

# Solvent free synthesis of $\gamma$ -valerolactone by homogeneous hydrogenation of biomass-derived levulinic acid

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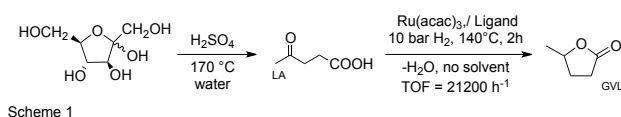
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We report here the catalyst design and development for the green synthesis of  $\gamma$ -valerolactone (GVL), a proposed sustainable liquid from biomass-based levulinic acid in the presence of recyclable Ru-based catalysts operating under solvent free conditions. The catalyst systems developed in this study will contribute to Sustainability.

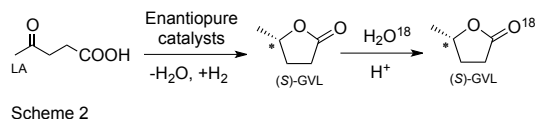
The gradual replacement of fossil resources of chemical industry with renewable ones is one of the most pressing challenge of mankind and crucial part of the sustainable development. Biomass could be an ideal alternative as it is one of the most abundant carbon resources and globally available on the Earth. The rapidly accelerating research on biomass conversion has led to the identification of several platform molecules such 5-hydroxymethylfurfural (1), levulinic acid (LA) (2) and  $\gamma$ -valerolactone (GVL) (3) which could either replace the currently used fossil-based chemicals or serve as renewable feedstock for their production. Due to the outstanding chemical and physical properties, GVL has been considered as a sustainable liquid (3) and can be used for production of several value added chemicals.

Since the most effective protocol to manufacture GVL is the selective hydrogenation of LA, we developed Ru-based hydrogenation catalyst systems operating under solvent free conditions that can quantitatively convert LA to GVL.

We demonstrated that GVL could be obtained from LA using molecular hydrogen in the presence of a catalyst *in situ* generated from 0.016 mol% Ru(acac)<sub>3</sub>, and 10 eqv. of electronically and sterically characterized phosphine (R<sub>n</sub>P(C<sub>6</sub>H<sub>4</sub>-*m*-SO<sub>3</sub>Na)<sub>3-n</sub> (n = 1 or 2; R = Me, Pr, *i*Pr, Bu, Cp) ligands. The high pressure *in situ* spectroscopy verified that catalyst still remained active even after several consecutive runs (4). Further catalyst development resulted in the identification of chelating type bidentate Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub> (n=1–3) ligands modified Ru-based catalysts that completely convert LA to GVL in the absence of any additives under solvent free conditions with TOF of 21 200 h<sup>-1</sup> (Scheme 1) To demonstrate the stability and resistance of the catalyst, the conversion of non-purified LA obtained by dehydration of fructose and the successfully catalyst recycling for 10 consecutive runs were also completed (5)



Since GVL has a chiral center the synthesis of optically active (*R*)-GVL or (*S*)-GVL can have much of interest. It could either be used as a chiral building block in synthetic schemes or applied as a chiral reaction media in catalysis. We have shown that optically active form can be obtained by reduction of LA utilizing chiral phosphine modified Ru-catalysts however, the stability of the chiral center is crucial in subsequent applications. The latter was investigated in details applying O<sup>18</sup>-labelling technique (Scheme 2).



Our contribution will show the catalyst design and development for production of GVL including its optically active form by the use of homogeneous Ru-based catalysts. The optimization of reaction conditions (pressure, temperature, catalyst and ligand concentration dependence) and the investigation of the stability of the chiral center will be presented as well.

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