

## Supplementary Information

# Radical $\alpha$ -Addition Involved Electrooxidative [3+2] Annulation of Phenols and Electron-Deficient Alkenes

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## 1. General Information

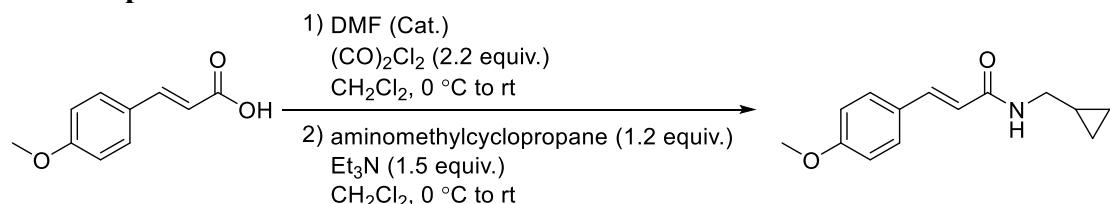
<sup>1</sup> H NMR (400 MHz) spectra were recorded on a Bruker Avance 400 spectrometer and <sup>1</sup> H NMR (500 MHz) spectra were recorded on a Bruker Avance 500 spectrometer in CDCl<sub>3</sub> [using CDCl<sub>3</sub> (for 1 H, δ = 7.26) or (CD<sub>3</sub>)<sub>2</sub>SO (for 1 H, δ = 2.50) as the internal standard]. <sup>13</sup>C NMR (101 MHz) spectra were recorded on a Bruker Avance 400 spectrometer and <sup>13</sup>C NMR (126 MHz) spectra were recorded on a Bruker Avance 500 spectrometer in CDCl<sub>3</sub> [using CDCl<sub>3</sub> (for <sup>13</sup>C, δ = 77.0 or (CD<sub>3</sub>)<sub>2</sub>SO (for <sup>13</sup>C, δ = 39.52) as internal standard]. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of doublet of doublet, dt = doublet of triplet, m = multiplet, s br = single broad. High-resolution mass spectra were obtained with a Water XEVO G2 Q-Tof (Waters Corporation). X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractionmeter. Melting points were uncorrected and were recorded on a Buchi B-54 melting point apparatus. Flash column chromatography was performed using Merck silica gel 60 with distilled solvents. Commercially available reagents were purchased from Energy Chemical, J & K Scientific, Adamas-beta and Sigma-Aldrich Co., Inc.

$\alpha, \beta$ -unsaturated carbonyl compounds **2a**,<sup>1</sup> **2b**,<sup>2</sup> **2c**,<sup>3</sup> **2d**,<sup>1</sup> **2e**,<sup>3</sup> **2f**,<sup>4</sup> **2g**,<sup>5</sup> **2h**,<sup>6</sup> **2i**,<sup>7</sup> **2j**,<sup>8</sup> **2k**,<sup>1</sup> **2l**,<sup>9</sup> **2m**,<sup>9</sup> **2q**,<sup>10</sup> **2r**,<sup>10</sup> and phenols **1ad**,<sup>11</sup> **1ag**,<sup>12</sup> **1ah**,<sup>13</sup> **1ai**,<sup>13</sup> **1aj**,<sup>13</sup> **1ak**,<sup>13</sup> **1al**,<sup>14</sup> were known compounds and prepared according to the literature procedures. Phenols **1a**, **1aa**, **1ab**, **1ac**, **1ae**, **1af**, **1am**, were purchased and used directly without further purification.

## 2. Synthesis of $\alpha, \beta$ -unsaturated carbonyl compounds

$\alpha, \beta$ -unsaturated carbonyl compounds **2n**, **2o**, **2p** were prepared by the procedure shown below.

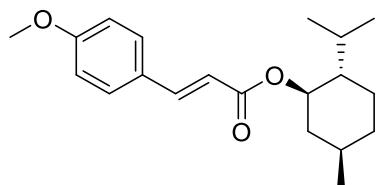
### General procedure :



To a solution of (E)-3-(4-methoxyphenyl)acrylic acid (0.894 g, 5.02 mmol) and drops of DMF (cat.) in CH<sub>2</sub>Cl<sub>2</sub> was slowly added (CO)<sub>2</sub>Cl<sub>2</sub> (0.9 mL, 10.64 mmol) at 0 °C. The reaction mixture was warm to room temperature, and stirred under nitrogen atmosphere for 1h. The solvent was removed under vacuo to afford a crude acyl chloride product. The crude product was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, Et<sub>3</sub>N (1.0 mL, 7.19 mmol) and aminomethylcyclopropane (0.5 mL, 5.84 mmol) were added. The reaction mixture was

stirred at room temperature before it was cooled to 0 °C and quenched with water. The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 5:1) to give **2p** (0.914 g) in 78% yield as a white solid, mp: 84-85 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.23-0.26 (m, 2H), 0.51-0.55 (m, 2H), 0.97-1.05 (m, 1H), 3.24 (dd, *J* = 7.0, 5.5 Hz, 2H), 3.82 (s, 3H), 5.74 (s, 1H), 6.28 (d, *J* = 15.5 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 15.5 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 3.43, 10.77, 44.55, 55.32, 114.20, 118.34, 127.58, 129.27, 140.49, 160.78, 166.05; ESIHRMS: Found: m/z 232.1340. Calcd for C<sub>14</sub>H<sub>18</sub>O<sub>2</sub>: (M+H)<sup>+</sup> 232.1338.

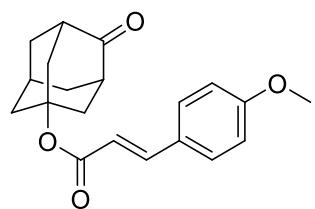
**(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl (*E*)-3-(4-methoxyphenyl)acrylate (2n)**



Following general procedure, **2n** was synthesised in 29% yield (487.2 mg, 1.540 mmol) from the reaction of (*E*)-3-(4-methoxyphenyl)acrylic acid (1.294 g, 7.262 mmol) and *L*-menthol (938.6 mg, 6.006 mmol); White solid, mp 52-53°C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.79 (d, *J* = 6.9 Hz, 3H), 0.89-0.94 (m, 7H), 1.04 (q, *J* = 12.0 Hz, 1H), 1.06-1.14 (m, 1H), 1.41-1.57 (m, 2H), 1.67-1.73 (m, 2H), 1.88-1.97 (m, 1H), 2.02-2.09 (m, 1H), 3.84 (s, 3H), 4.81 (ddd, *J* = 11.0, 10.5, 4.5 Hz, 1H), 6.30 (d, *J* = 16.0 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 16.0 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 16.42, 20.77, 22.05, 23.53, 26.32, 31.41, 34.31, 41.06, 47.22, 55.34, 74.00, 114.25, 116.21, 127.27, 129.65, 144.00, 161.24, 166.91; ESIHRMS: Found: m/z 317.2114. Calcd for C<sub>20</sub>H<sub>29</sub>O<sub>3</sub>: (M+H)<sup>+</sup> 317.2117.

**(1s,3R,5S,7s)-4-oxoadamantan-1-yl (*E*)-3-(4-methoxyphenyl)acrylate (2o)**



Following general procedure, **2o** was obtained in 30% yield (977.1 mg, 2.99 mmol) from the reaction of (*E*)-3-(4-methoxyphenyl)acrylic acid (2.167 g, 12.16 mmol) and 5-hydroxyadamantan-2-one (1.678 g, 10.10 mmol); white solid, mp 120-121 °C.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.96 (d, *J* = 12.9 Hz, 2H), 2.04-2.09 (m, 2H), 2.35-2.40 (m, 2H), 2.40-2.46 (m, 3H), 2.50 (d, *J* = 11.7 Hz, 2H), 2.68 (s, 2H), 3.84 (s, 3H), 6.23 (d, *J* = 16.0 Hz, 1H), 6.90 (d, *J* = 9.0 Hz, 2H), 7.45 (d, *J* = 9.0 Hz, 2H), 7.55 (d, *J* = 16.0 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 29.85, 38.21, 40.00, 41.41, 47.07, 55.35, 114.28, 116.80, 127.11, 129.67, 144.04, 161.31, 166.24, 215.78; ESIHRMS: Found: m/z 327.1594. Calcd for C<sub>20</sub>H<sub>23</sub>O<sub>4</sub>: (M+H)<sup>+</sup> 327.1596.

### 3. Information for reaction set up:

#### 3.1. Small scale reaction



**Supplementary Figure 1.** Experimental setup diagram for the small scale reaction.

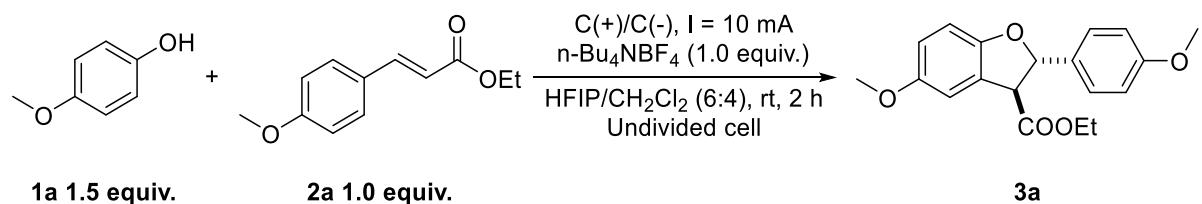
#### 3.2. Large scale reaction



**Supplementary Figure 2.** Experimental setup diagram for the large scale reaction.

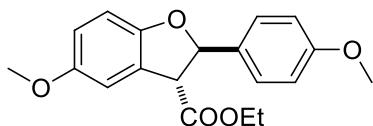
#### 4. Electrooxidative annulation of phenols and electron-deficient alkenes

**General procedure:**



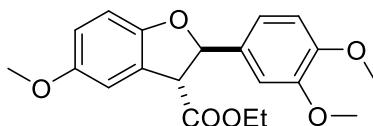
In an oven-dried undivided three-necked flask (10 mL) equipped with a stir bar, ethyl 4-methoxycinnamate (**2a**) (62.0 mg, 0.301 mmol), *p*-methoxylphenol (**1a**) (58.0 mg, 0.467 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (100.3 mg, 0.305 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2, 10 mL) were added. The flask was equipped with graphite rod electrode (Φ 6 mm) as the anode and cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under room temperature and nitrogen atmosphere for 2 h. After evaporation of solvent, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10 : 1) to afford product **3a** (81.4 mg, 0.248 mmol) in 82% yield.

**Ethyl 5-methoxy-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-carboxylate (3a)**



Yellow solid, mp 45-46 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.34 (t,  $J = 7.2$ , 3H), 3.78 (s, 3H), 3.80 (s, 3H), 4.21-4.35 (m, 3H), 6.05 (d,  $J = 8.0$ , 1H), 6.78-6.83 (m, 2H), 6.89-6.92 (m, 2H), 6.96-6.97 (m, 1H), 7.34-7.38 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  14.16, 55.16, 55.90, 55.93, 61.48, 85.60, 109.70, 110.91, 113.98, 114.66, 124.87, 127.22, 132.60, 153.32, 154.24, 159.57, 170.54; ESIHRMS: Found:  $m/z$  351.1204. Calcd for  $\text{C}_{19}\text{H}_{20}\text{O}_5\text{Na}$ : ( $\text{M}+\text{Na}$ ) $^+$  351.1208.

### Ethyl-2-(3,4-dimethoxyphenyl)-5-methoxy-2,3-dihydrobenzofuran-3-carboxylate (3b)

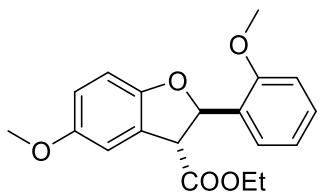


According to the general procedure, the reaction of **2b** (71.5 mg, 0.303 mmol), **1a** (59.1 mg, 0.476 mmol),  $n\text{-Bu}_4\text{NBF}_4$  (100.3 mg, 0.305 mmol) and HFIP/ $\text{CH}_2\text{Cl}_2$  (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 5:1) afforded 89.3 mg (82%) of **3b** as yellow solid, mp 57-58 °C.

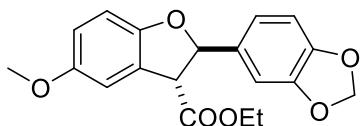
### Procedure for gram scale synthesis

In an oven-dried two-necked flask (100 mL) equipped with a stir bar, (*E*)-ethyl 3-(3,4-dimethoxyphenyl)acrylate (**2b**) (1.208 g, 5.113 mmol), p-methoxylphenol (**1a**) (0.956g, 7.701 mmol),  $n\text{-Bu}_4\text{NBF}_4$  (1.687 g, 5.123 mmol) and HFIP/ $\text{CH}_2\text{Cl}_2$  (36/24 mL) were added. The bottle was equipped with graphite rod ( $\Phi$  6 mm) as the anode and cathode. The reaction mixture was stirred and electrolyzed at a constant current of 50 mA under room temperature and nitrogen atmosphere for 6 h. After evaporation of solvent, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 5 : 1) to afford product **3b** (1.199g, 3.346 mmol) in 66% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.33 (t,  $J = 7.2$ , 3H), 3.77 (s, 3H), 3.86 (s, 3H), 3.87 (s, 3H), 4.20-4.35 (m, 3H), 6.01 (d,  $J = 8.0$ , 1H), 6.76-6.83 (m, 2H), 6.85 (d,  $J = 8.0$ , 1H), 6.92-6.99 (m, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  14.22, 55.86, 55.89, 55.98, 61.58, 85.84, 108.990, 109.81, 110.94, 111.09, 114.71, 118.42, 124.92, 132.95, 149.04, 149.16, 153.31, 154.33, 170.58; ESIHRMS: Found:  $m/z$  359.1508. Calcd for  $\text{C}_{20}\text{H}_{23}\text{O}_6$ : ( $\text{M}+\text{H}$ ) $^+$  359.1495.

**Ethyl-5-methoxy-2-(2-methoxyphenyl)-2,3-dihydrobenzofuran-3-carboxylate (3c)**

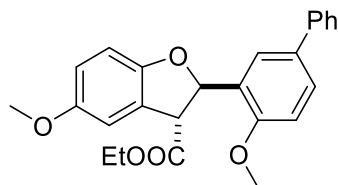
According to the general procedure, the reaction of **2c** (63.4 mg, 0.307 mmol), **1a** (61.1 mg, 0.492 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (102.0 mg, 0.310 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2.5 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10:1) afforded 53.1 mg (53%) of **3c** as pale yellow solid, mp 78-79 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.33 (t, *J* = 7.2 Hz, 3H), 3.74 (s, 3H), 3.79 (s, 3H), 4.14 (d, *J* = 6.4 Hz, 1H), 4.20-4.35 (m, 2H), 6.33 (d, *J* = 6.4 Hz, 1H), 6.77 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.83-6.86 (m, 2H), 6.87-6.89 (m, 1H), 6.91-6.95 (m, 1H), 7.24-7.29 (m, 1H), 7.40-7.42 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 14.30, 55.20, 55.48, 55.97, 61.26, 82.29, 109.76, 110.34, 110.67, 114.69, 120.50, 125.41, 125.41, 128.89, 129.30, 153.62, 154.16, 155.88, 171.40; ESIHRMS: Found: *m/z* 351.1204. Calcd for C<sub>19</sub>H<sub>20</sub>NaO<sub>5</sub>: (M+Na)<sup>+</sup> 351.1208.

**Ethyl-2-(benzo[d][1,3]dioxol-5-yl)-5-methoxy-2,3-dihydrobenzofuran-3-carboxylate (3d)**

According to the general procedure, the reaction of **2d** (71.5 mg, 0.303 mmol), **1a** (59.1 mg, 0.476 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (100.3 mg, 0.305 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 5:1) to afford 89.3 mg (82%) of **3d** as pale solid, mp 60-61 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.33 (t, *J* = 7.2, 3H), 3.77 (s, 3H), 4.19-4.34 (m, 3H), 5.94 (s, 2H), 5.99 (d, *J* = 7.6 Hz, 1H), 6.74-6.84 (m, 3H), 6.88-6.89 (m, 3H), 6.93-6.94 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 14.21, 55.98, 56.08, 61.60, 85.68, 101.11, 106.23, 108.24, 109.78, 110.97, 114.78, 119.53, 124.72, 134.51, 147.58, 147.97, 153.27, 154.34, 170.52; ESIHRMS: Found: *m/z* 365.1000. Calcd for C<sub>19</sub>H<sub>18</sub>O<sub>6</sub>Na: (M+Na)<sup>+</sup> 365.1001.

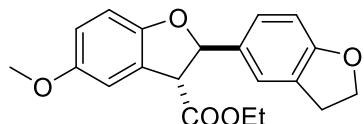
**Ethyl-5-methoxy-2-(4-methoxy-[1,1'-biphenyl]-3-yl)-2,3-dihydrobenzofuran-3-carboxylate (3e)**



According to the general procedure, the reaction of **2e** (85.3 mg, 0.302 mmol), **1a** (62.6 mg, 0.504 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (103.1 mg, 0.313 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10:1) to afford 99.0 mg (74%) of **3e** as white solid, mp 98-99 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.35 (t, *J* = 7.2 Hz, 3H), 3.76 (s, 3H), 3.85 (s, 3H), 4.22 (d, *J* = 6.4 Hz, 1H), 4.23-4.38 (m, 2H), 6.40 (d, *J* = 6.4 Hz, 1H), 6.79 (ddd, *J* = 8.8, 2.8, 0.8 Hz, 1H), 6.86 (dd, *J* = 2.8, 0.8 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 7.27-7.32 (m, 1H), 7.38-7.42 (m, 2H), 7.50-7.54 (m, 3H), 7.67 (dd, *J* = 2.4, 0.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 14.35, 55.44, 55.56, 56.01, 61.33, 82.37, 109.86, 110.65, 110.77, 114.76, 124.83, 125.40, 126.72, 126.81, 127.42, 128.65, 129.65, 133.71, 140.70, 153.60, 154.22, 155.49, 171.41; ESIHRMS: Found: m/z 427.1518. Calcd for C<sub>25</sub>H<sub>24</sub>O<sub>5</sub>Na: (M+Na)<sup>+</sup> 427.1521.

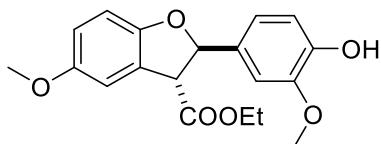
### Ethyl-5-methoxy-2,2',3,3'-tetrahydro-[2,5'-bibenzofuran]-3-carboxylate (**3f**)



According to the general procedure, the reaction of **2f** (65.6 mg, 0.301 mmol), **1a** (60.3 mg, 0.486 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (101.3 mg, 0.308 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 1.5 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10:1) afforded 71.3 mg (77%) of **3f** as yellow solid, mp 50-51 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.32 (t, *J* = 7.2 Hz, 3H), 3.18 (t, *J* = 8.8 Hz, 2H), 3.77 (s, 3H), 4.19-4.34 (m, 3H), 4.56 (t, *J* = 8.8 Hz, 2H), 6.00 (d, *J* = 7.8 Hz, 1H), 6.74-6.78 (m, 3H), 6.94-6.95 (m, 1H), 7.15 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.24-7.25 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 14.30, 29.63, 56.06, 56.14, 61.60, 71.45, 86.08, 109.27, 109.82, 111.01, 114.78, 122.77, 125.03, 126.30, 127.67, 132.67, 153.43, 154.33, 160.33, 170.70; ESIHRMS: Found: m/z 362.1204. Calcd for C<sub>19</sub>H<sub>20</sub>NaO<sub>5</sub>: (M+Na)<sup>+</sup> 363.1208.

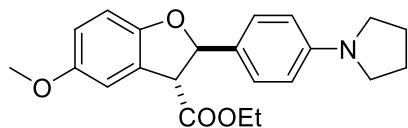
### Ethyl-2-(4-hydroxy-3-methoxyphenyl)-5-methoxy-2,3-dihydrobenzofuran-3-carboxylate (**3g**)



According to the general procedure, the reaction of **2g** (73.2 mg, 0.329 mmol), **1a** (62.0 mg, 0.499 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (110.0 mg, 0.334 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) electrolyzed under nitrogen atmosphere at room temperature for 2 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10:1) afforded 73.8 mg (65%) of **3g** as bright yellow liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.33 (t, *J* = 7.2 Hz, 3H), 3.78 (s, 3H), 3.88 (s, 3H), 4.20-4.35 (m, 3H), 5.64 (s, 1H), 6.00 (d, *J* = 8.4 Hz, 1H), 6.77-6.82 (m, 2H), 6.90-6.93 (m, 3H), 6.77-6.82 (m, 2H), 6.94-6.95 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 14.25, 55.96, 56.05, 56.09, 61.60, 86.00, 108.46, 109.84, 111.00, 114.48, 114.79, 119.16, 124.99, 132.43, 145.78, 146.70, 153.37, 154.38, 170.63; ESIHRMS: Found: *m/z* 345.1328. Calcd for C<sub>19</sub>H<sub>21</sub>NaO<sub>6</sub>: (M+H)<sup>+</sup> 345.1338.

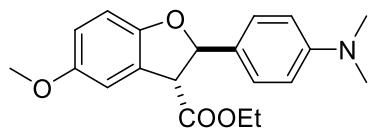
### Ethyl-5-methoxy-2-(4-(pyrrolidin-1-yl)phenyl)-2,3-dihydrobenzofuran-3-carboxylate (**3h**)



According to the general procedure, the reaction of **2h** (74.2 mg, 0.303 mmol), **1a** (60.0 mg, 0.483 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (101.2 mg, 0.307 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 1.5 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 10:1) afforded 71.5 mg (64%) of **3h** as gray liquid.

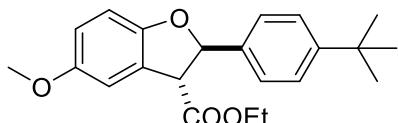
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.33 (t, *J* = 7.2 Hz, 3H), 1.97-2.03 (m, 4H), 3.24-3.32 (m, 4H), 3.79 (s, 3H), 4.19-4.34 (m, 3H), 5.99 (d, *J* = 8.4 Hz, 1H), 6.54-6.57 (m, 2H), 6.78 (d, *J* = 1.6 Hz, 2H), 6.95-6.96 (m, 1H), 7.27-7.30 (m, 2H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ = 14.22, 25.38, 47.63, 55.76, 55.99, 61.39, 86.48, 109.71, 110.83, 111.61, 114.61, 125.35, 127.32, 148.00, 153.51, 154.08, 170.81; ESIHRMS: Found: *m/z* 368.1860. Calcd for C<sub>22</sub>H<sub>26</sub>NO<sub>4</sub>: (M+H)<sup>+</sup> 368.1862.

### Ethyl-2-(4-(dimethylamino)phenyl)-5-methoxy-2,3-dihydrobenzofuran-3-carboxylate (**3i**)



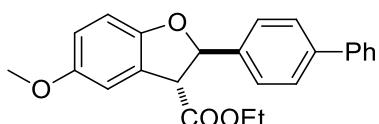
According to the general procedure, the reaction of **2i** (66.2 mg, 0.302 mmol), **1a** (57.6 mg, 0.464 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (101.5 mg, 0.308 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate =10:1) afforded 86.0 mg (83%) of **3i** as pale yellow solid, mp 55-56 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.33 (t, *J* = 7.2 Hz, 3H), 2.95 (s, 6H), 3.78 (s, 3H), 4.20-4.33 (m, 3H), 5.99 (d, *J* = 8.0 Hz, 1H), 6.70-6.74 (m, 2H), 6.78 (d, *J* = 1.6 Hz, 2H), 6.94-6.96 (m, 1H), 7.26-7.31 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 14.24, 40.49, 55.75, 56.01, 61.44, 86.23, 109.75, 110.88, 112.42, 114.65, 125.27, 127.18, 127.86, 150.69, 153.50, 154.14, 170.78; ESIHRMS: Found: *m/z* 342.1704. Calcd for C<sub>20</sub>H<sub>24</sub>NO<sub>4</sub>: (M+H)<sup>+</sup>342.1705.

**Ethyl-2-(4-(*tert*-butyl)phenyl)-5-methoxy-2,3-dihydrobenzofuran-3-carboxylate  
(3j)**



According to the general procedure, the reaction of **2j** (72.3 mg, 0.311 mmol), **1a** (58.3 mg, 0.470 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (102.8 mg, 0.312 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 30:1) afforded 55.0 mg (50%) of **3j** as colorless liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.33-1.36 (m, 12H), 3.79 (s, 3H), 4.23-4.35 (m, 3H), 6.09 (d, *J* = 7.6 Hz, 1H), 6.79-6.80 (m, 2H), 6.97 (s, 1H), 7.36-7.42 (m, 4H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 14.22, 31.25, 34.53, 55.88, 55.97, 61.54, 85.63, 109.78, 111.95, 114.72, 124.87, 125.59, 137.62, 151.31, 153.45, 154.26, 170.64; ESIHRMS: Found: *m/z* 377.1733. Calcd for C<sub>22</sub>H<sub>26</sub>NO<sub>4</sub>: (M+H)<sup>+</sup>377.1729.

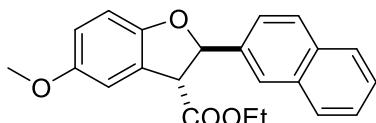
**Ethyl-2-([1,1'-biphenyl]-4-yl)-5-methoxy-2,3-dihydrobenzofuran-3-carboxylate  
(3k)**



According to the general procedure, the reaction of **2k** (76.2 mg, 0.302 mmol), **1a** (63.8 mg, 0.514 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (100.8 mg, 0.306 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2.5 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20:1) afforded 33.9 mg (30%) of **3k** as pale yellow solid, mp 64-65 °C.

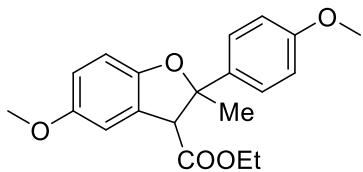
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.36 (t, *J* = 7.2 Hz, 3H), 3.79 (s, 3H), 4.23-4.37 (m, 3H), 6.15 (d, *J* = 7.8 Hz, 1H), 6.79-6.88 (m, 2H), 6.97 (d, *J* = 2.4 Hz, 1H), 7.34-7.37 (m, 1H), 7.45 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.57-7.61 (m, 4H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 14.26, 56.02, 56.09, 61.69, 85.50, 109.88, 111.03, 114.81, 124.72, 126.25, 127.09, 127.41, 127.46, 128.77, 139.69, 140.61, 141.27, 153.41, 154.37, 170.60; ESIHRMS: Found: *m/z* 397.1412. Calcd for C<sub>24</sub>H<sub>22</sub>NaO<sub>4</sub>: (M+Na)<sup>+</sup> 397.1416.

### Ethyl-5-methoxy-2-(naphthalen-2-yl)-2,3-dihydrobenzofuran-3-carboxylate (3l)



According to the general procedure, the reaction of **2l** (69.0 mg, 0.305 mmol), **1a** (60.8 mg, 0.490 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (101.8 mg, 0.309 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2.5 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20:1) afforded 35.1 mg (33%) of **3l** as pale yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.35 (t, *J* = 7.2 Hz, 3H), 3.79 (s, 3H), 4.24-4.38 (m, 3H), 6.27 (d, *J* = 8.0 Hz, 1H), 6.83 (ddd, *J* = 8.8, 2.8, 0.8 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.97-6.98 (m, 1H), 7.48-7.51 (m, 3H), 7.83-7.87 (m, 3H), 7.90 (d, *J* = 0.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 14.26, 56.05, 56.14, 61.69, 85.88, 109.91, 111.08, 114.90, 123.31, 124.76, 124.93, 126.21, 126.36, 127.69, 128.08, 128.78, 133.14, 133.22, 137.99, 153.54, 154.44, 170.63; ESIHRMS: Found: *m/z* 371.1286. Calcd for C<sub>24</sub>H<sub>19</sub>NaO<sub>4</sub>: (M+H)<sup>+</sup> 371.1283.

### Ethyl-5-methoxy-2-(4-methoxyphenyl)-2-methyl-2,3-dihydrobenzofuran-3-carboxylate (3m)

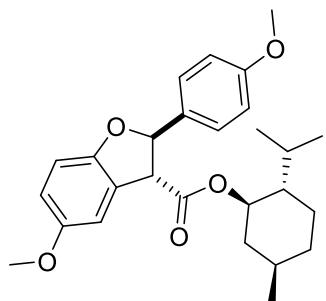


According to the general procedure, the reaction of **2m** (66.5 mg, 0.302 mmol), **1a** (56.8 mg, 0.458 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (100.8 mg, 0.306 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2.5 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20:1 then 10:1) afforded 79.4 mg (82%) of **3m** as yellow liquid. These two diastereomers could be separated by flash column chromatography, but the stereochemistry of each isomer was not assigned.

isomer 1:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.33 (t,  $J = 7.0$  Hz, 3H), 1.72 (s, 3H), 3.74 (s, 3H), 3.79 (s, 3H), 4.24-4.34 (m, 2H), 4.38 (s, 1H), 6.73 (s, 1H), 6.77 (d,  $J = 8.5$  Hz, 1H), 6.84 (d,  $J = 8.5$  Hz, 1H), 6.88 (d,  $J = 8.0$  Hz, 2H), 7.48 (d,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  14.24, 24.73, 55.22, 55.91, 60.10, 61.21, 90.55, 109.84, 111.75, 113.66, 114.79, 125.44, 125.85, 138.54, 153.14, 154.27, 158.78, 170.63; ESIHRMS: Found:  $m/z$  365.1363. Calcd for  $\text{C}_{20}\text{H}_{22}\text{NaO}_5$ : ( $\text{M}+\text{Na}$ ) $^+$  365.1365.

isomer 2:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.86 (t,  $J = 7.2$  Hz, 3H), 1.85 (s, 3H), 3.60-3.66 (m, 1H), 3.71-3.75 (m, 1H), 3.76 (s, 3H), 3.78 (s, 3H), 4.22 (s, 1H), 6.76-6.87 (m, 5H), 7.34-7.36 (m, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  13.60, 29.18, 55.19, 55.92, 60.74, 91.05, 110.09, 111.62, 113.17, 114.88, 125.79, 126.69, 133.87, 153.44, 154.22, 158.87, 170.12; ESIHRMS: Found:  $m/z$  365.1364. Calcd for  $\text{C}_{20}\text{H}_{22}\text{NaO}_5$ : ( $\text{M}+\text{Na}$ ) $^+$  365.1365.

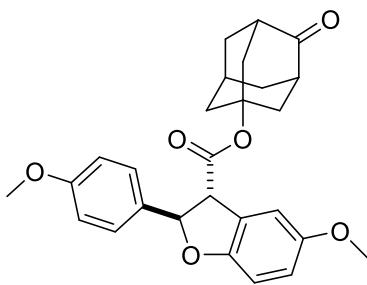
**(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl-5-methoxy-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-carboxylate (3n)**



According to the general procedure, the reaction of **2n** (95.9 mg, 0.303 mmol), **1a** (61.8 mg, 0.498 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (109.6 mg, 0.333 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 1.5 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate =30:1) afforded 101.8 mg (77%) of **3n** as colorless liquid.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.73 (d,  $J = 7.0$  Hz, 3H), 0.85 (d,  $J = 7.0$  Hz, 2H), 0.85-0.92 (m, 5H), 0.98 – 1.12 (m, 2H), 1.41-1.54 (m, 2H), 1.67-1.71 (m, 2H), 1.74 – 1.92 (m, 1H), 2.01-2.05 (m, 1H), 3.77 (s, 3H), 3.81 (s, 3H), 4.22 (t, 7.5 Hz, 1H), 4.78-4.84 (m, 1H), 6.01 (d,  $J = 8.0$  Hz, 1H), 6.78-6.81 (m, 2H), 6.89 – 6.94 (m, 3H), 7.32-7.35 (m, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  15.83, 16.21, 20.69, 20.89, 21.96, 22.91, 23.32, 25.95, 26.15, 31.38, 34.06, 34.11, 40.76, 40.88, 47.00, 47.03, 55.26, 55.94, 55.99, 56.32, 56.47, 75.59, 85.83, 85.90, 109.79, 109.87, 110.45, 110.64, 114.02, 114.88, 115.30, 124.96, 125.23, 127.17, 127.28, 132.70, 153.36, 153.44, 154.25, 154.31, 159.59, 170.30, 170.34; ESIHRMS: Found:  $m/z$  461.2302. Calcd for  $\text{C}_{27}\text{H}_{34}\text{O}_5\text{Na}$ : ( $\text{M}+\text{Na}$ ) $^+$  461.2304.

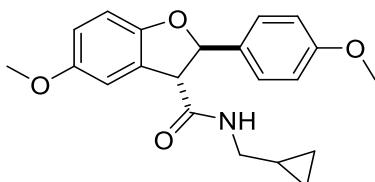
**(1s,3R,5S,7S)-4-oxoadamantan-1-yl-5-methoxy-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-carboxylate (3o)**



According to the general procedure, the reaction of **2o** (99.2 mg, 0.304 mmol), **1a** (58.2 mg, 0.469 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (100.6 mg, 0.306 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate =5:1) afforded 97.5 mg (72%) of **3o** as white solid, mp 114-115 °C.

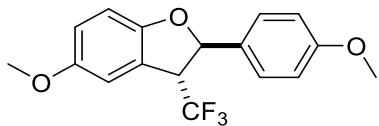
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.93-1.97 (m, 2H), 2.02-2.05 (m, 2H), 2.36-2.40 (m, 5H), 2.43-2.49 (m, 2H), 2.67 (s, 2H), 3.77 (s, 3H), 3.80 (s, 3H), 4.17 (d, *J* = 8.0 Hz, 1H), 5.94 (d, *J* = 8.0 Hz, 1H), 6.78 (s, 2H), 6.88-6.91 (m, 3H), 7.31 (d, *J* = 8.8 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 29.81, 38.01, 39.92, 41.20, 41.24, 46.91, 55.26, 55.99, 56.65, 79.27, 85.54, 109.75, 110.99, 114.05, 114.49, 124.98, 127.29, 132.63, 153.37, 154.26, 159.64, 169.39, 214.97; ESIHRMS: Found: *m/z* 471.1789. Calcd for C<sub>27</sub>H<sub>28</sub>O<sub>6</sub>Na: (M+Na)<sup>+</sup> 471.1784.

### ***N*-(cyclopropylmethyl)-5-methoxy-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-amine (**3p**)**



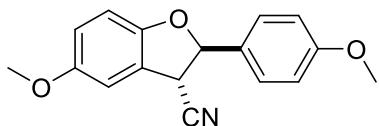
According to the general procedure, the reaction of **2p** (71.7 mg, 0.310 mmol), **1a** (117.4 mg, 0.946 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (103.7 mg, 0.315 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate =5:1) afforded 53.2 mg (49%) of **3p** as white solid, mp 137-138 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.17-0.21 (m, 2H), 0.47-0.52 (m, 2H), 0.86-0.99 (m, 1H), 3.15-3.18 (m, 2H), 3.77 (s, 3H), 3.80 (s, 3H), 4.05 (d, *J* = 6.8 Hz, 1H), 5.73-5.79 (m, 1H), 5.88 (d, *J* = 6.8 Hz, 1H), 6.79-6.82 (m, 2H), 6.83-6.86 (m, 1H), 6.87-6.90 (m, 2H), 7.31-7.35 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 3.32, 3.36, 10.72, 44.54, 55.30, 56.06, 58.65, 87.44, 110.32, 110.69, 114.06, 115.00, 125.63, 127.00, 132.98, 154.07, 154.55, 159.57, 170.52; ESIHRMS: Found: *m/z* 376.1520. Calcd for C<sub>21</sub>H<sub>23</sub>NO<sub>4</sub>Na: (M+Na)<sup>+</sup> 376.1525.

**5-methoxy-2-(4-methoxyphenyl)-3-(trifluoromethyl)-2,3-dihydrobenzofuran (3q)**

According to the general procedure, the reaction of **2q** (62.3mg, 0.308 mmol), **1a** (58.1mg, 0.468 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (104.1 mg, 0.316 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate =40:1) afforded 43.0 mg (43) of **3p** as pale yellow solid, mp 42-43 °C.

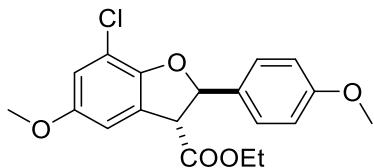
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.9 (s, 3H), 3.70 (s, 3H), 3.90-3.98 (m, 1H), 5.65 (d, *J*= 5.6 Hz, 1H), 6.75-6.77 (m, 2H), 6.78-6.82 (m, 3H), 7.16-7.20 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 55.27, 55.56 (q, *J* = 28.7 Hz), 55.98, 83.15 (q, *J* = 2.6 Hz), 110.15, 111.35, 114.24, 116.24, 120.42 (q, *J*= 2.0 Hz), 125.77 (q, *J*= 279.8 Hz), 126.79, 132.34, 154.47, 154.52, 159.83; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -70.73 (d, *J* = 9.3 Hz); ESIHRMS: Found: *m/z* 325.1038. Calcd for C<sub>17</sub>H<sub>16</sub>O<sub>3</sub>F<sub>3</sub>: (M+H)<sup>+</sup> 325.1052.

**5-methoxy-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-carbonitrile (3r)**

In an oven-dried undivided three-necked flask (10 mL) equipped with a stir bar, **2r** (53.3 mg, 0.3113 mmol), *p*-methoxylphenol (**1a**) (59.1 mg, 0.476 mmol), *n*-Bu<sub>4</sub>NPF<sub>6</sub> (197.5 mg, 0.51 M) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2, 10 mL) were added. The flask was equipped with graphite rod electrode (φ6 mm) as the anode and cathode. The reaction mixture was stirred and electrolyzed at a constant potential of 2.5 V under room temperature and nitrogen atmosphere for 10 h. After evaporation of solvent, the crude residue was dissolved in CDCl<sub>3</sub> along with 20 μL CHCl<sub>2</sub>CHCl<sub>2</sub> as internal standard for crude <sup>1</sup>H NMR. The result showed that the target product **3r** was detected in 48% yield. Purification by flash column chromatography on silica gel gave an inseparable mixture containing **2r** and **3r** (**2r**:**3r** = 1:1.15).

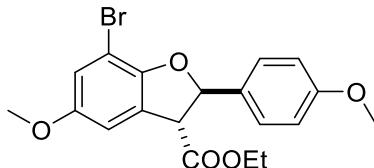
Yellow liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.22 (t, *J*= 8.5 Hz, 2H), 3.79 (s, 3H), 4.32 (d, *J* = 9.5Hz, 1H), 4.60 (t, *J* = 8.5 Hz, 2H), 5.73 (d, *J* = 9.5 Hz, 1H), 6.80 (d, *J* = 8.5 Hz, 1H), 6.83-6.85 (m, 2H), 6.92 (s, 1H), 7.21 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.29-7.31 (m, 1); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 29.46, 42.09, 56.02, 71.52, 87.66, 109.54, 109.79, 110.78, 116.29, 118.10, 122.24, 122.53, 126.13, 128.05, 129.67, 152.90, 155.00, 160.96; ESIHRMS: Found: *m/z* 316.0944. Calcd for C<sub>18</sub>H<sub>15</sub>NO<sub>3</sub>Na: (M+Na)<sup>+</sup> 316.0950.

**Ethyl-7-chloro-5-methoxy-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-**

**carboxylate (3aa)**

According to the general procedure, the reaction of **2a** (62.9 mg, 0.305 mmol), **1aa** (73.7 mg, 0.465 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (104.8 mg, 0.318 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate =20:1) afforded 89.0 mg (80%) of **3aa** as yellow liquid.

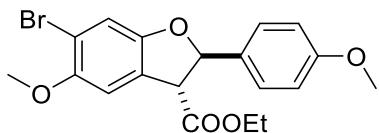
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.32 (t, *J* = 7.2 Hz, 3H), 3.76 (s, 3H), 3.80 (s, 3H), 4.12-4.34 (m, 3H), 6.10 (d, *J* = 8.0 Hz, 1H), 6.81 (dd, *J* = 2.4, 0.8 Hz, 1H), 6.86 (dd, *J* = 2.4, 1.2 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 14.17, 55.24, 56.11, 56.50, 61.74, 86.18, 110.07, 114.07, 114.78, 114.89, 126.16, 127.35, 131.88, 149.49, 154.50, 159.78, 169.99; ESIHRMS: Found: *m/z* 385.0815. Calcd for C<sub>19</sub>H<sub>19</sub>O<sub>5</sub>NaCl: (M+Na)<sup>+</sup> 385.0819.

**Ethyl-7-bromo-5-methoxy-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-carboxylate (3ab)**

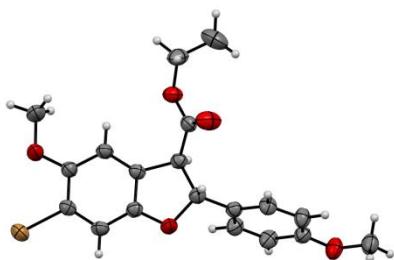
According to the general procedure, the reaction of **2a** (62.6 mg, 0.304 mmol), **1ab** (93.8 mg, 0.462 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (100.7 mg, 0.306 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate =10:1) afforded 117.6 mg (95%) of **3ab** as brown liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.32 (t, *J* = 7.2 Hz, 3H), 3.76 (s, 3H), 3.80 (s, 3H), 4.20-4.33 (m, 3H), 6.10 (d, *J* = 7.6 Hz, 1H), 6.88-6.92 (m, 3H), 6.95 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.32-7.36 (d, *J* = 2.8, 8.4 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 14.19, 55.27, 56.18, 56.81, 61.77, 85.88, 102.18, 110.86, 114.08, 117.35, 125.75, 127.32, 131.96, 150.92, 154.65, 159.76, 170.05; ESIHRMS: Found: *m/z* 429.0315. Calcd for C<sub>19</sub>H<sub>19</sub>O<sub>5</sub>NaBr: (M+Na)<sup>+</sup> 429.0314.

**Ethyl-6-bromo-5-methoxy-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-carboxylate (3ac)**



According to the general procedure, the reaction of **2a** (62.9 mg, 0.305 mmol), **1ac** (93.1 mg, 0.459 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (102.4 mg, 0.311 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2.5 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate =10:1) afforded 97.0 mg (78%) of **3ac** as white solid, mp 93-94°C. Recrystallization from petroleum ether/ethyl acetate gave colorless crystals.



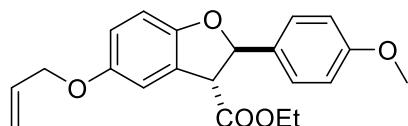
CCDC: 1968793. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.33 (t, *J* = 7.2 Hz, 3H), 3.81 (s, 3H), 3.85 (s, 3H), 4.19 (dd, *J* = 7.6, 1.2 Hz, 1H), 4.20-4.36 (m, 2H), 6.03 (d, *J* = 7.6 Hz, 1H), 6.88-6.92 (m, 2H), 6.97 (d, *J* = 1.2 Hz, 1H), 7.09 (s, 1H), 7.29-7.34 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 14.25, 55.30, 55.87, 57.15, 61.72, 86.12, 109.53, 112.41, 114.13, 114.43, 123.90, 127.22, 132.26, 150.71, 153.65, 159.76, 170.20; ESIHRMS: Found: *m/z* 429.0313. Calcd for C<sub>19</sub>H<sub>19</sub>O<sub>5</sub>NaBr: (M+Na)<sup>+</sup> 429.0314.

**Supplementary Table 1. Crystal data and structure refinement for 3ac**

Empirical formula	C <sub>19</sub> H <sub>19</sub> BrO <sub>5</sub>
Formula weight	407.25
Temperature/K	291(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.9606(3)
b/Å	9.9217(4)
c/Å	11.8105(4)
α/°	72.290(3)
β/°	88.750(3)
γ/°	63.972(4)
Volume/Å <sup>3</sup>	891.11(6)
Z	2
ρ <sub>calcd</sub> /g/cm <sup>3</sup>	1.518
μ/mm <sup>-1</sup>	3.376
F(000)	416.0
Crystal size/mm <sup>3</sup>	0.28 × 0.25 × 0.24

Radiation	CuK $\alpha$ ( $\lambda = 1.54184$ )
2 $\Theta$ range for data collection/ $^\circ$	7.926 to 148.154
Index ranges	-11 $\leq$ h $\leq$ 7, -12 $\leq$ k $\leq$ 8, -14 $\leq$ l $\leq$ 14
Reflections collected	5844
Independent reflections	3476 [ $R_{\text{int}} = 0.0212$ , $R_{\text{sigma}} = 0.0211$ ]
Data/restraints/parameters	3476/0/229
Goodness-of-fit on $F^2$	1.047
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0299$ , $wR_2 = 0.0782$
Final R indexes [all data]	$R_1 = 0.0312$ , $wR_2 = 0.0795$
Largest diff. peak/hole / e $\text{\AA}^{-3}$	0.40/-0.64

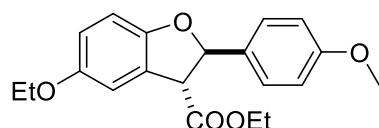
**Ethyl-5-(allyloxy)-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-carboxylate(3ad)**



According to the general procedure, the reaction of **2a** (63.8 mg, 0.309 mmol), **1ad** (64.2 mg, 0.472 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (103.3 mg, 0.314 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate =20:1) afforded 89.3 mg (81%) of **3ad** as yellow liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  1.34 (t, *J* = 7.1 Hz, 3H), 3.80 (s, 3H), 4.21-4.35 (m, 3H), 4.50 (ddd, *J* = 5.6, 1.6 Hz, 2H), 5.29 (ddt, *J* = 10.4, 2.8, 1.2 Hz, 1H), 5.42 (ddt, *J* = 17.2, 3.2, 1.6 Hz, 1H), 6.02-6.11 (m, 2H), 6.78-6.84 (m, 2H), 6.89-6.93 (m, 2H), 6.98-7.00 (m, 1H), 7.34-7.37 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  14.19, 55.19, 55.92, 61.50, 69.78, 85.63, 109.72, 111.98, 113.99, 115.81, 117.43, 124.85, 127.24, 132.59, 133.49, 153.23, 153.48, 159.59, 170.54; ESIHRMS: Found: *m/z* 377.1359. Calcd for C<sub>21</sub>H<sub>22</sub>O<sub>5</sub>Na: (M+Na)<sup>+</sup> 377.1365.

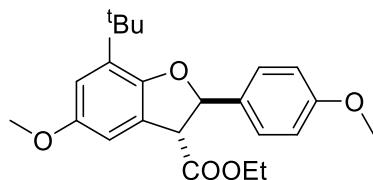
**Ethyl-5-ethoxy-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-carboxylate(3ae)**



According to the general procedure, the reaction of **2a** (62.5 mg, 0.303 mmol), **1ae** (63.3 mg, 0.458 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (101.6 mg, 0.319 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 1.5 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate =10:1) afforded 67.7 mg (65%) of **3ae** as yellow liquid . <sup>1</sup>H NMR (400

MHz, CDCl<sub>3</sub>) δ 1.33 (t, *J* = 7.2 Hz, 3H), 1.40 (t, *J* = 7.2 Hz, 3H), 3.80 (s, 3H), 3.99 (q, *J* = 7.2 Hz, 2H), 4.21-4.34 (m, 3H), 6.03 (d, *J* = 8.0 Hz, 1H), 6.78-6.80 (m, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.94-6.96 (m, 1H), 7.35 (d, *J* = 8.8 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 14.22, 14.89, 55.23, 56.00, 61.52, 64.33, 85.63, 109.75, 111.70, 114.03, 115.57, 124.85, 127.27, 132.68, 153.32, 153.58, 159.61, 170.64; ESIHRMS: Found: *m/z* 365.1368. Calcd for C<sub>20</sub>H<sub>22</sub>O<sub>5</sub>Na: (M+Na)<sup>+</sup> 365.1365.

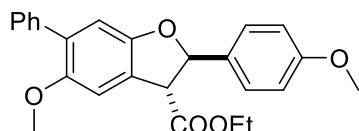
**Ethyl-7-(tert-butyl)-5-methoxy-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-carboxylate (3af)**



According to the general procedure, the reaction of **2a** (63.6 mg, 0.308 mmol), **1af** (83.8 mg, 0.465 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (103.4 mg, 0.314 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 1.5 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate =20:1) afforded 105.6 mg (89%) of **3af** as yellow liquid .

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.34 (t, *J* = 7.2 Hz, 3H), 1.39 (s, 9H), 3.78 (s, 3H), 3.81 (s, 3H), 4.16 (d, *J* = 8.4 Hz, 1H), 4.22-4.35 (m, 2H), 6.05 (d, *J* = 8.4 Hz, 1H), 6.79 (s, 2H), 6.91 (d, *J* = 7.2 Hz, 2H), 7.35 (d, *J* = 7.2 Hz, 2H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 14.28, 29.15, 34.32, 55.26, 55.89, 56.18, 61.46, 84.94, 106.96, 113.22, 113.98, 124.65, 127.00, 133.51, 134.05, 151.43, 153.93, 159.42, 171.01; ESIHRMS: Found: *m/z* 407.1830. Calcd for C<sub>23</sub>H<sub>28</sub>O<sub>5</sub>Na: (M+Na)<sup>+</sup> 407.1834.

**Ethyl-5-methoxy-2-(4-methoxyphenyl)-6-phenyl-2,3-dihydrobenzofuran-3-carboxylate (3ag)**

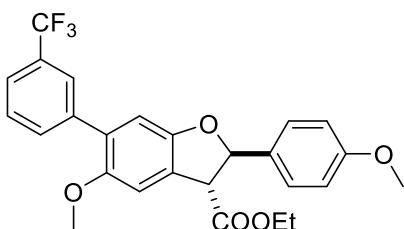


According to the general procedure, the reaction of **2a** (63.1 mg, 0.306 mmol), **1ag** (92.1 mg, 0.460 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (102.4 mg, 0.311 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate =20:1) afforded 88 mg (71%) of **3ag** as yellow liquid .

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.38 (t, *J* = 7.2 Hz, 3H), 3.77 (s, 3H), 3.83 (s, 3H), 4.25-4.41 (m, 3H), 6.09 (d, *J* = 8.0 Hz, 1H), 6.90 (s, 1H), 6.93 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 1.2 Hz, 1H), 7.32-7.37 (m, 1H), 7.38-7.45 (m, 4H), 7.53-7.56 (m, 2H); <sup>13</sup>C NMR (101

MHz, CDCl<sub>3</sub>) δ 14.27, 55.25, 56.17, 56.58, 61.57, 85.72, 109.13, 111.66, 114.08, 123.34, 127.04, 127.29, 127.96, 129.40, 132.20, 132.69, 138.33, 151.29, 153.46, 159.66, 170.66; ESIHRMS: Found: *m/z* 427.1516. Calcd for C<sub>25</sub>H<sub>24</sub>O<sub>5</sub>Na: (M+Na)<sup>+</sup> 427.1521.

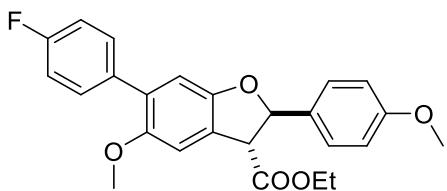
**Ethyl-5-methoxy-2-(4-methoxyphenyl)-6-(3-(trifluoromethyl)phenyl)-2,3-dihydrobenzofuran-3-carboxylate (3ah)**



According to the general procedure, the reaction of **2a** (62.8 mg, 0.305 mmol), **1ah** (124.0 mg, 0.462 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (101.0 mg, 0.307 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 1 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate =15:1) afforded 95.2 mg (66%) of **3ah** as pale yellow liquid.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.36 (t, *J* = 7.2 Hz, 3H), 3.77 (s, 3H), 3.82 (s, 3H), 4.24-4.38 (m, 3H), 6.07 (d, *J* = 7.5 Hz, 1H), 6.86 (s, 1H), 6.92 (d, *J* = 8.5 Hz, 2H), 7.05 (s, 1H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.52 (dd, *J* = 7.5, 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.78 (s, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 14.31, 55.31, 56.17, 56.50, 61.69, 85.81, 109.07, 111.53, 114.12, 123.77 (q, *J* = 3.8 Hz), 124.22 (q, *J* = 272.2 Hz), 124.25, 126.32 (q, *J* = 3.8 Hz), 127.29, 128.42, 130.34 (q, *J* = 32.0 Hz), 130.44, 132.59, 132.75, 139.04, 151.17, 153.52, 159.71, 170.56; <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -62.52; ESIHRMS: Found: *m/z* 495.1395. Calcd for C<sub>26</sub>H<sub>23</sub>O<sub>5</sub>NaF<sub>3</sub>: (M+Na)<sup>+</sup> 495.1395.

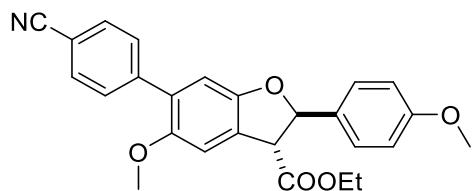
**Ethyl-6-(4-fluorophenyl)-5-methoxy-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-carboxylate (3ai)**



According to the general procedure, the reaction of **2a** (63.2 mg, 0.306 mmol), **1ai** (100.6 mg, 0.461 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (103.2 mg, 0.313 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate =25:1) afforded 88.6 mg (68%) of **3ai** as yellow liquid. <sup>1</sup>H NMR (400

MHz, CDCl<sub>3</sub>) δ 1.36 (t, *J* = 7.2 Hz, 3H), 3.75 (s, 3H), 3.82 (s, 3H), 4.23-4.39(m, 3H), 6.07 (d, *J* = 7.6 Hz, 1H), 6.84 (s, 1H), 6.90-6.94 (m, 2H), 7.03 (d, *J* = 1.2 Hz, 1H), 7.06-7.12 (m, 2H), 7.35-7.39 (m, 2H), 7.46-7.51 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 14.30, 55.30, 56.17, 56.56, 61.62, 85.78, 109.14, 111.56, 114.12, 114.89 (d, *J* = 21.4 Hz), 123.50, 127.30, 131.03 (d, *J* = 8.0 Hz), 131.12, 132.66, 134.24 (d, *J* = 3.1 Hz), 151.20, 153.49, 159.71, 162.05 (d, *J* = 247.1 Hz), 170.65; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -115.53 (m); ESIHRMS: Found: *m/z* 445.1418. Calcd for C<sub>25</sub>H<sub>23</sub>O<sub>5</sub>FNa: (M+Na)<sup>+</sup> 445.1427.

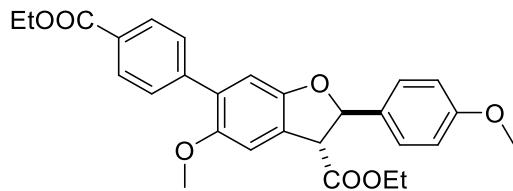
**Ethyl-6-(4-cyanophenyl)-5-methoxy-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-carboxylate (3aj)**



According to the general procedure, the reaction of **2a** (62.6 mg, 0.304 mmol), **1aj** (101.4 mg, 0.450 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (102.2 mg, 0.310 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate =5:1) afforded 124.8 mg (95%) of **3aj** as yellow solid, mp 44-45 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.36 (t, *J* = 7.1 Hz, 3H), 3.77 (s, 3H), 3.81 (s, 3H), 4.23-4.39 (m, 3H), 6.07 (d, *J* = 8.0 Hz, 1H), 6.84 (s, 1H), 6.90-6.93 (m, 2H), 7.06 (d, *J* = 1.2 Hz, 1H), 7.34-7.38 (m, 2H), 7.60-7.63 (m, 2H), 7.67-7.70 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 14.27, 55.28, 56.10, 56.44, 61.70, 85.88, 109.17, 110.56, 111.28, 114.13, 119.03, 124.93, 127.25, 129.87, 130.15, 131.75, 132.43, 143.16, 151.14, 153.53, 159.74, 170.42; ESIHRMS: Found: *m/z* 430.1657. Calcd for C<sub>26</sub>H<sub>24</sub>NO<sub>5</sub>: (M+H)<sup>+</sup> 430.1654.

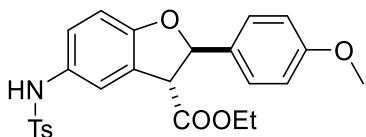
**Ethyl-6-(4-(ethoxycarbonyl)phenyl)-5-methoxy-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-carboxylate (3ak)**



According to the general procedure, the reaction of **2a** (62.4 mg, 0.303 mmol), **1ak** (123.0 mg, 0.452 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (99.6 mg, 0.303 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate =5:1) afforded 122.4 mg (85%) of **3ak** as bright yellow liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.36 (t, *J* = 7.2 Hz, 3H), 1.41 (t, *J* = 7.2 Hz, 3H), 3.75 (s, 3H), 3.81 (s, 3H), 4.23-4.37 (m, 3H), 4.40 (q, *J* = 7.2 Hz, 2H), 6.07 (d, *J* = 8.0 Hz, 1H), 6.87 (s, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 7.04 (d, *J* = 0.8 Hz, 1H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 8.07 (d, *J* = 8.8 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 14.30, 14.34, 55.31, 56.187, 56.59, 60.86, 61.66, 85.82, 109.27, 111.49, 114.13, 124.26, 127.29, 129.00, 129.24, 129.42, 131.06, 132.60, 143.03, 151.31, 153.52, 159.72, 166.55, 170.56; ESIHRMS: Found: *m/z* 477.1908. Calcd for C<sub>28</sub>H<sub>29</sub>NO<sub>7</sub>: (M+H)<sup>+</sup>477.1913.

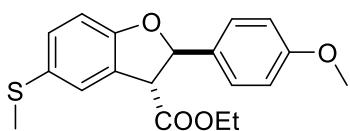
**Ethyl-2-(4-methoxyphenyl)-5-((4-methylphenyl)sulfonamido)-2,3-dihydrobenzofuran-3-carboxylate (3al)**



According to the general procedure, the reaction of **2a** (63.1, 0.306 mmol), **1al** (122.9 mg, 0.467 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (104.3 mg, 0.317 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate =4:1) afforded 117.2 mg (83%) of **3al** as white solid, mp 103-104 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.28 (t, *J* = 7.2 Hz, 3H), 2.39 (s, 3H), 3.80 (s, 3H), 4.16-4.28 (m, 3H), 6.03 (d, *J* = 7.6 Hz, 1H), 6.68 (s, 1H), 6.69 (d, *J* = 8.8 Hz, 1H), 6.83 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 7.15-7.18 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 14.13, 21.50, 55.30, 55.32, 61.75, 86.06, 109.95, 114.12, 121.83, 125.15, 125.88, 127.26, 127.32, 129.20, 129.52, 132.14, 136.01, 143.65, 157.69, 159.77, 170.30; ESIHRMS: Found: *m/z* 490.1290. Calcd for C<sub>25</sub>H<sub>25</sub>NO<sub>6</sub>NaS: (M+Na)<sup>+</sup>490.1300.

**Ethyl-2-(4-methoxyphenyl)-5-(methylthio)-2,3-dihydrobenzofuran-3-carboxylate (3am)**



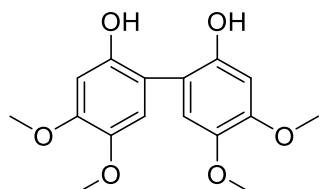
According to the general procedure, the reaction of **2a** (62.4, 0.303 mmol), **1am** (65.1 mg, 0.464 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (101.6 mg, 0.309 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) was electrolyzed under nitrogen atmosphere at room temperature for 2.5 h. The subsequent purification by flash column chromatography on silica gel (petroleum ether : ethyl acetate =30:1) afforded 62.5 mg (60%) of **3am** as pale yellow liquid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.33 (t, *J* = 7.2 Hz, 3H), 2.46 (s, 3H), 3.80 (s, 3H), 4.21-4.35 (m, 3H), 6.06 (d, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 8.8 Hz,

2H), 7.24 (ddd,  $J = 8.4, 2.0, 0.8$  Hz, 1H), 7.33 (d,  $J = 8.8$  Hz, 2H), 7.36-7.38 (m, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  14.24, 18.52, 55.29, 55.49, 61.68, 85.88, 110.33, 114.12, 125.18, 126.12, 127.29, 129.04, 130.81, 132.37, 158.05, 159.74, 170.45; ESIHRMS: Found:  $m/z$  367.0981. Calcd for  $\text{C}_{19}\text{H}_{20}\text{O}_4\text{NaS}$ : ( $\text{M}+\text{Na}$ ) $^+$  367.0980.

## 5. Mechanistic studies

### 5.1. Synthesis of 4,4',5,5'-tetramethoxy-[1,1'-biphenyl]-2,2'-diol (5)



In an oven-dried two-necked flask, a stir bar, **2a** (62.2 mg, 0.302 mmol), **1o** (70.0 mg, 0.454 mmol),  $n\text{-Bu}_4\text{NBF}_4$  (100.3 mg, 0.305 mmol) and HFIP/ $\text{CH}_2\text{Cl}_2$  (3:2 10 mL) were added. The flask was equipped with graphite rod ( $\phi$  6 mm) as the anode and cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under room temperature and nitrogen atmosphere for 75 min. After evaporation of solvent, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 2 : 1) to afford product **5** (50.3 mg) in 87% yield as brown solid, mp 166-167 °C.  $^1\text{H}$  NMR (500 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  3.68 (s, 6H), 3.73 (s, 6H), 6.53 (s, 2H), 6.77 (s, 2H), 8.87 (s, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $(\text{CD}_3)_2\text{SO}$ )  $\delta$  55.49, 56.39, 101.41, 115.93, 116.62, 141.84, 147.98, 148.63; ESIHRMS: Found:  $m/z$  329.0996. Calcd for  $\text{C}_{16}\text{H}_{18}\text{O}_6\text{Na}$ : ( $\text{M}+\text{Na}$ ) $^+$  329.1001.

### 5.2. Computational studies

All the calculations were performed using Gaussian 16 software packages.<sup>16</sup> Solution-phase geometry optimizations of all of the minima and transition states involved were carried out at the (U)B3LYP<sup>17</sup>/6-31G(d)<sup>18</sup> level of theory with an empirical dispersion term (Grimme-D3(0))<sup>19</sup> as implemented. SMD solvation model<sup>20</sup> for the mix solvent system of  $\text{CF}_3\text{CH}_2\text{OH}/\text{CH}_2\text{Cl}_2$  (3:2) was adopted. Vibrational frequency analysis was calculated at the same level of theory to validate each structure as either a minimum or a transition state and to evaluate its zero-point energy and thermal corrections at 298 K. For each transition state, the intrinsic reaction coordinate (IRC) analysis was conducted to ensure that it connects the right reactant and product.<sup>21</sup> To obtain more accurate energies, single point energy calculations were performed at the SMD/(U)M06-2X<sup>22</sup>/6-311+G(d,p)<sup>23</sup> level of theory with an empirical dispersion term (Grimme-D3(0))<sup>19</sup> as implemented. Unless otherwise specified, all of the conformers were located but only the ones with the lowest Gibbs energies were reported.

**Table 1.** Thermal correction of Gibbs free energy (TCG, hartree) and single point energies (SP,

hartree) in solvent CF<sub>3</sub>CH<sub>2</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> (3:2) for all species involved in this study

Compounds	TCG	SP	Compounds	TCG	E
<b>2a</b>	0.194273	-691.286591	<b>Int-a-II</b>	0.311269	-1112.617674
<b>II</b>	0.092267	-421.308446	<b>TS-b-I</b>	0.308129	-1112.565178
<b>TS-a-I</b>	0.310336	-1112.577527	<b>Int-b-I</b>	0.309109	-1112.574783
<b>Int-a-I</b>	0.309134	-1112.588731	<b>Int-b-II</b>	0.311694	-1112.611122

## Cartesian coordinates for all optimized geometries

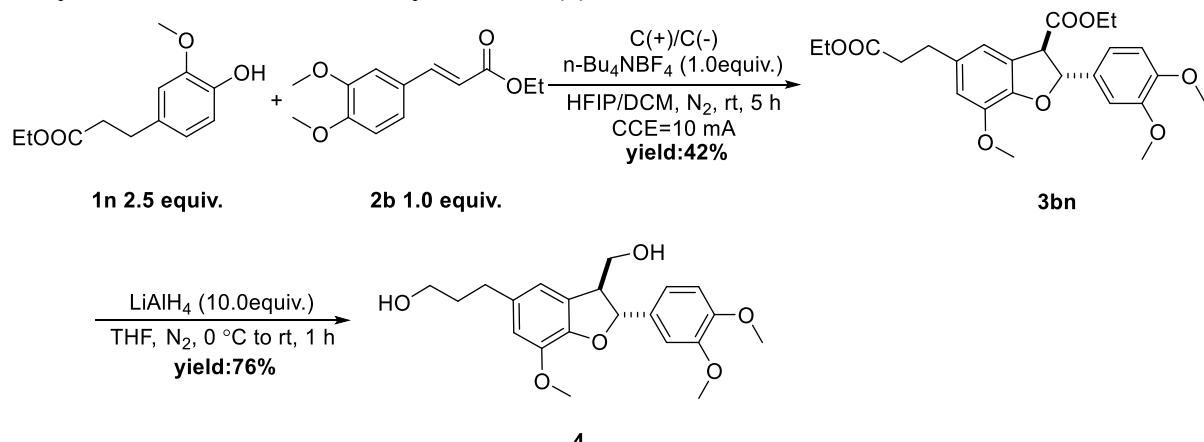
<b>2a</b>				O	2.16840900	0.59004200	-0.00000200	
C	2.67141200	-1.40348800	-0.00097000	C	3.14944300	-0.46184200	-0.00002000	
C	1.33033400	-1.06437200	-0.00103200	H	4.11517400	0.04474700	-0.00003800	
C	0.92094300	0.28928500	-0.00037700	H	3.05363800	-1.08092900	0.89802500	
C	1.92425300	1.27508600	0.00023900	H	3.05360300	-1.08092900	-0.89806100	
C	3.27919200	0.94955000	0.00034600					
C	3.65918700	-0.39951900	-0.00024200	<b>TS-a-I</b>				
H	2.98789400	-2.44231000	-0.00150000	C	2.92356400	-1.06385900	-1.24827500	
H	0.58924800	-1.85826100	-0.00168500	C	1.57329600	-1.01470200	-0.96138400	
H	1.63606700	2.32350800	0.00069700	C	1.10090900	-1.05015500	0.38282400	
H	4.02023200	1.74020200	0.00087000	C	2.08177300	-1.15425500	1.40602900	
C	-0.47385800	0.70547700	-0.00027700	C	3.43941300	-1.20112200	1.12604200	
H	-0.64196600	1.78225700	-0.00061500	C	3.87296900	-1.15150600	-0.21100800	
C	-1.57149200	-0.08139300	0.00031200	H	3.27910400	-1.03726700	-2.27413200	
H	-1.52077300	-1.16534500	0.00086500	H	0.86606300	-0.95150900	-1.78109500	
C	-2.91188900	0.51484600	0.00038400	H	1.75427500	-1.18469800	2.44219400	
O	-3.86913400	-0.43923200	0.00062000	H	4.15121500	-1.27196400	1.94025800	
C	-5.24449800	0.02262600	0.00013200	C	-0.27386300	-0.97924900	0.73619500	
H	-5.40665200	0.64393500	-0.88703700	H	-0.51979300	-1.03206700	1.79313100	
H	-5.40693100	0.64497900	0.88651700	C	-1.35780900	-0.74561800	-0.16368900	
C	-6.12853200	-1.20734800	0.00071700	H	-1.19848800	-1.01628900	-1.20494100	
H	-7.18097300	-0.90305600	0.00035500	C	-2.70834900	-1.17217400	0.32960300	
H	-5.94456200	-1.81990300	-0.88871200	O	-3.59209700	-1.23591300	-0.67806800	
H	-5.94486700	-1.81883200	0.89094600	C	-4.97728200	-1.48946500	-0.31193000	
O	-3.17069900	1.71462600	-0.00073500	H	-5.28761700	-0.71340900	0.39441400	
O	4.94391600	-0.84205400	-0.00020300	H	-5.03536800	-2.46082000	0.18896300	
C	6.00029900	0.12429000	0.00064600	C	-5.78667800	-1.45541400	-1.59057700	
H	6.92658300	-0.45304600	0.00061100	H	-6.84220900	-1.63689300	-1.36024800	
H	5.96124400	0.75494800	-0.89552400	H	-5.70114500	-0.47814400	-2.07808900	
H	5.96069100	0.75396200	0.89748400	H	-5.44660400	-2.22754200	-2.28931300	
				O	-2.99251000	-1.39865900	1.49472200	
<b>II</b>				O	5.17262900	-1.18737300	-0.60564700	
C	0.86199700	0.27791000	0.00000300	C	6.19019200	-1.29983400	0.39533700	
C	0.35357700	-1.04482800	0.00001100	H	7.13645400	-1.31752500	-0.14832100	
C	-1.00723500	-1.24721600	0.00001400	H	6.17393600	-0.43979800	1.07528100	
C	-1.94624100	-0.14231700	0.00001700	H	6.07905100	-2.22742500	0.96924900	
C	-1.37921500	1.19470200	-0.00000400	C	-0.39858900	1.64766800	-1.03057000	
C	-0.02463600	1.39047800	-0.00000600	C	-1.65578400	1.13285400	-0.52633900	
H	1.02868700	-1.89268700	0.00001500	C	-2.15388200	1.62610100	0.78559900	
H	-1.42020000	-2.25186300	0.00001700	C	-1.14007000	2.15131700	1.68538100	
H	-2.06984400	2.03303300	-0.00001400	C	0.11844500	2.40220500	1.23182500	
H	0.40912100	2.38627900	-0.00001600	C	0.48746200	2.20433900	-0.15176100	
O	-3.19544700	-0.33491400	-0.00000100	H	-0.14983300	1.48366000	-2.07190900	

H	-1.43051200	2.37086200	2.70852900	C	0.15739700	2.88925900	-1.23338800
H	0.88021500	2.81190200	1.89046800	C	-0.23116700	2.57334500	0.13441200
O	-3.35498600	1.52321100	1.10783800	H	0.20142200	1.43747200	1.88697900
O	1.74412300	2.64199600	-0.44039100	H	1.53240200	2.60263100	-2.84230700
C	2.17026900	2.58595100	-1.80507000	H	-0.46854800	3.60299700	-1.76373000
H	1.52079700	3.20044400	-2.44107500	O	3.10830200	0.91382700	-1.60972800
H	3.18475000	2.98862800	-1.81603500	O	-1.33429500	3.27253100	0.53321700
H	2.18073000	1.55528800	-2.17459900	C	-1.84294500	2.99827900	1.84051100
H	-2.44820700	0.99998300	-1.25974800	H	-1.10656700	3.25444300	2.61285800
				H	-2.72756900	3.62744700	1.95550200
<b>Int-a-I</b>				H	-2.12403000	1.94236400	1.93651700
C	-3.00388900	-1.01549000	1.27589300	H	2.50553000	1.05234400	0.93774700
C	-1.65381800	-0.93630800	0.99316900				
C	-1.16372300	-1.03977200	-0.34647800	<b>Int-a-II</b>			
C	-2.14314800	-1.23841200	-1.36414800	C	3.28399300	0.24729600	-1.21356500
C	-3.50029100	-1.31541400	-1.08464900	C	1.99254600	-0.10931100	-0.87593300
C	-3.94521700	-1.20107400	0.24393800	C	1.72192800	-0.93559700	0.25873000
H	-3.36510400	-0.93771200	2.29764800	C	2.84991100	-1.36326200	1.01820400
H	-0.95738600	-0.79548100	1.81273800	C	4.14800000	-1.00701800	0.68149500
H	-1.81135600	-1.32458600	-2.39607300	C	4.37727200	-0.19496600	-0.44310700
H	-4.20388800	-1.46139700	-1.89637500	H	3.48113600	0.87725300	-2.07654200
C	0.20116700	-0.95293200	-0.69543700	H	1.17330500	0.25708900	-1.48576900
H	0.46486000	-1.05739700	-1.74417500	H	2.68381500	-1.99001100	1.89114100
C	1.32217100	-0.61892100	0.23315500	H	4.97242200	-1.35832600	1.29145400
H	1.09136500	-0.89567800	1.26778500	C	0.42308500	-1.33025900	0.64765300
C	2.59657800	-1.37653400	-0.13599900	H	0.31382800	-1.92663400	1.54831700
O	3.56903400	-1.14898200	0.75853600	C	-0.83875100	-0.91014800	-0.06586100
C	4.87045000	-1.72924700	0.46668200	H	-0.67803200	-0.91789800	-1.14720100
H	5.19518300	-1.35972800	-0.51131500	C	-1.94752200	-1.90964700	0.22730900
H	4.76425100	-2.81699800	0.40946500	O	-2.48676700	-2.41970900	-0.87194700
C	5.80572100	-1.30291800	1.57792100	C	-3.58384400	-3.37082400	-0.69661400
H	6.80358300	-1.71668300	1.39556600	H	-4.37852700	-2.87250900	-0.13376700
H	5.88547700	-0.21123200	1.62118500	H	-3.21242400	-4.21392100	-0.10679000
H	5.45133600	-1.66791700	2.54811000	C	-4.03048100	-3.78730300	-2.08064300
O	2.72403600	-2.11373900	-1.09722500	H	-4.85590000	-4.50235500	-1.99482500
O	-5.24991700	-1.25848300	0.63701700	H	-4.37897700	-2.92220400	-2.65478500
C	-6.25299200	-1.45278200	-0.36351400	H	-3.21151200	-4.26691500	-2.62723600
H	-7.20459300	-1.47012800	0.17132700	O	-2.31264600	-2.20922400	1.36193100
H	-6.25623700	-0.62978000	-1.08871600	O	5.60565800	0.21815700	-0.86731100
H	-6.11124500	-2.40516600	-0.88887700	C	6.75615500	-0.19576900	-0.12561500
C	0.47316700	1.68619300	0.86797500	H	7.61278300	0.24708200	-0.63746100
C	1.63439400	0.94746200	0.27914700	H	6.71766400	0.17183100	0.90710000
C	2.08201100	1.39123000	-1.11130800	H	6.85649100	-1.28807700	-0.12332700
C	1.24477400	2.34552900	-1.82728200	C	-1.29302700	0.51032600	0.31503000

C	-1.39966400	1.47453100	-0.68778200	H	-5.52139700	-1.51633400	-0.57019000
C	-1.54391700	0.88944000	1.65229000	H	-5.01504400	-3.11412200	-1.20418800
C	-1.71682100	2.80691300	-0.39491300	C	-1.63581900	2.05824100	1.17176500
H	-1.21625600	1.20365000	-1.72391800	C	-0.51941300	1.75360000	1.88562900
C	-1.85497000	2.21855900	1.93986500	C	0.76843800	1.56488100	1.23174300
C	-1.93741400	3.18394000	0.93327200	C	0.76637300	1.57809700	-0.26148300
H	-2.04000800	2.49096300	2.97507000	C	-0.40273800	2.09720000	-0.93532100
H	-2.17993800	4.20670500	1.19725900	C	-1.58521000	2.24399400	-0.26540900
O	-1.45887600	0.01779300	2.71152700	H	-2.57953800	2.18444600	1.69092200
H	-1.70132300	-0.88654700	2.40769600	H	-0.37489500	2.25760200	-2.00896300
O	-1.77938600	3.65285000	-1.47358000	O	1.81079600	1.33462000	1.86937900
C	-2.07939500	5.02648800	-1.22816100	O	-2.67838000	2.60668000	-0.99309600
H	-1.32147300	5.49413900	-0.58641500	C	-3.96578200	2.63718200	-0.36523800
H	-2.07449500	5.51183000	-2.20650700	H	-4.01996600	3.41307900	0.40742100
H	-3.06895100	5.14557700	-0.76838300	H	-4.67129200	2.87460700	-1.16367100
				H	-4.21835700	1.66114400	0.06566000
				H	-0.55258900	1.64702300	2.96581900
<b>TS-b-I</b>				H	1.72578600	1.86736700	-0.68595400
C	-1.94406200	-2.01893000	1.18895600				
C	-0.70378500	-1.471118400	0.89287900				
C	-0.43985400	-0.90811000	-0.36926300	<b>Int-b-I</b>			
C	-1.47413600	-0.90932100	-1.31283600	C	-1.95251800	-2.01450300	1.27971800
C	-2.73113400	-1.451115900	-1.03184900	C	-0.77493000	-1.34671800	0.96488900
C	-2.97015600	-2.00862400	0.22964800	C	-0.49356900	-0.95435800	-0.35514100
H	-2.14644500	-2.45052500	2.16488200	C	-1.43586600	-1.25655000	-1.34182400
H	0.06027100	-1.46301100	1.66477400	C	-2.62662800	-1.92662000	-1.04475100
H	-1.30080800	-0.47089300	-2.29222100	C	-2.88877800	-2.30741100	0.27633100
H	-3.50241800	-1.43089800	-1.79278500	H	-2.16841500	-2.31673300	2.30048300
C	0.85873000	-0.25638500	-0.71060300	H	-0.06903900	-1.12550300	1.76052100
H	0.96877900	-0.06787800	-1.77873000	H	-1.24440800	-0.96215600	-2.37104100
C	2.06864300	-0.74642100	-0.11957800	H	-3.32960000	-2.14187900	-1.84106200
H	2.06852400	-1.32705000	0.79430800	C	0.76080000	-0.17733100	-0.71225300
C	3.35561300	-0.35139600	-0.65844900	H	0.86326400	-0.14786900	-1.80505300
O	4.38179200	-0.89648700	0.03111700	C	2.00947200	-0.76562700	-0.15605300
C	5.71675500	-0.55639000	-0.42342900	H	1.97942200	-1.52769400	0.61303900
H	5.83666900	0.53120700	-0.37466100	C	3.30196700	-0.31754000	-0.62248100
H	5.82149200	-0.86427200	-1.46936300	O	4.31944800	-0.93684000	0.01877800
C	6.69412500	-1.27677600	0.48168600	C	5.65994200	-0.54477000	-0.37207300
H	7.71928800	-1.04546900	0.17221900	H	5.77358100	0.53176800	-0.20494700
H	6.56643900	-0.96050700	1.52266100	H	5.78546100	-0.73820700	-1.44292200
H	6.55112300	-2.36140200	0.42493500	C	6.62522800	-1.35475900	0.46809600
O	3.51747200	0.39593300	-1.62510300	H	7.65449900	-1.08780200	0.20426900
O	-4.15482400	-2.56077800	0.62396400	H	6.47708900	-1.15302200	1.53456600
C	-5.24789700	-2.54323200	-0.29684300	H	6.48940600	-2.42750900	0.29235100
H	-6.08260500	-3.01543700	0.22500800	O	3.47905000	0.52995700	-1.50125900

O	-4.01498500	-2.96361000	0.68913200	H	-0.46897500	-0.84775700	1.53346600
C	-5.00718900	-3.28128500	-0.28869500	C	-1.27721400	-1.13948300	-0.39187900
H	-5.80664000	-3.78969300	0.25418000	H	-1.10987500	-1.20720100	-1.46042000
H	-5.40652700	-2.37538300	-0.76171100	C	-2.56219500	-1.55010900	0.11390800
H	-4.60775200	-3.95112600	-1.06049300	O	-3.32944300	-2.13659300	-0.82056300
C	-1.55080300	2.57523500	1.12832800	C	-4.64975700	-2.57775700	-0.40000600
C	-0.49597700	2.111127900	1.84521500	H	-5.19697600	-1.71301300	-0.01070500
C	0.66158400	1.51982300	1.19237500	H	-4.53229800	-3.30372300	0.41116800
C	0.62681200	1.37486400	-0.32011000	C	-5.32390900	-3.18187800	-1.61332000
C	-0.55170500	1.97608900	-1.00768200	H	-6.32619700	-3.52797300	-1.33817900
C	-1.58335300	2.52151600	-0.32662400	H	-5.42042200	-2.44154000	-2.41480500
H	-2.39550900	3.00145600	1.65906400	H	-4.75332300	-4.03705900	-1.99132400
H	-0.58607900	1.93384100	-2.09281200	O	-2.94380700	-1.39518500	1.28636500
O	1.64059100	1.11220000	1.83380600	O	5.17187200	-1.92126900	-0.58254900
O	-2.64016500	3.01389800	-1.04841000	C	6.13333600	-2.02472800	0.46964900
C	-3.73042900	3.63900900	-0.36628500	H	7.07339300	-2.29792100	-0.01408900
H	-3.40218800	4.51596000	0.20526200	H	6.25765900	-1.06859600	0.99318200
H	-4.41756500	3.96059000	-1.15173700	H	5.85460700	-2.80354800	1.19048000
H	-4.24846700	2.93663400	0.29824200	C	-0.88190900	3.79619700	0.44704100
H	-0.48429300	2.16332500	2.92983700	C	-1.52059200	2.99842100	1.39734300
H	1.54788400	1.83409100	-0.70230500	C	-1.35069400	1.61235400	1.41799800
				C	-0.48843900	1.00419200	0.47625800
<b>Int-b-II</b>				C	0.12693800	1.80636000	-0.48699800
C	2.98491700	-1.50828600	-1.32386500	C	-0.05815300	3.19219300	-0.51091100
C	1.65231700	-1.17886000	-1.09567800	H	-1.04119400	4.86814700	0.45978800
C	1.18131900	-0.91914600	0.20101400	H	0.79126800	1.36520100	-1.22321100
C	2.09572000	-1.00311500	1.25620400	O	-1.99620700	0.91355000	2.40766800
C	3.43731500	-1.33121700	1.04713700	O	0.61378300	3.86366000	-1.50093200
C	3.88775900	-1.58715800	-0.25415700	C	0.47682100	5.28313800	-1.55874100
H	3.34533800	-1.71043700	-2.32841300	H	0.84203500	5.75938700	-0.63970200
H	0.98112500	-1.12560500	-1.94739200	H	1.09002000	5.60724900	-2.40236900
H	1.75808600	-0.80510300	2.27105900	H	-0.56568500	5.57924600	-1.73273500
H	4.10989500	-1.38665600	1.89520600	H	-2.17358100	3.44831400	2.13977700
C	-0.25673900	-0.51999000	0.51080900	H	-2.28553000	0.02851400	2.07847000

## 6. Synthesis of 3,4'-di-O-methycedrusin (4)



In an oven-dried undivided three-necked flask (10 mL) equipped with a stir bar, ethyl-3-(4-hydroxy-3-methoxyphenyl)propanoate (172.1 mg, 0.767 mmol), ethyl 4-methoxycinnamate (**2b**) (71.5 mg, 0.303 mmol), *n*-Bu<sub>4</sub>NBF<sub>4</sub> (100.3 mg, 0.305 mmol) and HFIP/CH<sub>2</sub>Cl<sub>2</sub> (3:2 10 mL) were added. The bottle was equipped with graphite rod electrode (Φ 6 mm) as the anode and cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under room temperature and nitrogen atmosphere for 5 h. After evaporation of solvent, the crude residue was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 8 : 1) to afford product **3bn** (54.1 mg, 0.126 mmol) in 42% yield as a yellow liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.23 (t, *J* = 7.2 Hz, 3H), 1.32 (t, *J* = 7.5 Hz, 3H), 2.59 (t, *J* = 8.0 Hz, 2H), 2.90 (t, *J* = 8.0 Hz, 2H), 3.84-3.88 (m, 9H), 4.12 (q, *J* = 7.5 Hz, 2H), 4.19-4.32 (m, 3H), 6.04 (d, *J* = 8.5 Hz, 1H), 6.69 (s, 1H), 6.80 (s, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 6.93 (s, 1H), 6.96 (d, *J* = 8.5 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 14.14, 14.19, 30.82, 36.31, 55.83, 55.85, 55.99, 56.00, 60.34, 61.52, 86.62, 109.17, 110.93, 112.72, 116.30, 118.73, 125.21, 132.50, 134.16, 144.16, 146.20, 149.05, 170.60, 172.80; ESIHRMS: Found: *m/z* 481.1839. Calcd for C<sub>25</sub>H<sub>30</sub>O<sub>8</sub>Na: (M+Na)<sup>+</sup> 481.1838.

To a solution of LiAlH<sub>4</sub> (69.7 mg, 1.84 mmol) in dry THF (3 mL) was added a solution of **3bn** (84.2 mg, 0.184 mmol) dissolved in dry THF (3 mL) dropwise at 0 °C. The reaction was continued at 0 °C for 5 min and at ambient temperature for additional 1 h. After the residual LiAlH<sub>4</sub> had been destroyed by adding water dropwise to the cooled mixture, concentrated HCl was then added dropwise until two clear layers formed. After separation, the aqueous layer was extracted with ethyl acetate (10 mL x 3) and the combined extracts were then dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and evaporated at reduced pressure. The residue was purified by column chromatography with ethyl acetate- petroleum ether as eluent (4:1) to afford product **4** (52.1 mg, 0.139 mmol) in 76% yield as a colorless liquid. The <sup>1</sup>H and <sup>13</sup>C NMR data (shown below) of this compound were identical to the reported ones.<sup>15</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.77 (s br, 2H), 1.77-1.90 (m, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 3.60 (dd, *J* = 5.5, 12.0 Hz, 1H), 3.67 (t, *J* = 6.5 Hz, 2H), 3.84 (s, 3H), 3.85 (s, 3H), 3.87 (s, 3H), 3.89 (d, *J* = 5.0 Hz, 1H), 3.95 (dd, *J* = 11.0, 6.0 Hz, 1H), 5.55 (d, *J* = 7.5 Hz, 1H), 6.66 (s, 1H), 6.67 (s, 1H), 6.82 (d, *J* = 8.5 Hz, 1H),

6.94-6.95 (m, 2H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  31.94, 34.54, 53.72, 55.87, 55.95, 62.19, 63.82, 87.71, 109.27, 110.90, 112.34, 115.95, 118.65, 127.71, 133.65, 135.35, 144.12, 146.48, 148.87, 149.05; ESIHRMS: Found:  $m/z$  397.1634. Calcd for  $\text{C}_{21}\text{H}_{26}\text{O}_6\text{Na}$ :  $(\text{M}+\text{Na})^+$  397.16927.

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**8. Copies of  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR Spectra**