### **Supporting Information**

## Rh(III)-catalysed C-H annulation of *cis*-stilbene acids with 2-diazo-1,3-diketones: Facile access to 6,7-dihydrobenzofuran-4(5*H*)-one and α-pyrone scaffolds

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### 1. General Information

Commercially available reagents and solvents were used without further purification. <sup>1</sup>H NMR spectra were recorded on NMR instrument operated at 500 MHz. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl<sub>3</sub>:  $\delta$  7.26 ppm). <sup>13</sup>C NMR spectra were recorded on NMR instrument operated at 125 MHz with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl<sub>3</sub>:  $\delta$  7.26 ppm). <sup>13</sup>C NMR spectra Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CDCl<sub>3</sub>:  $\delta$  77.5 ppm). The following abbreviations were used for <sup>1</sup>H NMR spectra to indicate the signal multiplicity: s (singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplet), t (triplet), q (quartet) and m (multiplet). HRMS was measured in ESI-MS mass spectrophotometer. Thin-layer chromatography was performed on MERCK precoated silica gel 60F-254 (0.5 mm) aluminium plates and visualized under UV light at 254 nm. Column chromatography was performed using silica gel #60-120 mesh size. All the starting materials **1a-l**<sup>1</sup> and **2a-h**<sup>2</sup>, were synthesized from previously reported methods.

### 2. Experimental procedures

#### 2.1. General procedure for synthesis of cis-stilbene acids 1a-l:

The compounds **1a-l** was obtained by Perkin condensation using 3,4-dimethoxyphenylacetic acid (1 equiv.) and various substituted benzaldehydes (0.8 equiv.) in presence of acetic anhydride (0.6 equiv.) and triethylamine (0.7 equiv.) refluxed under inert atmosphere for overnight at 110 °C. Upon completion of the reaction, the reaction was quenched with water and the solid precipitate formed was filtered. The reaction mixture was then washed with small amount of 20% (EA: Hex) to obtained the pure products in 54-78% yields.<sup>1</sup>

#### 2.2. General procedure for synthesis of 2a-h:

**Step 1: Preparation of sulphonyl azides:** To *p*-toluene sulfonyl chloride (1 equiv.), sodium azide (1.5 equiv.) was added in a round bottom flask which contain a mixture of solvent system - acetone: water (1:1) ratio and stirred for 1 h at room temperature. After the completion of the reaction, the reaction mixture was extracted with water and ethyl acetate (2 x 100 mL). The combined organic layers were dried over anhydrous  $Na_2SO_4$  and concentrated under the reduced pressure to obtain liquid product up to 98% yield.

**Step 2: Preparation of diazo compounds:** To 1,3-dicarbonyl compounds (1 equiv.) in acetonitrile, potassium carbonate (3 equiv.) was added at 0 °C. To this, sulphonyl azide (1 equiv.) was added and kept for stirring under room temperature for 1-3 h. After checking the completion of the reaction by

TLC, the reaction mixture was quenched with water and ethylacetate (2 x 100 mL). All the organic layers were dried over anhydrous  $Na_2SO_4$  and concentrated under reduced pressure. Finally, the crude product was purified by column chromatography on silica gel (eluent EA: Hex; 10%) to afford **2a-h**.<sup>2</sup>

### 2.3. General procedure for synthesis of 2,3-diphenyl-6,7-dihydrobenzofuran-4(5H)-ones (3a):

In an oven-dried pressure tube equipped with a magnetic stirring bar was added sequentially *cis*stilbene acid **3a** (1 equiv.), 2-diazocyclohexane-1,3-dione **2a** (1.1. equiv.),  $[Cp*RhCl_2]_2$  (2.5 mol%), AgOAc (1 equiv.) in 2 mL DCE. The reaction mixture was stirred at 100 °C for 3-4 h. After the completion of the reaction (monitored by TLC), solvent was evaporated under reduced pressure and extracted with ethyl acetate: water (2 x 100 ml). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent EA: Hex; 10%) to afford **3a**. The same procedure is followed for all the compounds listed in the manuscript **3a-y**, **4a-c**. For **5a-j** zinc acetate was added (1 equiv.) instead of sliver acetate and was stirred at 80 °C for 10-12 h.

## 2.4. General procedure for the synthesis of (E)-2-(3,4-dimethoxyphenyl)-6,6-dimethyl-3-(3,4,5trimethoxyphenyl)-6,7-dihydrobenzofuran-4(5H)-one oxime (4):

To 1 equiv. of compound **3c** in ethanol, 1.5 equiv. of hydroxylamine hydrochloride was added and 1.5 equiv. of sodium bicarbonate was added sequentially. Then reaction mixture was refluxed at 80 °C for 12 h. After the completion of the reaction (determined by TLC), the solvent was removed under vacuum and the crude reaction mixture was purified by flash chromatography using Hex:EA (80:20) % to obtain the desired product **4**.

## 2.5 General procedure for the synthesis of ethyl 3,3'',4,4'',5''-pentamethoxy-4'-methyl-6'-phenyl-[1,1':2',1''-terphenyl]-3'-carboxylate (5):

To a round bottom flask, compound 3w (1 equiv.) 10% palladium on activated carbon (2.5 equiv.) was weighed and subjected under vacuum for 10-15 min. *p*-Xylene was then added to the reaction mixture as a solvent along with purging of nitrogen gas. To the reaction mixture, 5 equiv. of styrene was added and refluxed for 24 h at 140 °C under nitrogen atmosphere. After the complete consumption of starting materials, the solvent is evaporated in vacuum. The crude reaction mixture is purified by column chromatography with 10 % EA: Hex to obtain compound **5** in 30% yield.

### 3. References

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- Bora, D.; Stephy Elza John; Mary Sravani Galla; Sathish, M.; Nagula Shankaraiah. Rh(III)-Catalysed Site-Selective Alkylation of β-Carbolines/Isoquinolines and Tandem c H/c N Functionalization to Construct Indolizine-Indole Frameworks. Molecular Catalysis 2022, 533, 112783–112783. https://doi.org/10.1016/j.mcat.2022.112783.

### 4. Spectral Information

### 6,6-Dimethyl-2,3-diphenyl-6,7-dihydrobenzofuran-4(5H)-one (3a):



White solid, 70% yield, mp:136-137 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ 7.41–7.37 (m, 4H), 7.35 (d, J = 7.7 Hz, 3H), 7.22 (t, J = 7.0 Hz, 3H), 2.86 (s, 2H), 2.39 (s, 2H), 1.20 (s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  193.4, 165.3, 149.3, 131.8, 130.1 128.3, 128.2, 127.8, 127.6, 126.1, 120.1, 119.7, 53.0, 37.7, 34.9, 28.6 ppm. HRMS (ESI-QTOF): m/z

 $[M+H]^+$  calcd. for  $C_{22}H_{20}O_2$  317.1542 found 317.1538.

### 2-(3,4-Dimethoxyphenyl)-6,6-dimethyl-3-phenyl-6,7-dihydrobenzofuran-4(5H)-one (3b):



Pale yellow solid, 70% yield, mp: 150-151 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.42–7.35 (m, 4H), 7.34–7.31 (m, 1H), 7.04 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.82 (d, *J* = 2.0 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 3.86 (s, 3H), 3.58 (s, 3H), 2.86 (s, 2H), 2.39 (s, 2H), 1.20 (s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  193.4, 164.8, 149.3, 148.7, 148.5, 132.2, 130.2, 128.2,

127.5, 122.9, 120.1, 118.7, 118.4, 110.9, 109.3, 55.8, 55.4, 52.9, 37.7, 34.9, 28.6 ppm. HRMS (ESI-QTOF): *m*/*z* [M+H]<sup>+</sup> calcd. for C<sub>24</sub>H<sub>24</sub>O<sub>4</sub> 377.1753 found 377.1753.

2-(3,4-Dimethoxyphenyl)-6,6-dimethyl-3-(3,4,5-trimethoxyphenyl)-6,7-dihydrobenzofuran-4(5H)-one (3c):



Yellow solid, 63% yield, mp:141-142 °C <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.07 (dd, J = 8.4, 2.0 Hz, 1H), 6.91 (d, J = 2.0 Hz, 1H), 6.79 (d, J = 8.5 Hz, 1H), 6.68 (s, 2H), 3.87 (d, J = 1.9 Hz, 6H), 3.78 (s, 6H), 3.66 (s, 3H), 2.86 (s, 2H), 2.41 (s, 2H), 1.21 (s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, Chloroform-*d*)  $\delta$  193.5, 164.9, 153.0, 149.4, 148.8, 148.5,

127.3, 122.8, 119.9, 119.0, 118.3, 110.9, 109.3, 99.9, 60.8, 56.1, 55.8, 55.5, 53.1, 37.7, 34.9, 28.6 ppm. HRMS (ESI-QTOF): *m/z* [M+H]<sup>+</sup> calcd. for C<sub>27</sub>H<sub>30</sub>O<sub>7</sub> 467.2070 found 467.2067. *2,3-Bis(3,4-dimethoxyphenyl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5H)-one* (3d):



Yellow solid, 67% yield, mp: 135-135 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.04 (dd, J = 8.4, 2.0 Hz, 1H), 6.99–6.96 (m, 2H), 6.94 (d, J = 2.0 Hz, 1H), 6.87 (d, J = 8.6 Hz, 1H), 6.77 (d, J = 8.5 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.81 (s, 3H), 3.66 (s, 3H), 2.86 (s, 2H), 2.40 (s, 2H), 1.20 (s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  193.5, 164.3, 148.7, 148.5, 148.4,

124.4, 123.0, 122.7, 120.0, 118.9, 118.1, 113.6, 111.0, 110.9, 109.2, 55.9, 55.8, 55.8, 55.6, 53.0, 37.7, 34.9, 28.6 ppm. HRMS (ESI-QTOF): m/z [M+H]<sup>+</sup> calcd. for C<sub>26</sub>H<sub>28</sub>O<sub>6</sub> 437.1964 found 437.1941.

### 2-(3,4-Dimethoxyphenyl)-6,6-dimethyl-3-(p-tolyl)-6,7-dihydrobenzofuran-4(5H)-one (3e):



Bright yellow solid, 58% yield, mp:133-134 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.30–7.25 (m, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.03 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.87 (d, *J* = 1.7 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 3.85 (s, 3H), 3.61 (s, 3H), 2.84 (s, 2H), 2.38–2.36 (m, 5H), 1.19 (s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  193.4, 164.8, 149.2, 148.6, 148.5, 137.1,

130.1, 129.0, 128.9, 123.1, 120.1, 118.7, 118.4, 110.9, 109.3, 55.8, 55.4, 53.0, 37.7, 34.9, 28.6, 21.3 ppm. HRMS (ESI-QTOF): *m*/*z* [M+H]<sup>+</sup> calcd. for C<sub>25</sub>H<sub>26</sub>O<sub>4</sub> 391.1909 found 391.1906.

2-(3,4-Dimethoxyphenyl)-3-(4-isopropylphenyl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5H)-one (3f):



White solid, 60% yield, mp:131-132 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ 7.33 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.11 (dd, J = 8.4, 2.0 Hz, 1H), 6.79 (d, J = 8.5 Hz, 1H), 6.75 (d, J = 2.0 Hz, 1H), 3.87 (s, 3H), 3.52 (s, 3H), 2.93 (dt, J = 13.8, 6.9 Hz, 1H), 2.86 (s, 2H), 2.40 (s, 2H), 1.25 (d, J = 6.9 Hz, 6H), 1.20 (s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):

δ 193.5, 164.8, 148.1, 130.1, 129.4, 126.3, 123.0, 118.5, 110.9, 109.2, 55.8, 55.2, 52.9, 37.7, 34.9, 33.9, 28.6, 23.9 ppm. HRMS (ESI-QTOF): m/z [M+H]<sup>+</sup> calcd. for C<sub>27</sub>H<sub>30</sub>O<sub>4</sub> 419.2222 found 419.2205.

 $\label{eq:constraint} 3-(4-Chlorophenyl)-2-(3,4-dimethoxyphenyl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5H)-one$ 

(**3g**):



White solid, 68% yield, mp:136-136 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ 7.35 (d, J = 1.7 Hz, 3H), 6.97 (dd, J = 8.4, 2.0 Hz, 1H), 6.86 (d, J = 2.0 Hz, 1H), 6.78 (d, J = 8.5 Hz, 1H), 3.87 (s, 3H), 3.68 (s, 3H), 2.86 (s, 2H), 2.40 (s, 2H), 1.20 (s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  193.5, 165.1, 149.6, 148.9, 148.6, 133.4, 131.7, 130.6, 128.4, 122.5, 119.8,

119.1, 117.1, 111.0, 109.3, 55.8, 55.5, 52.9, 37.7, 34.9, 28.6 ppm. HRMS (ESI-QTOF): *m*/*z* [M+H]<sup>+</sup> calcd. for C<sub>24</sub>H<sub>23</sub>ClO<sub>4</sub> 411.1363 found 411.1340.

# 2-(3,4-Dimethoxyphenyl)-6,6-dimethyl-3-(4-nitrophenyl)-6,7-dihydrobenzofuran-4(5H)-one (3h):



Bright yellow solid, 78% yield, mp:161-161 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.23–8.20 (m, 2H), 7.62–7.59 (m, 2H), 6.89 (d, J = 7.8 Hz, 2H), 6.77 (d, J = 8.4 Hz, 1H), 3.87 (s, 3H), 3.70 (s, 3H), 2.88 (s, 2H), 2.42 (s, 2H), 1.22 (s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  193.5, 165.6, 150.6, 149.5, 148.9, 147.0, 139.4, 131.4, 123.3, 121.8, 119.7,

111.1, 109.6, 55.9, 55.7, 52.8, 37.6, 35.0, 28.6 ppm. HRMS (ESI-QTOF): m/z [M+H]<sup>+</sup> calcd. for C<sub>24</sub>H<sub>23</sub>NO<sub>6</sub>422.1604 found 422.1599.

## 4-(2-(3,4-Dimethoxyphenyl)-6,6-dimethyl-4-oxo-4,5,6,7-tetrahydrobenzofuran-3-yl)benzonitrile (3i):



Yellow solid, 75%, yield, mp: 169-169 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.65 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H), 6.91 (dd, J = 8.4, 2.0 Hz, 1H), 6.83 (d, J = 2.0 Hz, 1H), 6.78 (d, J = 8.5 Hz, 1H), 3.88 (s, 3H), 3.68 (s, 3H), 2.87 (s, 2H), 2.41 (s, 2H), 1.21 (s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  193.4, 165.5, 150.3, 149.4, 148.8, 137.3, 131.8, 131.2,

121.9, 119.5, 119.5, 118.9, 116.7, 111.1, 111.1, 109.6, 55.9, 55.6, 52.8, 37.6, 35.0, 28.6 ppm. HRMS (ESI-QTOF): *m*/*z* [M+H]<sup>+</sup> calcd. for C<sub>25</sub>H<sub>23</sub>NO<sub>4</sub> 402.1705 found 402.1679.

## 2-(3,4-Dimethoxyphenyl)-6,6-dimethyl-3-(4-(trifluoromethyl)phenyl)-6,7-dihydrobenzofuran-4(5H)-one (3j):



Pale yellow solid, 61% yield, mp:136-137 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.64–7.53 (m, 4H), 6.96 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.79–6.76 (m, 2H), 3.87 (s, 3H), 3.62 (s, 3H), 2.87 (s, 2H), 2.41 (s, 2H), 1.21 (s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 193.4, 165.2, 150.1, 149.1, 148.7, 136.1, 130.8, 125.0, 122.2, 119.7, 119.2, 117.0, 111.1, 109.4, 55.8,

55.4, 52.9, 37.7, 35.0, 28.6 ppm. HRMS (ESI-QTOF): *m*/*z* [M+H]<sup>+</sup> calcd. for C<sub>25</sub>H<sub>23</sub>F<sub>3</sub>O<sub>4</sub> 445.1627 found 445.1619.

## 3-(Benzo[d][1,3]dioxol-5-yl)-2-(3,4-dimethoxyphenyl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5H)-one (3k):



White solid, 55% yield, mp:157-158 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  6.95 (td, J = 6.0, 1.8 Hz, 3H), 6.89–6.85 (m, 2H), 6.71 (d, J = 8.2 Hz, 1H), 5.94 (s, 2H), 3.91 (s, 3H), 3.82 (s, 3H), 2.83 (s, 2H), 2.39 (s, 2H), 1.20 (s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  193.5, 164.9, 149.0, 148.5, 148.5, 147.5, 147.2, 124.2, 124.1, 122.6, 120.4, 113.5, 111.0,

108.3, 106.7, 101.1, 55.9, 55.8, 53.1, 37.7, 34.8, 29.7, 28.6 ppm. HRMS (ESI-QTOF): *m*/*z* [M+H]<sup>+</sup> calcd. for C<sub>25</sub>H<sub>24</sub>O<sub>6</sub> 421.1651 found 421.1622.

## 2-(3,4-Dimethoxyphenyl)-6,6-dimethyl-3-(thiophen-2-yl)-6,7-dihydrobenzofuran-4(5H)-one (3l):



Brown solid, 52% yield, mp:220-221 °C, <sup>1</sup>H NMR (500 MHz, Chloroformd)  $\delta$  7.37–7.34 (m, 1H), 7.18–7.16 (m, 1H), 7.11 (dd, J = 8.4, 1.9 Hz, 1H), 7.06 (dd, J = 5.1, 3.6 Hz, 1H), 6.94 (s, 1H), 6.81 (d, J = 8.4 Hz, 1H), 3.88 (s, 3H), 3.68 (s, 3H), 2.84 (s, 2H), 2.40 (s, 2H), 1.20 (s, 6H).<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  193.1, 164.8, 150.7, 149.1, 148.6, 132.7, 128.5, 127.0,

126.3, 122.5, 120.3, 119.2, 110.9, 109.5, 77.3, 77.0, 76.8, 55.8, 55.5, 52.9, 37.6, 34.9, 28.6 ppm. HRMS (ESI-QTOF): *m*/*z* [M+H]<sup>+</sup> calcd. for C<sub>22</sub>H<sub>22</sub>O<sub>4</sub>S 383.1317 found 383.1294.

3-(Furan-3-yl)-6,6-dimethyl-2-phenyl-6,7-dihydrobenzofuran-4(5H)-one (3m):



White solid, 68% yield, mp:180-181 °C,<sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.41 (dd, J = 1.8, 0.7 Hz, 1H), 7.14 (dd, J = 8.4, 2.0 Hz, 1H), 7.00 (d, J = 2.0 Hz, 1H), 6.92 (dd, J = 3.3, 0.7 Hz, 1H), 6.86 (d, J = 8.5 Hz, 1H), 6.50 (dd, J = 3.3, 1.8 Hz, 1H), 3.90 (s, 3H), 3.80 (s, 3H), 2.83 (s, 2H), 2.42 (s,

2H), 1.19 (s, 6H) ppm. <sup>13</sup>C NMR (126 MHz, Chloroform-*d*) δ 193.1, 165.2, 151.0, 149.3,148.5, 145.3,141.6, 122.8, 119.8, 119.3, 111.5, 111.4, 110.8, 110.1, 110.1, 108.3, 55.9, 55.7, 53.0, 37.6, 34.8, 28.5 ppm. HRMS (ESI-QTOF): *m*/*z* [M+H]<sup>+</sup> calcd. for C<sub>22</sub>H<sub>22</sub>O<sub>5</sub> 367.1545 found 367.1538.

### 6,6-Dimethyl-2-(4-nitrophenyl)-3-phenyl-6,7-dihydrobenzofuran-4(5H)-one (3n):



Yellow solid, 76% yield, mp:215-217 °C, <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  8.11 – 8.07 (m, 2H), 7.54– 7.52 (m, 2H), 7.42 (dd, J = 5.0, 1.8 Hz, 3H), 7.38 (dd, J = 6.7, 3.0 Hz, 2H), 2.90 (s, 2H), 2.42 (s, 2H), 1.22 (s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, Chloroform-*d*)  $\delta$  192.2, 166.5, 136.1, 130.9, 129.7, 128.6, 128.4, 125.9, 123.8, 52.9, 37.7, 34.9, 28.6 ppm. HRMS (ESI-QTOF): *m*/*z* [M+H]<sup>+</sup> calcd. for C22H19NO<sub>4</sub> 362.1392 found 362.1383.

### 2-(3,4-Dimethoxyphenyl)-3-phenyl-6,7-dihydrobenzofuran-4(5H)-one (4a):



Pale yellow solid, 59% yield, mp:116-117 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.40–7.31 (m, 5H), 7.04 (dd, J = 8.4, 2.0 Hz, 1H), 6.81 (d, J = 2.0 Hz, 1H), 6.77 (d, J = 8.5 Hz, 1H), 3.86 (s, 3H), 3.57 (s, 3H), 3.00 (t, J = 6.3 Hz, 2H), 2.53–2.48 (m, 2H), 2.23 (p, J = 6.4 Hz, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  193.9, 165.6, 149.0, 148.7, 148.5, 132.3, 130.2, 128.2,

127.5, 122.8, 121.3, 118.7, 111.0, 109.3, 55.8, 55.4, 38.6, 23.8, 22.4 ppm. HRMS (ESI-QTOF): *m/z* [M+H]<sup>+</sup> calcd. for C<sub>22</sub>H<sub>20</sub>O<sub>4</sub> 349.1440 found 349.1433.

### 2-(3,4-Dimethoxyphenyl)-3,6-diphenyl-6,7-dihydrobenzofuran-4(5H)-one (4b):



Brown liquid, 42%, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.43–7.40 (m, 3H), 7.38 (dd, *J* = 7.6, 3.3 Hz, 3H), 7.33 (q, *J* = 10.9, 10.0 Hz, 4H), 7.06 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.82 (d, *J* = 2.1 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 3.86 (s, 3H), 3.64 (td, *J* = 11.1, 5.5 Hz, 1H), 3.58 (s, 3H), 3.34 – 3.14 (m, 2H), 2.85–2.73 (m, 2H) ppm. <sup>13</sup>C NMR (125)

MHz, CDCl<sub>3</sub>): δ 192.5, 164.8, 149.6, 148.8, 148.5, 142.5, 132.1, 130.2, 128.8, 128.3, 127.6, 127.2, 126.7, 122.7, 121.2, 118.8, 118.4, 55.8, 55.4, 45.8, 41.0, 31.5 ppm. HRMS (ESI-QToF): *m*/*z* [M+H]<sup>+</sup> calcd. for C<sub>28</sub>H<sub>24</sub>O<sub>4</sub> 425.1753 found 425.1740.

### 6-(3,4-Dimethoxyphenyl)-1,3-dimethyl-5-phenylfuro[2,3-d]pyrimidine-2,4(1H,3H)-dione (4c):



White solid, 67% yield, mp:138-138 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.51–7.48 (m, 2H), 7.44–7.40 (m, 2H), 7.39–7.36 (m, 1H), 7.08 (dd, J = 8.4, 2.1 Hz, 1H), 6.82 (d, J = 8.5 Hz, 1H), 6.80 (d, J = 2.1 Hz, 1H), 3.88 (s, 3H), 3.67 (s, 3H), 3.57 (s, 3H), 3.39 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  158.0, 154.5, 150.5, 149.0, 148.6, 145.4, 130.5, 130.2,

128.4, 128.2, 121.8, 118.8, 118.7, 111.1, 109.2, 98.0, 55.9, 55.4, 29.5, 28.2 ppm. HRMS (ESI-QToF): *m/z* [M+H]<sup>+</sup> calcd. for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>O<sub>5</sub> 393.1450 found 393.1442.

*Methyl* (4*R*)-3-(3,4-dimethoxyphenyl)-6-methyl-2-oxo-4-phenyl-3,4-dihydro-2H-pyran-5carboxylate (5a):



Pale yellow, 78%, mp:124-125 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.23–7.19 (m, 3H), 7.02–6.98 (m, 2H), 6.77 (dd, J = 1.9 Hz, 1H), 6.72-6.71 (m, 1H), 6.44 (d, J = 1.9 Hz, 1H), 3.81 (s, 3H), 3.56 (s, 3H), 3.40 (s, 3H), 2.44 (s, 3H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  166.4, 161.6, 161.2, 150.7, 148.4, 148.0, 136.5, 128.2, 127.8, 125.1, 123.5, 123.3, 114.6, 113.9, 110.4,

55.7, 55.6, 52.2, 18.8 ppm. HRMS (ESI-QToF): *m*/*z* [M+H]<sup>+</sup> calcd. for C<sub>22</sub>H<sub>22</sub>O<sub>6</sub> 383.1495 found 516.2111 [M+H]<sup>+</sup>.

Isopropyl 3-(3,4-dimethoxyphenyl)-6-methyl-2-oxo-4-(3,4,5-trimethoxyphenyl)-3,4-dihydro-2Hpyran-5-carboxylate (5b):



Bright yellow, 67% yield, mp: 140-141 °C <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ 6.74 (d, J = 1.0 Hz, 2H), 6.54 (s, 1H), 6.26 (s, 2H), 4.83 (dq, J = 12.5, 6.3 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 3.63 (d, J = 2.5 Hz, 9H), 2.43 (s, 3H), 0.94 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  165.6, 161.5, 160.8, 153.1, 150.4, 148.5, 148.3, 138.0, 131.6, 125.4, 123.2, 123.2, 114.9, 113.7, 110.6,

105.8, 69.5, 60.9, 56.1, 55.8, 55.7, 21.2, 18.5 ppm. HRMS (ESI-QToF): m/z [M+H]<sup>+</sup> calcd. for C<sub>27</sub>H<sub>30</sub>O<sub>9</sub> 499.1968 found 499.1938.

## *Benzyl* 3-(3,4-dimethoxyphenyl)-6-methyl-2-oxo-4-(3,4,5-trimethoxyphenyl)-3,4-dihydro-2Hpyran-5-carboxylate (5c):



Pale yellow solid, 47%, mp:135-136 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.27–7.26 (m, 2H), 6.94 (d, J = 6.6 Hz, 2H), 6.73 (d, J = 2.1 Hz, 2H), 6.50 (s, 1H), 6.21 (s, 2H), 4.89 (s, 2H), 3.82 (s, 3H), 3.78 (s, 3H), 3.61 (s, 3H), 3.55 (s, 6H), 2.43 (s, 3H) ppm.<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  166.0, 161.4, 161.3, 153.1, 150.2, 148.5,

148.3, 138.0, 134.1, 131.4, 128.6, 128.4, 128.4, 125.4, 123.2, 123.2, 114.4, 113.6, 110.6, 105.6, 68.0, 60.9, 56.0, 55.8, 55.7, 18.7 ppm. HRMS (ESI-QTOF): m/z [M+H]<sup>+</sup> calcd. for C<sub>31</sub>H<sub>30</sub>O<sub>9</sub> 547.1968 found 547.1933.

### *Ethyl 4-(3,4-dimethoxyphenyl)-6-methyl-2-oxo-3-phenyl-2H-pyran-5-carboxylate* (5d):



White solid, 70% yield, mp:130.6-131.2 °C <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.22 – 7.20 (m, 3H), 7.01 (dd, *J* = 6.5, 3.1 Hz, 2H), 6.76 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.44 (d, *J* = 2.0 Hz, 1H), 3.81 (s, 3H), 3.56 (s, 3H), 2.45 (s, 3H), 0.80 (t, *J* = 7.1 Hz, 3H) ppm. <sup>13</sup>C NMR (125 MHz, Chloroform-*d*)  $\delta$  165.9, 161.6, 161.2, 150.8, 148.4,

148.0, 136.6, 128.1, 128.0, 125.1, 123.5, 114.7, 114.0, 110.5, 61.5, 55.7, 55.6, 29.6, 18.7, 13.3 ppm . HRMS (ESI-QTOF): *m*/*z* [M+H]<sup>+</sup> calcd. for C<sub>27</sub>H<sub>30</sub>O<sub>7</sub> 395.1495 found 395.1488 [M+H]<sup>+</sup>.

## *Ethyl* 4-(4-cyanophenyl)-3-(3,4-dimethoxyphenyl)-6-methyl-2-oxo-3,4-dihydro-2H-pyran-5carboxylate (5e):



Yellow solid, 72% yield, mp:172-172 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ 7.52 (d, J = 8.5 Hz, 2H), 7.15 (d, J = 8.5 Hz, 2H), 6.68 (d, J = 8.4 Hz, 1H), 6.57 (dd, J = 8.3, 2.0 Hz, 1H), 6.50 (d, J = 2.0 Hz, 1H), 3.91 (q, J =7.1 Hz, 2H), 3.82 (s, 3H), 3.65 (s, 3H), 2.49 (s, 3H), 0.87 (t, J = 7.1 Hz, 3H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  165.1, 162.7, 160.9, 148.8,

148.7, 148.3, 141.5, 131.8, 128.9, 124.2, 124.1, 123.5, 118.0, 113.6, 113.5, 112.0, 110.6, 61.7, 55.7, 19.0, 13.5 ppm. HRMS (ESI-QTOF): *m/z* [M+H]<sup>+</sup> calcd. for C<sub>24</sub>H<sub>21</sub>NO<sub>6</sub> 420.1447 found 420.1455.

*Ethyl* 4-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)-6-methyl-2-oxo-3,4-dihydro-2H-pyran-5carboxylate (5f):



Pale yellow solid, 67% yield, mp:104-105 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.21–7.18 (m, 2H), 6.98–6.94 (m, 2H), 6.74–6.66 (m, 2H), 6.46 (d, *J* = 1.8 Hz, 1H), 3.93 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 3.62 (s, 3H), 2.45 (s, 3H), 0.89 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  165.6, 161.6,

161.3, 149.6, 148.6, 148.2, 135.0, 134.3, 132.8, 129.4, 129.1, 128.4, 126.4, 124.8, 123.7, 123.5, 114.3, 113.8, 110.6, 99.9, 61.7, 55.7, 55.6, 29.7, 18.8, 13.4 ppm. HRMS (ESI-QTOF): m/z [M+H]<sup>+</sup> calcd. for C<sub>23</sub>H<sub>21</sub>ClO<sub>6</sub> 429.1105 found 429.1102.

*Ethyl* 3-(3,4-dimethoxyphenyl)-6-methyl-4-(naphthalen-2-yl)-2-oxo-3,4-dihydro-2H-pyran-5carboxylate (5g):



White solid, 69% yield, mp: 171-176 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.79–7.70 (m, 3H), 7.47–7.41 (m, 2H), 7.30 (dd, J = 8.2, 7.1 Hz, 1H), 7.09 (dd, J = 7.1, 1.0 Hz, 1H), 6.77 (dd, J = 8.3, 2.0 Hz, 1H), 6.58 (d, J = 8.4 Hz, 1H), 6.34 (d, J = 2.0 Hz, 1H), 3.71 (s, 2H), 3.59 – 3.48 (m, 2H), 3.20 (s, 3H), 2.51 (s, 3H), 0.35 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (125 MHz,

CDCl<sub>3</sub>):  $\delta$  165.3, 161.7, 161.5, 150.3, 148.3, 147.7, 134.2, 133.0, 130.8, 128.5, 128.3, 126.5, 126.2, 126.0, 125.4, 125.1, 124.9, 122.6, 115.2, 112.9, 110.3, 61.1, 55.6, 55.1, 19.1, 12.8 ppm. HRMS (ESI-QTOF): m/z [M+H]<sup>+</sup> calcd. for C<sub>27</sub>H<sub>24</sub>O<sub>6</sub> 445.1651 found 445.1665.

*Ethyl* 3-(3,4-dimethoxyphenyl)-6-methyl-2-oxo-4-(3,4,5-trimethoxyphenyl)-3,4-dihydro-2Hpyran-5-carboxylate (5h):



Bright yellow solid, 70% yield, mp:105-106 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  6.75 (s, 2H), 6.55 (s, 1H), 6.25 (s, 2H), 3.96 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H), 3.63 (s, 9H), 2.44 (s, 3H), 0.90 (t, *J* = 7.1 Hz, 3H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  166.1, 161.5, 161.1, 153.0, 150.4, 148.5, 148.3, 138.0, 131.7, 125.4, 123.3, 123.1 114.7, 113.7, 110.6,

105.7, 61.7, 60.9, 56.1, 55.8, 55.7, 18.6, 13.5 ppm. HRMS (ESI-QToF): m/z [M+H]<sup>+</sup> calcd. for C<sub>26</sub>H<sub>28</sub>O<sub>9</sub> 485.1812 found 485.1812.

## *Ethyl* 3-(3,4-dimethoxyphenyl)-6-methyl-2-oxo-4-(thiophen-3-yl)-3,4-dihydro-2H-pyran-5carboxylate (5i):



White solid, 58% yield, mp:122-124 °C <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ 7.28 (dd, J = 5.0, 1.2 Hz, 1H), 6.89 (dd, J = 5.0, 3.6 Hz, 1H), 6.85 (dd, J = 3.6, 1.2 Hz, 1H), 6.82 (dd, J = 8.3, 1.9 Hz, 1H), 6.78 (d, J = 8.3 Hz, 1H), 4.01 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 3.66 (s, 3H), 2.43 (s, 3H), 0.98 (t, J = 7.1 Hz, 3H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  165.8, 161.2,

160.6, 148.8, 148.4, 143.9, 136.8, 128.4, 128.1, 126.7, 125.3, 124.5, 123.2, 114.9, 113.5, 110.6, 61.8, 55.7, 18.7, 13.5 ppm. HRMS (ESI-QToF): *m*/*z* [M+H]<sup>+</sup> calcd. for C<sub>21</sub>H<sub>20</sub>O<sub>6</sub>S 401.1059 found 401.1051.

# *Ethyl* 4-(*benzo*[*d*][1,3]*dioxo*l-5-*y*l)-3-(3,4-*dimethoxyphenyl*)-6-*methyl*-2-*oxo*-3,4-*dihydro*-2*H*-*pyran*-5-*carboxylate* (5j):



White solid, 55% yield, mp:116-117 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  6.73 (d, J = 8.3 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 6.62 (dd, J = 8.3, 1.9 Hz, 1H), 6.58–6.56 (m, 1H), 6.54–6.52 (m, 1H), 6.49 (d, J = 1.7 Hz, 1H), 5.90 (s, 2H), 3.95 (q, J = 7.1 Hz, 2H), 3.84 (s, 3H), 3.64 (s, 3H), 2.43 (s, 3H), 0.92 (t, J = 7.1 Hz, 3H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  166.1,

161.7, 160.9, 150.9, 149.0, 148.5, 147.2, 147.0, 128.5, 126.8, 124.4, 120.7, 114.9, 111.6, 110.8, 110.5, 108.1, 101.0, 61.6, 55.8, 18.7, 13.6 ppm. HRMS (ESI-QToF): m/z [M+H]<sup>+</sup> calcd. for C<sub>24</sub>H<sub>22</sub>O<sub>8</sub> 439.1393 found 439.1359.

## (E)-2-(3,4-dimethoxyphenyl)-6,6-dimethyl-3-(3,4,5-trimethoxyphenyl)-6,7-dihydrobenzofuran-4(5H)-one oxime (6):



White solid, 70% yield, mp:123-124 °C, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$ 7.62 (s, 1H), 6.99 (dd, J = 8.5, 2.0 Hz, 1H), 6.80 (d, J = 2.0 Hz, 1H), 6.75 (d, J = 8.5 Hz, 1H), 6.59 (s, 2H), 3.89 (s, 3H), 3.85 (s, 3H), 3.78 (s, 6H), 3.62 (s, 3H), 2.67 (s, 2H), 2.57 (s, 2H), 1.15 (s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  154.0, 152.3, 150.3, 147.7, 147.3, 147.2, 136.2, 128.3, 122.5, 117.1, 117.0, 114.4, 109.9, 107.6, 106.3, 59.7, 55.0, 54.8, 54.4, 36.3, 35.1, 31.4, 27.7 ppm. HRMS (ESI-QToF): *m*/*z* [M+H]<sup>+</sup> calcd. for C<sub>27</sub>H<sub>31</sub>NO<sub>7</sub> 482.2179 found 482.2173.

### Ethyl 3,3'',4,4'',5''-pentamethoxy-4'-methyl-6'-phenyl-[1,1':2',1''-terphenyl]-3'-carboxylate (7):



Yellow liquid, 30% yield, <sup>1</sup>H NMR (500 MHz, Chloroform-*d*)  $\delta$  7.32 (d, *J* = 4.5 Hz, 1H), 7.30–7.28 (m, 2H), 7.18 (d, *J* = 7.3 Hz, 2H), 7.10–7.08 (m, 1H), 6.99–6.92 (m, 1H), 6.26 (s, 2H), 5.99 (bncs, 2H), 4.37 (q, *J* = 7.2 Hz, 1H), 3.70 (s, 3H), 3.59 (s, 6H), 3.38 (s, 6H), 2.46 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H) ppm.<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  168.3, 158.9, 150.9, 141.5, 140.4, 140.4, 137.8, 136.1, 130.3, 128.4, 126.7, 125.5, 108.4, 107.3, 98.6, 60.0, 59.8, 54.9,

54.2, 28.6, 18.3, 12.7 ppm. HRMS (ESI-QTOF): *m*/*z* [M+H]<sup>+</sup> calcd. for C<sub>33</sub>H<sub>34</sub>O<sub>7</sub> 543.2383 found 543.2365.

### 5. Mechanistic investigation

### 5.1 (H/D)-exchange experiment

To an oven-dried pressure tube equipped with magnetic stir bar, **1a** (1 equiv.),  $CD_3OD$  (10 equiv.),  $[Cp*RhCl_2]_2$  (2.5 mol%), AgOAc (1 equiv.) in 2 mL DCE was added. The reaction mixture was stirred at 100 °C for 1 h. Then the solvent was evaporated under reduced pressure and the residue was purified by column chromatography using hexane: ethyl acetate (60:40). The result of <sup>1</sup>H NMR of isolated compounds revealed 30% incorporation of deuterium at *ortho*-position.





### 5.2 Competitive measurements (EWG vs EDG)

To an oven dried pressure tube equipped with a magnetic bead **1e** (1 equiv.), **1h** (1 equiv.), with **2a** (1 equiv.), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (2.5 mol%), AgOAc (1 equiv.) and DCE 2 ml was added. The reaction mixture was stirred for 1 h and the crude reaction mixture is purified by flash chromatography and mixture of spots was isolated. Then trimethoxy benzene (1 equiv.) was added to the resulting purified mixture and directly recorded <sup>1</sup>H NMR. The spectra resulted that product **3h/3e** has been formed with a ratio of 2:1 concluding that **1h** acts 2 times faster than **1e**.



Figure S2. Competitive reactivity measurements: electron-withdrawing acid vs electron-donating acid.

### 5.3 ESI-MS studies

To an oven-dried pressure tube equipped with magnetic stir bar, *cis*-stilbene acid **1a** (1 equiv.), 2diazo-5,5-dimethylcyclohexane-1,3-dione **2a** (1.1. equiv.),  $[Cp*RhCl_2]_2$  (2.5 mol%), AgOAc (1 equiv.) in 2 mL DCE was added. The reaction mixture was stirred at 100 °C for 1 h. The samples were withdrawn from the pressure tube and the mass of the crude mixture was recorded at subsequent intervals (0, 1, 5, 8, 12, 18, 22, 30 and 60 min.) to predict the intermediates of the catalytic cycle.



Figure S3. HRMS-(ESI-QToF) mechanistic studies of the reaction.





Compound 3b. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)





















































