Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

A sustainable approach to empower the bio-based future: upgrading of biomass *via* process intensification

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Contents

General procedure for upgrading of biomass via hydrodeoxygenation of vanillin

Vanillin (1mmol) was dissolved in 4.5 mL of water and 0.5mL methanol, to which 25mg of the catalyst, AgPd@g-C_3N_4, was added and the contents were sonicated for 5 min. To this mixture, 1mL of water and 1.5mmol of formic acid was added. The total mixture was then introduced into the coil reactor (10m) by syringe pump (under constant flow) at 0.1 mL/min while maintaining the reaction zone temperature at 70 ^{o}C. The product mixture was then collected at the exit port and extracted into ethyl acetate. The organic layer was then washed with water, dried over anhydrous sodium sulfate and the ensuing crude product was purified by flash chromatography on a silica gel column using ethyl acetate-hexane (5:95) as a mobile phase.

Note: Mixture of water and methanol were used as a solvent in the reaction. Water helped with dispersibility of the bimetallic AgPd@g-C_3N_4 catalyst, while methanol assisted with the solubility of the vanillin.

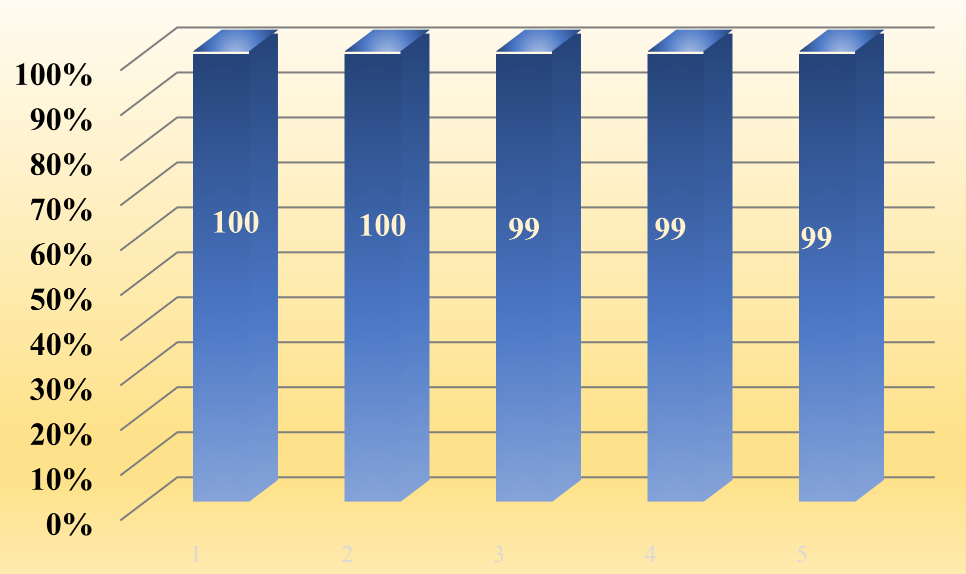
General procedure for the synthesis of GVL

Levulinic acid (1mmol) was dissolved in 4.5mL of water and 0.5mL methanol, to which 25mg of the catalyst, AgPd@g-C_3N_4, was added and the contents were sonicated for 5 min. To this mixture, 1mL of water and 1.5mmol of formic acid was added. The total mixture was then introduced into the coil reactor (10m) by syringe pump (under constant flow) at 0.1 mL/min while maintaining the reaction zone temperature at 70 ^{o}C. The product mixture was then collected at the exit port and was extracted into ethyl acetate. The organic layer was then washed with water, dried over anhydrous sodium sulfate and the ensuing crude product was purified by flash chromatography on a silica gel column using ethyl acetate-hexane (5:95) as a mobile phase.

Note: Mixture of water and methanol were used as a solvent in the reaction. Water helped with dispersibility of the bimetallic AgPd@g-C_3N_4 catalyst, while methanol assisted with the solubility of the levulinic acid.

Recycling of the AgPd@g-C_3N_4 catalyst for the hydrodeoxygenation of vanillin

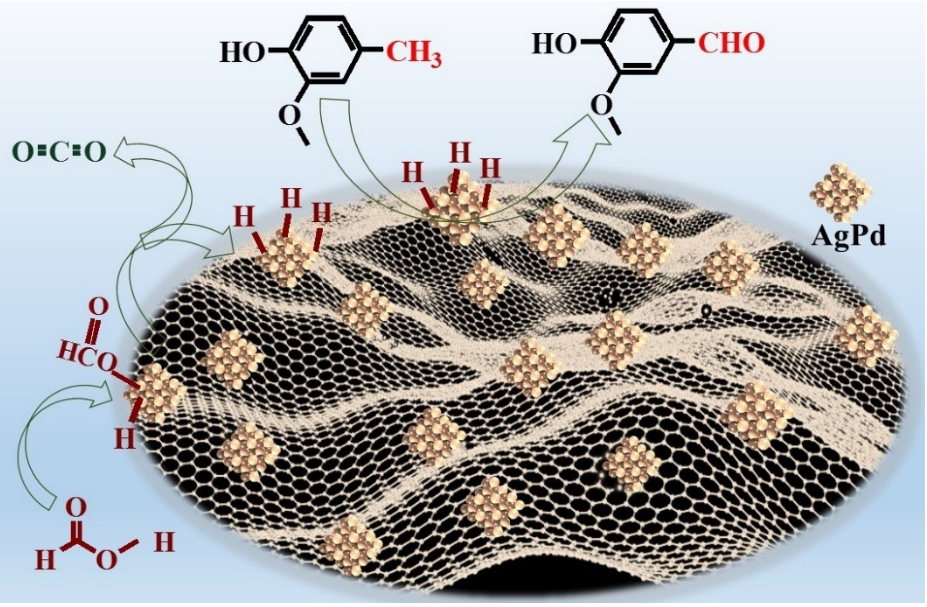
After completion of each reaction, the AgPd@g-C_3N_4 catalyst was recovered via centrifuge, rinsed with water (10L), dried under vacuum (4h) and subsequently used for an additional reaction. It was observed catalytic activity was not diminished even after fifth cycle and has the ability to be reused several times without losing activity.



S1. Recycling of AgPd@g-C_3N_4 catalyst

Plausible mechanism for hydrodeoxygenation of vanillin

In most of the reported methods for hydrodeoxygenation of vanillin, the use of high pressure of hydrogen has resulted in the formation of 4-hydroxymethyl-2-methoxyphenol as a by-product. However, in our study no such side product formation was discerned. A plausible mechanism for hydrodeoxygenation of vanillin is proposed (S2). The reaction presumably occurs via the adsorption of formic acid on the AgPd@g-C_3N_4 surface that leads to the formation of formate species. The migration of ensuing formate species to nearby AgPd alloy particles and their decomposition facilitates hydrodeoxygentaion of vanillin on the PdAg surface.



S2. Proposed pathways for hydrodeoxygenation of vanillin

GC-MS of the products

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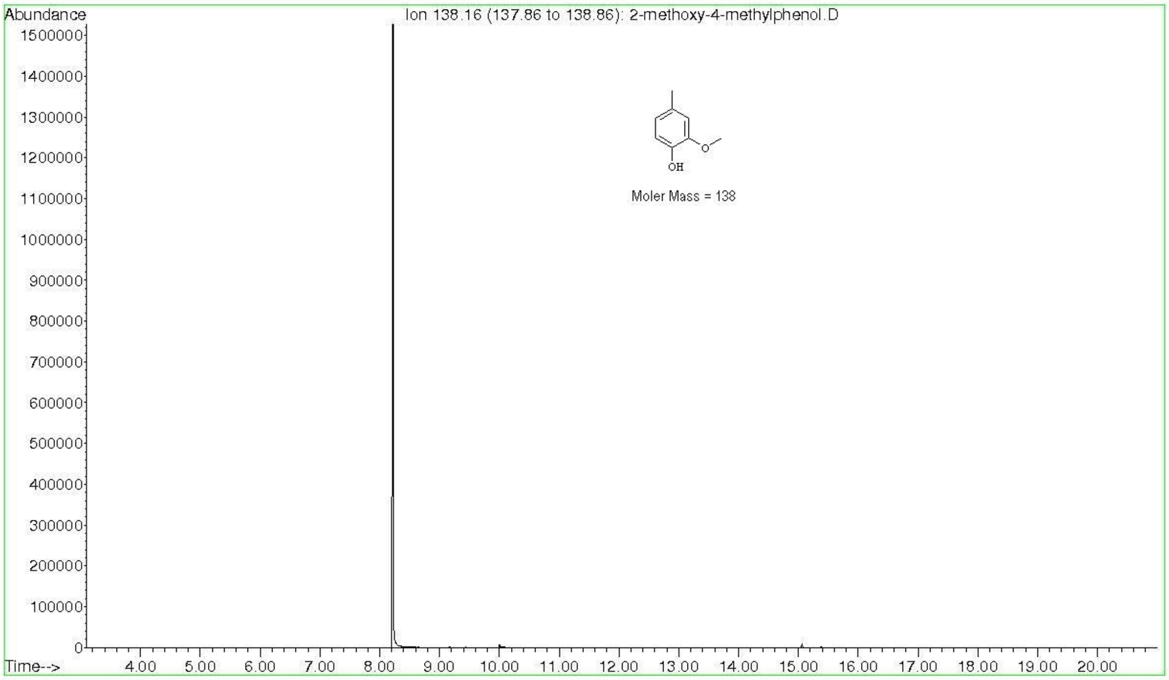

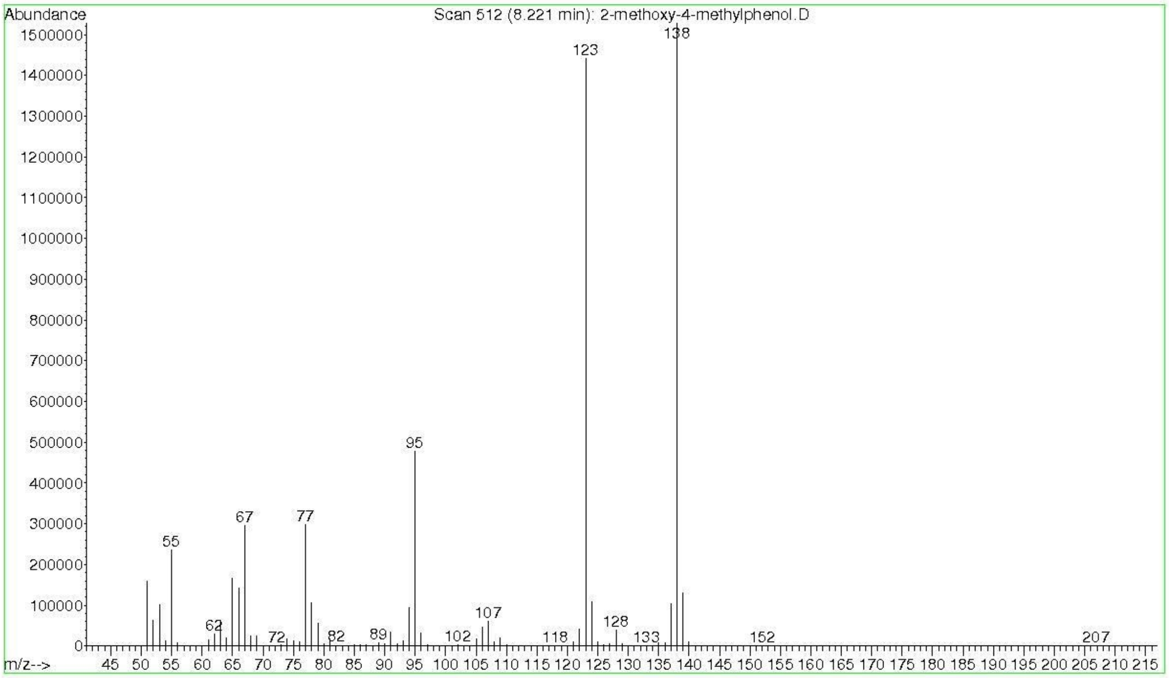

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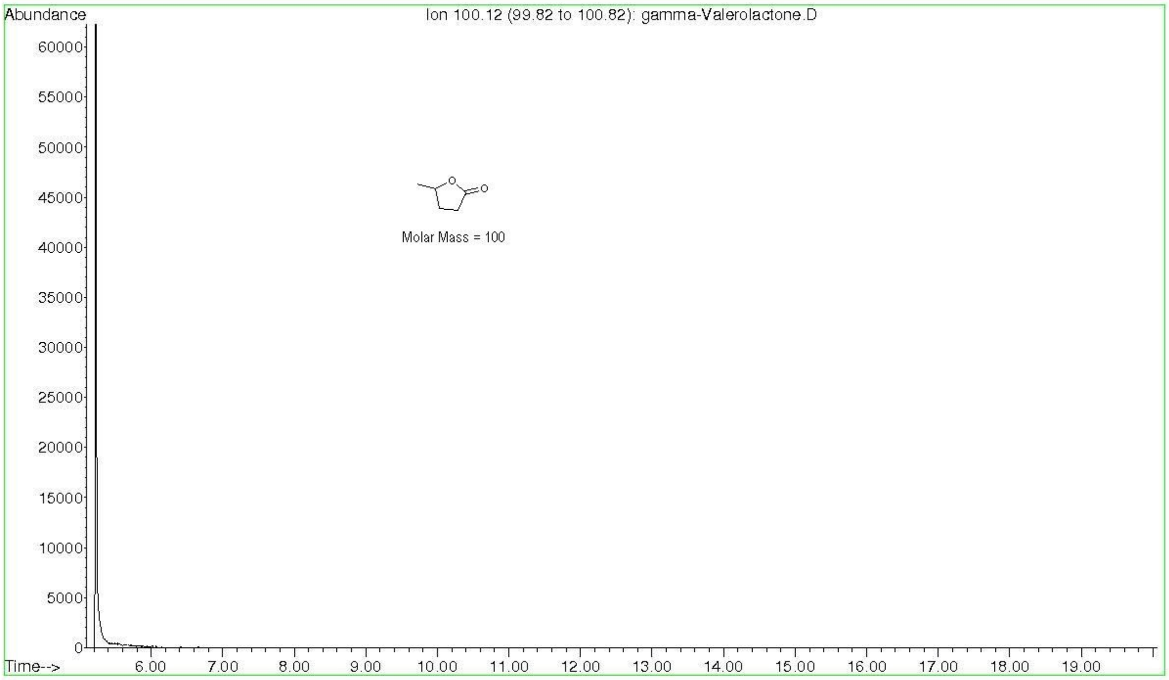
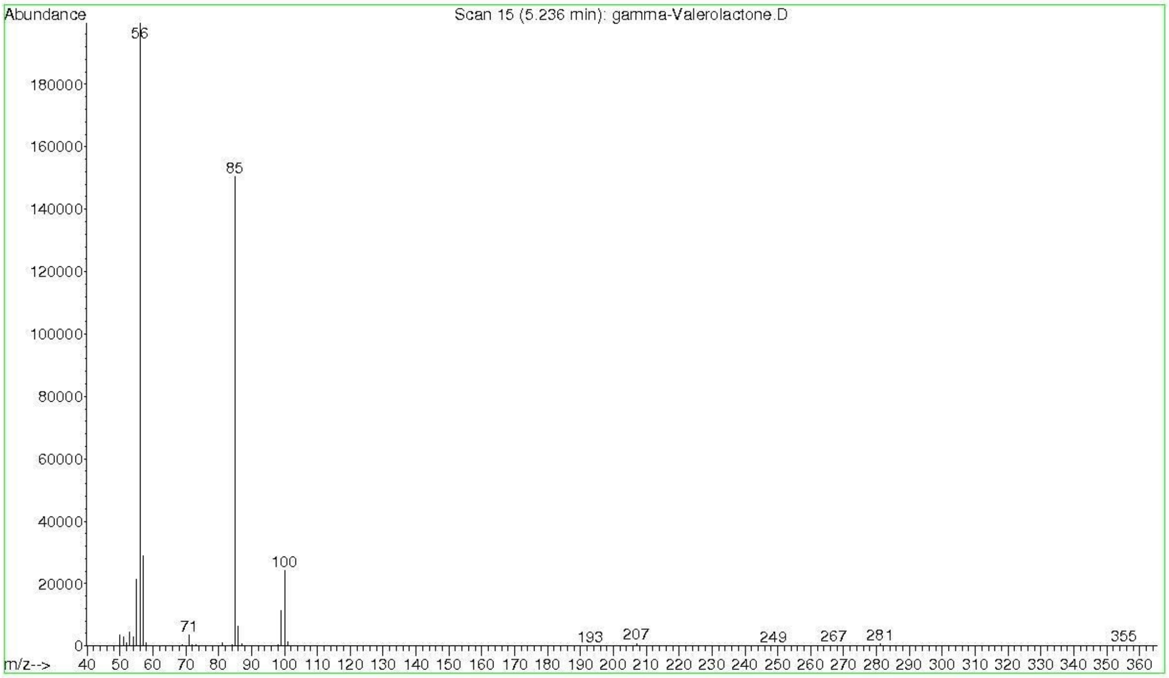
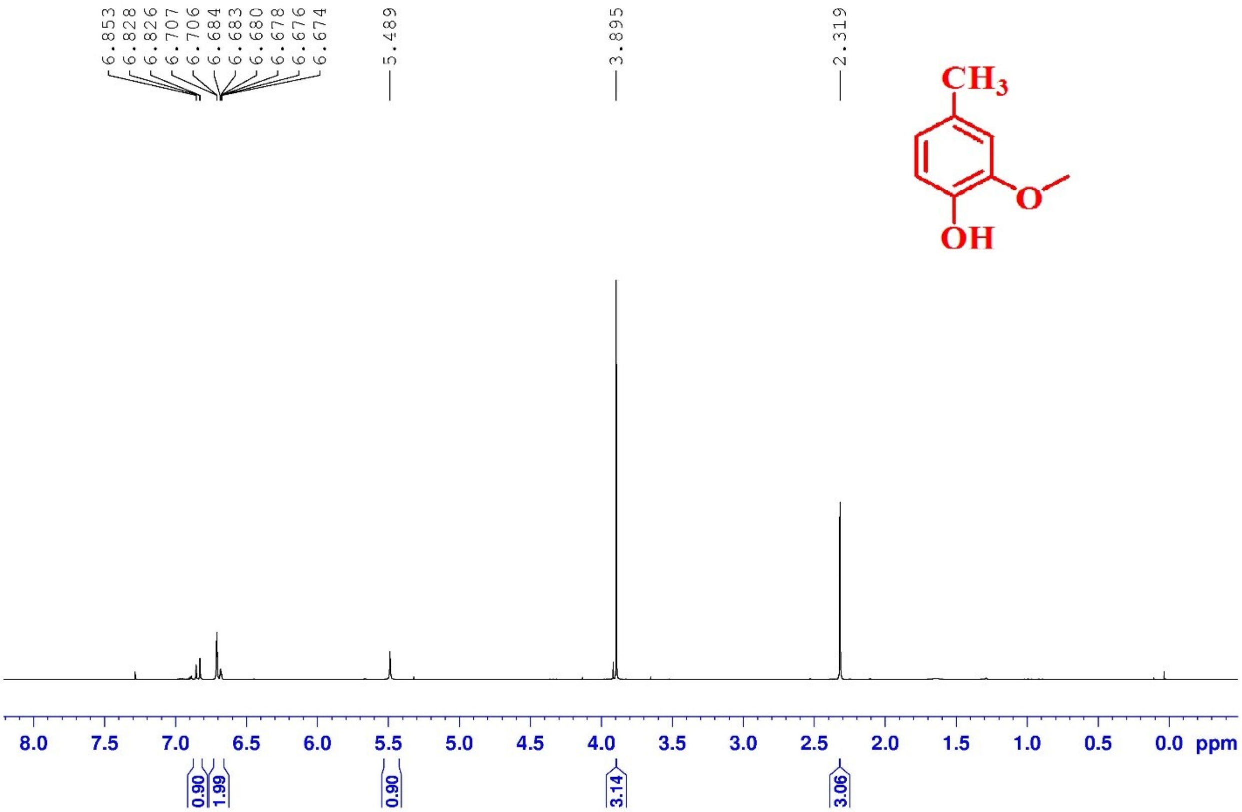
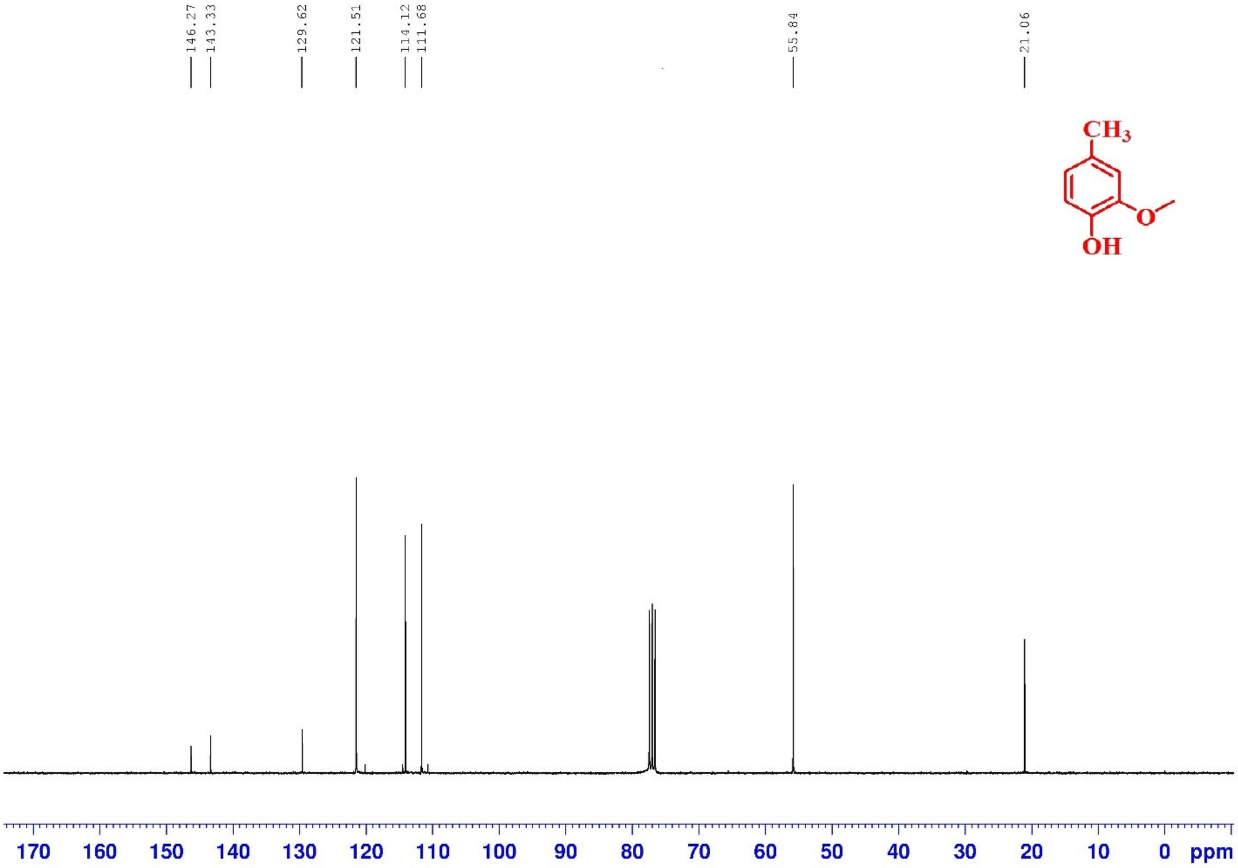




^{1}HNMR and ^{13}CNMR of the products

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20
10
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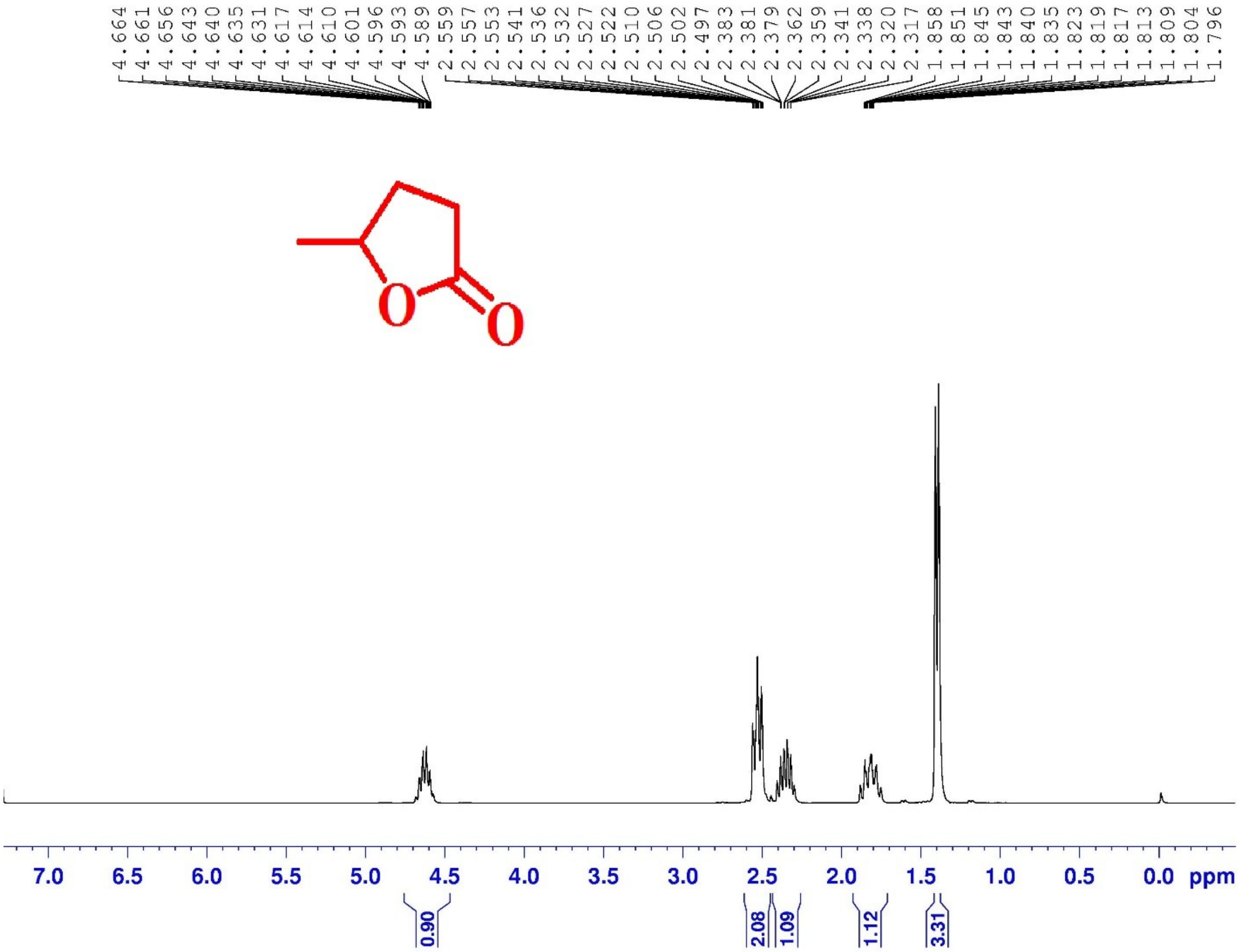

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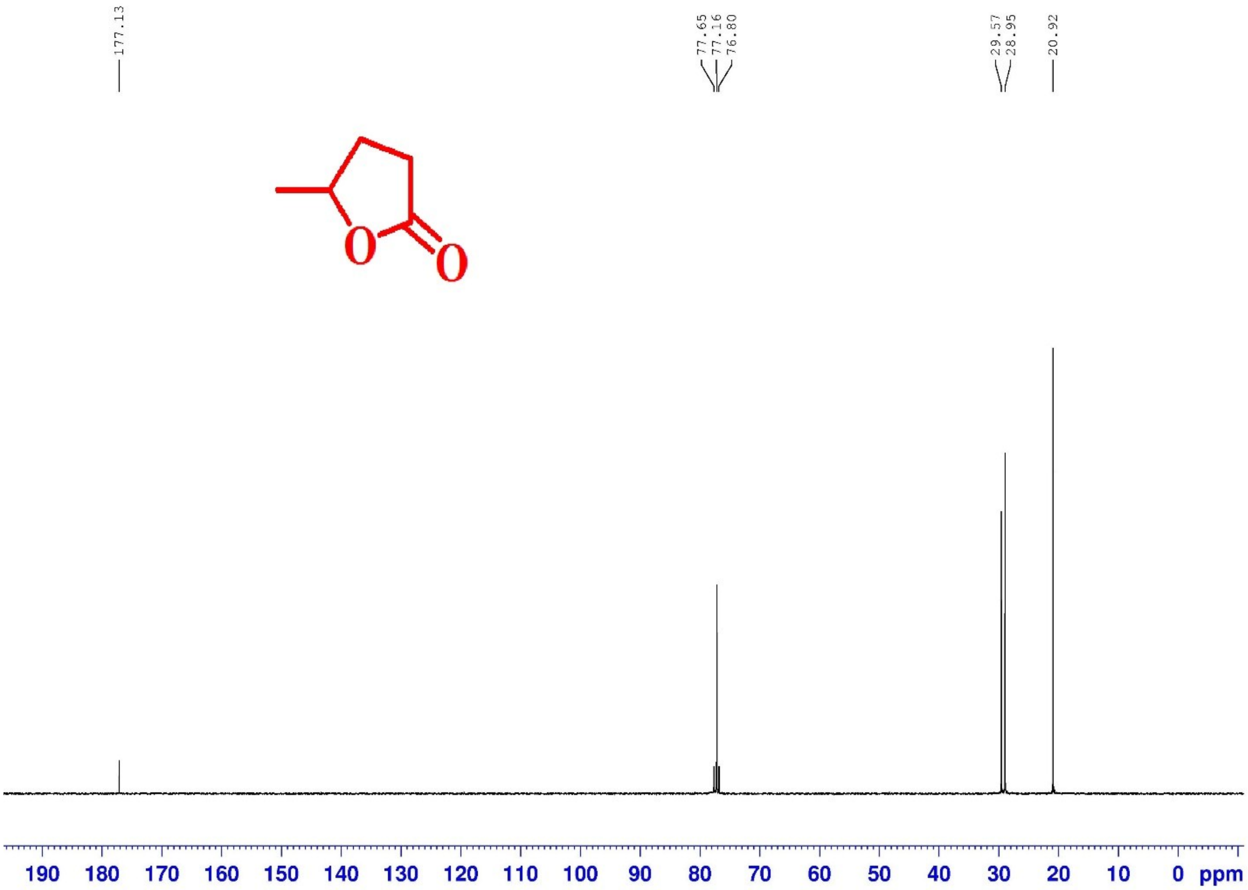
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