

## **Supporting Information**

### **Levulinic Acid-derived Reusable Cobalt Nanoparticles-catalyzed Sustainable Synthesis of $\gamma$ -Valerolactone**

Kathiravan Murugesan,<sup>†</sup> Ahmad S. Alshammari,<sup>†,‡</sup> Manzar Sohail<sup>†</sup> and Rajenahally V. Jagadeesh<sup>†\*</sup>

<sup>†</sup>Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein Str. 29a, Rostock, D-18059, Germany.

<sup>‡</sup>King Abdulaziz City for Science and Technology, Post Office Box 6086, Riyadh 11442, Saudi Arabia.

\* Corresponding author: E-mail: jagadeesh.rajenahally@catalysis.de

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## **S1. Materials and methods**

All substrates were obtained commercially from various companies and the purity has been checked before use. Cobalt (II) nitrate hexahydrate (cat no. 36418-100G) was purchased from Alfa aesar. Levulinic acid (4-Oxopentanoic acid or 4-Oxovalerianic acid) (cat no. L2009-50G) was purchased from Sigma-Aldrich. *N, N*-Dimethylformamide (DMF, code- 348435000; 99%) was obtained from Across Chemicals. Silica (Aerosil OX-50) was obtained from Evonik. The pyrolysis experiments were carried out in Nytech-Qex oven.

TEM measurements were performed at 200kV with an aberration-corrected JEM-ARM200F (JEOL, Corrector: CEOS). The microscope is equipped with a JED-2300 (JEOL) energy-dispersive x-ray-spectrometer (EDXS) and an Enfinum ER (GATAN) with Dual EELS for chemical analysis. The aberration corrected STEM imaging (High-Angle Annular Dark Field (HAADF) and Annular Bright Field (ABF)) were performed under the following conditions: HAADF and ABF both were done with a spot size of approximately 0.1 nm, a convergence angle of 30-36° and collection semi-angles for HAADF and ABF of 90-170 mrad and 11-22mrad respectively. Dual EELS was done at a CL of 4 cm, an illumination semi angle of 21.3 mrad and an entrance aperture semi angle of 19.8 mrad. The solid samples were deposited without any pretreatment on a holey carbon supported Cu-grid (mesh 300) and transferred to the microscope. The average particle diameter and size distribution were calculated using Java image tool software (ImageJ), based on the data of an average of 100-200 particles.

XPS (X-ray Photoelectron Spectroscopy) data was obtained with a VG ESCALAB220iXL (ThermoScientific) with monochromatic Al K $\alpha$  (1486.6 eV) radiation. The electron binding energies EB were obtained without charge compensation. For quantitative analysis the peaks were deconvoluted with Gaussian-Lorentzian curves, the peak area was divided by a sensitivity factor obtained from the element specific Scofield factor and the transmission function of the spectrometer. CasaXPS was used for XPS peak deconvolution.

XRD powder patterns were recorded on a Stoe STADI P diffractometer, equipped with a linear Position Sensitive Detector (PSD) using Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Processing and assignment of the powder patterns was done using the software WinXpow (Stoe) and the Powder Diffraction File (PDF) database of the International Centre of Diffraction Data (ICDD).

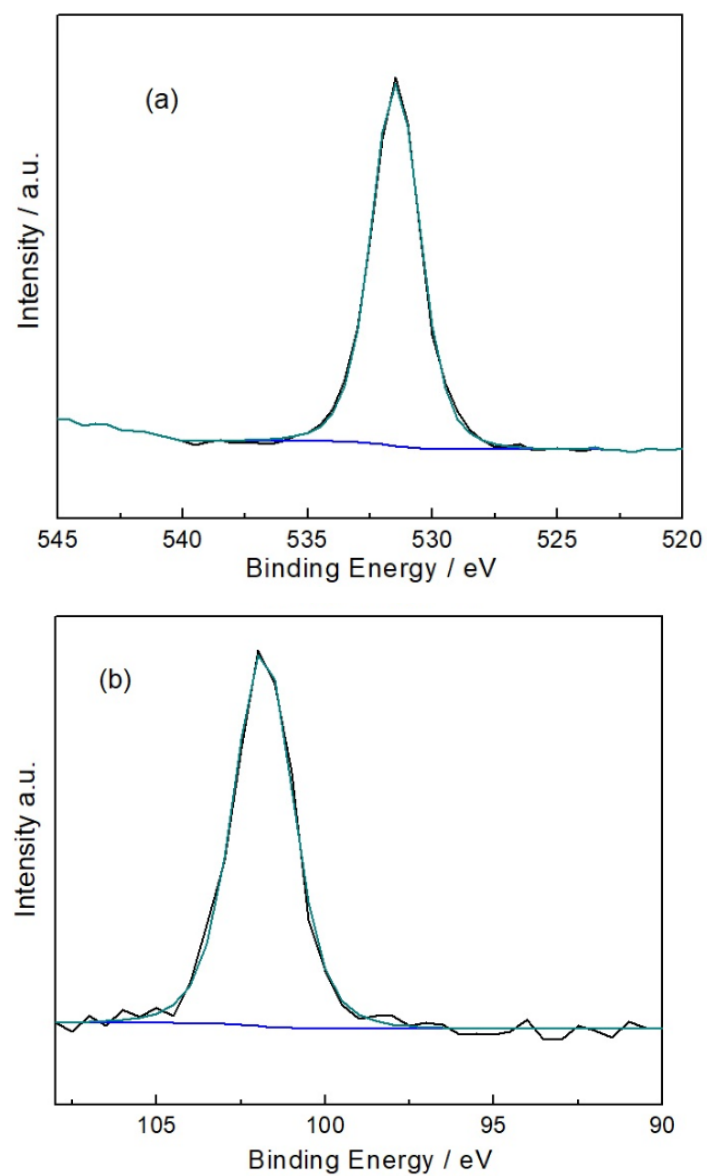
Thermogravimetric analysis (TGA) and the associated differential thermal analysis (DTA) were carried out in TA Instruments SDTQ600. Analysis was done in the presence of argon as inert purge with flow of 100 mL/min and heating rate of 10°C/min, heating from room temperature to 1200°C.

All catalytic experiments were carried out in 300 mL and 100 mL autoclaves (PARR Instrument Company). In order to avoid unspecific reactions, all catalytic reactions were carried out either in glass vials, which were placed inside the autoclave, or glass/Teflon vessel fitted autoclaves.

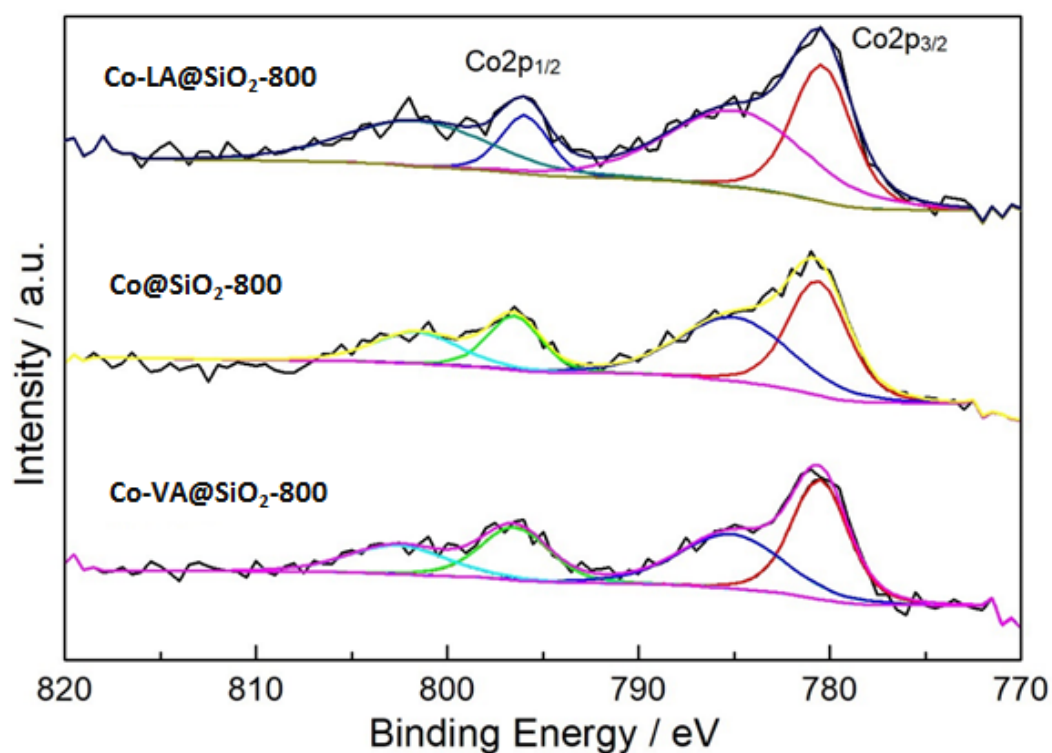
GC and GC-MS were recorded on Agilent 6890N instrument. GC conversion and yields were determined by GC-FID, HP6890 with FID detector, column HP530 m x 250 mm x 0.25  $\mu$ m.

$^1\text{H}$ ,  $^{13}\text{C}$  NMR data were recorded on a Bruker ARX 300 and Bruker ARX 400 spectrometers using DMSO- $d_6$ ,  $\text{CD}_3\text{OD}$  and  $\text{CDCl}_3$  solvents.

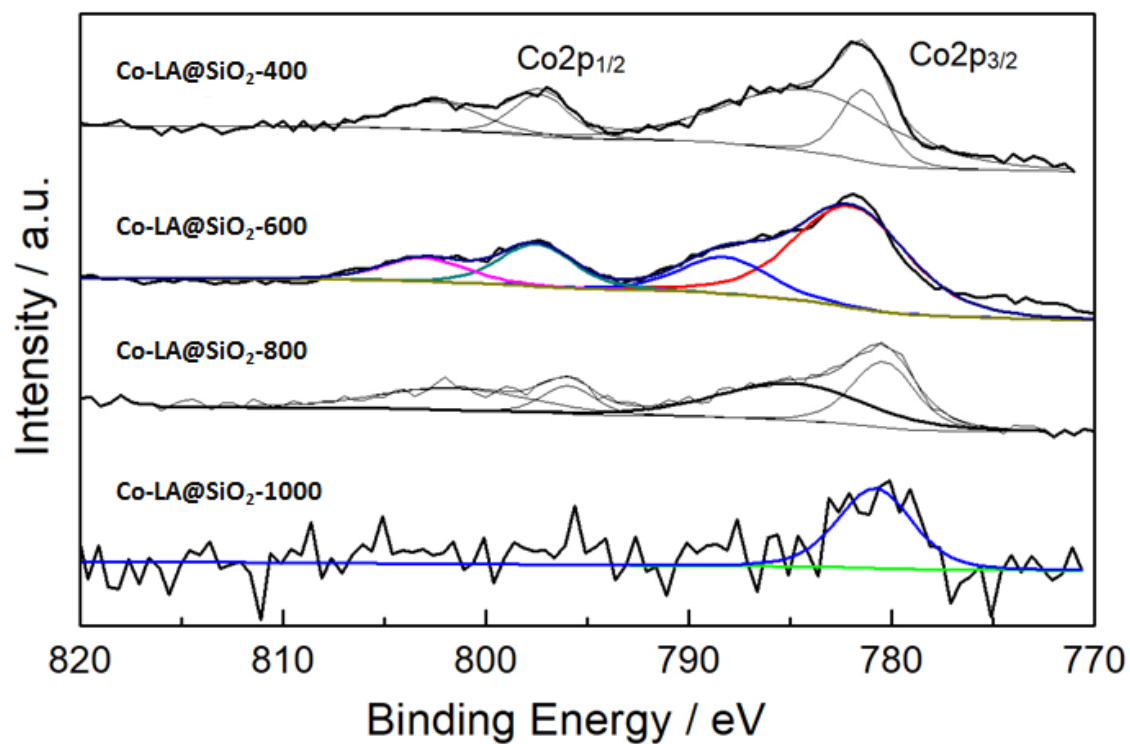
## **S2. XPS spectra**



**Figure S1.** XPS spectra of Co-LA@SiO<sub>2</sub>-800 a) O 1s spectra b) Si 2p spectra.

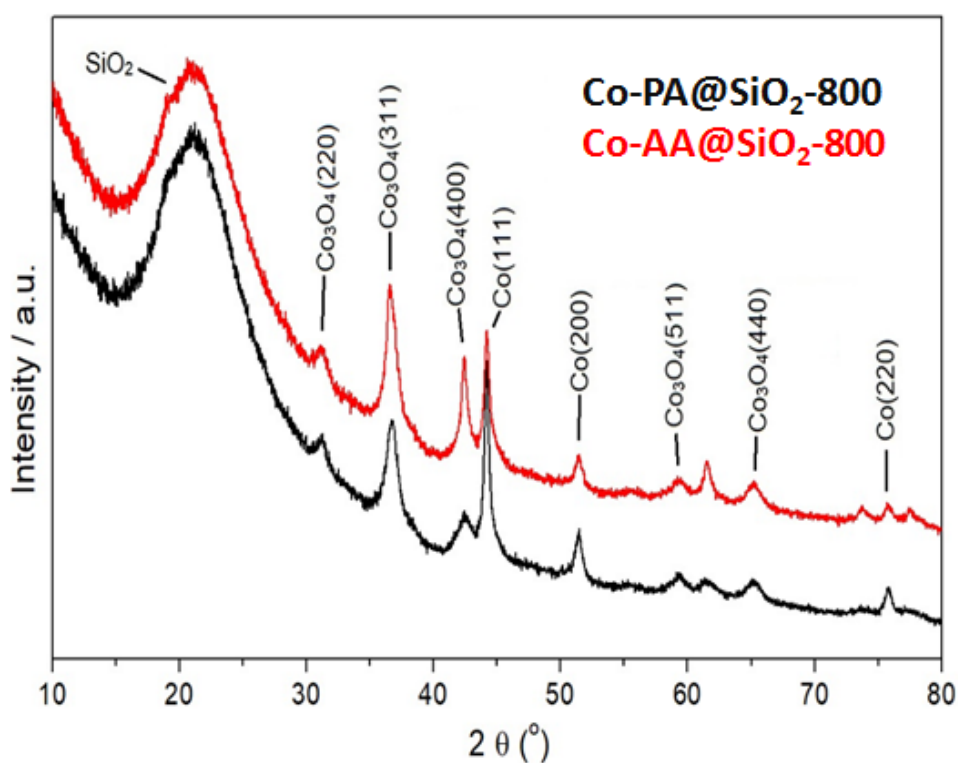


**Figure S2.** XPS Co<sub>2</sub>p spectra of Co-LA@SiO<sub>2</sub>-800, Co@SiO<sub>2</sub>-800 and Co-VA@SiO<sub>2</sub>-800 catalysts.



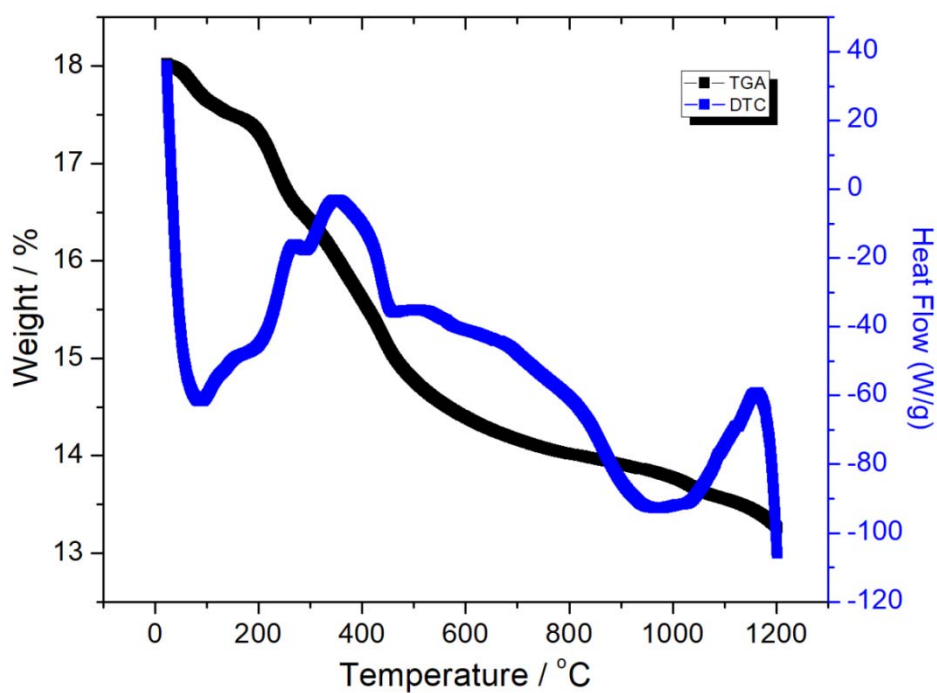
**Figure S3.** XPS Co<sub>2</sub>p spectra of Co-LA@SiO<sub>2</sub>-400-1000 catalysts

### S3. XRD spectra



**Figure S4.** XRD spectra of Co-PA@SiO<sub>2</sub>-800 and Co-AA@SiO<sub>2</sub>-800 (PA= Propionic acid; AA= Acetic Acid)

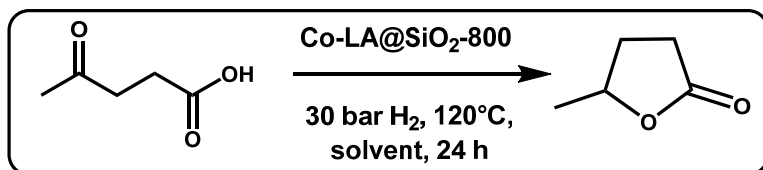
### S4. DSC-TGA spectra



**Figure S5.** DSC-TGA spectra of Co-LA@SiO<sub>2</sub> material.

## S5. Reaction optimization

**Table S1:** Screening of different solvents for the Co-catalyzed hydrogenation of levulinic acid to  $\gamma$ -valerolactone

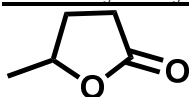


Entry	Solvent	Conversion (%)	Yield (%)
1	Dioxane	>99	97
2	Toluene	95	93
3	i-PrOH	95	93
4	<i>t</i> -amyl alcohol	90	88
5	MeOH	80	78
6	EtOH	70	68
7	THF	80	78
8	Water	5	2

Reaction conditions: 0.5 mmol levulinic acid, 6 mol % Cobalt catalyst (Co-LA@SiO<sub>2</sub>), 30 bar H<sub>2</sub>, 3 mL solvent, 120 °C, 24h, yields were determined by GC using n-hexadecane standard.

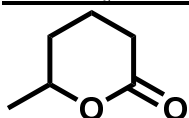
## S6. NMR data

### 5-Methyldihydrofuran-2(3H)-one



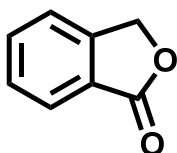
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  4.67 – 4.46 (m, 0H), 2.46 (dd,  $J$  = 9.3, 6.7 Hz, 1H), 2.35 – 2.18 (m, 1H), 1.86 – 1.64 (m, 0H), 1.32 (d,  $J$  = 6.2 Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  177.59 , 77.38 , 29.60 , 29.07 , 20.96 . Colorless oil.

### 6-Methyltetrahydro-2H-pyran-2-one



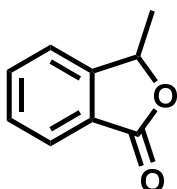
$^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  4.50 – 4.27 (m, 1H), 2.61 – 2.24 (m, 2H), 1.96 – 1.71 (m, 3H), 1.54 – 1.41 (m, 1H), 1.31 (d,  $J$  = 6.0 Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  172.03, 76.97 , 29.50 , 29.16 , 21.63 , 18.45 . Colorless oil.

### Isobenzofuran-1(3H)-one



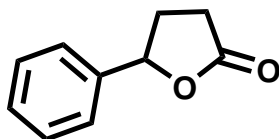
$^1\text{H}$  NMR (300 MHz, Chloroform-*d*)  $\delta$  7.88 – 7.79 (m, 1H), 7.70 – 7.55 (m, 1H), 7.52 – 7.39 (m, 2H), 5.25 (s, 2H).  $^{13}\text{C}$  NMR (75 MHz, Chloroform-*d*)  $\delta$  171.12 , 146.54 , 134.03 , 129.03 , 125.73 , 125.70 , 122.14 , 69.69 . White solid.

### 3-Methylisobenzofuran-1(3H)-one



$^1\text{H}$  NMR (300 MHz, Chloroform-*d*)  $\delta$  8.29 – 7.02 (m, 4H), 5.85 – 5.23 (m, 1H), 2.14 – 1.04 (m, 3H).  $^{13}\text{C}$  NMR (75 MHz, Chloroform-*d*)  $\delta$  170.50 , 151.18 , 134.08 , 129.05 , 125.61 , 125.51 , 121.59 , 77.77 , 20.38 . White solid.

### 5-phenyldihydrofuran-2(3H)-one

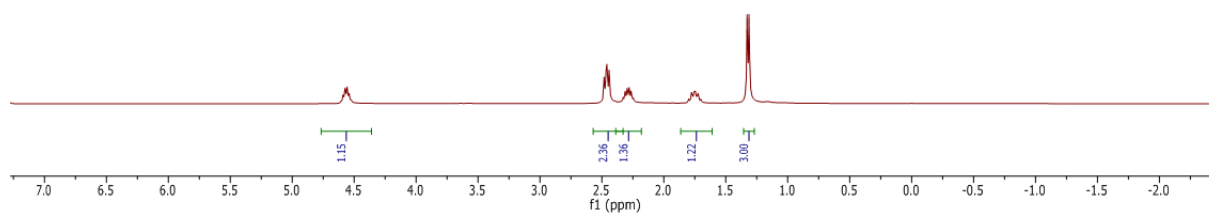
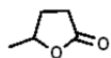


$^1\text{H}$  NMR (300 MHz, Chloroform-*d*)  $\delta$  7.50 – 6.86 (m, 5H), 5.41 (dd,  $J$  = 8.2, 6.0 Hz, 1H), 2.72 – 2.42 (m, 3H), 2.27 – 1.84 (m, 1H).  $^{13}\text{C}$  NMR (75 MHz, Chloroform-*d*)  $\delta$  177.03 , 139.41 , 128.77 , 128.45 , 125.33 , 81.29 , 30.97 , 29.00 . Off white solid.



## S7. NMR spectra

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Au1H CDCl<sub>3</sub> {C:\Bruker\TopSpin3.5pl6} 1808 43



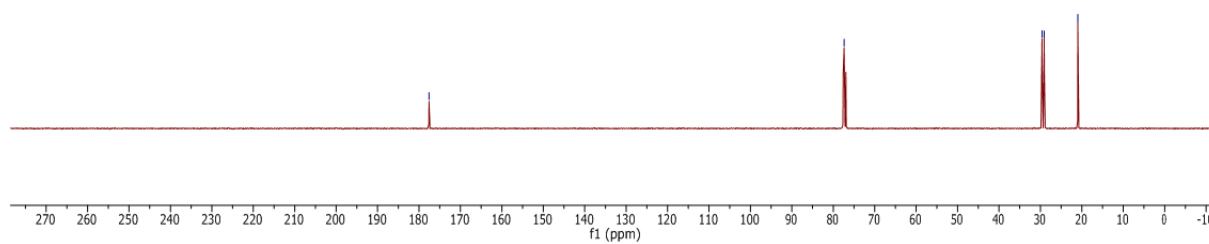
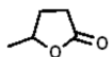
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177.59

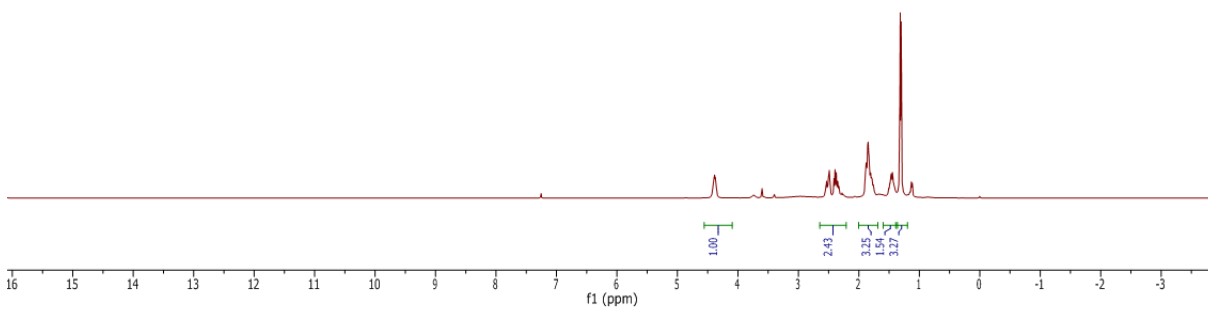
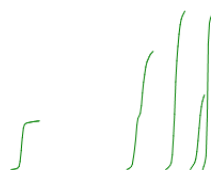
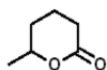
77.38

29.60  
29.07

20.96



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172.03

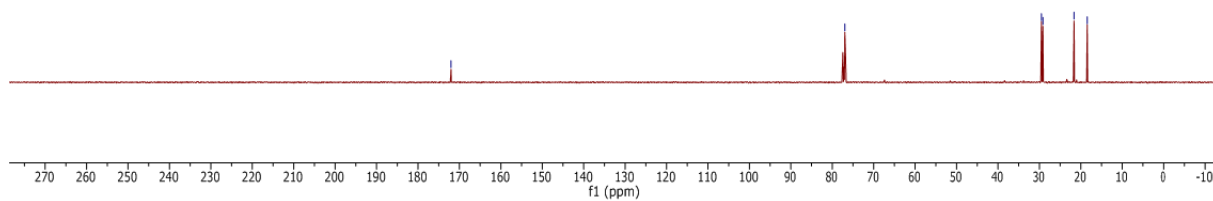
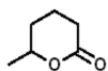
76.97

29.59

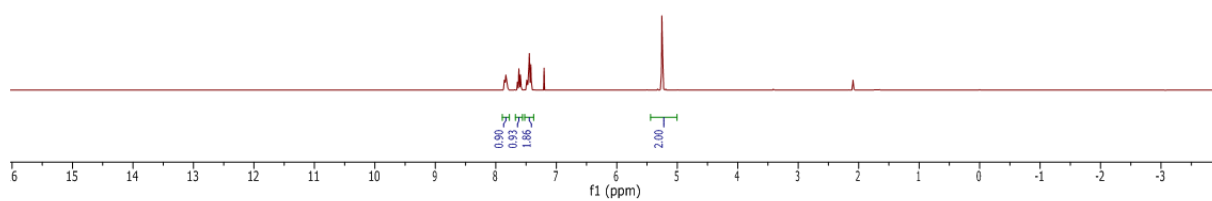
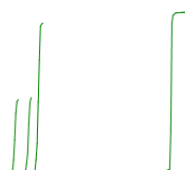
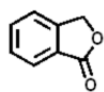
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21.63

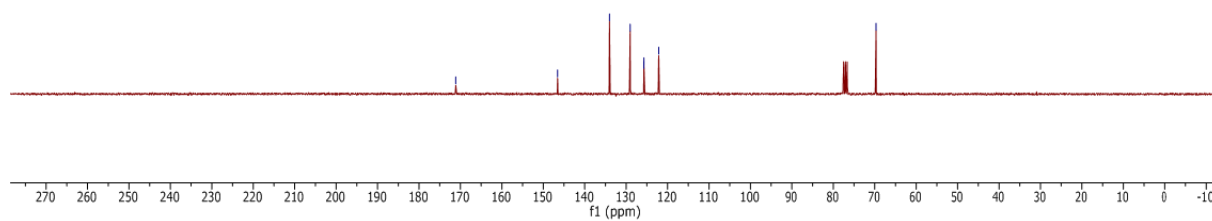
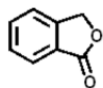
18.45



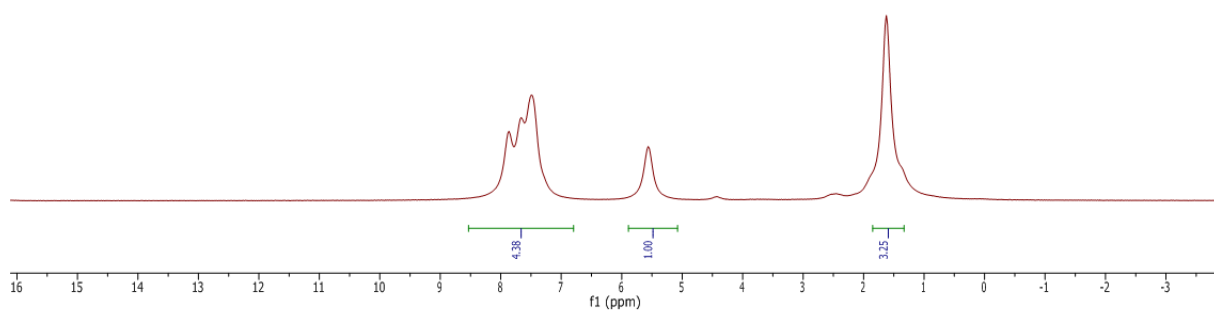
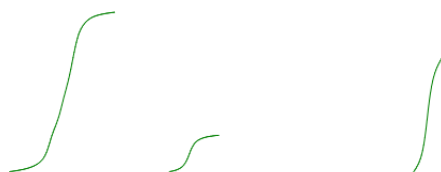
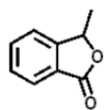
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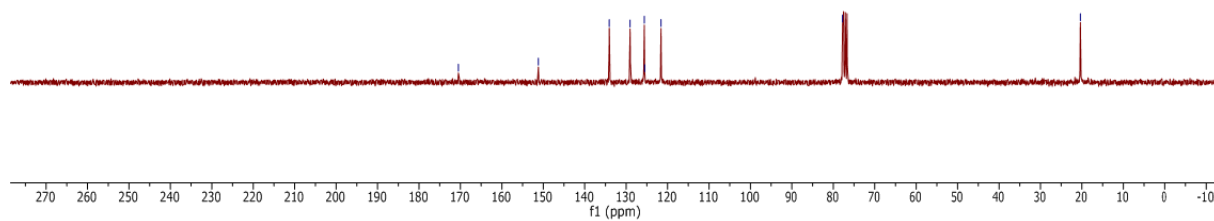
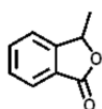
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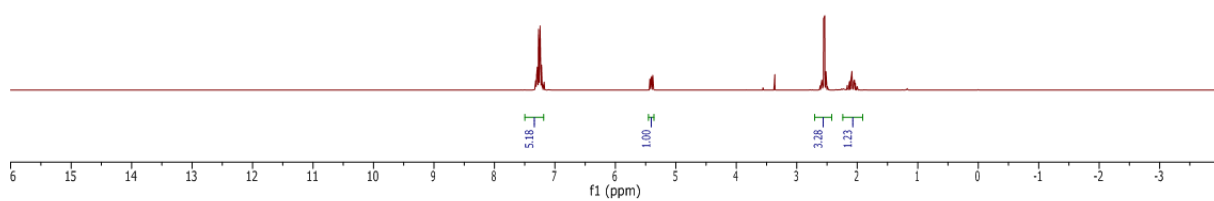
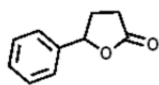
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