

## Supporting Information

### Novel Synthesis of 3-Phenyl-chromen-4-ones Using N-Heterocyclic Carbene as Organocatalyst: An Efficient Domino Catalysis Type Approach

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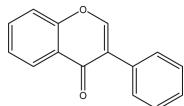
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#### **General Information:**

The melting points were determined on a MAC, DIGITAL MELTING POINT APPARATUS and were uncorrected.  $^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  (100 MHz) spectra were recorded on a Bruker Avance II 400 spectrometer. The chemical shifts are expressed in ppm: s, singlet; d, doublet; m, multiplet. The products were purified either by recrystallization or by column chromatography. The starting materials used were purchased from Aldrich Chemical Company and were used without any further purification. Elemental analyses were performed using a Vario EL III CHN-O- analyzer.

#### **Characterization Data of products:**



#### **3-Phenyl-chromen-4-one (3a)**

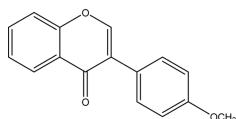
Pale yellow crystal, mp 150-155 °C

$^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta_{\text{H}}$  8.45 (s, 1H), 8.00 (d d,  $J$  = 8.50 Hz, 1.70 Hz, 1H), 7.65 (t,  $J$  = 7.46 Hz, 1H), 7.48 (d d,  $J$  = 8.05 Hz, 1.66 Hz, 1H), 7.40 (t,  $J$  = 7.45 Hz, 1H), 7.28 (t,  $J$  = 7.60 Hz, 2H), 7.25 (t,  $J$  = 7.40 Hz, 8.00 Hz, 1H), 7.22 (d d,  $J$  = 7.90 Hz, 1.67 Hz, 2H).

$^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta_{\text{c}}$  175.5, 157.1, 153.4, 135.5, 132.3, 130.2, 128.9, 128.1, 126.2, 124.1, 123.4, 123.1, 117.5.

EIMS ( $m/z$ ): 222 ( $\text{M}^+$ ).

Anal. Calc. for  $\text{C}_{15}\text{H}_{10}\text{O}_2$ ; C, 81.07; H, 4.54; O, 14.40. Found: C, 81.04; H, 4.56; O, 14.45.



#### **3-(4-Methoxy-phenyl)-chromen-4-one (3b)**

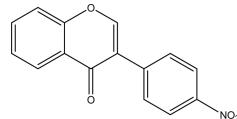
Yellow crystal, mp 220-222 °C;

$^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta_{\text{H}}$  8.73 (s, 1H), 8.02 (d d,  $J$  = 8.60 Hz, 2.12 Hz, 1H), 7.40 (d d,  $J$  = 7.95 Hz, 2.00 Hz, 1H), 7.36 (m, 3H), 7.28 (t,  $J$  = 7.50 Hz, 1H), 6.86 (d,  $J$  = 7.77 Hz, 2H), 3.65 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta_{\text{c}}$  175.5, 160.1, 157.2, 153.1, 135.6, 130.3, 127.3, 125.1, 124.1, 123.6, 123.2, 117.5, 114.3, 56.2.

EIMS ( $m/z$ ): 252 ( $\text{M}^+$ ).

Anal. calc. for  $\text{C}_{15}\text{H}_{10}\text{O}_2$ ; C, 76.18; H, 4.79; O, 19.03. Found: C, 76.20; H, 4.80; O, 19.01.



#### **3-(4-Nitro-phenyl)-chromen-4-one (3c)\***

Orange solid, mp 195-198 °C;

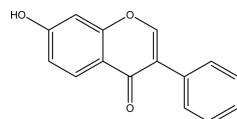
$^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta_{\text{H}}$  8.96 (s, 1H), 8.27 (d,  $J$  = 7.75 Hz, 2H), 7.99 (d d,  $J$  = 8.05 Hz, 1.79 Hz, 1H), 7.65 (d,  $J$  = 7.63 Hz, 2H), 7.50 (d d,  $J$  = 8.00 Hz, 1.72 Hz, 1H), 7.41 (t,  $J$  = 7.56 Hz, 1H), 7.32 (t,  $J$  = 7.49 Hz, 1H).

$^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta_{\text{c}}$  170, 157.06, 155.03, 149.14, 143.33, 135.17, 130.33, 127.37, 126.53, 126.46, 126.01, 126.0, 118.61.

EIMS ( $m/z$ ): 267 ( $\text{M}^+$ ).

Anal. Calc. for  $\text{C}_{15}\text{H}_{10}\text{O}_2$ ; C, 67.42; H, 3.39; N, 5.24; O, 23.95. Found: C, 67.40; H, 3.41; N, 5.25; O, 23.93.

\*The spectral data for this compound matches fairly with that of 7-Hydroxy-4'-nitroisoflavone described elsewhere.<sup>1</sup>



#### **7-Hydroxy-3-phenyl-chromen-4-one (3d)\***

White solid, mp 210-213 °C;

$^1\text{H-NMR}$  (400 MHz, DMSO- $d_6$ )  $\delta_{\text{H}}$  9.28 (s, 1H), 8.90 (s, 1H), 7.88 (d,  $J$  = 7.57 Hz, 1H), 7.50 (d d,  $J$  = 8.40 Hz, 1.83 Hz, 2H), 7.28 (t,  $J$  = 7.52 Hz, 2H), 7.20 (t,  $J$  = 7.43 Hz, 1H), 6.92 (s, 1H), 6.75 (d d,  $J$  = 8.20 Hz, 1.60 Hz, 1H).

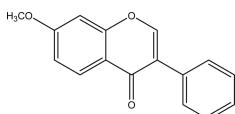
$^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta_{\text{c}}$  172.25, 161.86, 156.96, 153.03, 132.24, 127.74, 127.69, 127.14, 126.60, 124.0, 116, 115.63, 101.14.

EIMS ( $m/z$ ): 238 ( $\text{M}^+$ ).

Anal. Calc. for  $\text{C}_{15}\text{H}_{10}\text{O}_2$ ; C, 75.62; H, 4.23; O, 20.15.

Found: C, 75.63; H, 4.25; O, 20.11.

\*The spectroscopic data are in agreement with those reported in the literature.<sup>1</sup>



### 7-Methoxy-3-phenyl-chromen-4-one (3e)\*

White solid, mp 157-158 °C;

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>) δ<sub>H</sub> 8.90 (s, 1H), 7.90 (d, *J* = 7.51 Hz, 1H), 7.52 (d d, *J* = 8.42 Hz, 1.67 Hz, 2H), 7.33 (t, *J* = 7.60 Hz, 2H), 7.21 (t, *J* = 7.48 Hz, 1H), 6.90 (d, *J* = 1.47 Hz, 1H), 6.80 (d d, *J* = 8.48 Hz, 1.62 Hz, 1H), 3.62 (s, 3H).

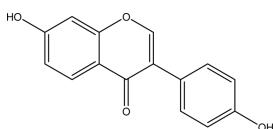
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ<sub>C</sub> 171.25, 162.31, 154.71, 152.03, 131.24, 126.74, 125.21, 124.69, 124.14, 122.0, 116.82, 112.56, 99.11, 54.04.

EIMS (*m/z*): 252 (M<sup>+</sup>).

Anal. Calc. for C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>; C, 76.18; H, 4.79; O, 19.03.

Found: C, 76.15; H, 4.81; O, 19.05.

\*The spectroscopic data are in agreement with those reported in the literature.<sup>1</sup>



### 7-Hydroxy-3-(4-hydroxy-phenyl)-chromen-4-one (Daidzin) (3f)\*

Pale yellow crystal, mp 320-321 °C;

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>) δ<sub>H</sub> 9.32 (s, 1H), 9.27 (s, 1H), 8.51 (s, 1H), 7.84 (d, *J* = 7.68 Hz, 1H), 7.05 (d, *J* = 7.61 Hz, 2H), 6.95 (s, 1H), 6.78 (d, *J* = 7.53 Hz, 2H), 6.75 (d d, *J* = 8.59 Hz, 1.71 Hz, 1H).

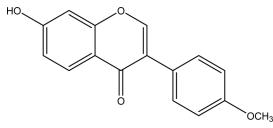
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ<sub>C</sub> 175.4, 165.1, 158.5, 157.9, 153.4, 132.1, 127.7, 125.1, 123.7, 116.6, 115.5, 110.8, 105.3.

EIMS (*m/z*): 254 (M<sup>+</sup>).

Anal. Calc. for C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>; C, 70.86; H, 3.96; O, 25.17.

Found: C, 70.83; H, 3.97; O, 25.19.

\*The spectroscopic data are in agreement with those reported in the literature.<sup>2,3</sup>



### 7-Hydroxy-3-(4-methoxy-phenyl)-chromen-4-one (Formononetin) (3g)\*

Colourless needles, mp 255-257 °C;

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>) δ<sub>H</sub> 9.26 (s, 1H), 8.80 (s, 1H), 7.84 (d, *J* = 7.59 Hz, 1H), 7.37 (d, *J* = 7.69 Hz, 2H), 6.92 (s, 1H), 6.83 (d, *J* = 7.58 Hz, 2H), 6.75 (d d, *J* = 8.28 Hz, 1.56 Hz, 1H), 3.64 (s, 3H).

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ<sub>C</sub> 169.25, 158.86,

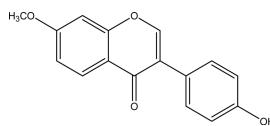
154.89, 153.96, 150.03, 125.57, 123.60, 121.0, 120.05, 113.0, 112.63, 109.94, 98.14, 54.04.

EIMS (*m/z*): 268 (M<sup>+</sup>).

Anal. Calc. for C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>; C, 71.64; H, 4.51; O, 23.86.

Found: C, 71.61; H, 4.55; O, 23.82.

\*The spectroscopic data are in agreement with those reported in the literature.<sup>4</sup>



### 3-(4-Hydroxy-phenyl)-7-methoxy-chromen-4-one (3h)\*

White solid, mp 218-220 °C;

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>) δ<sub>H</sub> 9.31 (s, 1H), 8.78 (s, 1H), 7.85 (d, *J* = 7.59 Hz, 1H), 7.35 (d, *J* = 7.53 Hz, 2H), 6.90 (s, 1H), 6.80 (m, 3H), 3.67 (s, 3H).

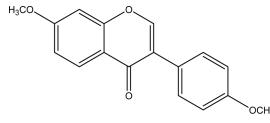
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ<sub>C</sub> 175.6, 161.31, 154.92, 151.03, 148.71, 126.95, 124.21, 122.0, 119.81, 115.82, 111.97, 111.56, 98.11, 53.04.

EIMS (*m/z*): 268 (M<sup>+</sup>).

Anal. Calc. for C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>; C, 71.64; H, 4.51; O, 23.86.

Found: C, 71.65; H, 4.55; O, 23.87.

\*The spectroscopic data are in agreement with those reported in the literature.<sup>1</sup>



### 7-Methoxy-3-(4-methoxy-phenyl)-chromen-4-one (3i)\*

White solid, mp 162-164 °C;

<sup>1</sup>H-NMR (400 Hz, DMSO-d<sub>6</sub>) δ<sub>H</sub> 8.80 (s, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 7.62 Hz, 2H), 6.94 (s, 1H), 6.82 (m, 3H), 3.69 (s, 3H), 3.64 (s, 3H).

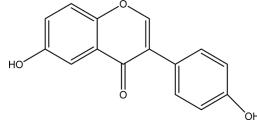
<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ<sub>C</sub> 172.25, 163.31, 157.89, 155.71, 153.03, 128.57, 126.20, 124, 123.05, 117.82, 113.56, 112.94, 100.11, 55.04, 55.03.

EIMS (*m/z*): 282 (M<sup>+</sup>).

Anal. Calc. for C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>; C, 72.33; H, 5.00; O, 22.67.

Found: C, 72.30; H, 5.1; O, 22.65.

\*The spectroscopic data are in agreement with those reported in the literature.<sup>1</sup>



### 3-(4-Hydroxy-phenyl)-7-methoxy-chromen-4-one (3j)\*

White solid, mp 160-162 °C;

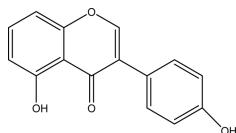
<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>) δ<sub>H</sub> 9.30 (s, 1H), 9.17 (s, 1H), 8.80 (s, 1H), 7.52 (s, 1H), 7.36 (d, *J* = 7.71 Hz, 2H), 7.28 (d, *J* = 7.80 Hz, 1H), 6.85 (d d, *J* = 8.85 Hz, 1.52 Hz, 1H), 6.80 (d, *J* = 7.81 Hz, 2H).

<sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ<sub>C</sub> 175.5, 157.8, 153.2,

153.1, 150.1, 127.9, 125.3, 125.1, 123.6, 122.6, 119.2, 116.5, 115.9.

EIMS (*m/z*): 254 (M<sup>+</sup>).

Anal. Calc. for C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>; C, 70.86; H, 3.96; O, 25.17. Found: C, 70.85; H, 3.99; O, 25.19.



### 5-Hydroxy-3-(4-hydroxy-phenyl)-chromen-4-one (3k)

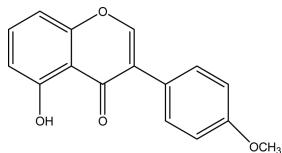
Crystalline solid, mp 168–170 °C,

<sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ<sub>H</sub> 9.35 (s, 1H), 9.27 (s, 1H), 8.83 (s, 1H), 7.35 (d, *J* = 7.57 Hz, 2H), 7.20 (t, *J* = 7.49 Hz, 1H), 7.00 (d d, *J* = 8.57 Hz, 1.69 Hz, 1H), 6.81 (d, *J* = 7.58 Hz, 2H), 6.76 (d d, *J* = 8.68 Hz, 1.62 Hz, 1H).

<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ<sub>C</sub> 175.5, 162.6, 158.8, 157.9, 153.1, 136.8, 127.8, 125.1, 123.6, 115.9, 112.8, 110.5, 110.1.

EIMS (*m/z*): 254 (M<sup>+</sup>).

Anal. Calc. for C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>; C, 70.86; H, 3.96; O, 25.17. Found: C, 70.82; H, 3.99; O, 25.17.



### 5-Hydroxy-3-(4-methoxy-phenyl)-chromen-4-one (3l)

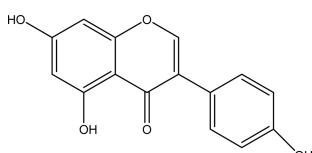
Crystalline solid, mp 140–142 °C;

<sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ<sub>H</sub> 9.34 (s, 1H), 8.78 (s, 1H), 7.35 (d, *J* = 7.66 Hz, 2H), 7.19 (t, *J* = 7.43 Hz, 1H), 7.02 (d d, *J* = 8.62 Hz, 1.61 Hz, 1H), 6.83 (d, *J* = 7.66 Hz, 2H), 6.80 (d d, *J* = 8.71 Hz, 1.58 Hz, 1H), 3.65 (s, 3H).

<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ<sub>C</sub> 175.4, 162.5, 160.1, 158.8, 153.4, 136.9, 127.5, 125.1, 123.6, 114.1, 113.1, 110.5, 110.2, 55.8.

EIMS (*m/z*): 268 (M<sup>+</sup>).

Anal. Calc. for C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>; C, 71.64; H, 4.51; O, 23.86. Found: C, 71.63; H, 4.53; O, 23.89.



### 5,7-Dihydroxy-3-(4-hydroxy-phenyl)-chromen-4-one

### (Genistein) (3m)\*

Off-white powder, mp 295 °C;

<sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ<sub>H</sub> 9.40–9.20 (s\*, 3H), 8.78 (s, 1H), 7.33 (d, *J* = 7.72 Hz, 2H), 6.81 (d, *J* = 7.67 Hz, 2H), 6.54 (s, 1H), 6.25 (s, 1H).

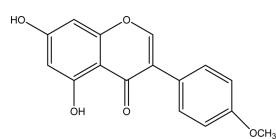
\*three nearly overlapped singlets.

<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ<sub>C</sub> 176.03, 161.88, 157.41, 155.83, 154.92, 151.71, 126.95, 122.56, 119.81, 111.97, 101.92, 96.33, 90.78.

EIMS (*m/z*): 270 (M<sup>+</sup>).

Anal. Calc. for C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>; C, 66.67; H, 3.73; O, 29.60. Found: C, 66.66; H, 3.75; O, 29.62.

\*The spectroscopic data are in agreement with those reported in the literature.<sup>5</sup>



### 5,7-Dihydroxy-3-(4-methoxy-phenyl)-chromen-4-one

### (Biochanin A) (3n)\*

Tan powder, mp 211–212 °C;

<sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ<sub>H</sub> 9.28–9.35 (s\*, 2H), 8.77 (s, 1H), 7.35 (d, *J* = 7.53 Hz, 2H), 6.88 (d, *J* = 7.50 Hz, 2H), 6.58 (s, 1H), 6.20 (s, 1H), 3.66 (s, 3H)

\*two overlapped singlets

<sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ<sub>C</sub> 183.03, 168.88, 165.92, 162.89, 162.83, 158.71, 133.57, 133.56, 128.05, 117.94, 108.92, 103.33, 97.78, 60.04.

EIMS (*m/z*): 284 (M<sup>+</sup>).

Anal. Calc. for C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>; C, 67.60; H, 4.25.; O, 28.14. Found: C, 67.63; H, 4.21; O, 28.13.

\*The spectroscopic data are in agreement with those reported in the literature.<sup>6</sup>

## References

1. Gao, G. Y.; Li, D. J.; Keung, W. M. *Bioorganic & Medicinal Chemistry* **2003**, *11*, 4069.
2. Kuruto-Niwa, R.; Ito, T.; Goto, H.; Nakamura, H.; Nozawa, R.; Terao, Y. *Environmental Toxicology and Pharmacology* **2007**, *23*, 121.
3. Whalley, J. L.; Bond, T. J.; Botting, N. P. *Bioorganic & Medicinal Chemistry Letters* **1998**, *8*, 2569.
4. Granados-Covarrubias, E. H.; Maldonado, L. A. *Tetrahedron Letters* **2009**, *50*, 1542.
5. Selepe, M. A.; Drewes, S. E.; van Heerden, F. R. *J. Nat. Prod.* **2010**, *73*, 1680.
6. Fokialakis, N.; Alexi, X.; Aligiannis, N.; Siriani, D.; Meligova, A. K.; Pratsinis, H.; Mitakou, S.; Alexis, M. N. *Bioorganic & Medicinal Chemistry* **2012**, *20*, 2962.