q, *J* = 8.0 Hz), 7.39-7.45 (3H, m), 7.48-7.52 (3H, m), 7.61 (1H, d, *J* = 8.0 Hz), 7.77 (1H, s). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 12.6, 20.4, 106.3, 115.0, 116.8, 119.7, 120.3, 126.4, 127.7, 129.0, 129.0, 131.3, 133.2, 152.8, 160.2. IR (KBr) 2979, 2924, 2225, 1429, 1182, 835, 706 cm<sup>-1</sup>. MS (EI) *m/z* 247 (M<sup>+</sup>, 100%), 232 (M<sup>+</sup>-CH<sub>3</sub>, 65%). HRMS Calcd for C<sub>17</sub>H<sub>13</sub>ON: 247.0997. Found: 247.0995.

**2-Benzyl-6-cyano-3-phenylbenzofuran (3ga):** Colorless crystals. Mp 147.5-148.5 °C (Hexane : EtOAc = 2 : 1). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 4.24 (2H, s), 7.26 (2H, dd, *J* = 7.6, 8.0 Hz), 7.33 (2H, dd, *J* = 6.4, 7.2 Hz), 7.42-7.54 (7H, m), 7.64 (1H, d, *J* = 8.0 Hz), 7.76 (1H, s). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 32.9, 106.7, 115.3, 118.7, 119.5, 120.6, 126.6, 126.9, 128.0, 128.5, 128.8, 129.0, 129.1, 131.0, 133.0, 136.8, 153.0, 156.6. IR (KBr) 3032, 2924, 2220, 2495, 1431, 980, 700 cm<sup>-1</sup>. MS (EI) *m/z* 309 (M<sup>+</sup>, 100%), 232 (M<sup>+</sup>-C<sub>6</sub>H<sub>5</sub>, 54%). HRMS Calcd for C<sub>22</sub>H<sub>15</sub>ON: 309.1153. Found: 309.1166.

**6-Cyano-2-(*p*-chloro-*o*-fluorophenyl)phenylmethyl-3-phenylbenzofuran (4ga):** Colorless crystals. Mp 156-158 °C (Hexane : EtOAc = 2 : 1). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 6.04 (1H, s), 7.18 (2H, dd, *J* = 7.6, 1.6 Hz), 7.32-7.38 (6H, m), 7.42-7.51 (5H, m), 7.54 (1H, dd, *J* = 8.0, 1.2 Hz), 7.64 (1H, dd, *J* = 8.0, 0.8 Hz), 7.80 (1H, dd, *J* = 1.2, 0.8 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 41.7 (d, *J* = 3.0 Hz), 107.5, 112.7 (d, *J* = 9.1 Hz), 115.7, 117.4 (d, *J* = 3.0 Hz), 119.2, 119.2 (d, *J* = 25.0 Hz), 119.9, 121.2, 126.9, 127.8, 128.3, 128.4, 128.4, 129.0, 129.1, 129.2, 130.2, 132.0 (d, *J* = 3.8 Hz), 132.7, 133.6 (d, *J* = 13.6 Hz), 138.4, 153.2, 154.8, 160.0 (d, *J* = 249.3 Hz). IR (KBr) 3072, 2229, 1568, 1495, 1415, 1255, 980, 702 cm<sup>-1</sup>. MS (EI) *m/z* 428 (M<sup>+</sup>, 74%), 308 (M<sup>+</sup>-C<sub>6</sub>H<sub>3</sub>CNF, 20%), 276 (M<sup>+</sup>-152, 100%). HRMS Calcd for C<sub>29</sub>H<sub>17</sub>ON<sub>2</sub>F: 428.1325. Found: 428.1316.

**3-Acetyl-6-cyano-2-methylbenzofuran (3ha):** Colorless crystals. Mp 131-132 °C (Et<sub>2</sub>O). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 2.65 (3H, s), 2.84 (3H, s), 7.60 (1H, d, *J* = 8.0 Hz), 7.76 (1H, s), 8.11 (1H, d, *J* = 8.0 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 15.7, 31.1, 107.6, 115.1, 117.8, 119.0, 122.6, 127.8, 130.5, 152.2, 165.8,

193.2. IR (KBr) 3095, 2222, 1664, 1394  $\text{cm}^{-1}$ . MS (EI)  $m/z$  199 ( $\text{M}^+$ , 62%), 184 ( $\text{M}^+ - \text{CH}_3$ , 100%). HRMS Calcd for  $\text{C}_{12}\text{H}_9\text{O}_2\text{N}$ : 199.0633. Found: 199.0616.

**3-Benzoyl-6-cyano-2-phenylbenzofuran (3ia):** Colorless crystals. Mp 149-151 °C (Hexane : EtOAc = 2 : 1).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31-7.38 (5H, m), 7.50-7.55 (2H, m), 7.66-7.68 (3H, s), 7.81 (2H, dd,  $J = 8.4, 1.2$  Hz), 7.90 (1H, s).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  108.2, 115.5, 115.9, 119.0, 122.4, 127.5, 128.3, 128.6, 128.6, 128.6, 129.7, 130.7, 132.7, 133.6, 137.1, 152.5, 160.6, 191.3. IR (KBr) 3059, 2224, 1641, 1377, 908  $\text{cm}^{-1}$ . MS (EI)  $m/z$  323 ( $\text{M}^+$ , 100%), 246 ( $\text{M}^+ - \text{C}_6\text{H}_5$ , 29%). HRMS Calcd for  $\text{C}_{22}\text{H}_{13}\text{O}_2\text{N}$ : 323.0946. Found: 323.0943.

**6-Cyano-3-(*p*-cyano-*o*-fluorophenyl)-2-(*p*-cyanophenyl)benzofuran (4ja):** Colorless crystals. Mp >245 °C (EtOAc).  $^1\text{H-NMR}$  (400 MHz, Benzene- $d_6$ )  $\delta$  6.47 (1H, dd,  $J = 7.6, 7.6$  Hz), 6.60 (1H, dd,  $J = 1.6, 9.2$  Hz), 6.68 (1H, d,  $J = 7.6$  Hz), 6.70 (1H, dd,  $J = 1.6, 7.6$  Hz), 6.84 (2H, d,  $J = 8.4$  Hz), 6.96 (1H, dd,  $J = 1.6, 8.0$  Hz), 7.01 (2H, d,  $J = 8.4$  Hz), 7.13 (1H, s).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  109.2, 112.0, 113.6, 114.8 (d,  $J = 9.1$  Hz), 116.0, 116.9 (d,  $J = 2.2$  Hz), 118.0, 118.7, 120.6 (d,  $J = 25.0$  Hz), 121.2, 124.2 (d,  $J = 15.1$  Hz), 127.3, 127.5, 129.0 (d,  $J = 3.8$  Hz), 132.66, 132.69, 132.8 (d,  $J = 3.8$  Hz), 132.9, 153.0, 153.4, 159.5 (d,  $J = 252.3$  Hz).  $^{19}\text{F-NMR}$  (376 MHz,  $\text{CDCl}_3$ ) -161.7. IR (KBr) 3072, 2924, 2227, 1603, 1412, 1267, 976, 829  $\text{cm}^{-1}$ . MS (EI)  $m/z$  363 ( $\text{M}^+$ , 100%). HRMS Calcd for  $\text{C}_{23}\text{H}_{10}\text{ON}_3\text{F}$ : 363.0807. Found: 363.0814.

**2-(*p*-Chlorophenyl)-6-dimethylamino-3-phenyl-4,5,7-trifluorobenzofuran (3dd):** Colorless crystals. Mp 138-139 °C (Hexane).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.99 (6H, t,  $J = 1.6$  Hz), 7.25 (2H, d,  $J = 8.8$  Hz), 7.43 (5H, br), 7.47 (2H, d,  $J = 8.8$  Hz).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  43.9 (dd,  $J = 3.0, 3.8$  Hz), 115.2 (d,  $J = 16.7$  Hz), 116.7, 127.7 (d,  $J = 10.6$  Hz), 128.0, 128.1, 128.3, 128.7, 128.8, 130.0, 131.1, 134.7, 138.2 (m), 139.8 (dd,  $J = 3.8, 242.5$  Hz), 140.3 (ddd,  $J = 6.0, 12.9, 253.1$  Hz), 143.5 (ddd,  $J = 4.6, 12.2, 240.2$  Hz), 150.5.  $^{19}\text{F-NMR}$  (376 MHz,  $\text{CDCl}_3$ ) -153.1 (dd,  $J = 17.7, 18.4$  Hz), -153.4 (d,  $J = 17.7$  Hz), -154.7 (d,  $J = 18.4$  Hz). IR (KBr) 2951, 2873, 2806, 1518, 1433, 991  $\text{cm}^{-1}$ . MS (EI)  $m/z$  401 ( $\text{M}^+$ , 100%), 386 ( $\text{M}^+ - \text{CH}_3$ , 17%). HRMS Calcd for  $\text{C}_{22}\text{H}_{15}\text{ONF}_3\text{Cl}$ : 401.0794. Found: 401.0772. CCDC 879722 contains the supplementary crystallographic data for compound **3dd**.

**2-(*p*-Chlorophenyl)-6-diphenylamino-3-phenyl-4,5,7-trifluorobenzofuran (3de):** Colorless crystals. Mp 162-163.5 °C (Hexane).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.03 (2H, t,  $J = 7.2$  Hz), 7.08 (4H, d,  $J = 8.0$  Hz), 7.25-7.30 (6H, m), 7.44-7.50 (7H, m).  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  116.9, 119.0 (m), 120.6 (m), 121.2, 122.9, 127.6, 128.3, 128.6, 128.9, 128.9, 129.3, 130.0, 130.7, 135.2, 138.0 (m), 140.6 (ddd,  $J = 3.8,$

15.9, 252.3 Hz), 144.6 (td,  $J = 3.8$ , 250.8 Hz), 144.6 (ddd,  $J = 2.2$ , 14.4, 247.0 Hz), 146.2, 151.8.  $^{19}\text{F}$ -NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -148.4 (d,  $J = 13.2$  Hz), -151.4 (d,  $J = 20.3$  Hz), -151.5 (d,  $J = 13.2$ , 20.3 Hz). IR (KBr) 3059, 3035, 1591, 1516, 1495, 1450, 1093, 997, 694  $\text{cm}^{-1}$ . MS (EI)  $m/z$  525 ( $\text{M}^+$ , 100%). HRMS Calcd for  $\text{C}_{32}\text{H}_{19}\text{ONF}_3\text{Cl}$ : 525.1107. Found: 525.1098. CCDC 879725 contains the supplementary crystallographic data for compound **3aa**.

**6-Butylthio-2-(*p*-chlorophenyl)-3-phenyl-4,5,7-trifluorobenzofuran (3df)**: Colorless crystals. Mp 79-81 °C (Hexane).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.91 (3H, t,  $J = 7.2$  Hz), 1.45 (2H, tt,  $J = 6.8$ , 6.8 Hz), 1.57 (2H, tt,  $J = 7.6$ , 7.6 Hz), 2.92 (2H, t,  $J = 7.2$  Hz), 7.28 (2H, d,  $J = 8.8$  Hz), 7.46 (5H, br), 7.51 (2H, d,  $J = 9.2$  Hz).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.6, 21.6, 31.8, 35.0, 108.7 (dd,  $J = 20.5$ , 22.0 Hz), 117.0, 121.3 (d,  $J = 15.9$  Hz), 127.5, 128.4, 128.6, 128.8, 128.9, 129.9, 130.6, 135.4, 137.5 (dd,  $J = 6.0$ , 12.8 Hz), 140.0 (ddd,  $J = 3.8$ , 17.4, 250.8 Hz), 143.9 (ddd,  $J = 3.1$ , 3.8, 248.6 Hz), 146.4 (ddd,  $J = 2.3$ , 12.9, 238.7 Hz), 152.0.  $^{19}\text{F}$ -NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -135.8 (d,  $J = 17.7$  Hz), -140.0 (d,  $J = 21.8$  Hz), -151.7 (dd,  $J = 17.7$ , 21.8 Hz). IR (KBr) 2958, 1504, 1481, 1263, 989, 825  $\text{cm}^{-1}$ . MS (EI)  $m/z$  446 ( $\text{M}^+$ , 100%). HRMS Calcd for  $\text{C}_{24}\text{H}_{18}\text{OSF}_3\text{Cl}$ : 446.0719. Found: 446.0714.

**2-(*p*-Chlorophenyl)-3-phenyl-6-(*p*-tolylthio)-4,5,7-trifluorobenzofuran (3dg)**: Colorless crystals. Mp 139.5-140 °C (Hexane).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.30 (3H, s), 7.08 (2H, d,  $J = 7.6$  Hz), 7.26-7.30 (4H, m), 7.44 (5H, br), 7.49 (2H, d,  $J = 8.8$  Hz).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  21.1, 108.5 (dd,  $J = 19.7$ , 21.2 Hz), 117.1, 122.3 (d,  $J = 15.2$  Hz), 127.4, 128.5, 128.6, 128.9, 130.0, 130.3, 130.5, 131.0, 135.5, 137.5, 137.6 (m), 140.1 (ddd,  $J = 4.5$ , 17.4, 251.5 Hz), 143.8 (ddd,  $J = 3.0$ , 3.8, 250.1 Hz), 146.2 (ddd,  $J = 1.5$ , 14.4, 240.2 Hz), 152.4.  $^{19}\text{F}$ -NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -135.1 (d,  $J = 18.8$  Hz), -139.3 (d,  $J = 21.4$  Hz), -151.0 (dd,  $J = 18.8$ , 21.4 Hz). IR (KBr) 3035, 2918, 1504, 1493, 1479, 1261, 993, 829, 706  $\text{cm}^{-1}$ . MS (EI)  $m/z$  480 ( $\text{M}^+$ , 100%). HRMS Calcd for  $\text{C}_{27}\text{H}_{16}\text{OSF}_3\text{Cl}$ : 480.05625. Found: 480.05344. Two carbon peak of aromatic region was piled up in  $^{13}\text{C}$ -NMR.

**2-(*p*-Chlorophenyl)-6-methyl-3-phenyl-4,5,7-trifluorobenzofuran (3dh)**: Colorless crystals. Mp 163-164.5 °C (Hexane).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.37 (3H, t,  $J = 2.4$  Hz), 7.27 (2H, d,  $J = 8.8$  Hz), 7.44- 7.47 (5H, m), 7.50 (2H, d,  $J = 8.8$  Hz).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  7.8, 111.2 (dd,  $J = 20.8$ , 17.8 Hz), 116.8, 118.6 (d,  $J = 15.6$  Hz), 127.9, 128.3, 128.4, 128.8, 130.0, 130.0, 131.0, 135.0, 137.6 (dd,  $J = 12.6$ , 7.4 Hz), 139.8 (ddd,  $J = 247.8$ , 16.3, 4.4 Hz), 141.4 (d,  $J = 20.3$  Hz), 144.7 (ddd,  $J = 238.9$ , 12.7, 6.0 Hz), 150.8.  $^{19}\text{F}$ -NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -146.5 (d,  $J = 18.8$  Hz), -149.4 (d,  $J = 20.3$  Hz), -153.8 (dd,  $J = 18.8$ , 20.3 Hz). IR (KBr) 3062, 2925, 1514, 1441, 1277, 1065, 951, 829  $\text{cm}^{-1}$ . MS (EI)  $m/z$  372 ( $\text{M}^+$ , 100%). HRMS Calcd for  $\text{C}_{21}\text{H}_{12}\text{OF}_3\text{Cl}$ : 372.0529. Found: 372.0522.

**2-(*p*-Chlorophenyl)-3-phenyl-4,5,7-trifluorobenzofuran (3di):** Colorless crystals. Mp 119-120 °C (Methanol). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 6.96 (1H, ddd, *J* = 6.0, 9.6, 10.4 Hz), 7.27 (2H, d, *J* = 8.8 Hz), 7.44 (5H, s), 7.49 (2H, d, *J* = 8.8 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 101.2 (dd, *J* = 21.9, 25.0 Hz), 117.0, 121.6 (td, *J* = 3.1, 15.1), 127.6, 128.4, 128.5, 128.9, 129.9, 130.0, 130.8, 135.3, 137.6 (dd, *J* = 7.5, 12.1 Hz), 139.9 (ddd, *J* = 3.8, 15.1, 248.5 Hz), 142.6 (ddd, *J* = 3.0, 10.6, 247.0 Hz), 145.3 (ddd, *J* = 9.1, 12.9, 241.0 Hz), 151.9. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -141.8 (dd, *J* = 10.9, 19.1 Hz), -145.8 (dd, *J* = 10.9, 20.3 Hz), -153.1 (ddd, *J* = 6.0, 19.1, 20.3 Hz). IR (KBr) 3076, 1651, 1522, 1483, 1421, 1257, 1101, 968, 825 cm<sup>-1</sup>. MS (EI) *m/z* 358 (M<sup>+</sup>, 100%). HRMS Calcd for C<sub>20</sub>H<sub>10</sub>OF<sub>3</sub>Cl: 358.0372. Found: 358.0375. CCDC 879724 contains the supplementary crystallographic data for compound **3di**.

**2-(*p*-Chlorophenyl)-3-phenyl-4,5,6,7-tetrafluorobenzofuran (3dj):** Colorless crystals. Mp 148-149 °C (Hexane). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.27 (2H, d, *J* = 8.8 Hz), 7.42-7.48 (7H, m). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 115.7 (d, *J* = 15.6 Hz), 116.4, 127.3, 128.3, 128.7, 128.89, 128.94, 129.9, 130.4, 134.0 (ddd, *J* = 5.2, 11.9, 250.8 Hz), 135.4, 137.0 (m), 137.5 (td, *J* = 14.9, 244.8 Hz), 138.9 (td, *J* = 13.8, 247.8 Hz), 140.0 (tdd, *J* = 3.0, 12.6, 251.6 Hz), 152.0. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -151.1 (dd, *J* = 19.1, 20.3 Hz), -163.6 (dd, *J* = 19.2, 20.3 Hz), -165.1 (ddd, *J* = 2.3, 20.3, 20.3 Hz), -166.8 (ddd, *J* = 2.3, 20.3, 20.3). IR (KBr) 3070, 1531, 1477, 1093, 1082, 1005, 833 cm<sup>-1</sup>. MS (EI) *m/z* 376 (M<sup>+</sup>, 100%). HRMS Calcd for C<sub>20</sub>H<sub>9</sub>OF<sub>4</sub>Cl: 376.0278. Found: 376.0258.

**2,8-Bis(*p*-chlorophenyl)-4,5-difluoro-3,6-diphenylbenzo[2,1-*b*;3,4-*b'*]difuran (4dj):** Colorless crystals. Mp 149-150 °C (Hexane). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.29 (4H, d, *J* = 8.4 Hz), 7.45-7.52 (10H, m), 7.56 (4H, d, *J* = 8.8 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 117.7 (dd, *J* = 7.5, 10.4 Hz), 117.9, 128.2, 128.2, 128.3, 128.4, 128.8, 130.1, 131.4, 134.7, 140.3 (dd, *J* = 16.4, 247.1 Hz), 150.4. <sup>19</sup>F-NMR (376 MHz, CDCl<sub>3</sub>) δ -156.2. IR (KBr) 3070, 1531, 1477, 1093, 1082, 1005, 833 cm<sup>-1</sup>. MS (EI) *m/z* 566 (M<sup>+</sup>, 100%). HRMS Calcd for C<sub>34</sub>H<sub>18</sub>O<sub>2</sub>F<sub>2</sub>Cl<sub>2</sub>: 566.0652. Found: 566.0657. One carbon peak of aromatic region was piled up in <sup>13</sup>C-NMR. CCDC 879723 contains the supplementary crystallographic data for compound **4dj**.

**6-Benzoyl-2-(*p*-chlorophenyl)-3-phenyl-4,5,6-trifluorobenzofuran (3dk):** Colorless crystals. Mp 167-168 °C (Hexane). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.30 (2H, d, *J* = 8.8 Hz), 7.48 (5H, br), 7.52 (4H, m), 7.66 (1H, t, *J* = 7.2 Hz), 7.93 (2H, d, *J* = 7.2 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 113.9 (dd, *J* = 20.1, 19.3 Hz), 117.1, 122.8 (d, *J* = 16.4 Hz), 127.2, 128.6, 128.8, 128.9, 129.0, 129.0, 129.8, 130.0, 130.3, 134.4, 135.7, 136.8, 137.4 (dd, *J* = 6.7, 12.6 Hz), 140.0 (ddd, *J* = 4.5, 15.6, 252.3 Hz), 140.1 (ddd, *J* = 4.5,

4.5, 251.6 Hz), 143.0 (ddd,  $J = 5.2, 14.1, 244.8$  Hz), 153.3, 187.6.  $^{19}\text{F}$ -NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -142.7 (d,  $J = 21.4$  Hz), -147.1 (dd,  $J = 19.2$  Hz), -151.4 (dd,  $J = 19.2, 21.4$  Hz). IR (KBr) 3059, 1676, 1508, 1294, 1003  $\text{cm}^{-1}$ . MS (EI)  $m/z$  462 ( $\text{M}^+$ , 100%), 385 ( $\text{M}^+ - \text{C}_6\text{H}_5$ , 15%). HRMS Calcd for  $\text{C}_{27}\text{H}_{14}\text{O}_2\text{F}_3\text{Cl}$ : 462.0634. Found: 462.0623.

**2-(*o*-Chloro-*p*-cyanophenyl)-1-(*p*-chlorophenyl)-2-phenyl-1-ethanone (8da):** In a two-necked flask equipped with a reflux condenser were placed **1d** (0.5 mmol, 115.0 mg), **7a** (0.25 mmol, 38.8 mg),  $\text{RhH}(\text{PPh}_3)_4$  (5 mol%, 14.4 mg), 1,2-bis(diphenylphosphino)ethane (10 mol%, 10.0 mg), and tributylsilane (0.25 mmol, 65  $\mu\text{L}$ ) in chlorobenzene (1 mL) under an argon atmosphere, and solution was stirred under reflux for 6 h. Then, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel giving **8da** (54.9 mg, 60%) as colorless crystals. Mp 130-131  $^\circ\text{C}$  (Hexane : EtOAc = 2 : 1).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.39 (1H, s), 7.08 (1H, d,  $J = 8.0$  Hz), 7.27 (2H, d,  $J = 6.8$  Hz), 7.33- 7.42 (5H, m), 7.47 (1H, dd,  $J = 2.0, 8.0$  Hz), 7.69 (1H, d,  $J = 2.0$  Hz), 7.93 (2H, d,  $J = 8.8$  Hz).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  56.7, 112.5, 117.3, 128.3, 129.1, 129.4, 129.6, 130.2, 130.4, 131.8, 132.5, 134.3, 134.6, 135.3, 140.0, 143.1, 195.1. IR (KBr) 3066, 3028, 2233, 1732, 1685, 1587, 1495, 1317, 1128, 1055, 742, 698  $\text{cm}^{-1}$ . MS (EI)  $m/z$  365 ( $\text{M}^+$ , 1%), 226 ( $\text{M}^+ - \text{COC}_6\text{H}_4\text{Cl}$ , 2%), 139 ( $\text{COC}_6\text{H}_4\text{Cl}$ , 100%). HRMS Calcd for  $\text{C}_{21}\text{H}_{13}\text{ONCl}_2$ : 365.0374. Found: 365.0357.

**2-(*o*-Chloro-*p*-cyanophenyl)-1,2-diphenyl-1-ethanone (8aa):** Colorless crystals. Mp 141.5-142  $^\circ\text{C}$  (Hexane : EtOAc = 2 : 1).  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.47 (1H, s), 7.11 (1H, d,  $J = 8.0$  Hz), 7.28 (2H, d,  $J = 7.2$  Hz), 7.33 (1H, t,  $J = 7.2$  Hz), 7.33-7.44 (4H, m), 7.46 (1H, dd,  $J = 1.6, 8.0$  Hz), 7.54 (1H, t,  $J = 7.6$  Hz), 7.69 (1H, d,  $J = 1.6$  Hz), 8.00 (2H, d,  $J = 7.6$  Hz).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  56.6, 112.3, 117.4, 128.1, 128.8, 128.9, 129.5, 130.4, 131.8, 132.4, 133.4, 134.6, 135.6, 135.9, 143.5, 196.3. IR (KBr) 3062, 3033, 2229, 1682, 1217, 704  $\text{cm}^{-1}$ . MS (EI)  $m/z$  331 ( $\text{M}^+$ , 0.4%), 105 (COPh, 100%). HRMS Calcd for  $\text{C}_{21}\text{H}_{14}\text{ONCl}$ : 331.0764. Found: 331.0764.

**1,2-Bis(*p*-methoxyphenyl)-2-(*o*-chloro-*p*-cyano)-1-ethanone (8ba):** Colorless oil.  $^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.78 (3H, s), 3.82 (3H, s), 6.36 (1H, s), 6.89 (2H, d,  $J = 8.8$  Hz), 6.90 (2H, d,  $J = 8.8$  Hz), 7.12 (1H, d,  $J = 8.0$  Hz), 7.20 (2H, d,  $J = 8.8$  Hz), 7.45 (1H, dd,  $J = 1.2$  Hz, 8.0 Hz), 7.67 (1H, d,  $J = 2.4$  Hz), 7.98 (2H, d,  $J = 8.4$  Hz).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  55.2, 55.4, 55.8, 112.0, 113.9, 114.7, 117.5, 127.8, 128.9, 130.3, 130.5, 131.2, 131.8, 132.3, 134.5, 144.1, 159.2, 163.6, 194.9. IR (neat) 2935, 2839, 2231, 1676, 1599, 1510, 1254, 1169, 1032  $\text{cm}^{-1}$ . MS (EI)  $m/z$  391 ( $\text{M}^+$ , 10%), 376 ( $\text{M}^+ - \text{CH}_3$ , 5%), 135 ( $\text{H}_3\text{CC}_6\text{H}_4\text{CO}$ , 100%). HRMS Calcd for  $\text{C}_{23}\text{H}_{18}\text{O}_3\text{NCl}$ : 391.0975. Found: 391.0967.

**2-(*o*-Chloro-*p*-nitrophenyl)-1-(*p*-chlorophenyl)-2-phenyl-1-ethanone (8db):** Colorless oil. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 6.42 (1H, s), 7.15 (1H, d, *J* = 8.4 Hz), 7.28 (2H, d, *J* = 6.8 Hz), 7.34-7.44 (5H, m), 7.94 (2H, d, *J* = 8.8 Hz), 8.03 (1H, dd, *J* = 2.4, 8.8 Hz), 8.29 (1H, d, *J* = 2.4 Hz). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 56.7, 121.7, 124.4, 128.4, 129.2, 129.4, 129.7, 130.3, 131.8, 134.2, 134.6, 135.3, 140.1, 144.8, 147.3, 195.0. IR (neat) 3099, 2925, 1685, 1520, 1350, 768 cm<sup>-1</sup>. MS (EI) *m/z* 385 (M<sup>+</sup>, 2%), 139 (C<sub>10</sub>H<sub>7</sub>ClO, 100%). HRMS Calcd for C<sub>20</sub>H<sub>13</sub>O<sub>3</sub>NC<sub>12</sub>: 385.0272. Found: 385.0264.

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8. Crystallographic data excluding structure factors have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 879722-879726 for compounds **3aa**, **3dd**, **3de**, **3di**, and **4dj**. A copy of the data can be obtained free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK or e-mail: deposit@ccdc.cam.ac.uk.