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# Regioselective Synthesis of Aurone Derivatives via $PBu_3$-Catalyzed Cyclization of 2-Alkynoylphenols

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Aurone derivatives were synthesized in good to high yields by $PBu_3$-catalyzed intramolecular 5-exo cyclization of 2-alkynoylphenols. The reaction proceeds in high regioselectivity without forming 6-endo cyclization products.

**Keywords** 2-alkynoylphenol, $PBu_3$, intramolecular cyclization, aurone

## Introduction

Flavonoids are a large class of plant natural products and exhibit multiple biological activities.[1] Aurones, 2-benzylidenzofuran-3(2*H*)-ones, constitute a minor subclass of flavonoids and are responsible for the pigmentation of the flowers and fruits.[2] Aurones also exhibit a broad variety of biological activities such as antifeedant activity, antibacterial activity or antifungal activity[3] and have been used as anticancer agents, anti-inflammatory agents or antioxidants.[4] Therefore, the syntheses of aurone derivatives are well established and keep being developed.[5]

The popular method to synthesis aurone derivatives is based on the condensation of benzofuran-3(2*H*)-ones with benzaldehydes.[6] However, the aldol-like reaction requires the synthesis of benzofuran-3(2*H*)-ones which is usually carried out under harsh reaction conditions and yields are modest. Oxidative cyclisation of 2'-hydroxychalcones are also reported to prepare aurones.[7] Li and Pale groups reported the regioselective synthesis of aurones respectively from metal-catalyzed cyclization of 2-(1-hydroxyprop-2-ynyl)phenols.[8] These methods, however, usually cannot completely prevent the formation of flavones (6-endo cyclisation product) and metal catalyst such as gold or silver is needed. 2-Alkynoylphenols have been widely used to prepare flavone derivatives by 6-endo cyclization.[9] For example, Doi and co-workers synthesized flavones regioselectively from 2-alkynoylphenols.[9a,9b] On the contrary, synthesis of aurone derivatives from 2-alkynoylphenol by 5-exo-digonal cyclization is limited because 6-endo-digonal cyclization is generally a favorable process that has been reported as a Baldwin's rule in 1976.[9a,10]

Due to the electron-withdrawing effect of carbonyl group, acetylenic ketones have been widely used as electron-deficient alkynes in organic synthesis.[11] Recently, we reported the synthesis of polysubstituted alkenes from acetylenic ketones.[12] In continuation of our research interest in this field, we wish to report herein a facile synthesis of aurone derivatives by $PBu_3$-catalyzed cyclization of 2-alkynoylphenols via the intramolecular addition of acetylenic ketones.

## Results and Discussion

Initially, the intramolecular addition reaction of 2-alkynoylphenol **1a** catalyzed by various bases was investigated. The results are summarized in Table 1. It was found that no reaction happened when 2-alkynoylphenol **1a** was dissolved in $CH_2Cl_2$ and stirred at room temperature for 24 h (Table 1, entry 1). 5-Exo cyclization product **2a** was isolated in 66% yield and trace 6-endo cyclization product **3a** was formed when 5 mol% $PPh_3$ was added as catalyst (Table 1, entry 4). Gratifyingly, **2a** was isolated in 95% yield with high regioselectivity when the reaction was catalyzed by 5 mol% $PBu_3$ (Table 1, entry 5). $Et_3N$, pyridine, tri-*t*-butylphosphine (TTBuP) or $Bu_3PO$ can not be used as catalyst to promote the reaction (Table 1, entries 2, 3, 6 and 7). When the $PBu_3$-catalyzed cyclization reaction of **1a** was carried out in solvents other than $CH_2Cl_2$, **2a** was isolated in inferior yields (Table 1, entries 8—11). An increase in the amount of $PBu_3$ has no apparent effect on the yield while a lower yield of **2a** was obtained when a reduced amount of $PBu_3$ was used (Table 1, entries 13 and 14). Therefore, we used 5 mol% $PBu_3$ in $CH_2Cl_2$ at room temperature as the general reaction

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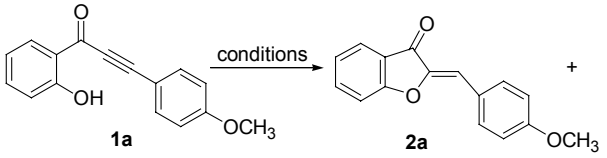
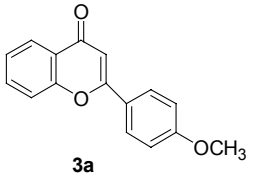
conditions in the subsequent studies.

**Table 1** Investigation of cyclization of 2-alkynoylphenol **1a**[a]




3a

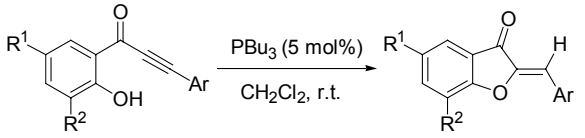
| Entry | Solvent | Catalyst | *T*/℃ | Time/h | Ratio of **2a**/**3a**[b] | Yield[c]/% |
|---|---|---|---|---|---|---|
| 1 | $CH_2Cl_2$ | NONE | r.t. | 24 | — | NR |
| 2 | $CH_2Cl_2$ | $NEt_3$ | r.t. | 24 | — | NR |
| 3 | $CH_2Cl_2$ | Pyridine | r.t. | 24 | — | NR |
| 4 | $CH_2Cl_2$ | $PPh_3$ | r.t. | 24 | >98∶2 | 66 |
| 5 | $CH_2Cl_2$ | $PBu_3$ | r.t. | 1 | >98∶2 | 95 |
| 6 | $CH_2Cl_2$ | $Bu_3PO$ | r.t. | 10 | — | NR |
| 7 | $CH_2Cl_2$ | TTBuP | r.t. | 24 | — | NR |
| 8 | Toluene | $PBu_3$ | r.t. | 1 | >98∶2 | 89 |
| 9 | THF | $PBu_3$ | r.t. | 1 | >98∶2 | 86 |
| 10 | $CH_3CN$ | $PBu_3$ | r.t. | 1 | 86∶14 | 79 |
| 11 | DMSO | $PBu_3$ | r.t. | 1 | 68∶32 | 61 |
| 12 | $CH_2Cl_2$ | $PBu_3$ | 40 | 1 | >98∶2 | 87 |
| 13[d] | $CH_2Cl_2$ | $PBu_3$ | r.t. | 1 | >98∶2 | 92 |
| 14[e] | $CH_2Cl_2$ | $PBu_3$ | r.t. | 1 | >98∶2 | 90 |

[a] Reaction conditions: **1a** (0.5 mmol) and 5 mol% of catalyst in 2 mL of solvent. [b] The ratio of **2a** and **3a** was determined by crude $^1$H NMR. [c] Isolated yield. [d] 10 mol% $PBu_3$ was used. [e] 2 mol% $PBu_3$ was used.

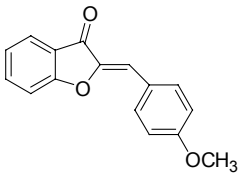
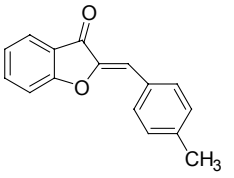
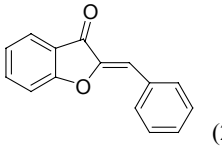
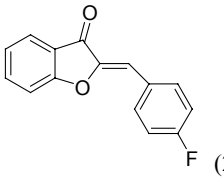
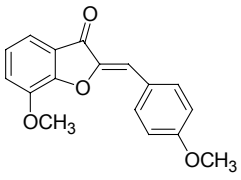
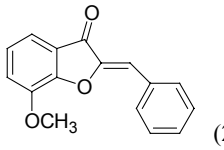
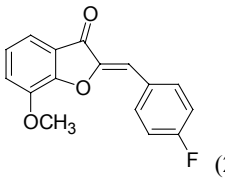
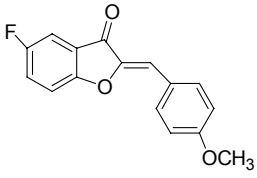
With the optimal reaction conditions in hand, the scope and generality of the intramolecular cyclization reaction of 2-alkynoylphenol was investigated. The results are compiled in Table 2. Table 2 shows that the cyclization reactions of various 2-alkynoylphenol possessing either a methoxy, fluoro or *t*-Bu group on the left benzene ring or methyl, fluoro or methoxy group on the right benzene ring proceed smoothly. The corresponding aurone derivatives were obtained in good to excellent yield. The products **2** were obtained in 81%—95% yields when electron-donating groups such as methyl (Table 1, entry 2), methoxy (Table 1, entries 1, 5, 6) or *t*-Bu (Table 1, entries 11, 12) attached to the left or right benzene ring, while the yields of **2** are lower (62%—83%) when the substrates contain fluoro either in the left or right benzene ring (Table 1, entries 4, 7—10, 13).

The molecular structure of compound **2b** was con-

**Table 2** $PBu_3$-catalyzed cyclization of 2-alkynoylphenols




**1** **2**

| Entry | Substrate **1** ($R^1$, $R^2$, Ar) | Product **2** | Yield/% |
|---|---|---|---|
| 1 | H, H, *p*-$CH_3OC_6H_4$ (**1a**) |  (**2a**) | 95 |
| 2 | H, H, *p*-$CH_3C_6H_4$ (**1b**) |  (**2b**) | 93 |
| 3 | H, H, $C_6H_5$ (**1c**) |  (**2c**) | 92 |
| 4 | H, H, *p*-$FC_6H_4$ (**1d**) |  (**2d**) | 80 |
| 5 | H, $CH_3O$, *p*-$CH_3OC_6H_4$ (**1e**) |  (**2e**) | 87 |
| 6 | H, $CH_3O$, $C_6H_5$ (**1f**) |  (**2f**) | 81 |
| 7 | H, $CH_3O$, *p*-$FC_6H_4$ (**1g**) |  (**2g**) | 75 |
| 8 | F, H, *p*-$CH_3OC_6H_4$ (**1h**) |  (**2h**) | 83 |

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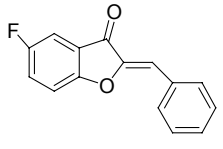
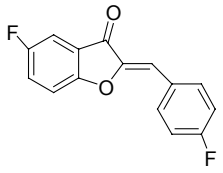
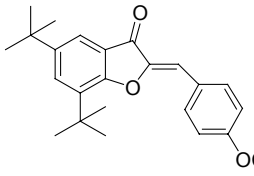
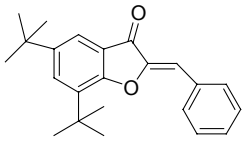
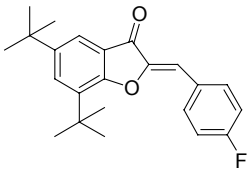
Continued

| Entry | Substrate **1** ($R^1$, $R^2$, Ar) | Product **2** | Yield/ % |
|---|---|---|---|
| 9 | F, H, $C_6H_5$ (**1i**) |  (**2i**) | 76 |
| 10 | F, H, *p*-$FC_6H_4$ (**1j**) |  (**2j**) | 62 |
| 11 | *t*-Bu, *t*-Bu, *p*-$CH_3OC_6H_4$ (**1k**) |  (**2k**) | 93 |
| 12 | *t*-Bu, *t*-Bu, $C_6H_5$ (**1l**) |  (**2l**) | 90 |
| 13 | *t*-Bu, *t*-Bu, *p*-$FC_6H_4$ (**1m**) |  (**2m**) | 79 |

firmed by X-ray diffraction analysis (Figure 1). Figure 1 shows that 5-exo cyclization of 2-alkynoylphenol was induced by $PBu_3$ to afford aurone derivatives and the reaction proceeds with *Z*-isomer selectivity.

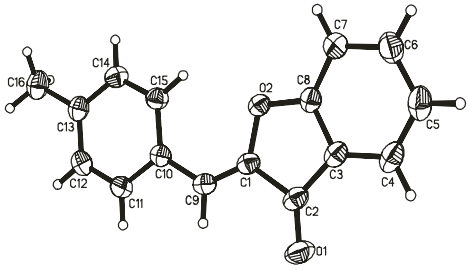
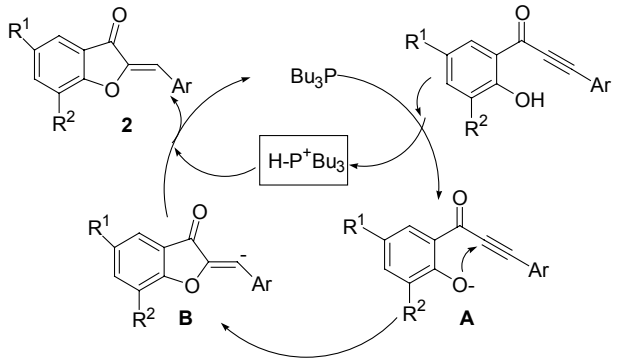



**Figure 1** The molecular structure of compound **2b**.

Based on the reported literature[9b,13] and the above experimental results, a plausible mechanism for the formation of aurone derivatives was depicated in Scheme 1. First, the $PBu_3$ acted as a base to deprotonate the phenolic hydroxyl group to generate the intermediate **A** and the resulting phenoxide **A** employed 5-exo cyclization to form vinyl carbanion **B**, which was probably arising from the kinetically controlled nucleophilic attach at the $\alpha$-carbonyl carbon. The vinyl carbanion **B** was rapidly protonated by the protonated phosphines $H\text{-}P^+Bu_3$ to give **2**.

**Scheme 1** A plausible mechanism for the formation of aurones




## Conclusions

In conclusion, we have demonstrated a convenient and transition-metal-free procedure for the regioselective syntheses of aurone derivatives in good to high yields from the $PBu_3$-catalyzed intramolecular cyclization of 2-alkynoylphenol. The method induces exclusive formation of 5-exo cyclization without formation of the 6-endo cyclized product.

## Experimental

All solid products were recrystallized from ethyl acetate and hexane, and the melting points are uncorrected. All reactions were carried out under an air atmosphere. $^1H$ NMR and $^{13}C$ NMR spectra were recorded on a BRUKER AVANCE-300 in $CDCl_3$ with TMS as the internal standard. The starting material 2-alkynoylphenols were prepared according to previously reported procedure.[9b]

**Typical procedure for the synthesis of aurone derivatives 2**

5 mol% $PBu_3$ was added to a solution of 2-alkynoylphenol **1** (0.5 mmol) in $CH_2Cl_2$ (2 mL) and the reaction mixture was stirred at room temperature. After the completion of the reaction (monitored by TLC), the reaction mixture was diluted with water and extracted with ethyl acetate (5 mL×3). The combined organics were dried over anhydrous $Na_2SO_4$ and the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (ethyl acetate/petroleum ether=1/20, *V*/*V*) to afford product **2**.

**(*Z*)-2-(4-Methoxybenzylidene)benzofuran-3(2*H*)-one (2a)** Yellow solid; m.p. 135−136 ℃; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$: 7.90 (d, $J$=8.6 Hz, 2H), 7.81 (d, $J$=7.4 Hz, 1H), 7.67−7.62 (m, 1H), 7.33 (d, $J$=8.2 Hz, 1H), 7.27−7.19 (m, 1H), 6.99 (d, $J$=8.6 Hz, 2H), 6.89

(s, 1H), 3.87 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 184.6, 165.8, 161.0, 145.9, 136.6, 133.5, 125.0, 124.5, 123.3, 121.9, 114.5, 113.4, 112.9, 55.4; IR (KBr) *v*: 1697, 1651, 1595, 1473, 883, 748, 696 cm$^{-1}$; HRMS (EI) calcd for $C_{16}H_{12}O_3$ ($M^+$) 252.0786, found 252.0782.

**(*Z*)-2-(4-Methylbenzylidene)benzofuran-3(2*H*)-one (2b)** Yellow solid; m.p. 93－94 ℃; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$: 7.83 (d, $J$=7.1 Hz, 3H), 7.68－7.63 (m, 1H), 7.35－7.22 (m, 4H), 6.90 (s, 1H), 2.41 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 184.6, 165.9, 146.4, 140.4, 136.7, 131.5, 129.7, 129.5, 124.5, 123.3, 121.7, 113.3, 112.9, 21,6; IR (KBr) *v*: 1710, 1655, 1596, 1465, 883, 746, 690 cm$^{-1}$; HRMS (EI) calcd for $C_{16}H_{12}O_2$ ($M^+$) 236.0837, found 236.0831.

**(*Z*)-2-Benzylidenebenzofuran-3(2*H*)-one (2c)** Yellow solid; m.p. 100－101 ℃; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$: 7.93 (d, $J$=7.2 Hz, 2H), 7.82 (d, $J$=7.4 Hz, 1H), 7.69－7.64 (m, 1H), 7.49－7.33 (m, 4H), 7.26－7.20 (m, 1H), 6.91 (s, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 183.7, 165.1, 145.8, 135.9, 131.3, 130.5, 128.9, 127.9, 123.6, 122.4, 120.6, 112.0, 111.9; IR (KBr) *v*: 1712, 1658, 1598, 1450, 883, 746, 686 cm$^{-1}$; HRMS (EI) calcd for $C_{15}H_{10}O_2$ ($M^+$) 222.0681, found 222.0673.

**(*Z*)-2-(4-Fluorobenzylidene)benzofuran-3(2*H*)-one (2d)** Yellow solid; m.p. 146－147 ℃; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$: 7.93－7.81 (m, 3H), 7.69－7.67 (m, 1H), 7.35－7.33 (m, 1H), 7.26－7.16 (m, 3H), 6.87 (s, 1H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$: 183.6, 165.0, 162.4 (d, $J$=250.9 Hz), 145.4, 135.9, 132.5 (d, $J$=8.4 Hz), 127.5 (d, $J$=3.3 Hz), 123.7, 122.5, 120.6, 115.1 (d, $J$=21.7 Hz), 111.9, 110.8; IR (KBr) *v*: 1714, 1658, 1598, 1473, 881, 750, 696 cm$^{-1}$; HRMS *m*/*z* (ESI) calcd for $C_{15}H_{10}FO_2$ ($M+H^+$) 241.0665, found 241.0659.

**(*Z*)-2-(4-Methoxybenzylidene)-7-methoxybenzofuran-3(2*H*)-one (2e)** Yellow solid; m.p. 136－137 ℃; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$: 7.92 (d, $J$=8.7 Hz, 2H), 7.40－7.37 (m, 1H), 7.17－7.10 (m, 2H), 7.00 (d, $J$=8.7 Hz, 2H), 6.92 (s, 1H), 4.03 (s, 3H), 3.87 (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$: 183.6, 160.1, 154.5, 144.9, 144.8, 132.6, 124.0, 122.7, 122.3, 117.2, 114.7, 113.5, 112.9, 55.3, 54.3; IR (KBr) *v*: 1693, 1643, 1598, 1438, 896, 833, 754 cm$^{-1}$; HRMS *m*/*z* (ESI) calcd for $C_{17}H_{15}O_4$ ($M+H^+$) 283.0970, found 283.0965.

**(*Z*)-2-Benzylidene-7-methoxybenzofuran-3(2*H*)-one (2f)** Yellow solid; m.p. 143－144 ℃; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$: 7.95 (d, $J$=6.7 Hz, 2H), 7.48－7.39 (m, 4H), 7.17 (s, 2H), 6.93 (s, 1H), 4.04 (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$: 183.8, 154.8, 145.8, 144.9, 131.2, 130.6, 128.9, 127.9, 122.9, 122.0, 117.7, 114.8, 112.5, 55.3; IR (KBr) *v*: 1703, 1651, 1600, 1438, 904, 754, 688 cm$^{-1}$; HRMS *m*/*z* (EI) calcd for $C_{16}H_{12}O_3$ ($M^+$) 252.0786, found 252.0777.

**(*Z*)-2-(4-Fluorobenzylidene)-7-methoxybenzofuran-3(2*H*)-one (2g)** Yellow solid; m.p. 148－149 ℃; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$: 7.98－7.93 (m, 2H), 7.41－7.38 (m, 1H), 7.20－7.13 (m, 4H ), 6.89 (s, 1H), 4.04 (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$: 183.8, 162.5 (d, $J$=251.1 Hz), 154.7, 145.4, 144.9, 132.7 (d, $J$=8.4 Hz), 127.5, 123.0, 121.9, 117.6, 115.2 (d, $J$=21.8 Hz), 114.8, 111.4; IR (KBr) *v*: 1714, 1654, 1598, 1440, 900, 833, 74 2 cm$^{-1}$; HRMS *m*/*z* (ESI) calcd for $C_{16}H_{12}FO_3$ ($M+H^+$) 271.0770, found 271.0765.

**(*Z*)-2-(4-Methoxybenzylidene)-5-fluorobenzofuran-3(2*H*)-one (2h)** Yellow solid; m.p. 152－153 ℃; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$: 7.89 (d, $J$=8.7 Hz, 2H), 7.48－7.26 (m, 3H), 7.00 (d, $J$=8.7 Hz, 2H), 6.91 (s, 1H), 3.88 (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$: 182.8, 160.8, 160.3, 157.7 (d, $J$=242.9 Hz), 145.4, 132.6, 123.8, 122.9 (d, $J$=25.8 Hz), 121.6 (d, $J$=7.7 Hz), 113.5, 113.3, 113.0 (d, $J$=7.7 Hz), 109.0 (d, $J$=24.1 Hz), 54.4; IR (KBr) *v*: 1697, 1649, 1597, 1454, 817, 792 cm$^{-1}$; HRMS *m*/*z* (ESI) calcd for $C_{16}H_{12}FO_3$ ($M+H^+$) 271.0770, found 271.0765.

**(*Z*)-2-Benzylidene-5-fluorobenzofuran-3(2*H*)-one (2i)** Yellow solid; m.p. 119－120 ℃; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$: 7.92 (d, $J$=6.9 Hz, 2H), 7.48－7.33 (m, 6H), 6.92 (s, 1H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$: 183.1, 161.1, 157.8 (d, $J$=242.9 Hz), 146.4, 131.0, 130.6, 129.2, 127.9, 123.2 (d, $J$=25.7 Hz), 121.3 (d, $J$=8.0 Hz), 113.1 (d, $J$=7.9 Hz), 112.9, 109.1 (d, $J$=24.1 Hz); IR (KBr) *v*: 1708, 1651, 1604, 1485, 904, 813, 777 cm$^{-1}$; HRMS *m*/*z* (ESI) calcd for $C_{15}H_{10}FO_2$ ($M+H^+$) 241.0665, found 241.0659.

**(*Z*)-2-(4-Fluorobenzylidene)-5-fluorobenzofuran-3(2*H*)-one (2j)** Yellow solid; m.p. 132－133 ℃; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$: 7.92 (dd, $J$=8.5, 5.6 Hz, 2H), 7.48－7.29 (m, 3H), 7.16 (t, $J$=8.6 Hz, 2H), 6.88 (s, 1H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$: 184.0, 163.6 (d, $J$=242.6 Hz), 161.9, 158.8 (d, $J$=242.3 Hz), 147.0, 133.7 (d, $J$=8.3 Hz), 128.3 (d, $J$=2.9 Hz), 124.4 (d, $J$=25.5 Hz), 122.2 (d, $J$=8.9 Hz), 116.2 (d, $J$=21.8 Hz), 114.1 (d, $J$=8.0 Hz), 112.7, 110.2 (d, $J$=23.9 Hz); IR (KBr) *v*: 1710, 1658, 1597, 1485, 827, 798 cm$^{-1}$; HRMS *m*/*z* (ESI) calcd for $C_{15}H_9F_2O_2$ ($M+H^+$) 259.0570, found 259.0565.

**(*Z*)-2-(4-Methoxybenzylidene)-5,7-di-*tert*-butylbenzofuran-3(2*H*)-one (2k)** Yellow solid; m.p. 166－167 ℃; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$: 7.91 (d, $J$=8.7 Hz, 2H), 7.66－7.62 (m, 2H), 7.00 (d, $J$=8.7 Hz, 2H), 6.87 (s, 1H), 3.88 (s, 3H), 1.56 (s, 9H), 1.36 (s, 9H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$: 184.5, 161.7, 159.9, 145.3, 144.7, 133.8, 132.0, 130.2, 124.2, 120.7, 117.2, 113.5, 111.6, 54.4, 33.8, 33.3, 30.5, 28.6; IR (KBr) *v*: 1691, 1639, 1600, 1462, 829 cm$^{-1}$; HRMS *m*/*z* (ESI) calcd for $C_{24}H_{29}O_3$ ($M+H^+$) 365.2117, found 365.2111.

**(*Z*)-2-Benzylidene-5,7-di-*tert*-butylbenzofuran-3(2*H*)-one (2l)** Yellow solid; m.p. 76－77 ℃; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$: 7.95 (d, $J$=6.8 Hz, 2H), 7.66 (d, $J$=6.8 Hz, 2H), 7.47－7.43 (m, 3H), 6.88 (s, 1H), 1.56 (s, 9H), 1.36 (s, 9H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 184.8, 162.0, 145.8, 145.6, 134.0, 131.6, 130.6, 130.2, 128.7, 128.0, 120.5, 117.3, 111.2, 33.9, 33.4, 30.5, 28.6; IR (KBr) *v*: 1705, 1651, 1593, 1446, 902, 785 cm$^{-1}$; HRMS *m*/*z* (EI) calcd for $C_{23}H_{26}O_2$ ($M^+$), 334.1933, found 334.1932.

**(*Z*)-2-(4-Fluorobenzylidene)-5,7-di-*tert*-butylbenzofuran-3(2*H*)-one (2m)** Yellow solid; m.p. 138—139 ℃; $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$: 8.01—7.92 (m, 2H), 7.66 (d, $J$=4.7 Hz, 2H), 7.19—7.14 (m, 2H), 6.85 (s, 1H) 1.55 (s, 9H), 1.36 (s, 9H); $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$: 184.6, 162.3 (d, $J$=250.4 Hz), 161.9, 145.7, 145.5, 133.9, 132.1 (d, $J$=8.3 Hz), 130.6, 127.8 (d, $J$=3.0 Hz), 120.4, 117.3, 115.2 (d, $J$=21.7 Hz), 110.0, 33.8, 33.3, 30.5, 28.6; IR (KBr) $v$: 1699, 1651, 1593, 1487, 823, 781 cm$^{-1}$; HRMS $m/z$ (ESI) calcd for $C_{23}H_{26}FO_2$ ($M+H^+$) 353.1917, found 353.1911.

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## Supporting Information

The cif file of compound **2b** is available. Single crystal data for compound **2b** (CCDC 1022096) has been deposited in the Cambridge Crystallographic Data Center.

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