

## Electronic Supplementary Information

### “Vanillin based polymers: I. An electrochemical route to polyvanillin”

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#### 1. Synthesis of divanillin (**2**)

Divanillin was prepared following the literature procedure<sup>7</sup> by horseradish peroxidase catalyzed oxidative dimerization of vanillin using 3% hydrogen peroxide as the oxidant, as a gray powder in 95% yield, and was confirmed by comparison of the NMR spectra with published data<sup>13</sup>.

#### 2. Synthesis of meso-hydrovanilloin (**4**)

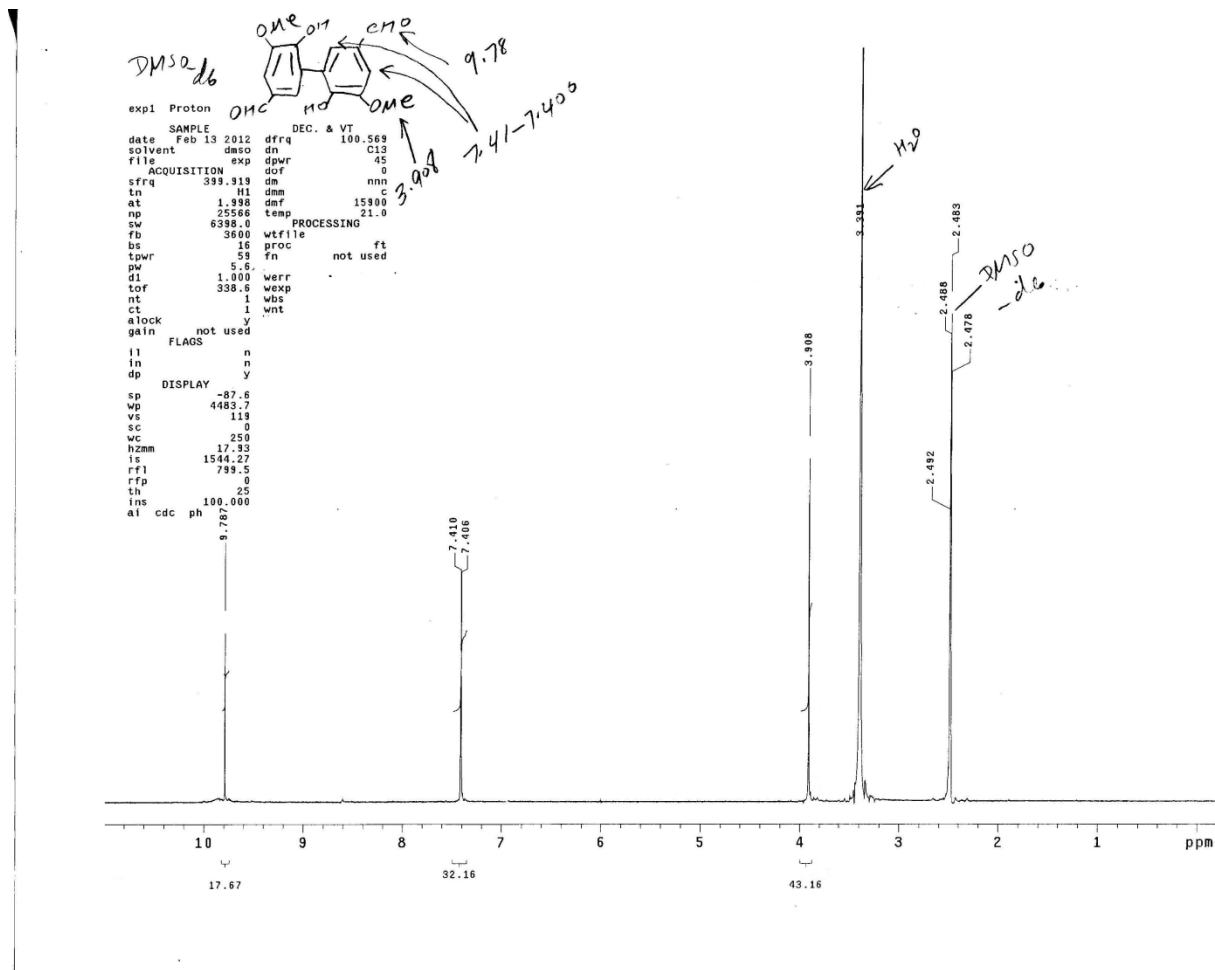
meso-Hydrovanilloin was prepared by electrolytic reduction of vanillin using the literature procedure<sup>9</sup>, with the exception of using concentrated hydrochloric acid in place of sulfur dioxide gas for the neutralization step, gray powder, 88% yield.

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>), δ 3.65 (s, 6H, 2x OCH<sub>3</sub>), 4.44 (s, 2H, 2X CH-O), 4.94 (bs, 2H, 2X OH), 6.62 (m, 4H, Ar-5,5',6,6'), 6.73 (s, 2H, Ar-3,3'), 8.69 (s, 2H, Ar-OH). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>), δ 55.9 (2xOCH<sub>3</sub>), 77.4 (2X CH-O), 112.1(C-3,3'), 114.7(C-6,6'), 120.3(C-4,4'), 134.6(C-5,5'), 145.6 (C-2,2'), 147.1(C-1,1').

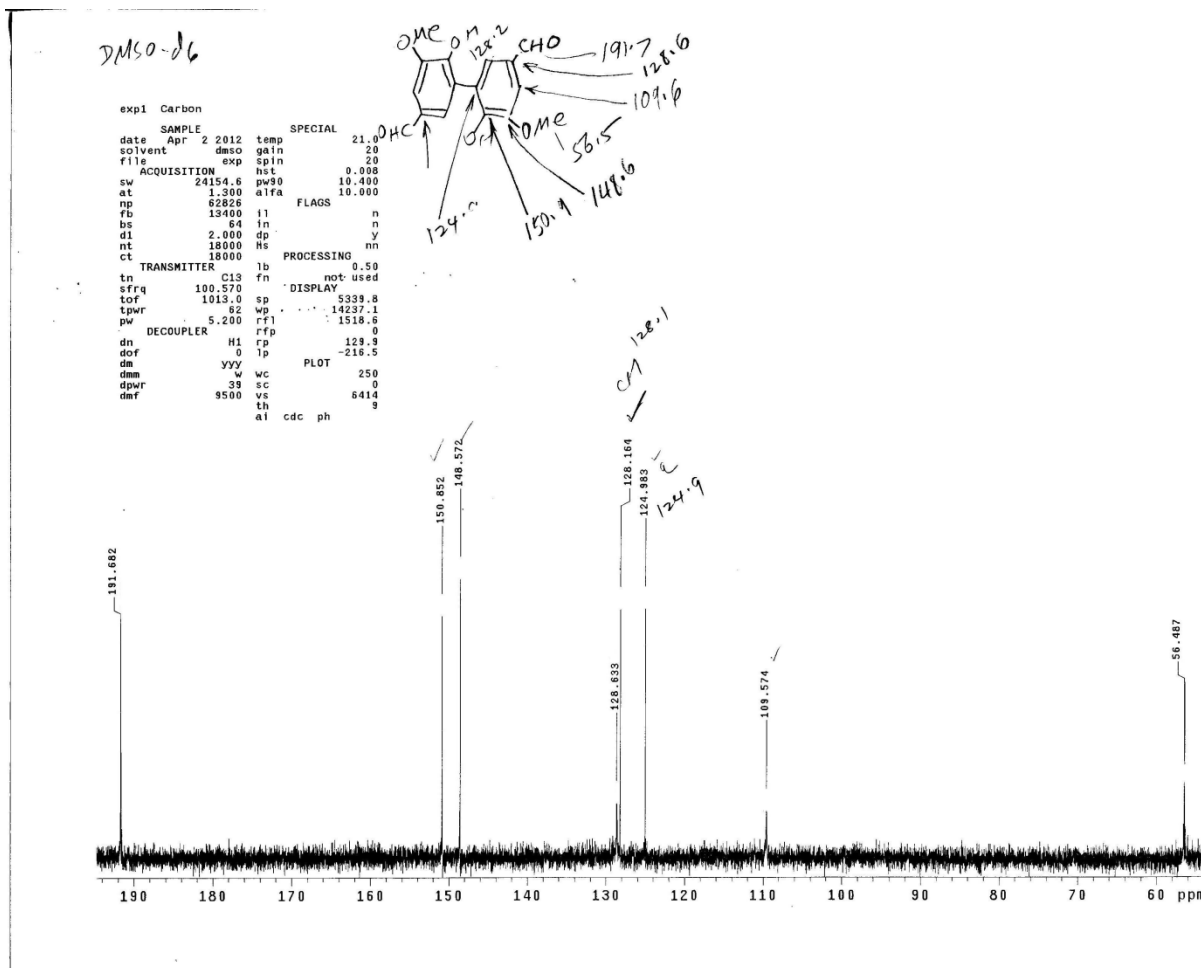
#### 3. Synthesis of polyvanillin (**3**)

A mixture of divanillin (1.057 g, 3.5 mmol) and sodium hydroxide (0.80 g, 20 mmol) in 20 mL of distilled water was placed in a 100 mL beaker, which served as the catholyte compartment of the electrolysis apparatus. A solution of sodium hydroxide (0.20 g, 5 mmol) in 5 mL of water was used as the anolyte in the inside porous cup (28.5x127 mm) of the apparatus. Two lead plates (25x90 mm) were used as the electrodes, and a current of 1.1 amperes was maintained across the cell using a 12V supply for 3hrs. Then catholyte was filtered, cooled in ice and acidified with concentrated hydrochloric acid. The gray precipitate formed was filtered, repeatedly washed with distilled water, and dried in an oven at 50 °C, overnight to yield polyvanillin as a gray powder, 0.968g, 91 % yield. Found: C, 59.34; H, 5.65 %. Calc. for C<sub>16</sub>H<sub>16</sub>O<sub>6</sub>.H<sub>2</sub>O: C, 59.62; H, 5.63%. <sup>1</sup>H and <sup>13</sup>C NMR spectra of **3** are shown in figures 4a and b. UV/Vis spectrum data of **3** are given in table 1.

1. Spectroscopic data of divanillin (2)

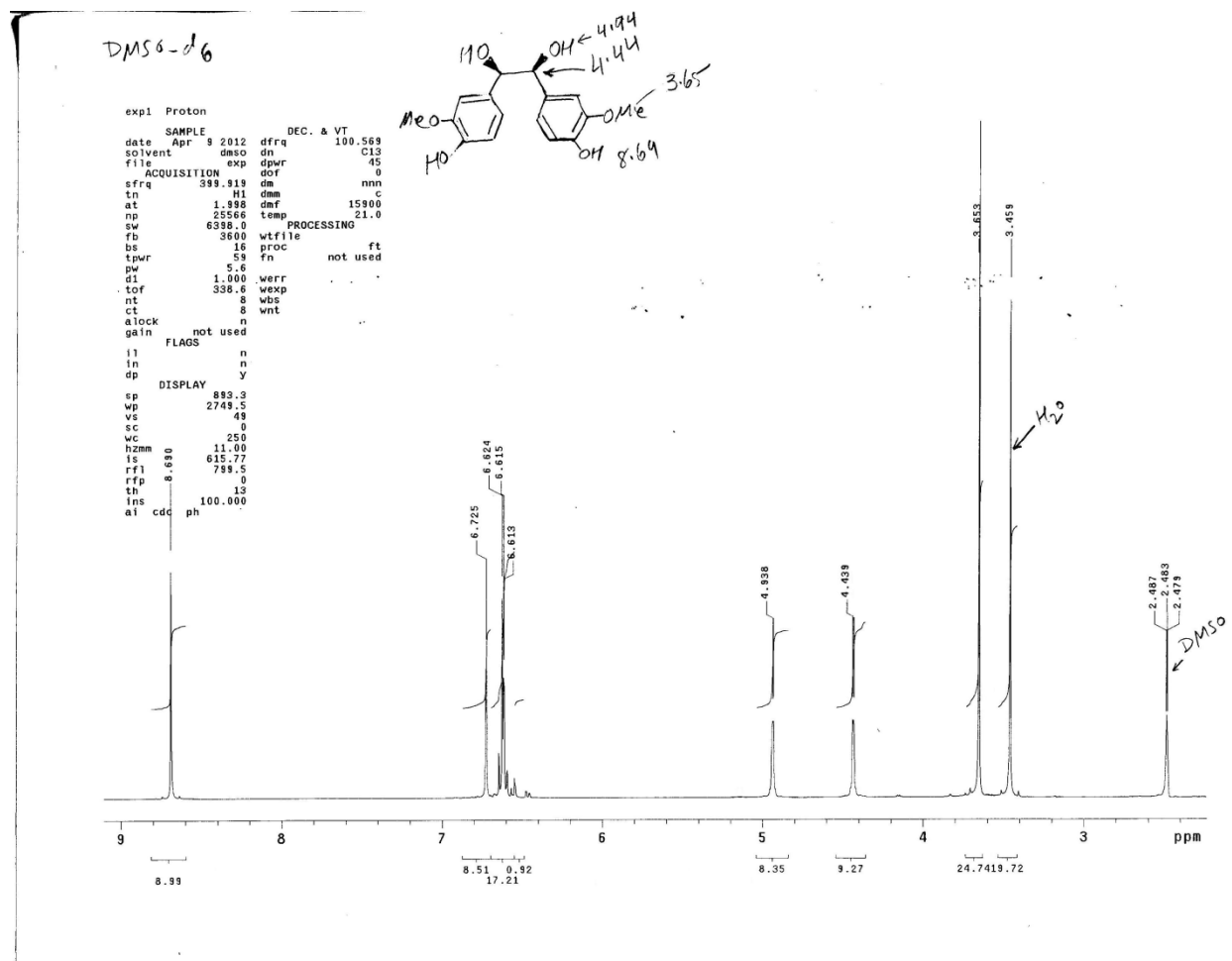


<sup>1</sup>H NMR spectrum of divanillin (2), DMSO-d<sub>6</sub>, 400 MHz

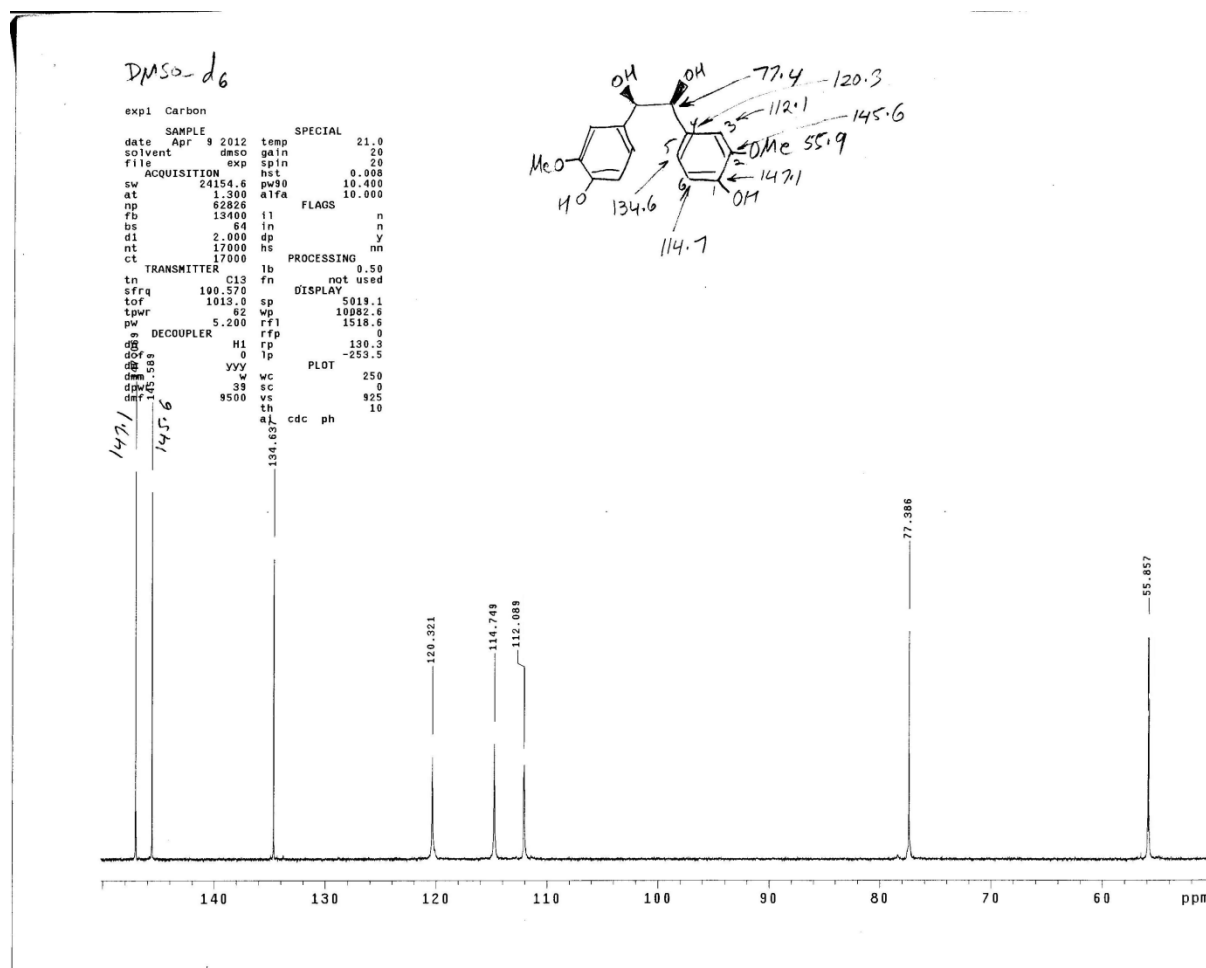


<sup>13</sup>C NMR spectrum of divanillin (2), DMSO-d<sub>6</sub>, 100 MHz

## 2. Spectroscopic data of *meso*-hydrovanilloin (**4**)

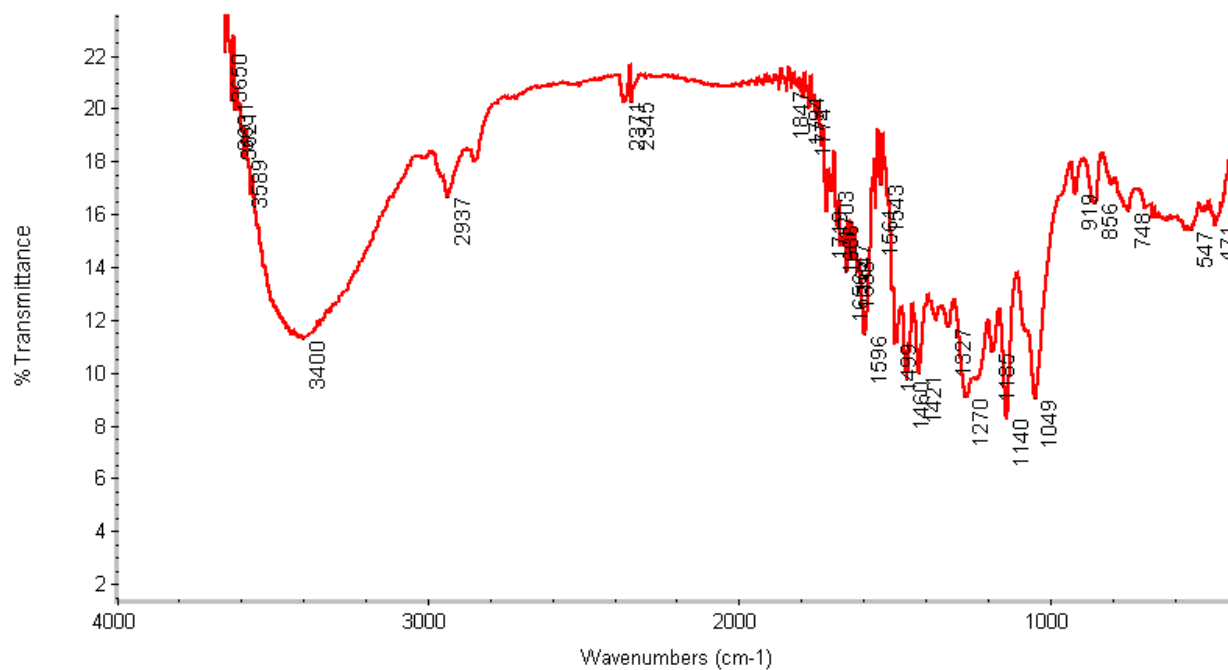


<sup>1</sup>H NMR spectrum of *meso*-hydrovanilloin (**4**), DMSO-*d*<sub>6</sub>, 400 MHz

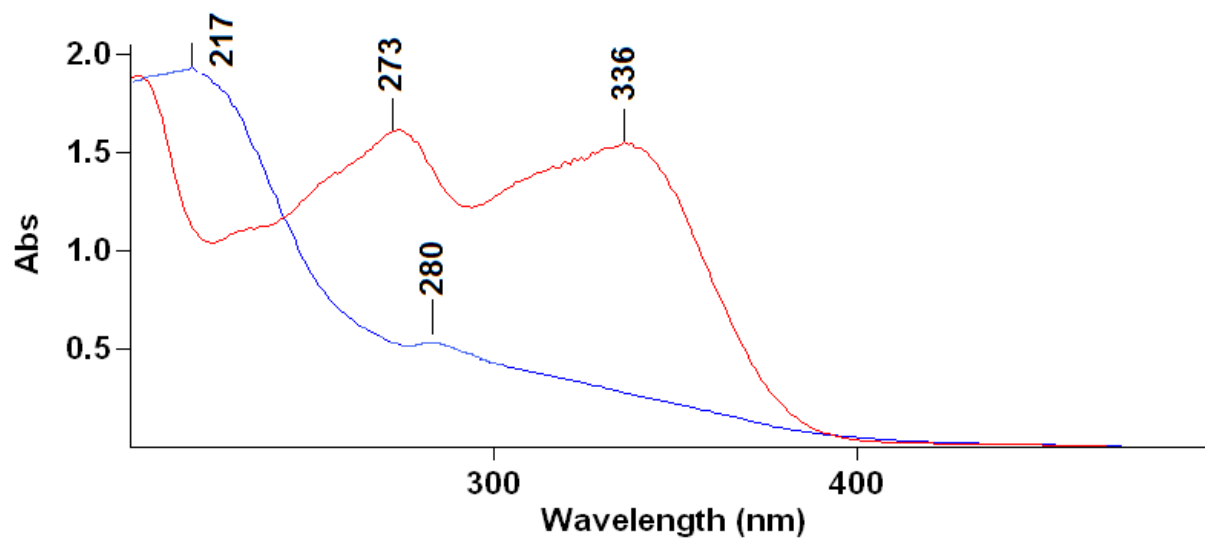


<sup>13</sup>C NMR spectrum of *meso*-hydrovanilloin (**4**), DMSO-*d*<sub>6</sub>, 100 MHz

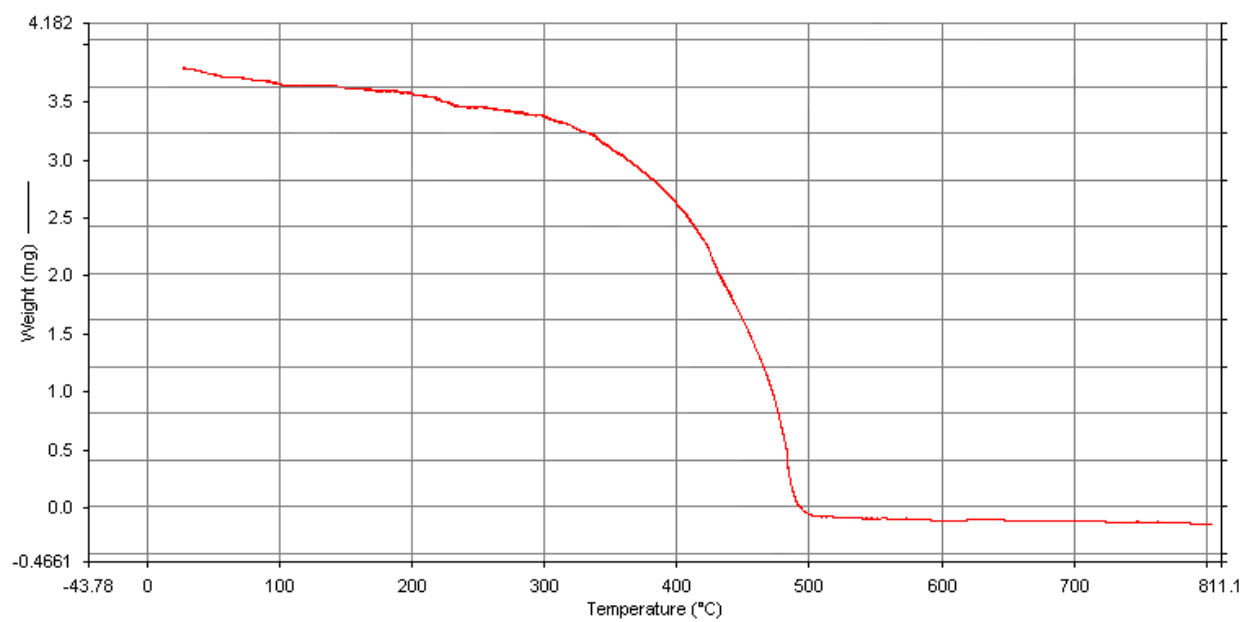
### 3. Spectroscopic data of polyvanillin (3)



FT-IR spectrum of polyvanillin (3), KBr



UV-Vis spectra for polyvanillin (3) \_\_\_\_\_ and divanillin (2) \_\_\_\_\_  
1.1x10<sup>-4</sup> M solutions in 0.01 M aqueous sodium hydroxide



TGA of polyvanillin (**3**), in air, 10 °C/min.