

Asymmetric reduction of levulinic acid to γ -valerolactone: synthesis of a chiral platform molecule

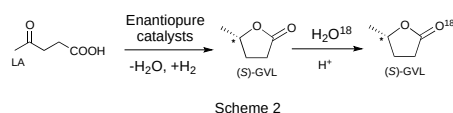
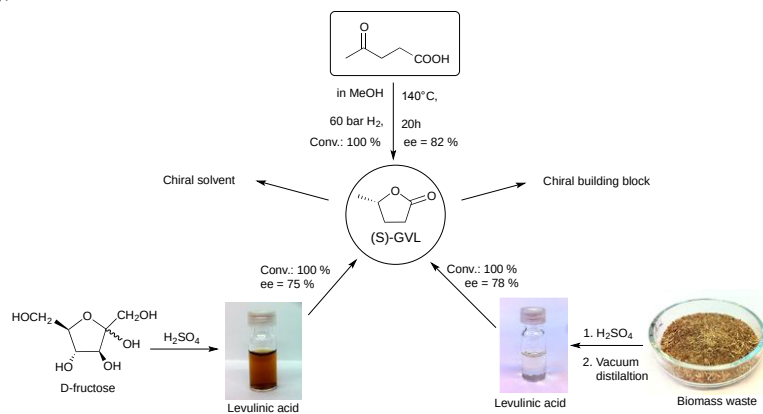
László T. Mika*; József M. Tukacs, Bálint Fridrich

Department of Chemical and Environmental Process Engineering, Budapest University of Technology and Economics, Budapest, Hungary. *Műegyetem rkp. 3. H-1111*
laszlo.t.mika@mail.bme.hu

Recently, the gradual replacement of fossil resources with renewable ones is one of the most pressing challenge of chemical industry. 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 as levulinic acid¹ (LA) and γ -valerolactone (GVL),² 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 liquid² and can be used for production of several value added chemicals and fuels.

Since GVL has a chiral center the synthesis of optically active (*R*)-GVL or (*S*)-GVL can have much of interest. These species could either be used as a chiral building blocks in synthetic schemes or applied as chiral reaction media in catalysis. Since the most effective protocol to obtain GVL is the selective reduction of levulinic acid³ we investigated this transformation in the presence of chiral catalysts.

We have shown that optically active GVL can be obtained by asymmetric hydrogenation of LA using chiral phosphine (BINAP, SEGPHOS) modified Ru-catalysts. Under optimized conditions, (*S*)-GVL can be directly synthesized from levulinic acid with 75–82 % of enantioselectivity (Scheme 1). Since the stability of the chiral center is crucial in subsequent applications, it was investigated in details applying O¹⁸-labelling technique (Scheme 2).



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

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