

Electronic Supplementary Information

Cobalt Schiff base with ionic substituents on ligand as an efficient catalyst for the oxidation of 4-methyl guaiacol to vanillin

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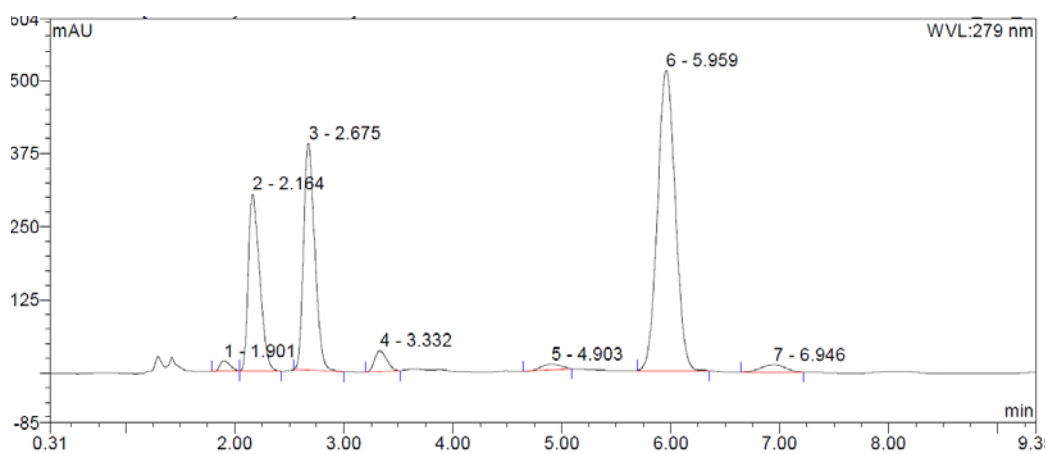
1. Experimental materials and methods

All the chemicals were of AR grade. They were commercially purchased from Sigma-Aldrich, Acros and used without further treatment. FT-IR spectra were recorded on a Bruker APEX-III spectrometer using KBr pellets in 400-4000 cm^{-1} region. ESI-MS analysis was performed on a Bruker Esquire 3000 (Bruker-Franzen Analytik, Bermen, Germany) equipped with an ion trap analyzer system. ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) analysis was performed on a Perkin-Elmer ELAN 6100, equipped with a standard pneumatic nebulizer and an automatic sampler as used. Indium was used as internal standard in order to correct potential instrument drift.

2. Reaction medium analysis

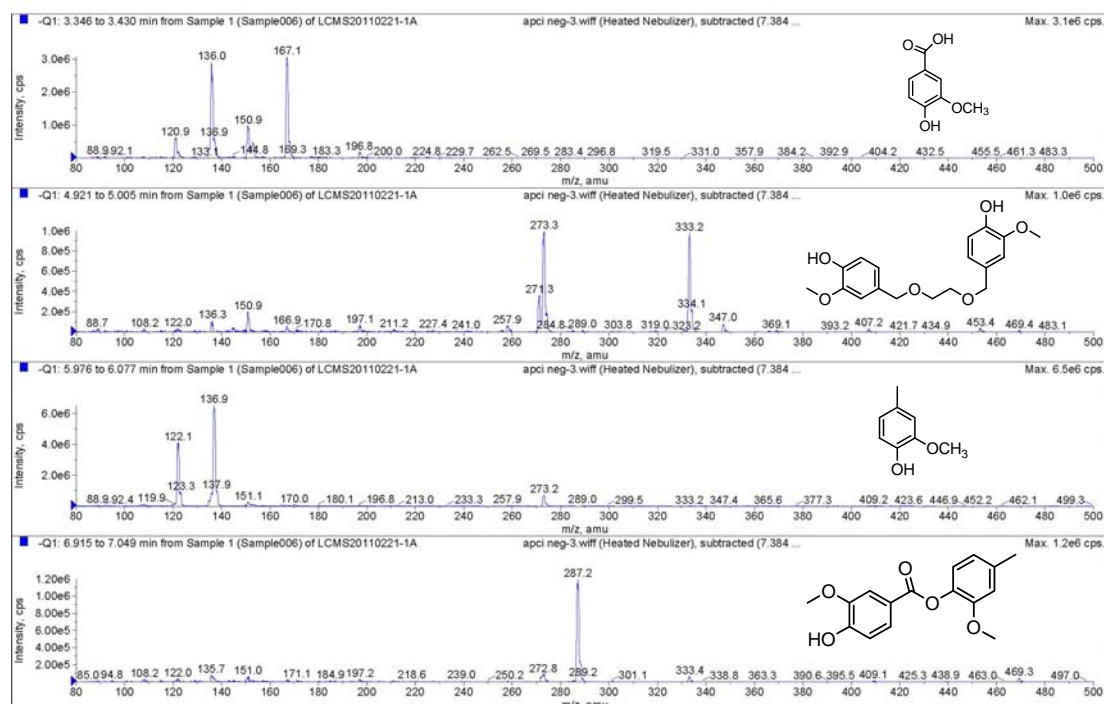
A 5.0 cm diameter, two-bladed impeller was used for stirring at approximately 1000 r.p.m. The end of the tube was positioned about 1 cm above the impeller blades. The mixture was left to stabilize at this temperature for a further 1 h, and then the oxygen was introduced (40 ml min⁻¹) to initiate the reaction. About 0.5 ml of sample withdrawn from the reaction mixture was acidified by hydrochloric acid (1:1, volume ratio) to pH =2~3 and diluted with methanol. The diluted sample was analyzed on a HPLC (DIONEX, Ultamate3000, RP-18 column 25 cm column, UV 279 nm). The definition of conversion, selectivity and isolated yield are as follows: conversion = amount of reactant consumed divided by the amount of reactant charged; selectivity = the amount of a particular product formed divided by the total amount of reactant consumed; isolated yield= the amount of a isolated particular product divided by the total amount of reactant charged. It should be noted that the sample should be analyzed immediately after acidification to avoid autoxidation.

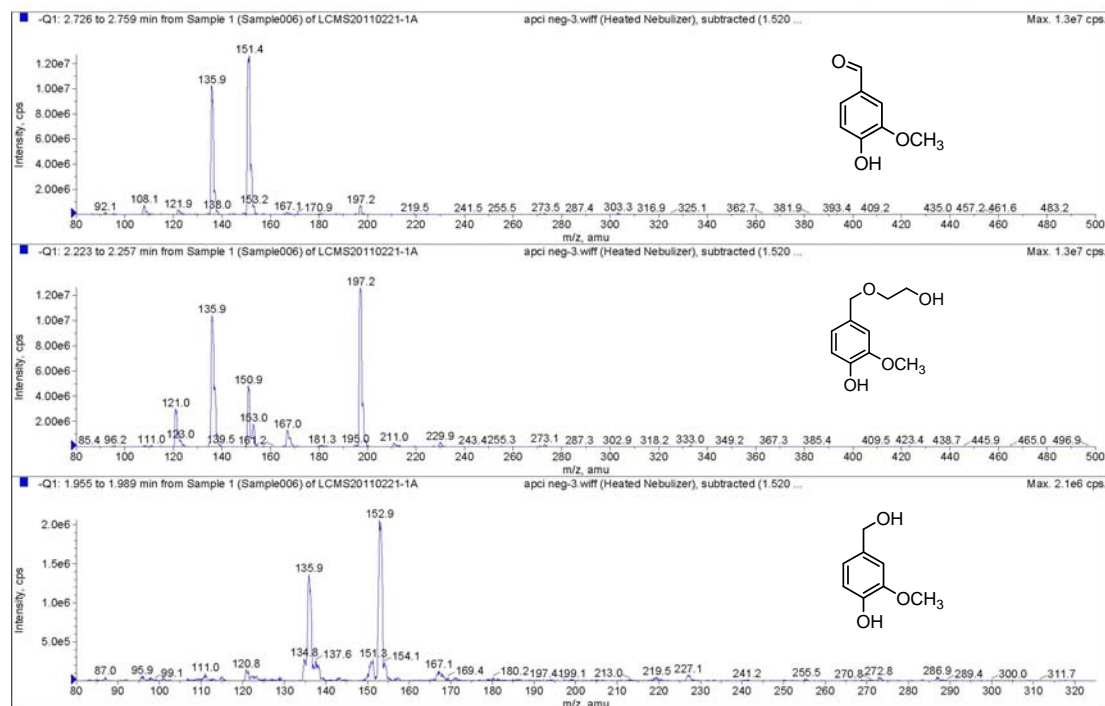
3. The liquid phase spectrogram of the 5h reaction solution.



Analysis contions: HPLC-MS (chrompak: kromasil 100-5, C18, 150*4.6mm, E30334. Dionex Summit HPLC and Applied Biosystem API2000 combined), Mobile phase Methanol: Water=50:50(V/V), T=40°C, UV 279nm.

4. The corresponding mass spectrogram of the above liquid phase peaks.





5. Effect of temperature

To determine whether reaction temperatures have any significant effect on the oxidation, reaction temperatures from 55 °C to 95 °C (Table 1, entries 1–5) were investigated. It seems that the reaction time and selectivity increased as the temperature decreased from 95 °C to 65 °C, and the selectivity reached a maximum at 65 °C and then decreased. However, when the temperature was lower than 65 °C, the reaction time increased remarkably. This may be the fact that higher temperature enhanced gas-liquid transfer and shortened the reaction time. However, when the temperature was higher than 85 °C, the over-oxidation product increased remarkably. Those results showed that temperature was also a key factor in this reaction, where a suitable temperature was 75 °C for the Co-[Salen-Py][PF₆]₂ catalyst system.

Table S1. Influence of temperature in the oxidation of 2-methoxy-4-methyl phenol

Entry	Temperature (°C)	Time (h)	Conv. (%)	Sel. (%)
1	55	42	100	82
2	65	30	100	90
3	75	18	100	86
4	85	15	100	75
5	95	9	100	70

Reaction conditions: 4-methyl guaiacol (40g; 290 mmol), molecular oxygen flow rate (40ml/min), stirring rate 1000 r.p.m., NaOH (38.3 g; 957 mmol), ethylene glycol (155 g), water 20g, Co-[Salen-Py][PF₆]₂ (1.0 g; 1.38 mmol).