

ELECTRONIC SUPPLEMENTARY INFORMATION

Catalytic activity of HKUST-1 on the oxidation of *trans*-ferulic acid to vanillin

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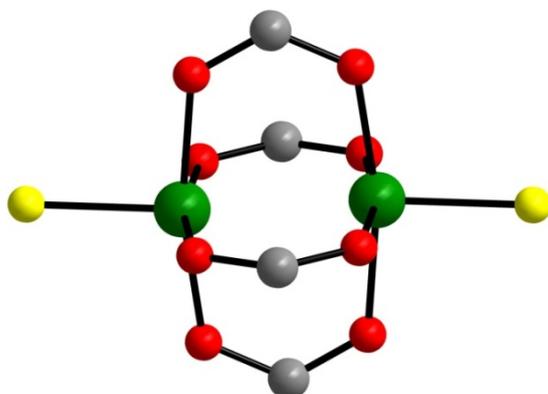
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1. Scheme of the binuclear $[\text{Cu}_2(\text{O}_2\text{CR})_4]$ building block



Scheme S1: Binuclear tetracarboxylate paddlewheel unit $[\text{Cu}_2(\text{O}_2\text{CR})_4]$. Potential uncoordinated metal sites are shown as yellow spheres. Green, red and grey spheres represent Cu, O and C atoms, respectively.

2. Materials and Measurements

All reagents and solvents were used as received from commercial suppliers without further purification. Powder X-ray diffraction (PXRD) data were collected under ambient conditions on a Bruker AXD D8 Advance diffractometer operated at 160 W (40 kV, 40 mA) for Cu $K\alpha_1$ ($\lambda = 1.5406 \text{ \AA}$). Thermal gravimetric analysis (TGA) was performed under N_2 at a heating rate of $2 \text{ }^\circ\text{C}/\text{min}$ using a TA Instruments Q500HR analyser. Inductively coupled plasma mass spectrometry was conducted on a Varian model ICP spectrometer. IR spectra were recorded using a Bruker TENSER 27 FT-IR spectrophotometer. Gas chromatography (GC) was performed using a Innovax column (30 mX 0.25 mm ID and 0.25 thickness) with a N_2 flow of $0.2 \text{ mL}/\text{min}$, FID $230 \text{ }^\circ\text{C}$, heating ramp of $10 \text{ }^\circ\text{C}$ from 50 to $230 \text{ }^\circ\text{C}$.

3. TGA plots

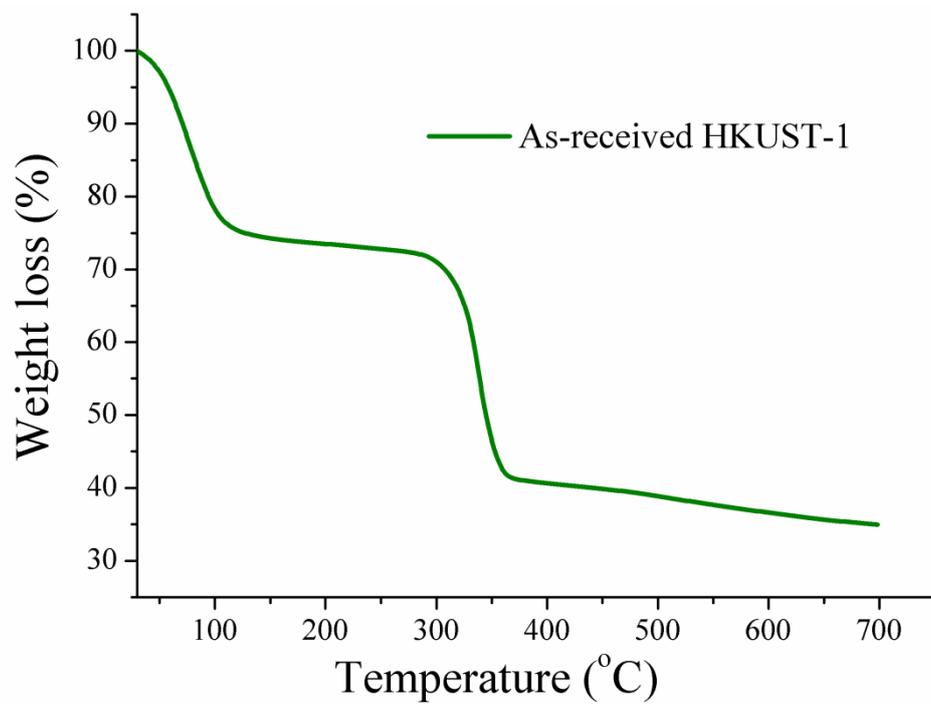


Fig. S1: TGA analysis of as-received HKUST-1 (green line).

4. Powder X-ray Diffraction Patterns

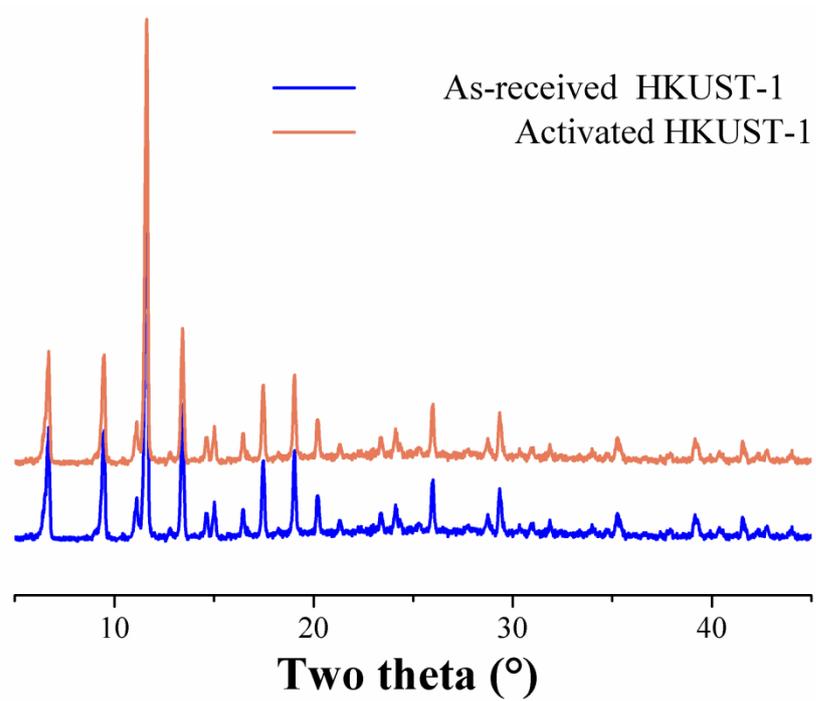


Fig. S2: PXRD patterns of as-received (blue) and desolvated (pink) HKUST-1.

5. Recyclability of the catalyst HKUST-1

Activated catalyst (HKUST-1), 0.05g (50 mg, 3.2 mol%), suspended in ethanol (200 mL) was mixed with 5.0 mL of H₂O₂ (30%v aqueous), 0.25mL of acetonitrile and 0.50g (2.57X10⁻³ mol) of ferulic acid. The reaction mixture was heated to 100 °C with a reflux condenser for 1 h. After the reaction was finished, the catalyst was recovered by filtration (see Table S1); the filtrate was extracted with ethyl acetate and washed with a saturated solution of NH₄Cl. The combined organic phases were dried with anhydrous Na₂SO₄, filtrated and concentrated under vacuum. Finally, the residue was purified by column chromatography (AcOEt-hexane 5:95).

Table. S1: Amount of activated catalyst for each cycle and the corresponding reaction yield.

| Cycle | Activated Catalyst (mg) [*] | Reaction Yield (%) |
|----------------|--------------------------------------|--------------------|
| 0 [‡] | 50 | - |
| 1 | 50 | 98 |
| 2 | 49 | 95 |
| 3 | 49 | 97 |
| 4 | 49 | 96 |
| 5 | 48 | 94 |
| 6 | 48 | 95 |
| 7 | 47 | 93 |
| 8 | 47 | 97 |
| 9 | 46 | 96 |
| 10 | 46 | 95 |

[‡] Cyc. 0 corresponds to only the activated HKUST-1 before any catalytic reaction.

^{*}The mass loss from Cycle 0 to Cycle 10 was due the manipulation of the catalyst during the filtration and activation processes. In each case, we adjusted the rest of the reactants accordingly with the amount of activated catalyst. The reaction yield was obtained after isolation of the vanillin by column chromatography purification.

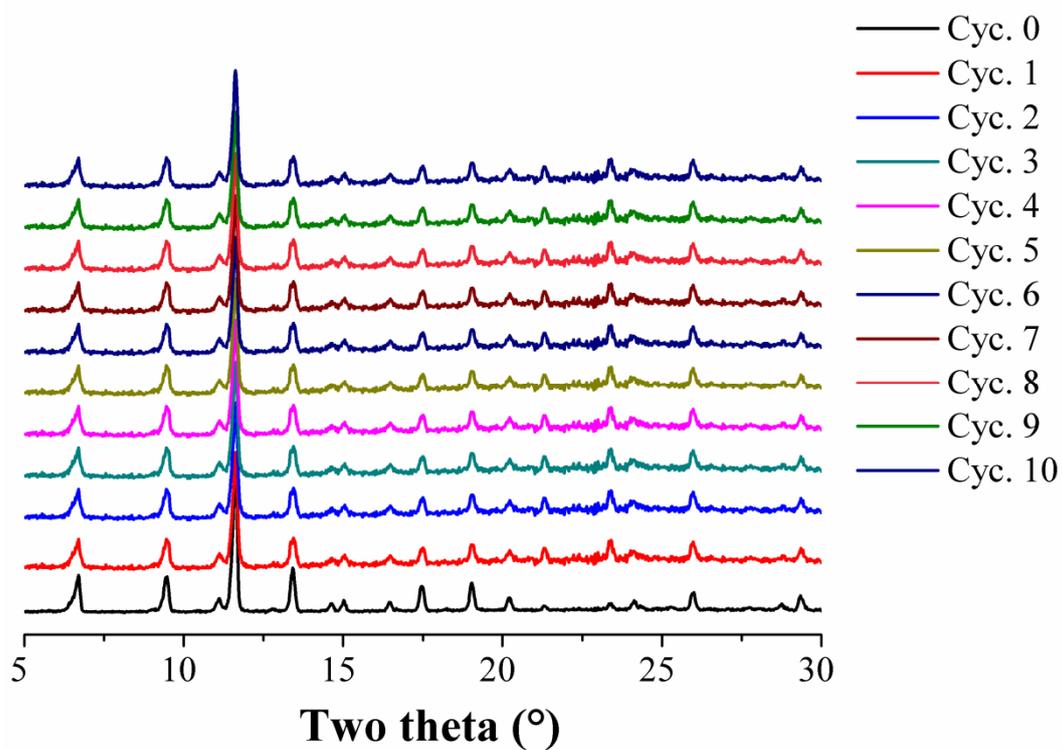


Fig. S3: PXRD patterns of the catalyst HKUST-1 after the catalytic reaction. Cyc. 0 corresponds to only activated HKUST-1. For each PXRD experiment it was used the same amount of catalyst (25 mg) to provide a better comparison.

6. Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Each of the 10 hot filtrates (coming from the catalytic reactions) were combined with OPTIMA grade nitric acid (180 μL) and OPTIMA grade sulphuric acid (180 μL). The mixture was heated to 90 $^{\circ}\text{C}$ for 2 h in an open container in a dust-free environment. The resulting solutions were diluted to 5.0 mL using 2% OPTIMA grade nitric acid. These stock solutions were diluted to 1:100 (v/v) with 2% nitric acid and analysed relative to a 50 ppb germanium internal standard on a Varian model ICP spectrometer using He collision gas mode.

Results

Analysis was done in CCT mode. The instrument passed its performance check. No analytes were observed to have tripped to analogue at any concentration measured and thus no cross calibration was necessary. A good calibration line was obtained for all elements. The washout samples are fine, indicating that there is no problem with carryover in this experiment. Cu was not found on samples 1 to 10. The detection limit of the Varian model ICP spectrometer was approximately from 0.4 ppm to 1 ppb.

7. FTIR Spectroscopy

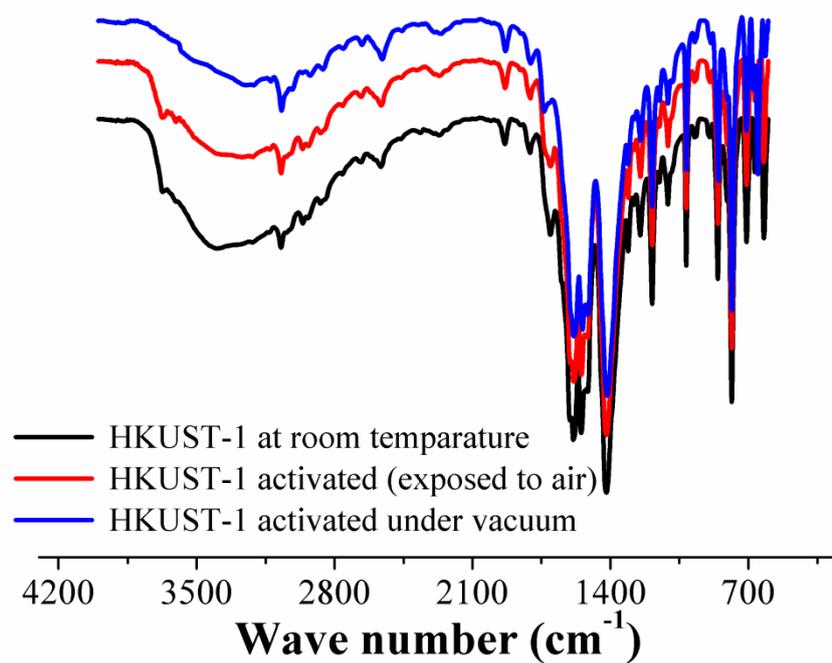
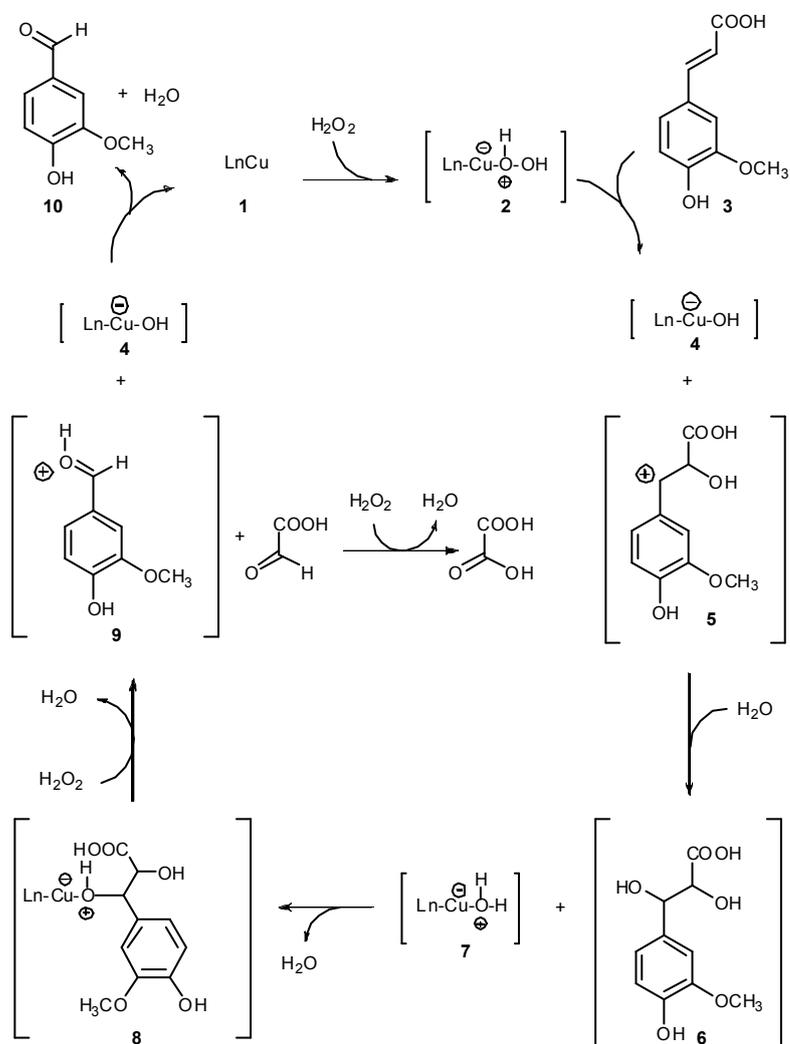


Fig. S4: FTIR spectra of the catalyst (HKUST-1) at 25 °C. Non-activated (black line), activated in a conventional oven (red line) and activated under vacuum (blue line).

8. Proposed Mechanism for the Oxidation of *trans*-ferulic Acid



Scheme S2: Proposed mechanism for the oxidation of *trans*-ferulic acid.

9. $^1\text{H-NMR}$ spectra

HKUST-1 Activated in a Conventional Oven (Exposed to Air) and $100\text{ }^\circ\text{C}$ for 1 h

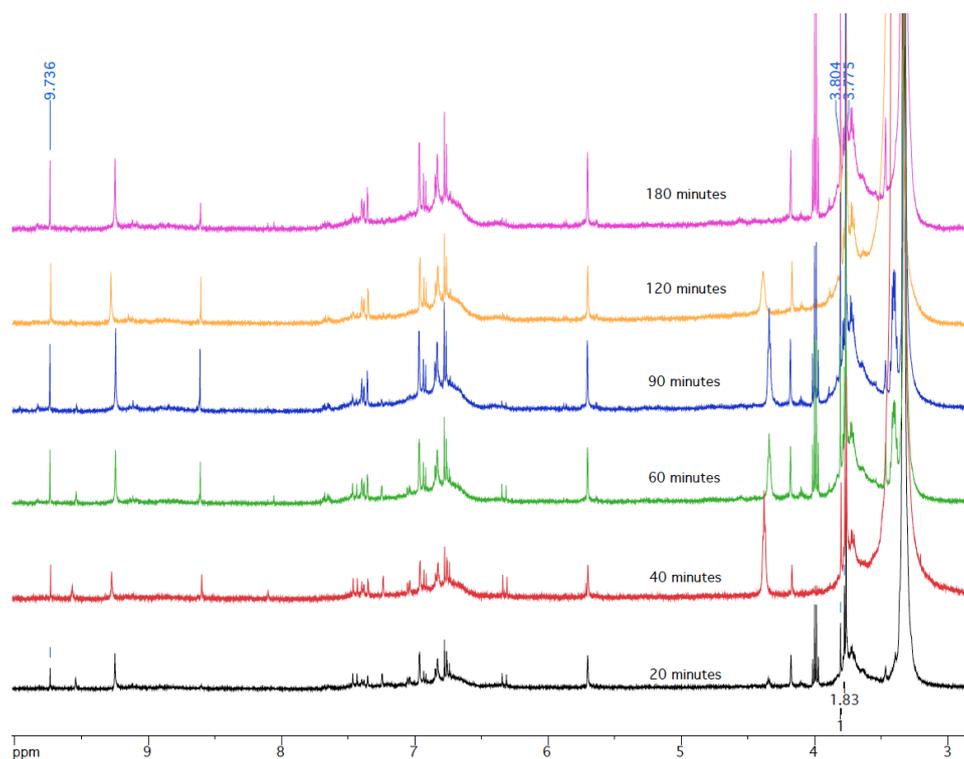


Fig. S5: $^1\text{H-NMR}$ spectra in the crude of reaction for the transformation of *trans*-ferulic acid to vanillin when the catalyst (HKUST-1) was activated in a conventional oven (exposed to air). Black line at 20 minutes, red line at 40 minutes, green line at 60 minutes, blue line 90 minutes, orange line 120 minutes and pink line at 180 minutes of the catalytic reaction.

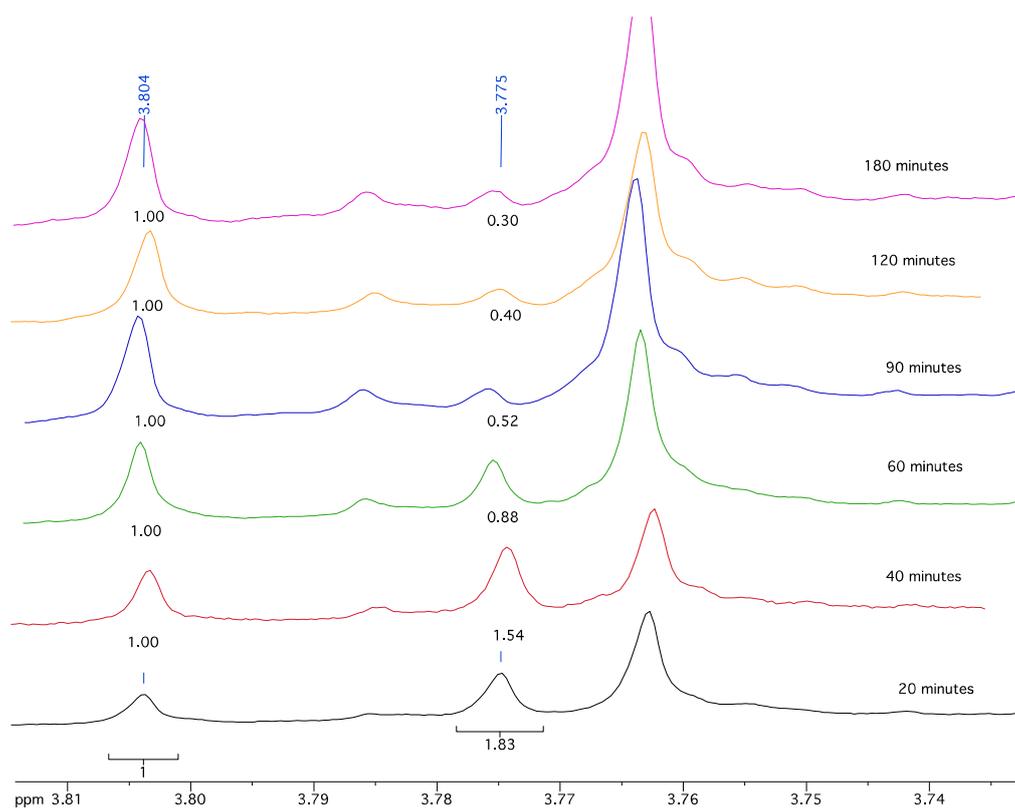


Fig. S6: ¹H-NMR integration spectra for the methoxy group of *trans*-ferulic acid (3.775 ppm) and methoxy group of vanillin (3.804 ppm), when the catalyst (HKUST-1) was activated in a conventional oven (exposed to air). Black line at 20 minutes, red line at 40 minutes, green line at 60 minutes, blue line 90 minutes, orange line 120 minutes and pink line at 180 minutes of the catalytic reaction.

10. ^1H -NMR and ^{13}C -NMR Spectra

HKUST-1 Activated under Vacuum (10^{-5} bar) and $100\text{ }^\circ\text{C}$ for 1 h

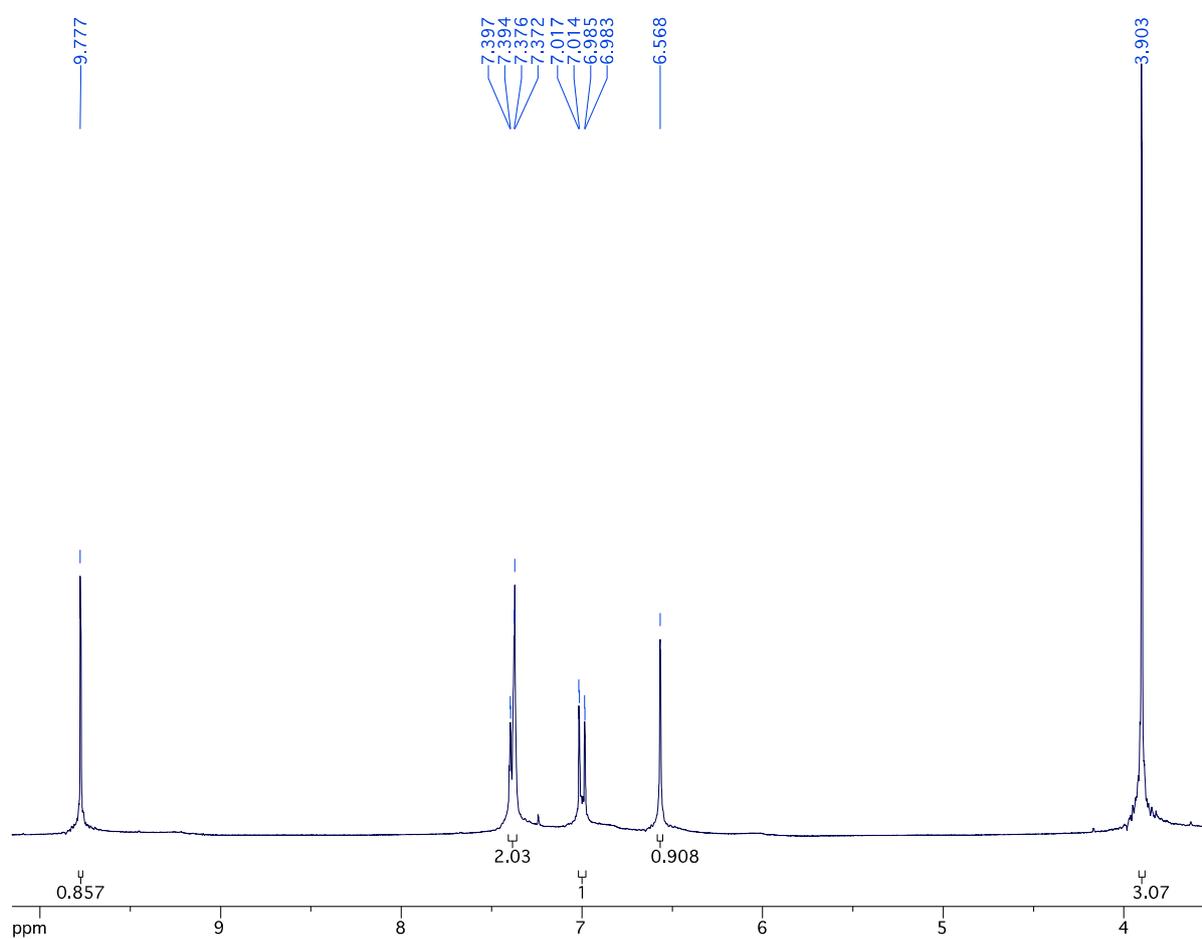


Fig. S7: ^1H -NMR spectra of vanillin after column chromatography purification on silica gel when the catalyst (HKUST-1) was activated under vacuum (10^{-5} bar) and $100\text{ }^\circ\text{C}$ for 1 h.

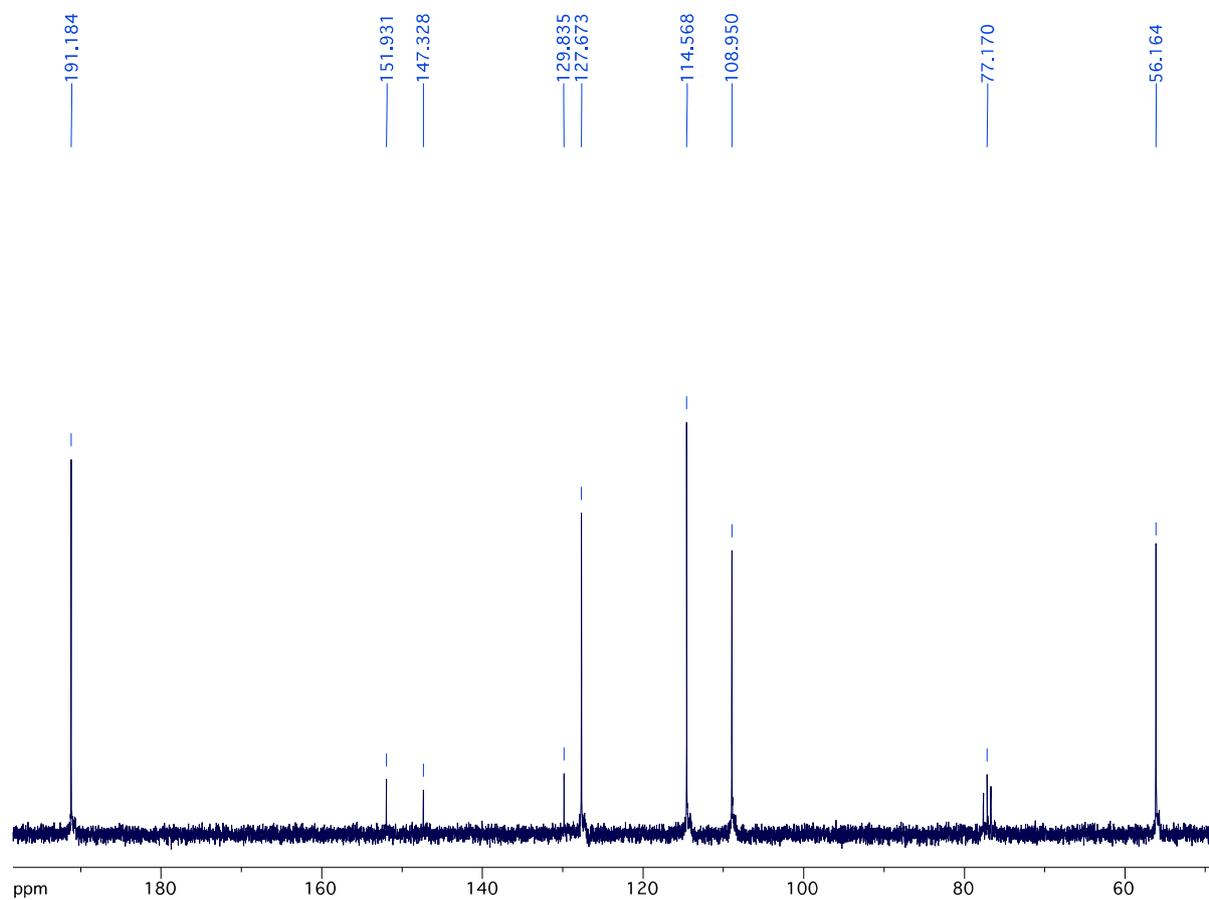


Fig. S8: ¹³C-NMR spectra of vanillin after column chromatography purification on silica gel when the catalyst (HKUST-1) was activated under vacuum (10^{-5} bar) and 100 °C for 1 h.

11. Preferred Catalytic Conditions

The best conditions in which the oxidation of *trans*-ferulic acid to vanillin took place were:

Activated catalyst (HKUST-1), 0.005g (3.2 mol%), suspended in ethanol (20 mL) was mixed with 0.5 mL of H₂O₂ (30%v aqueous), 0.025mL of acetonitrile and 0.050g (2.57X10⁻⁴ mol) of ferulic acid. The reaction mixture was heated to reflux for 1 h.

We investigated different concentrations of activated catalyst: 0.32 mol%, 1.6 mol%, 3.2 mol% and 4.8 mol%. In the cases of 0.32 mol% and 1.6 mol% GC analysis and showed a partial conversion of *trans*-ferulic acid to vanillin (see Table S2). In the case of 3.2 mol% and 4.8 mol% the conversion was satisfactory (see Table S2). We decided to use 3.2 mol% since, economically speaking, is more efficient than 4.8 mol%.

Table. S2: Amount of activated catalyst and the corresponding reaction yield.

| Amount of Activated Catalyst (mol%) | Reaction Yield (%) |
|-------------------------------------|--------------------|
| 0.32 | 11 |
| 1.6 | 65 |
| 3.2 | 98 |
| 4.8 | 98 |

Once we established the amount of catalyst (3.2 mol%) we carried out this reaction at 25 °C and 50 °C. Since we did not observe any conversion of *trans*-ferulic acid to vanillin, we always carried out any catalytic reaction at approximately 100 °C (reflux).