

**The development of a novel H<sub>2</sub>AuCl<sub>4</sub>@MOF catalyst and its catalytic application in the formation of dihydrochalcones**

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## Supporting Information

**General Information.** All  $^1\text{H}$  NMR, and  $^{13}\text{C}$  NMR spectra were recorded using Varian Unity Plus 400 (93.94 kG,  $^1\text{H}$  400 MHz) spectrometer at ambient temperature in  $\text{CDCl}_3$ . Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant, and integration. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR ESP spectrophotometer. Analytical thin layer chromatography was performed using EMD 0.25 mm silica gel 60-F plates. Flash column chromatography was performed on Sorbent Technologies 60 Å silica gel. Mass spectra were obtained using a Waters Q-TOF mass spectrometer. All reactions were performed under air unless otherwise.

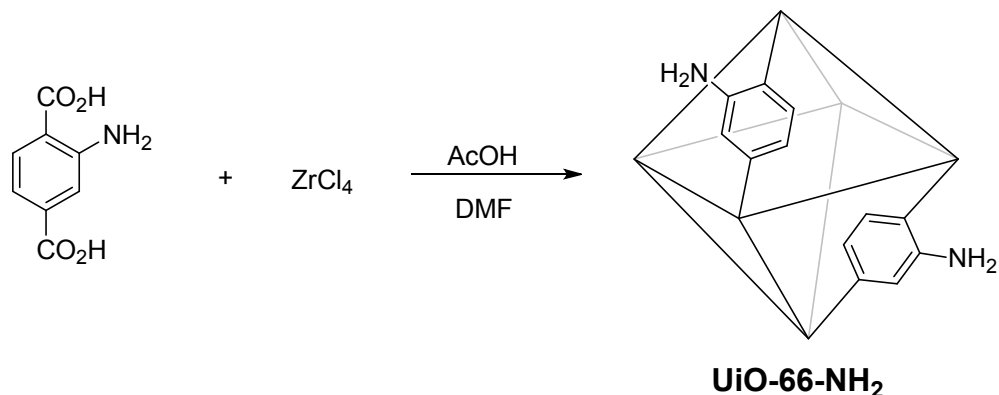
2*H*-chromenes (**1a-1g**) were prepared according to the published procedure.<sup>1</sup> Other reagents were used as received from Sigma-Aldrich and Alfa Aesar, and unless otherwise noted.

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(1) Y. Ashihara, Y. Nagata, K. Kurosawa, *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3298-5301.

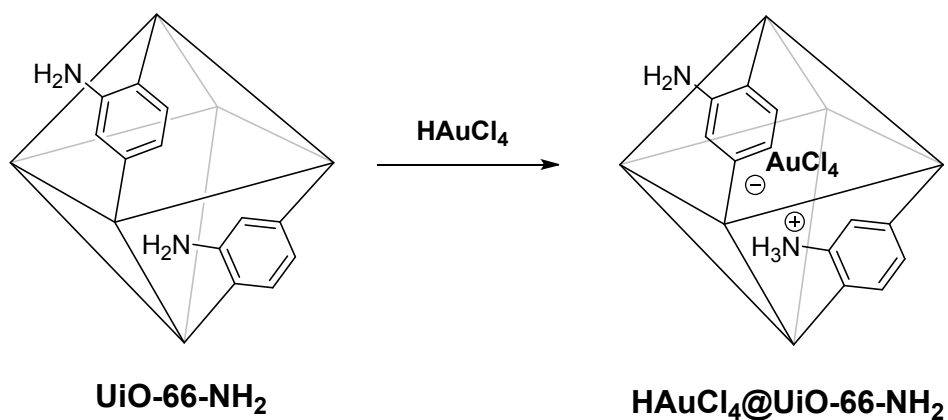
Material synthesis

### The synthesis of UiO-66-NH<sub>2</sub> metal-organic framework at nanoscale



ZrCl<sub>4</sub> (0.4 g, 1.7 mmol) in DMF (75 mL) was stirred with acetic acid (2.85 mL, 850 mmol) at 55 °C. A DMF solution (25 mL) of 2-aminoterephthalic acid (0.311 g, 1.7 mmol) was added to the previous mixture solution. Then, water (0.125 mL, 0.007 mmol) was added to the solution as well and the solution was sonicated at 60 °C. The mixture solution was further kept in a bath at 120 °C for 24 h. After 24 h, the solution was cooled to room temperature and the precipitate was collected by centrifugation. The obtained solid was washed with DMF (2 x 10 mL), ethanol (3 x 10 mL) and dried under reduced pressure (80 °C, 3 h).

**The synthesis of  $\text{HAuCl}_4@\text{UiO-66-NH}_2$  catalyst via post-synthetic modification of  $\text{UiO-66-NH}_2$**



0.3 g of UiO-66-NH<sub>2</sub> at nanoscale (0.17 mmol based on MW of 1766 g/mol) was suspended in 5 mL of CHCl<sub>3</sub>, then 5 mol% of HAuCl<sub>4</sub> (0.0085 mmol) was added. The mixture was stirred slowly at 25 °C for 12 h, after which the solvent was decanted. CHCl<sub>3</sub> was used to rinse the crystals once a day for two days. The crystals were dried under vacuum at 40 °C before use.

*For catalyst recycling:*

At the end of each reaction cycle, the catalyst was recovered by centrifugation of the solution mixture followed by washing with solvent (5 - 10 ml). After being immersed in the solvent for 12 h and dried at 40 °C under vacuum for 12 h, the catalyst was reused.

## Material characterization

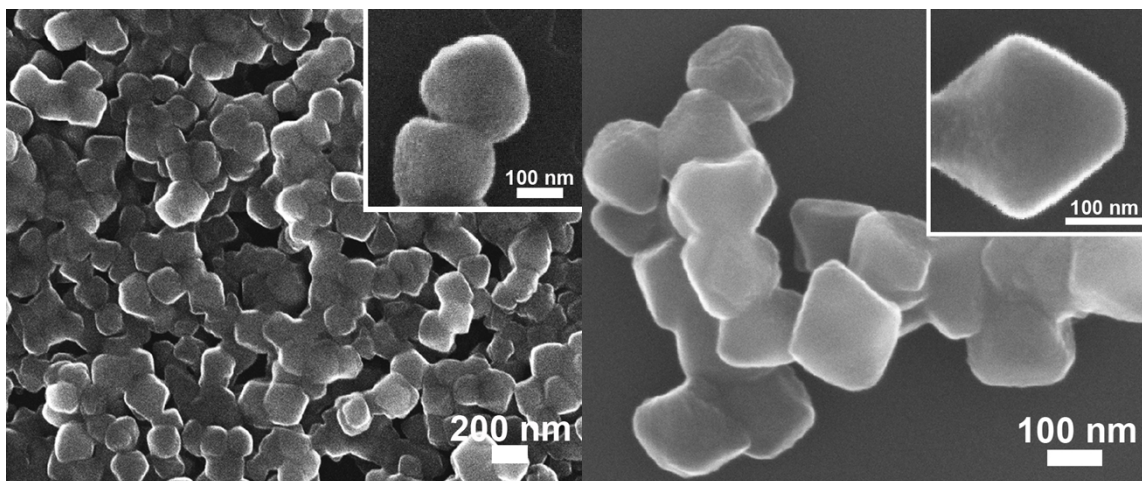


Figure S1. SEM images of UiO-66-NH<sub>2</sub> (left) and HAuCl<sub>4</sub>@UiO-66-NH<sub>2</sub> (right)

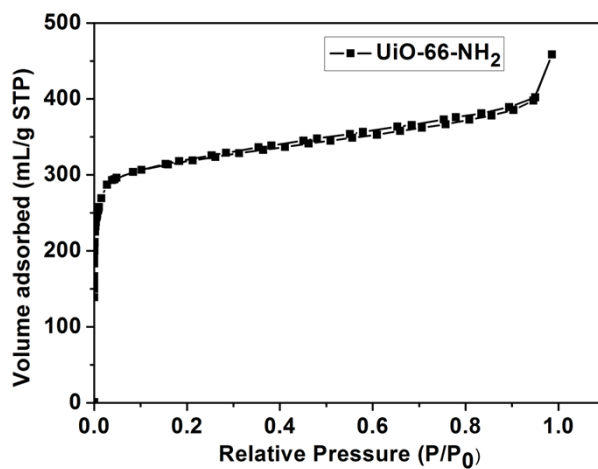


Figure S2. Nitrogen adsorption/desorption isotherms of UiO-66-NH<sub>2</sub> support.

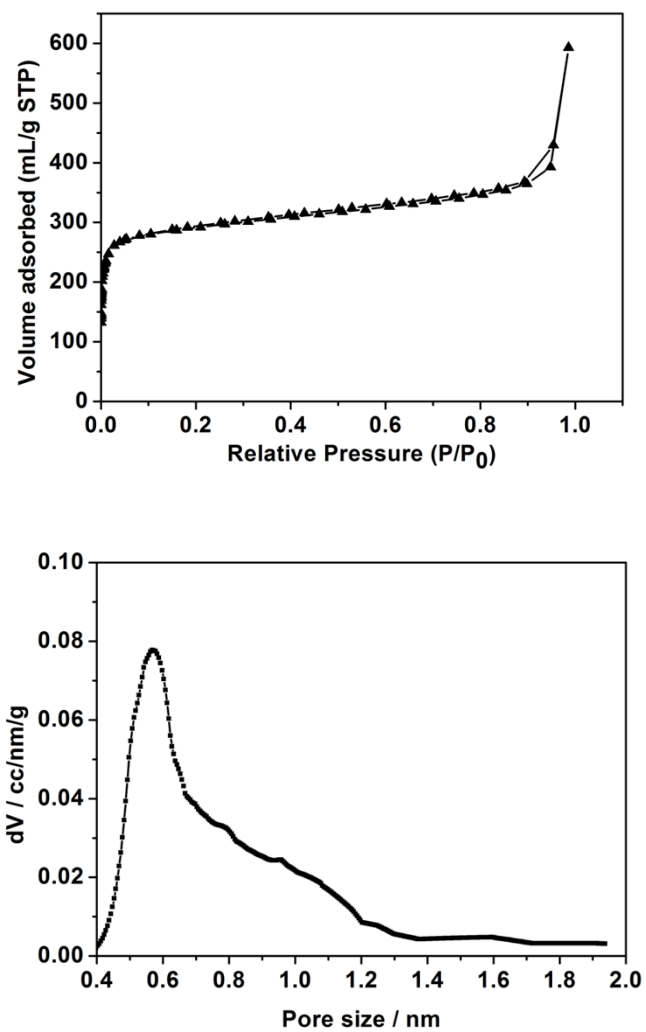


Figure S3. Nitrogen adsorption/desorption isotherms and pore size distribution of HAuCl<sub>4</sub>@UiO-66-NH<sub>2</sub>.

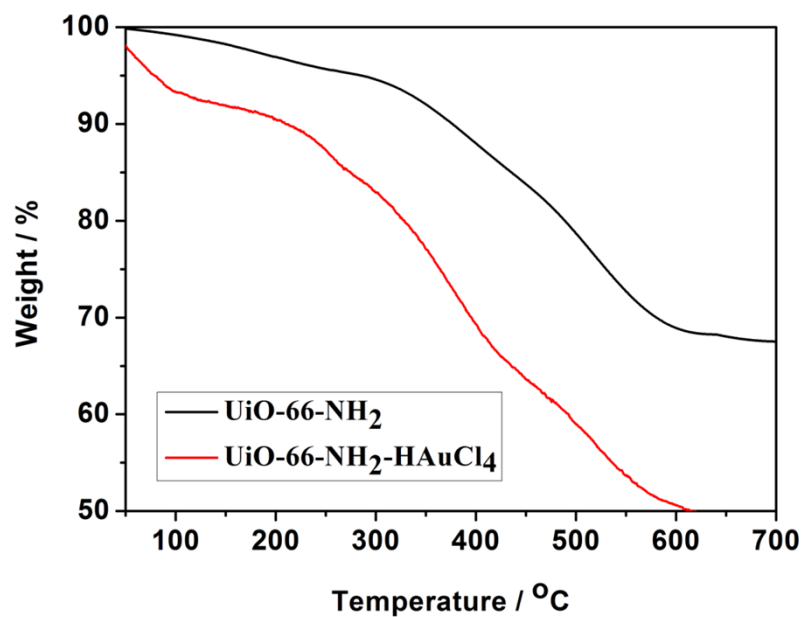


Figure S4. TGA curves of UiO-66-NH<sub>2</sub> and HAuCl<sub>4</sub>@UiO-66-NH<sub>2</sub>.

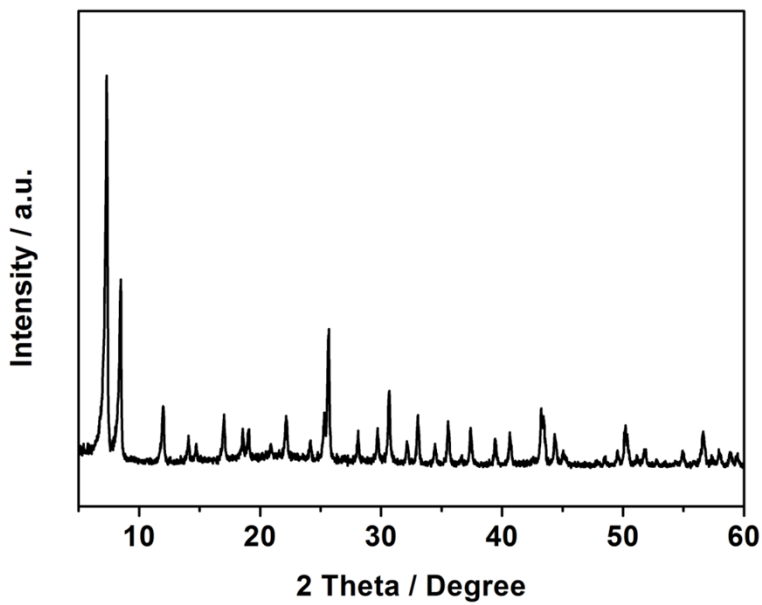
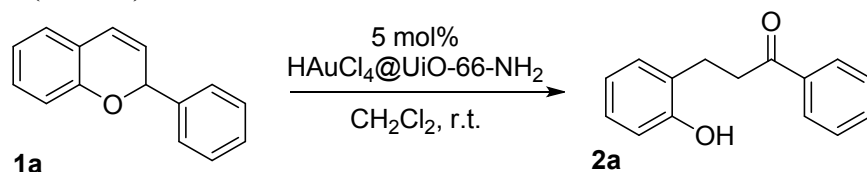


Figure S5. Powder XRD of 5 times recycled HAuCl<sub>4</sub>@UiO-66-NH<sub>2</sub> catalyst.

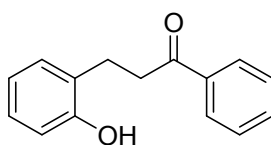
**General procedure used for the preparation of dihydrochalcone 1a by H<sub>2</sub>AuCl<sub>4</sub>@UiO-66-NH<sub>2</sub> catalyst (Table 2).**



To a reaction vessel equipped with stir bar in air was added 2*H*-chromene **1a** (113 mg, 0.5 mmol) and H<sub>2</sub>AuCl<sub>4</sub>@UiO-66-NH<sub>2</sub> catalyst (37 mg, 0.0025 mmol) in 2.5 mL dichloromethane. The mixture was stirred at room temperature for 12 hours. The reaction was purified without work-up by flash chromatography over silica gel column (elution with 95:5 – 90:10, hexanes:EtOAc) to afford the product **2a** as a colorless oil (92 mg, 81% yield).

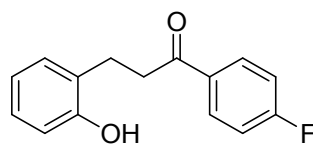
For detailed characterization data of dihydrochalcones **2a-2c**, please see literature reference.<sup>2</sup>

### 3-(2-hydroxyphenyl)-1-phenylpropan-1-one (2a)



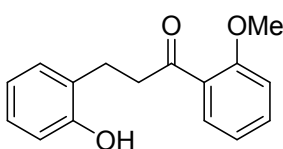
The crude mixture was purified by flash column chromatography with elution by 95:5 – 90:10, hexanes:EtOAc. **Yield:** 92 mg, 81%. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.42-7.98 (m, 5H), 6.86-7.26 (m, 4H), 3.45 (t, *J* = 6.0 Hz, 2H), 3.04 (t, *J* = 6.0 Hz, 2H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 202.0, 154.5, 136.0, 133.7, 130.5, 128.6, 128.3, 127.9, 127.7, 120.6, 117.4, 40.4, 23.3; **IR (thin film, cm<sup>-1</sup>):** 2935, 1726, 1686, 1611, 1545, 1451. **HRMS** *m/z* 227.1070 [(*M* + *H*<sup>+</sup>) calc'd for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>H<sup>+</sup>: 227.1067]. See ref 2 for details.

### 1-(4-fluorophenyl)-3-(2-hydroxyphenyl)propan-1-one (2b)



The crude mixture was purified by flash column chromatography with elution by 95:5 – 90:10, hexanes:EtOAc. **Yield:** 91.5 mg, 75%. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.01 (dd, *J* = 9.0, 5.4 Hz, 2H), 7.76 (s, 1H), 7.16-6.83 (m, 6H), 3.42 (t, *J* = 6.0 Hz, 2H), 3.03 (t, *J* = 6.0 Hz, 2H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 200.3, 167.8, 154.4, 132.6, 131.1, 131.0, 130.6, 128.0, 127.6, 120.8, 117.4, 116.0, 115.7, 40.3, 23.5; **IR (thin film, cm<sup>-1</sup>):** 3032, 2933, 2576, 1677, 1573, 1525, 1438, 1332, 1233; **HRMS** *m/z* 245.0968 [(*M* + *H*<sup>+</sup>) calc'd for C<sub>15</sub>H<sub>13</sub>FO<sub>2</sub>H<sup>+</sup>: 245.0972]. See ref 2 for details.

### 3-(2-hydroxyphenyl)-1-(2-methoxyphenyl)propan-1-one (2c)

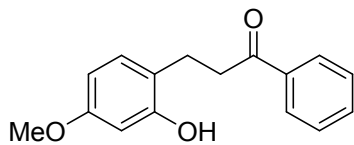


The crude mixture was purified by flash column chromatography with elution by 95:5 – 90:10, hexanes:EtOAc. **Yield:** 91 mg, 71%. **IR (thin film, cm<sup>-1</sup>):** 3231, 2488, 1932, 1659, 1594, 1433, 1278; **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.18 (s, 1H), 7.85 (m, 1H), 7.51 (m, 1H), 7.23-6.94 (m, 4H), 6.94-6.87 (m, 1H), 3.92 (s, 3H), 3.46 (t, *J* = 6.0 Hz, 2H), 3.02 (t, *J* = 6.0 Hz, 2H); **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ = 203.7, 159.4, 154.6, 134.5, 130.9, 130.6, 128.2, 127.7, 126.6, 120.6, 120.4, 117.4, 111.6, 55.5, 45.8, 23.8; **IR (thin film, cm<sup>-1</sup>):** 3425, 2534, 1943, 1663, 1455, 1301, 1275; **HRMS** *m/z* 257.1176 [(*M* + *H*<sup>+</sup>) calc'd for C<sub>16</sub>H<sub>16</sub>O<sub>3</sub>H<sup>+</sup>: 257.1172]. See ref 2 for details.

<sup>2</sup> Maiti, G.; Kayal, U.; Karmakar, R.; Bhattacharya, R. N. *Tetrahedron Lett.* **2012**, 53, 6321–6325.

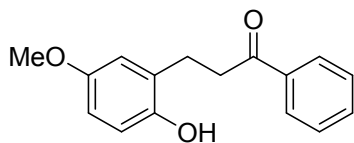


### 3-(2-hydroxy-4-methoxyphenyl)-1-phenylpropan-1-one (2d)



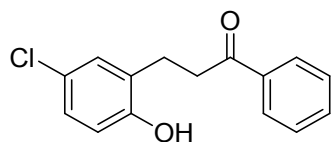
The crude mixture was purified by flash column chromatography with elution by 95:5 – 90:10, hexanes:EtOAc. **Yield:** 92 mg, 72%. **IR (thin film,  $\text{cm}^{-1}$ ):** 3418, 2534, 1943, 1657, 1591, 1461, 1301, 1275;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ ) 7.75-7.35 (m, 3H), 7.04-6.82 (m, 3H), 6.98-6.28 (m, 2H), 3.78 (s, 3H), 3.52 (t,  $J = 6.0$  Hz, 2H), 3.08 (t,  $J = 6.0$  Hz, 2H);  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  203.6, 159.2, 154.8, 132.8, 128.2, 124.9, 114.8, 114.3, 113.0, 109.5, 105.9, 55.6, 45.5, 26.1; **HRMS  $m/z$**  257.1174 [(M + H<sup>+</sup>) calc'd for  $\text{C}_{16}\text{H}_{16}\text{O}_3\text{H}^+$ : 257.1172].

### 3-(2-hydroxy-5-methoxyphenyl)-1-phenylpropan-1-one (2e)



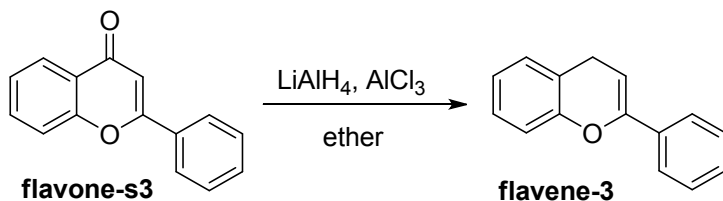
The crude mixture was purified by flash column chromatography with elution by 95:5 – 90:10, hexanes:EtOAc. **Yield:** 111 mg, 87%. **IR (thin film,  $\text{cm}^{-1}$ ):** 3428, 2539, 1947, 1667, 1591, 1460, 1303, 1277;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ ) 7.48-7.15 (m, 5H), 6.90-6.71 (m, 2H), 6.65 (s, 1H), 3.90 (s, 3H), 3.36 (t,  $J = 5.8$  Hz, 2H), 2.91 (t,  $J = 5.8$  Hz, 2H);  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  203.7, 153.5, 151.8, 131.2, 126.9, 126.5, 125.3, 119.0, 117.1, 109.6, 62.4, 45.5, 23.7; **HRMS  $m/z$**  257.1169 [(M + H<sup>+</sup>) calc'd for  $\text{C}_{16}\text{H}_{16}\text{O}_3\text{H}^+$ : 257.1172].

### 3-(5-chloro-2-hydroxyphenyl)-1-phenylpropan-1-one (2f)



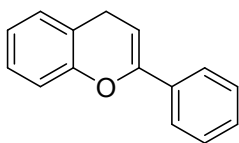
The crude mixture was purified by flash column chromatography with elution by 95:5 – 90:10, hexanes:EtOAc. **Yield:** 99 mg, 76%. **IR (thin film,  $\text{cm}^{-1}$ ):** 3465, 2889, 2353, 1676, 1607, 1512, 1414, 1317, 1183;  **$^1\text{H NMR}$**  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.43 (s, 1H), 7.87 (d,  $J = 8.0$  Hz, 2H), 7.65-6.75 (m, 6H), 3.42 (t,  $J = 6.0$  Hz, 2H), 2.97 (t,  $J = 6.0$  Hz, 2H);  **$^{13}\text{C NMR}$**  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.6, 158.3, 141.2, 137.1, 132.6, 132.3, 126.8, 122.6, 121.7, 120.8, 120.2, 108.2, 45.4, 22.1; **HRMS  $m/z$**  261.0676 [(M + H<sup>+</sup>) calc'd for  $\text{C}_{15}\text{H}_{13}\text{ClO}_2\text{H}^+$ : 261.0677].

### General procedure used for the deoxygenation of flavone<sup>3</sup>



A solution of flavone (2.00 g) in THF (30 ml) was added into a stirred solution of AlCl<sub>3</sub> (4.20 g) and LiAlH<sub>4</sub> (0.60 g) in ether (40 ml) at 0 °C over 20 min. Then wet ether was added to decompose the reactive AlCl<sub>3</sub> and LiAlH<sub>4</sub>, then the oil was isolated. Lastly, the product was recrystallized from methanol to give pure flav-2-ene 3.

### 2-phenyl-4H-chromene (flavene-3)



The crude mixture was purified by flash column chromatography with elution by 99:1 – 98:2, hexanes:EtOAc. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.87 (s, 2H), 7.67 – 6.99 (m, 7H), 5.86 – 5.58 (m, 1H), 3.77 (s, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 154.51, 152.13, 133.83, 128.82, 126.48, 123.35, 117.15, 114.58, 114.19, 26.92. **MS** *m/z* 209.0960 [(M + H<sup>+</sup>) calc'd for C<sub>15</sub>H<sub>13</sub>ClO<sub>2</sub>H<sup>+</sup>: 209.0961]. See ref 3 for details.

<sup>3</sup> Bird, T. G. C.; Brown, B. R.; Stuart, I. A.; Tyrrell, A. W. R. *J. Chem. Soc. Perkin Trans.* **1983**, 1, 1831-1846. Fichtner, C.; Remennikov, G.; Mayr, H. *Eur. J. Org. Chem.* **2001**, 4451-4456. M. M. Mishrikey, E. T. Østensen, *Acta Chem. Scand., Ser. B* **1976**, 30, 329-335.

