

Homogenous Catalysis for the Sustainable Valorization of Biomass

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Homogenous Catalysis for the Sustainable Valorization of Biomass

PhD Thesis

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August 2022

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To Amma

Preface

Around the world, small but clear-cut steps are taken to replace the fossil based economy to a more sustainable bio-circular economy based on renewable resources. The driving forces behind the green transition to bio-based economy are the global issue of climate change due to the harmful greenhouse gases, population growth, over dependency of many countries on fossil fuels, the need for countries for diversification of their energy sources. In this context, integrated biorefinery process that focuses on the sustainable production of biofuels/chemicals is considered as the most efficient approach for the valorization of biomass in a future sustainable bio-based economy.

The continued development of bio-based chemicals and fuels will lead to new feedstock demands, economic opportunities as well as new technologies development. The current level of research and industrial activity is very encouraging as a whole within the bio-based chemical targets wherein traditional sources of feedstock are replaced by biomass. Since, the sustainability aspects are not always clear if considered, therefore for future use, a true valuation is placed on biomass. The components of lignocellulosic biomass and other biomass components are valuable building blocks and we should utilize them in order to maximize the economic, environmental and social benefits of a variety of pathways to their use. It is essential upon us to identify the best apportioning of biomass to fuels/chemicals based on evaluation of requirements, best leading technology and the overall needs of the society. This will certainly help to employ a sustainable industry into the future.

In this context, catalysis is a unifying technology that play an important role in generating "drop- in" attractive especially in area of food and nutrition, flavors, cosmetics, pharmaceuticals, fine chemicals, lubricants, coatings, solvents, etc. Moreover, value-added chemicals with better performances are expected to grow considerably over the next coming years. In this regard, homogeneous catalysts emerges as a promising routes for the cost effective production of biofuels/chemicals viable for industry. Hence, the research towards this has a great potential. My PhD dissertation focuses on the benign method for biomass valorization using homogeneous catalysis as a tool and thereby gaining access to sustainable fuels/chemicals that might constitute an important partial solution for a swift green transition.

This thesis contains the results of the scientific research undertaken during my PhD studies at the department of chemistry, Technical University of Denmark (DTU). The research was carried out in the timeframe between June 2019–August 2022 under the supervision of Associate Professor Martin Nielsen and co-supervisor Associate Professor Susanne Mossin.

Kgs. Lyngby, 31-08-2022

Jalhithe Koranchalil

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I can't thank enough my parents, my Amma, grandmother, sisters and family members for their constant love, support and encouragement throughout my life. Extremely grateful for always believing in me. Without their support, it would have been impossible for me to complete my studies seamlessly. Also thanks to my cousins for cool advices and constant motivation. Last but not the least, I heartily thank my closest friends for the support and always being there in my hard and good times.

Abstract

Being the only sustainable hydrocarbon-based source, biomass plays an important role in our energy landscape and has the potential to have a negative carbon footprint. Gaining access to sustainable fuels and chemicals through biomass valorization can be considered as a formula for a swift green transition. Herein, I developed a benign method for converting biomass waste material to fuels and chemicals through the interplay between organometallic pincer catalyst and a Brønsted acid.

Homogeneous transition metal-based Ru-PNP complexes are well known for (de)hydrogenation reactions for small molecule transformation. However, PNP pincer complexes have never been reported for its activity under acidic conditions and here comes the novelty of my PhD project. I demonstrated that the right combination of Ru-PNP catalyst and a Brønsted acid is able to transform the biomass feedstock directly to GVL (gamma-valerolactone). GVL holds highly promising potential as a future biomass-derived sustainable fuel and feed compound in many chemical industries. It is therefore extremely attractive to directly convert biomass to GVL. However, such a transformation is elusive owing to the high complexity and relatively inert nature of biomass. In concise, low loadings of Ru-MACHO-BH allows for valorizing woody and starchy biomasses to GVL under mild conditions (30 bar H₂, 140 °C, H₃PO₄(aq), 24-72 hours) with yields ranging from 16-26 wt%. No chemical treatment or isolation is required for this gamechanging method and will represent the state-of-the-art for this transformation or for any transformations of biomass derived substrates for that matter. In addition to the raw biomass feedstock, we also investigated cellulose and hemicellulose as substrates to obtain insight into the underlying mechanisms and performances of the two main reaction pathways for the biomass.

Synthesis, characterization and some catalytic activities of a novel Ru-CNC pincer complex have also been demonstrated in the thesis as well. Exchanging the phosphorus arms with *N*heterocyclic carbenes results in a transition metal that is significantly more electron-rich to the extent that the metal-hydrido complex can deliver its hydrogen even under acidic conditions. Based on the preliminary results, this scenario opens for carrying out hydrodeoxygenation (HDO), CO_2 hydrogenation and several other transformations of potential substrates.

List of publications

- R. Padilla, S. Koranchalil, M. Nielsen,* Efficient and selective catalytic hydrogenation of furanic aldehydes using well defined Ru and Ir pincer complexes, *Green Chem.* **2020**, *22*, 6767-6772.
- R. Padilla,* S. Koranchalil,* M. Nielsen, Homogeneous Catalyzed Valorization of Furanics: A Sustainable Bridge to Fuels and Chemicals, *Catalysts* **2021**, *11*, 1371.
- S. Koranchalil, M. Nielsen,* Homogeneous catalytic direct conversion of biomass waste feedstock to gamma-valerolactone. *Manuscript in preparation*.
- S. Koranchalil, D. Lobo Justo Pinheiro, R. Padilla, M. Nielsen,* Homogeneous catalysis for the direct conversion of furfural to gamma-valerolactone. *Manuscript in preparation.*

List of abbreviations

- DHMF = 2,5-bis(hydroxymethyl)furan
- DMA = N,N-dimethylacetamide
- DMF = 2,5-dimethylfuran
- DMSO = dimethyl sulfoxide
- EMIM = ethyl-3-methylimidazolium
- GBL = γ -butyrolactone
- GC = Gas chromatography
- $GVL = \gamma$ -valerolactone
- HMF = 5-hydroxymethyl furfural
- HVA = γ -hydroxyvaleric acid
- LA = Levulinic acid
- LCB = Lignocellulosic biomass
- MTG = methanol to gasoline
- MTHF = 2-methyltetrahydrofuran
- MF = 2-methylfuran
- NMR = Nuclear Magnetic Resonance
- NHC = N-heterocyclic carbene
- PDO = 1,4-pentanediol
- PTSA = p-toluenesulfonic acid
- TPPS = tris(3-sulfonatophenyl)phosphane
- SDG = Sustainable Development Goal
- TGA = Thermogravimetric Analysis
- TMM = trimethylenemethane
- TON = Turn over number
- TOF = Turn over frequency

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1. Introduction

This chapter introduces the basic concepts of bio circular economy and the importance of biomass valorization in biorefineries, structural understanding of lignocellulosic biomass (LCB), biomass derived platform chemicals, catalysis, pincer complexes in homogeneous catalysis as well as examples of organometallic complexes in combination with acids. Finally, this chapter will outline the main objectives, scientific contents and the overall structure of the thesis.

1.1 The circular bio economy and biomass valorization

According to the latest report by Worldometer, the current world population is 8 billion as of 2022, and is estimated to be 10 billion in 2057.¹ This population growth results in pressing challenges on global issues to environmental problems and energy needs, which thereby affects the feasibility of reaching the UN Sustainable Development Goals (SDGs).² Disturbingly, environmental crises, such as climate change, global warming, waste disposal, depletion of non-renewable resources, have increased at an alarming rate over particularly the last three decades as a consequence of anthropogenic activities.³ For example, the extensive use of fossil fuels, which has been the resource of choice for most of our chemical and energy needs, not only causes depletion of non-renewable resources but also negatively impacts the release of greenhouse gases emissions.⁴⁻⁶

These global problems require imperative solutions where circular bio economy plays a pivotal role in which a low-/zero-carbon economy will contribute to resolving the major environmental crisis such as climate change through limiting global warming by 1.5 °C henceforth.^{7,8} The term bio circular economy is an integrated concept of both circular economy and bio economy.⁹ A circular bio economy focuses of efficient utilization of biomass waste and optimizing the value of biomass in terms of economic, environmental, and social aspects. This is achieved through a sustainable production of value-added products, such as food, bioenergy, and biomaterials.¹⁰ Improved resources and ecofriendly, lower greenhouse gases footprints, reduced dependence on fossil fuels, and valorization of waste into value-added products are the main advantages of circular bio economy.¹¹ Therefore, circular bio economy can be considered as a low-/zero-carbon economy as it exhibits potential development of a sustainable and greener environment.^{11,12}

Biorefining is one of the vital strategies of the bio based circular economy, and can be defined as sustainable processes that utilize biomass for the production of market products and metabolites.¹³ Moreover, waste biorefining receives much attention hence it deals with the waste management approach.¹⁴ In addition, biomass based solutions are of unique interest to the most challenging problems of expensive atmospheric CO₂ capture and storage.¹⁵ Biomass utilization constitutes an excellent strategy for indirectly removing CO₂ from the atmosphere. For this approach to have the maximal effect on atmospheric CO₂ removal, it requires that the biorefining processes focus on producing value-added commodities that can be used elsewhere

in the (chemical) industries. Simply producing green fuels comes with the caveat that the CO₂ quickly reenters the atmosphere. Biomass as fuel source has long been considered as carbon neutral to an approximation in the same way as emission free wind and solar (Figure 1.1, middle scenario).¹⁶ However, it can also stabilize a portion of carbon into chemicals and fuels (right scenario).¹⁷ In fact, it can be considered as the only perennial resource that has the potential to have a *negative* carbon footprint.¹⁷ Hence, biomass utilization should be prioritized to transform it to value-added compounds, be it for fuel or for fine-/bulk chemical industries.¹⁸



Figure 1.1: CO₂ cycles representing a negative carbon footprint with biomass valorization

In this context of biofuels and chemicals, biomass can be divided into mainly three categories such as first, second and third generation biomass. First-generation biomass includes edible biomasses that are composed of starchy carbohydrates, e.g. corn, wheat, sugarcane and barely. Fermentation process of these biomass yields bioethanol, one of the important drop-in biofuels.¹⁹ The main drawback of this type of biomass is the competition with the food resources. Non-food biomass, including byproducts and waste materials comes under second-generation biomass. Second-generation biofuels are produced from lignocellulosic biomass (wood, forestry residues, agricultural wastes such as wheat straw, rice husk, corn cob, sugarcane bagasse, industrial wastes such as paper sludge, grains from distilleries and urban wastes such as household and municipal solid waste).²⁰ The structural composition consists of cellulose, hemicellulose and lignin. Pretreatment is usually required for fermentation to biofuels and chemicals and the process is not economically viable due to the multistep process.²¹⁻²⁴ Finally, the third-generation biomass includes non-edible feedstock such as aquatic biomass (algae, micro-organisms). These feedstock contain unsaturated hydrocarbons to produce gasoline fuels or higher lipid content for biodiesel applications.²⁶ The economic challenges limits their industrial application considering the resource efficiency in processing.²⁷⁻²⁸

The availability of these biomass will play a vital role in recognizing the biggest driver for sustainability. Based on the recent report from the EU, the annual production of agricultural biomass was estimated at 956 Mt of dry matter of which food consumption covers 54% and 46% used for energy production or animal bedding.²⁹ Also, 80% of the agricultural biomass is used as

food and feed, which shows the limited potential of using the first-generation biomass for the production of fuels and chemicals.²⁹ In case of third-generation biomass, only 0.23 Mt of wet matter was estimated, which corresponds to 0.027 Mt of dry mass. On the contrary, an estimate of 18600 Mt of dry wait was reported for woody biomass, which makes more attractive as feedstock.²⁹ Greater than 18000 Mt of woody resources makes Europe competitive worldwide and further support sustainable processes. Moreover, the use of lignocellulosic residues will improve long-term sustainability of the industry, considering the availability volume and very lea impact on the food resources. In case growing population, the food and municipal wastes volume are high with an estimate of 61 Mt produced in Europe yearly.³⁰

In case of conversion strategies of biomass, the use of lignocellulosic biomass offer a promising alternative to the fossil-based industry. From the perspective of energy, lignocellulose has lower energy densities when compared to non-renewable resources such as coal, natural gas and oil.³¹ Conversion of biomass to platform molecules, e.g. ethanol, sugars, 2-methylfuran, hydrogenated products etc.) can provide biofuel diversification with several energy contents for various transport applications, including aviation/jet fuel. It can also offer potential feedstock in different areas in the chemical industries such as textiles, materials and pharmaceuticals, which is discussed later in this chapter.

In the Vision 2020 catalysis report by the US chemical industry report, one recommendation was to utilize renewable resources, e.g. cellulose and carbohydrates for the production of platform chemicals.³¹ It was expressed that the use of renewable raw materials should be increased by 13% until 2020. In addition, a platform for sustainable chemistry has been established by the EU demanding that 30% of the chemicals should come from the renewable resources by 2025.³² Some current biomass technologies have been criticized because of the low thermal conversion efficiencies, wherein a small part of the energy is converted into final fuel product.³³ Thus, the biofuels industry is practically in its infancy and, likely, advances in technologies and process integration will ultimately improve the overall economic efficiency and energy.

1.2 Lignocellulosic biomass

Lignocellulosic biomass (LCB) is an inexpensive and abundant feedstock and is composed of hemicellulose (23-32 wt%), cellulose (38-50 wt%) and lignin (15-25 wt%).³⁴ Figure 1.2 illustrates their chemical structures. The biomass fractions are generally isolated through pretreatment followed by hydrolysis. This include physical treatment such as milling, comminuting and steam whereas chemical methods involves acid or base hydrolysis. These are performed as a means of increasing the susceptibility of crystalline cellulose degradation. This objective is achieved by the pretreatment process by depolymerization of the lignin wall and extraction of the monomer units of corresponding polymers.³⁵

Hemicellulose (23% - 32%)



Figure 1.2: Chemical structures of lignocellulosic contents in biomass.

The hemicellulose fraction is an amorphous polymer that consists of different sugar monomers such as D-xylose, L-arabinose, D-galactose, D-glucose and D-mannose where xylose being the most abundant.³⁶ Depending upon the bond linkages and functional side groups as well as its abundance and distribution in plants, hemicellulose can be differentiated into xylans, mannas, mixed linkage beta-glucans and xyloglucans. Xylan in general contains β -(1,4) linked five carbon xylose monomers.³⁷ Pretreatment methods such as dilute acid hydrolysis produce xylose in good yield. In comparison with crystalline cellulose, the chemical treatment is very straightforward and yield high sugar yield. This is typically carried out by dilute H₂SO₄ acid hydrolysis.³⁸ Once extracted, the sugars can be used as a feedstock for the production of furfural via dehydration, one of the important platform chemicals.³⁹

Cellulose consists of linear chains of (1,4)-d-glucopyranose units linked 1–4 in the β configuration.⁴⁰ They are typically isolated along with hemicellulose and lignin which requires further hydrolysis step.⁴¹ Once isolated, further depolymerization of cellulose into glucose units is considered more difficult than analogous synthesis of xylose from hemicellulose. However, this can be achieved under harsher reaction conditions using mineral acids such as H₂SO₄ at elevated temperatures. Employing harsh reaction conditions favor the formation of degradation products such as hydroxymethyl furfural (HMF), levulinic acid (LA) and also insoluble humins.⁴² However glucose yield can be optimized through proper selection of acid concentration, temperature, and reaction time.⁴³

Lignin provides structural rigidity to the plant. It is an amorphous polymer which is composed of methoxylated phenylpropane units such as sinapyl alcohol, coumaryl alcohol and coniferyl alcohol.⁴⁴ Lignin surrounds the hemicellulose and cellulose, and one of the functions of pretreatment includes the depolymerization of lignin wall so as to access the carbohydrates fractions. Lignin as such can be isolated and used as a feedstock in the production of phenolic resins⁴⁵ and reports suggests the pyrolysis strategies can be utilized for bio-oils,⁴⁶ aromatics.^{47,48}

There are mainly three methods to convert biomass into platform chemicals/fuels (Scheme 1.1). The first method involves the biomass being treated at high temperature (pyrolysis) to produce either a mixture of hydrocarbons or syngas (gasification) using a heterogeneous catalyst.⁴⁹ This formed syngas can be further converted into alkenes by Fisher Tropsch (F-T) process or conversion to methanol and thereby to alkanes using known methanol to gasoline (MTG) technology.



Scheme 1.1: Conversion of lignocellulosic biomass

The second method is pretreatment wherein the lignocellulose is separated into three main components such as cellulose, hemicellulose and lignin. Then there is another method known as thermal decomposition or fermentation where biomass can be transformed into limited number of platform chemicals that can be further be used for the synthesis of other desired chemicals, mostly through catalytic conversions. The selection of these platform chemicals were done based on several factors such as the availability of technologies for its production, and its potential to be efficiently transformed into fuels and chemicals. Therefore, according to these set of criteria's the US department of energy include sugars (glucose, xylose), polyols (sorbitol, xylitol, glycerol), furans (furfural, 5-hydroxymethyl furfural) and acids (levulinic acid, succinic acid, lactic acid) as platform chemicals used in a biorefinery (Figure 1.3).⁵⁰



Figure 1.3: Platform chemicals derived from hemicellulose and hemicellulose

1.2.1 Lignocellulosic biomass to platform chemicals

Ethanol

Ethanol is the most abundant biofuel in the world and has been considered as an alternatives to gasoline and other transportation industries. The first- generation ethanol was commercially obtained from starch and sugar derived feedstock such as sugarcane and corn. The secondgeneration bioethanol is of great interest as it is obtained from lignocellulosic biomass. Enzymatic degradation methods are also employed to hydrolyze lignocellulosic components into simple sugars followed by fermentation to yield ethanol. There are numerous reviews available which describes the cost structure, process technologies and research needs.⁵¹⁻⁵⁸ Ethanol and other alcohols such as propanol and butanol are interesting precursors for the production of corresponding olefins via dehydration, building a bridge between biorefinery and petrochemical industries.⁵⁹ Ethylene production was carried out from ethanol at extremely high selectivity and conversion in a fluidized bed-reactor over activated alumina.⁶⁰ Vapor phase dehydration of ethanol to ethylene at 400 °C affords 99.5% conversion with 99.9% selectivity.⁶⁰ However, with the availability of cheap oil, the production of ethylene from ethanol was discontinued in favor of steam cracking processes. In Brazil, more recently, have announced projects to build ethanol to ethylene plants based on low-cost sugarcane.^{61,62} Ethanol can also undergo oxidation to commodity chemicals, e.g. ethanol oxidation to acetic acid is achieved over Au/TiO₂ or Au/MgAl₂O₄ with high selectivity and conversion.⁶³ Moreover, ethanol can also be oxidized over gold nano catalysts or Mo, V and Nb mixed oxides to afford acetic acid and ethyl acetate with high yield.^{64,65}

Furfural

The acid catalyzed hydrolysis of hemicellulose (xylan) in lignocellulosic biomass, yields C5 sugars known as xylose which then dehydrated further to furfural (Scheme 1.2).⁶⁶ Xylose can be hydrogenated into xylitol, which is wide applications in cosmetics and pharmaceutical industry.



Scheme 1.2: Xylose, furfural and derivatives.

Industrially, Raney nickel catalysts are mainly employed in hydrogenation reactions affording 98% yield.⁶⁷ However, the deactivation of the catalyst was the drawback due to the leaching of promoters and poisoning.⁶⁸ Later Ru/C catalysts were found to have higher activity than Raney nickel.⁶⁹ Reports suggests that employing Ru/SiO₂ and Ru/ZrO₂ 98% yield of xylitol was observed.⁷⁰ Industrial production of furfural is by the hydrolysis of agricultural/forestry wastes with concentrated sulphuric acid.⁷¹⁻⁷³ It is applied in the refining of lubricant oil, sand linker and as an important intermediate for the synthesis of furan, furfuryl alcohol, tetrahydrofuran, gamma-valerolactone. Acidic dehydration of xylose was achieved in biphasic system consisting of water/MIBK, yielding 85% furfural.⁷⁴ However, by using aqueous/toluene biphasic system over H-mordenite 98% yield was obtained.⁷⁵ Furfuryl alcohol is synthesized industrially is through furfural hydrogenation over Cu-Cr catalysts in the liquid or vapor phase.⁷⁶ However, there were many findings to have an alternative methods on using Cu-Cr catalysts. Thus, hydrogenation of furfural to furfuryl alcohol with 96.5% yield was obtained using Raney nickel impregnated with heteropolyacid salts.⁷⁷ Later Stevens reported a switchable system based on two fixed bed reactor with copper chromite and Pd/C catalysts for the hydrogenation of furfural and depending on the reaction conditions, furfural was selectively hydrogenated into furfuryl alcohol (97%), 2methyltetrahydrofuran (82%), 2-methylfuran (90%) and furan (98% yiled).⁷⁸ Ketone derivatives were achieved from furfural by aldol condensation.⁷⁹ Furfural was oxidized to fumaric acid by sodium chlorate with V₂O₅, which then subsequently hydrogenated to either succinic acid or 1,4butanediol selectively over Pd/C and Pd–Re/C catalysts respectively.⁸⁰

5-Hydroxymethyl furfural (HMF)

HMF and its derivatives are considered as an important platform chemical obtained by the catalytic conversion of C6 sugars (Scheme 1.3).⁸¹ HMF is obtained by the dehydration of fructose by solid acid catalysts or from glucose or even from cellulose by a multistep process.⁸²⁻⁸⁴ This resulted in a modest yield of HMF due to the formation of levulinic acid, formic acid and humins. In presence of a sulphated zirconia catalyst in a mixture of DMSO and acetone, 93.6% HMF was obtained with 72.8% selectivity.⁸⁵ A yield of 92% of HMF was obtained from fructose with H₂SO₄ in N,N-dimethylacetamide (DMA) solution using LiBr or KI additives.⁸⁶ The use of ionic liquids along with the catalysts gave higher yield from fructose,^{87,88} starch,⁸⁹ cellulose,^{90,91} and also from lignocellulose. 48% HMF was obtained from corn stover using ethyl-3-methylimidazolium chloride ([EMIM]Cl), LiCl₃ and HCl.⁸⁶



Scheme 1.3: Glucose, HMF, sorbitol and derivatives.

The hydrogenation of HMF yields 2,5-bis(hydroxymethyl)furan (DHMF), which is used in the manufacturing of polyurethane foams⁹² or 2,5-Dimethylfuran DMF. This is achieved using formic acid as a hydrogen donor using Ir or Ru complexes.⁹³ DMF was obtained with 95% yield by heating HMF in tetrahydrofuran in the presence of formic acid, H₂SO₄, and Pd/C catalyst.⁹⁴ Using a homogeneous catalyst RhCl₃ in a H₂O/toluene/HI mixture yielded 79% DMF.⁹⁵

Sorbitol, another important platform chemical which finds applications in food, pharmaceutical cosmetic industries and as a key intermediate in the synthesis of ascorbic acid (vitamin C).⁹⁶ It is industrially produced by the catalytic hydrogenation of glucose using Raney nickel catalysts.⁹⁷ Due to leaching issues, Ru/C were used in the continuous hydrogenation of glucose in a bed reactor.⁹⁸ Bach reaction using Ru on activated carbon yielded sorbitol in 99.7% yield.⁹⁸ Starch can be used for the synthesis of sorbitol as well, combining hydrogenation and hydrogenolysis steps on a on bifunctional Ru–HY catalysts, 95% yield was achieved.⁹⁹

Levulinic acid (LA)

At the industrial scale, biorefinery process was developed for the production of levulinic acid from hemicellulose and cellulose.^{100,101} Levulinic acid is another promising platform chemical which finds applications in fuel additives, oil additives, solvents, fragrances, pharmaceuticals.^{102,103} It is produced mainly from cellulose through acid dehydration via the formation of HMF. 61% of levulinic acid along with 82% formic acid was obtained from paper pulp using H₂SO₄ at 205 °C.¹⁰⁴ Using Lewis acid metal triflates together with Lewis acid assisted Brønsted acid complexes with phosphoric acid (In(OTf)₃/H₃PO₄) afforded the up to 75% yield from microcrystalline cellulose.¹⁰⁵ The production of levulinic acid from lignocellulosic feedstocks such as wheat straw and water hyacinth has been reported with 53% molar yield of levulinic acid.^{106,107}

γ-valerolactone (GVL)

In the past few years attention was highly focused on γ -valerolactone (GVL) obtained by hydrogenation of LA. GVL is a potential platform chemical, which can be synthesized directly from biomass derived products such as LA, furfural, and HMF, as well as via one-pot catalytic transformation of renewable sugars (cellulose, hemicellulose, glucose and xylose)^{108,109} or even direct production from real biomass. It is a five carbon cyclic ester with high boiling (~207 °C) and a low melting point (-31 °C).¹⁰⁹ Therefore, at ambient conditions, it is a colorless liquid which is stable in normal conditions and has low viscosity. The high polarity of GVL ensures its total miscibility with water.

The properties of GVL makes it both stable as well as reactive enough for the production of variety of compounds such as butane, valeric acid etc.¹¹⁰⁻¹¹³ GVL is mainly produced from LA through γ -hydroxyvaleric acid (HVA), which ring closes by intramolecular esterification and upon losing a water molecule produces GVL.¹¹⁴ Another possibility is through LA dehydration to angelica lactone followed by hydrogenation to GVL. In case of levulinate (esters), the reaction proceed in the same pathway as LA (Scheme 1.4).¹¹⁵



Scheme 1.4: Synthetic routes of GVL.

Moreover, it has been shown that it does not decompose, hydrolyze or form peroxides under ambient temperatures.^{116,117} These properties makes GVL a versatile platform chemical with wide varieties of applications (Figure 1.4). The combination of its relatively low vapor pressure even at high temperature and stability make it a promising solvent for organic synthesis.¹¹⁸ For e.g. it can be even used to solubilize lignocellulosic biomass.^{119,120} Furthermore, it is used as a green alternatives to hazardous solvents.¹²¹ The sweet, herbaceous odor is the main reason why it is been used for the production of perfumes and food additives.¹⁰⁹ Additionally, it is widely used in products such as nail paint, varnish, paints and coating removers.¹²²⁻¹²⁵ GVL can also be used as a monomer for polymer synthesis.¹²⁶ Yet another interesting application of GVL is its direct use as liquid fuel or as an additive current petroleum fuels. Horvath compared the mixtures

of 90 vol% convention gasoline with 10 vol% GVL or 10 vol% ethanol and observed that the mixture with GVL had a low vapor pressure, which improved the combustion at similar octane numbers.¹¹⁸ GVL has a similar combustion energy to that of ethanol (29.7 MJ kg⁻¹) and a higher energy density. An important problem using GVL as a pure fuel is its high solubility in water, however, water can be distilled off easily as GVL does not form azeotropic mixture.¹⁰⁹



Figure 1.4: Various applications of GVL.

 Ru/SiO_2 were employed for the continuous conversion of LA to GVL with 99% yield in supercritical CO_2 .¹²⁷ Another continuous hydrogenation of LA over Pt/TiO₂ or Pt/ZrO₂ catalysts afforded 95% yield over 100 hours.¹²⁸

GVL can further be hydrogenated for the production of fuel additives, such as 1,4-pentanediol (1,4-PDO), methyl tetrahydrofuran (2-MTHF) (Scheme 1.5). Leitner reported the hydrogenation of LA in presence of Ru catalyst and demonstrated that the selectivity can be tuned to different products such as GVL, 1,4-PDO or 2-MTHF depending upon the ligand modifications and additives used.¹²⁹ Thus, 1,4-PDO was obtained with the triphos ligand in 95% yield, 2-MTHF obtained in 92% yield upon using acidic ionic liquids.¹²⁹ GVL can also serve as a building block for the production of chemicals like butane, valeric acid and 5-nonanone.¹³⁰⁻¹³³ GVL is converted into pentanoic acid over Pd/Nb₂O₅ which is further ketonized over Ce-Zr mixed oxide to 5-nonanone.¹³⁴ This process can be further integrated to form gasoline-range C9 alkanes. This is performed by series of hydrogenation, dehydration and a second hydrogenation over Pd/Nb₂O₅ under 60 bar H₂ at 255 and 295 °C.¹³⁵



Scheme 1.5: Fuels and chemicals from GVL.

The homogeneous state-of-the-art examples for the hydrogenation of levulinic acid to GVL is discussed further in the Chapter 2. There are couple of examples where GVL is synthesized from sugars (C5 and C6) and polysaccharides (hemicellulose and cellulose) as well. A detailed discussion on such reported examples are addressed in Chapter 3 and 4 respectively.

1.3 Catalysis

Catalysis plays a very important role in producing fine-/bulk chemicals and fuels.¹³⁶ Now-a-days a wide variety of catalytic reactions have become indispensable. The term catalysis was first coined by Berzelius 150 years ago when he observed certain changes in substances that were brought in contact with minute amount of species called "ferments".¹³⁷ Later in 1895 Ostwald came up with a definition on catalyst that we follow now: "A catalyst is a substance that alters the rate of a chemical reaction by providing an alternative pathway with lower activation energy without itself undergoing permanent chemical change".¹³⁸ During a catalytic cycle a catalyst is bought in its active form and maybe present in serval intermediates. The number of times an active catalyst goes through a catalytic cycle is the turn over number (TON). That means he number of moles of substrate that a mole of catalyst can convert. Turn over frequency (TOF) is the TON per time. An organometallic catalyst consists of a central metal atom surrounded by ligands. The properties and activity is determined by the metal center and the ligands.¹³⁹ Important properties are the rate of the reactions and selectivity towards certain products.

Catalysis is mainly classified as homogeneous, heterogeneous and biological (enzyme) catalysis. It is estimated that 85% of all chemical processes are catalytically.¹⁴⁰ There are many homogeneously catalyzed processes that considerably contribute for producing bulk chemicals. For example, hydroformylation, carbonylation, hydrogenation, oxidation, hydrocyanation, and metathesis.¹⁴¹ The Ziegler-Natta catalyst (Ti and Zr) is well known for polymerization for the development of polyethylene, polybutene and other copolymers. Other important homogeneous

catalyst employed is in the Wacker's process using PdCl₂ for the oxidation of ethylene to acetaldehyde and Wilkinson's catalyst (Rh(PPh₃)₃Cl) for the hydrogenation of olefins. Also with fine chemicals that ensures high atom economies or E factors.¹⁴² Thus, for the green and sustainable production of chemicals are afforded by homogeneous catalysis rather than heterogeneous catalysis. Moreover, homogeneous catalysis overcome several potential drawbacks of heterogeneous catalysis such as lack of deeper understanding of reaction mechanism, selectivity, employing harsh reaction conditions. In homogeneous catalysis the reactants, products and catalyst remain in the same phase which makes it difficult for the separation. However, this challenge is made easy since the catalysts are unequivocally synthesized and characterized, the reaction kinetics are based on the active metal atom and because catalysts can be tailor-made upon designing with fine tuning the sterics and electronics as well. An important and striking advantage is that it is often possible to optimize homogenous catalysts step-by-step to solve a particular problem.

Combining the advantages of both homogeneous and heterogeneous catalysts there has been developments achieved by immobilizing homogeneous catalysts which have gained attention and developed into an important field in the catalysis research.^{143,144}

1.3.1 Pincer Catalysts in Catalysis

In 1976, Moulton and Shaw first discovered pincer metal compounds, which marked a new field in organometallic chemistry for the synthesis of a plethora of new metal complexes.¹⁴⁵ Over time such ligand scaffold complexes found large applications, particularly in homogeneous transition metal based catalysis. This ground breaking development has been achieved by their inherent physical and chemical properties that enable them robustness and stability even at higher temperatures. Pincer catalysts generally exhibits excellent catalytic activity even under mild reaction conditions, low catalyst loading with high atom efficiency and selectivity.¹⁴⁶ They serves as a very promising catalysts within sustainable chemistry.^{147,148} They have been particularly relevant for the activation of relatively inter molecules such as CO₂, and dehydrogenation reactions for energy production.

The structure of the ligand allows the multiple, creative modifications/tuning of the pincer arm. For example, the pincer arms can have different heteroatoms and functionalities. The first classical organometallic pincer complex is PCP (named according to the heteroatom of the pincer arm coordinate to its metal center).¹⁴⁹ There exists other pincer arms such as PNP, PNN, PCP, POP, SNS, CNC and CNN which resulted in the fully synthesized and characterized pincer complexes.¹⁵⁰⁻¹⁵⁴ Moreover, the variation of central atom for example N or Si has also resulted in the active metal ligand cooperation between pincer ligand and the metal center which lead to the discovery of non-innocent behavior of the pincer ligands. These observations helps to explore cheaper, abundant first row transition metals such as Mn, Fe, Co making the catalytic process green and sustainable. They have shown optimal activity in the field of hydrogen economy.¹⁵⁵⁻¹⁵⁹ Furthermore, the use of pincer complexes are applied for a wide series of chemical

transformations, for examples, olefination, hydroamination, hydrocarboxylation, hydrovinylation, aminomethylation, dehydrogenation of alkanes, alkane metathesis, N-formylation of amines, C-alkylation of secondary alcohols, α -alkylation of ketones, and alkylation of amines. In recent years an interesting discovery towards this was the participation of pincer complexes in biological systems as well.¹⁶⁰ The versatility of the pincer arm has also applications beyond catalysis for the development of sensors and mimicking biological systems.

Because of the wide applications of pincer complexes, especially for both hydrogenation and dehydrogenation, this work mainly focuses on the reactions utilizing PNP complexes of Ru which are generally known as Ru-PNP (Figure 1.5). The central metal atom is Ru which is in +2 oxidation state that is surrounded by tridentate ligand with two phosphorous donor arms and nitrogen bearing an amine proton. A spectator ligand, CO and two X-type ligand completes the octahedral geometry of the complexes. The ligands can be tuned by changing the sterics and electronics. For example, changing the substituents on the phosphorous atom can alter the reactivity and stability of the complexes in relation with the degree of electron density at the metal center. This also has an effect on the solubility of the complexes.



Figure 1.5: PNP Pincer complexes mainly used in the study

The Ru-MACHO was first developed in 2012 by Kuriyama for the hydrogenation of esters to alcohols and is patented by the Japanese company, Takasago International Corporation.^{161,162} Since then it was widely utilized for reactions such as transfer hydrogenation, other hydrogenation and dehydrogenations.¹⁶³ The same is true for the ⁱPr congener as well. Along with the catalytic studies of these complexes, several mechanistic investigation were also carried out.^{164,165} Hydrogenation reactions utilizing Ru-MACHO are normally base activated (Scheme 1.6). The activated complex acquires a square pyramidal geometry with a vacant coordination site.¹⁶⁶ In direct hydrogenation reactions the H₂ equilibrates between the amide ruthenium hydride form and amine ruthenium dihydride. A modified version of Ru-MACHO is the Ru-MACHO-BH which has a bohydride ligand instead of chlorido. The Ru-MACHO-BH has been shown to be thermally activated unlike with Ru-MACHO which usually requires base for its activation.¹⁶⁷ Both are commercially available and are extensively studied for hydrogenation and dehydrogenation addehydrogenation addehydrogenation and theydrogenation for hydrogenation and dehydrogenation reactions.¹⁶⁸⁻¹⁷³



Scheme 1.6: Base activation of Ru-MACHO

Participation of the ligand in bond activation reactions is called metal-ligand cooperation, i.e., the tridentate pincer motif, rather than behaving as an "innocent ligand", plays an active role which often involves profound, and reversible changes in the binding mode and electronics between the pincer ligand scaffold and the metal center. This was first demonstrated by Milstein and coworkers with a reversible de-aromatization/aromatization reactions of the pincer-metal (Figure 1.6).¹⁷⁴⁻¹⁷⁷ This opens into novel routes to catalytic bond activation of small molecules such as methane, N₂O and carbon dioxide. In this chemistry the metal-pincer group of the active catalytic species forms a template where the substrate is activated.



Figure 1.6: Demonstration of metal-ligand cooperation by Milstein.

The exceptional stability of PNP pincer ligands has inspired researchers to explore and expand by tuning different functional groups for harvesting new reactions. Beller reported the use of aliphatic PNP ligand for activation of various small molecules. The mechanistic involving aliphatic PNP ligands belong to the so-called Noyori-type pincer scaffold.^{178,179} The N-HO interaction depicted in the Scheme 1.7 activates the carbonyl functionality. The hydrogenation of carbonyl groups catalyzed by such complexes proceed through a concerted H⁺/H⁻ transfer to the substrate which is further followed by heterolytic cleavage of dihydrogen by the formed amido species.¹⁸⁰ This was further confirmed by the lost catalytic activity by replacing NH with an NMe group.¹⁸¹



Scheme 1.7: Simplified representation of catalytic cycle and transition state.

The use of pincer complexes for the biomass transformations is relatively new, however, they show promising performances and allowing the useful dehydrogenations, hydrogenation of esters, carboxylic acids and aldehydes at mild reaction conditions.^{182,183} In 2015, Beller screened various aliphatic PNP Ru and Ir complexes for the production of H₂ from biomass substrates such as cellulose, glucose, fructose, lignocellulose and cigarette filters (cellulose acetate).¹⁸⁴ Ru-MACHO was also shown to catalyze dehydrogenation of glycerol to obtain lactic acid.¹⁸⁵ Zhou reported an Ir-PNP trihydride complex for the hydrogenation of levulinic acid to GVL.¹⁸⁶ de Vries provided relevant contributions to the field of utilizing PNP pincer complexes for the transformation of various biomass derived substrates. For example, HMF into 2-hydroxy-3-methylcyclopent-2-enone (MCP) and to 1,2-cyclopentanediol.¹⁸⁷ In addition he also reported the activity of Ru-NNS complex for the selective hydrogenation of methyl levulinates.¹⁸⁸ Song made an important contribution in the field of biomass upgrading with first row transition metal pincer complexes, in particular with iron.¹⁸⁹

1.3.2 Organometallic complexes in combination with acids

The homogeneous one-pot direct transformations of bio based transformations remains elusive in literature. One of the important reasons is that the organometallic complexes, which can catalyse hydrogenation reactions under acidic environment, is very challenging due to the stability of complexes. However, they exists a very few examples of complexes that works under acidic environment. Figure 1.7 shows the reported organometallic complexes that are known to work under acidic conditions, which are utilized for catalysing different substrates. Fu reported the Ir bypyridine complexes (1) and investigated the stability of the complexes in strong acidic solution ($H_2SO_4(aq)$). Further they tested half sandwich Ir complexes to study the catalytic performance on acid hydrolysis of sugars and levulinic acid hydrogenation to GVL.¹⁹⁰ The direct conversion of fructose to GVL with a moderate yield was obtained using Shvo-catalyst (2) system combined with H_2SO_4 .¹⁹¹ Leitner reported a combination of Ru(acac)₃ and triphos ligand (catalyst formed *in-situ*) (3) that also shows activity under highly acidic conditions. The complexes were utilized for the transformation of biomass-derived substrates as well such as levulinic acid to GVL and beyond with acid additives such as p-TsOH and NH₄PF₆.¹⁹² Using the ruthenium(II)-complex [(Triphos)Ru(TMM)] (TMM = trimethylenemethane) (4) in the presence of HNTf₂, Leitner demonstrated the hydrogenation of CO₂ to methanol.¹⁹³

Metal PNP complex in hydrogenation catalysis in presence of a Brønsted acid has never been explored before. Nevertheless, there exist few examples on the use of pincer complexes, all of which are lutidine-based, that work under acidic conditions for hydrogenative purposes. For e.g. Schlaf introduced a couple of Ru NNN terpyridine complexes that are water and acid stable for the hydrogenation of aldehydes and ketones in sulfolane solution. In the presence of a dehydration co-catalyst triflic acid they directly convert 1,2-haxanediol to n-hexane and hexanol as well as glycerol to propane.¹⁹⁴ Later Goldberg reported an iridium pincer complex that catalyzes hydrogenolysis of 1,2-propanediol to n-propanol. (POCOP)IrH₂ in combination with trifluoromethanesulfonic acid 95% yield of n-propanol was obtained in aqueous dioxane at 125 °C under 7 bar H₂.¹⁹⁵ Recently Schlaf synthesized trans-[(2,9-dipyridyl-1,10-phenanthroline)(CH₃CN)₂Ru](OTf)₂ complex and tested for the hydrodeoxygenation of furfuryl alcohol and furfuryl acetate to 1,4-pentanediol and cyclopentanol in acid aqueous medium (triflic acid) at an elevated temperature (150–200 °C) and under 50 bar H₂.¹⁹⁶



Figure 1.7: Organometallic complexes that shows activity under acidic conditions.

However, there are no reports on using Noyori-type PNP pincer complexes as catalysts in the presence of Brønsted acid. Herein, I have shown the activity of PNP pincer complexes in presence of a Brønsted acid. This groundbreaking observations lead to explore important various transformations mainly within biomass valorization. Chapter 3-5 focuses on the study of biomass valorization into platform chemical, mainly GVL in a sustainable conditions utilizing the efficient activity of PNP pincer complex in acid, viable for industries. This eventually led me to succeed on the direct use of real biomass waste as feedstocks directly for such transformations.

1.4. Outlook and contents of the thesis

In this thesis, I have explored the homogeneous catalysis for the valorization of biomass for the production of fuels and chemicals within sustainable chemistry. This includes hydrogenation of biomass and biomass-derived platform chemicals using pincer complexes in combination with a Brønsted acid. My research findings describes here represents the first example biomass transformation to gamma-valerolactone (GVL) using homogeneous catalysis which holds highly promising potential as a future biomass-derived sustainable fuel and feed compound in many chemical industries

I have also explored the possibility of use of pincer PNP catalyst in combination with Brønsted acid. This will provides unprecedented insights to the previously undisclosed synergistic performance between a Noyori-type hydrogenation pincer catalyst and a Brønsted acid in cascade hydrogenation/protonolysis reactions, opening for a plethora of novel transformations.

Particularly, chapter 2 sheds light on the reaction mechanism in detail of all the steps involved in transforming biomass to GVL. This will provide a basic understanding and a background on the projects discussed in the following chapters. Chapter 3 describes the direct conversion of furfural to GVL using Ru-PNP complex in combination with either formic acid or phosphoric acid. Chapter 4 portrays the utilization of same combination of Ru-PNP with phosphoric acid for the direct transformation of sugars (C6 and C5) to GVL. The remarkable findings in this chapter paved the way to explore the real biomass feedstocks towards achieving the goal. Thus, chapter 5 discloses the direct valorization of woody and starchy biomasses. This ground-breaking direct route requires no chemical pretreatment or separation of the biomass waste and thus potentially saving energy tremendously in comparison with the existing thermochemical and hydrolysis-based approaches to produce fuels and chemicals from biomass.

Chapter 6 describes the synthesis and spectroscopic characterization of novel Ru-CNC pincer complex. This complex is found catalytically active for hydrogenation reactions under acidic and basic conditions. This project based on the new catalyst is in the developing stage. However, my very preliminary studies with some model substrates show the versatility of the catalytic system and is promising.

The confidentiality of the project in view of patent filing prevented prior publications of the scientific research results described herein. Appendices F-G includes manuscript drafts of the research results discussed in chapters 3 and 5 of the thesis that are currently in preparation and aiming to submit in high-impact factor journals. In addition, now that I have shown the feasibility of using PNP complexes in presence of acid, there will be openings for exploring plethora of transformations leading to several potential projects.

2. Mechanistic overview on the production of GVL from biomass

This chapter sheds light on the detailed reaction mechanisms of the transformations of biomass substrates to building block chemicals. Hence, this chapter will provide a background idea of the chemistry that are discussed in the chapters 3-5. This includes a complete reaction mechanism of hemicellulose, cellulose, glucose, fructose, furfural, HMF and LA towards the formation of GVL.

To obtain GVL, the lignocellulosic biomass should undergo a combination of cascade of events (Scheme 2.1). This mechanism can mainly be divided into two specific multistep cascade processes, one is the acid-mediated hydrolysis and the other metal catalyzed hydrogenation. This is achieved through an interplay of an acid and a metal catalyst. My catalytic system consists of a right combination of a pincer hydrogenation catalyst (Ru-MACHO-BH) and H₃PO₄(aq) as a Brønsted acid. This combination allows to integrate the myriad of cascade events of hydrolysis/isomerization/dehydration/rehydration/hydrogenation/lactonization. Herein, I will discuss the detailed mechanistic description adapted from literature preceding and relevant discussion of all steps from biomass to GVL.



Scheme 2.1: General mechanism on the production of GVL from cellulose and hemicellulose.

2.1 Cellulose to GVL

Cellulose is chemically very stable molecule formed by several glycosyl units linked through 1,4glycosidic bonds in linear fashion. Hydrogen bonds and van der Waals bonds combine them together, which, provide high mechanical strength.¹⁹⁷ Due to the presence of hydrogen bonds, the hydrolysis is significantly hard than the hydrolysis of hemicellulose. Hydrolysis even becomes harder in case of crystalline cellulose. At present, the commonly used catalysts for hydrolyzing cellulose to glucose are acid, alkali, cellulose and metal ions.^{198,199} A general reaction through which an acid decomposes cellulose is shown in Scheme 2.2.^{200,201}



Scheme 2.2: Acid catalyzed reaction mechanism of cellulose degradation to glucose

The acid transfers a proton to water forming hydronium ions, which transfers the proton to cellulose, initiating the chain scission. According to Brønsted-Lowry acid–base theory,²⁰² the acid can easily transfer its proton directly to cellulose, however since the polarity of water is high, it acts as a better proton acceptor than cellulose. The proton shares its electron density with the oxygen in the cellulose followed by addition of water molecule, subsequently breaking the glycosidic linkage. It is to note that one water molecule is consumed during the chain scission while one H⁺ ion is recovered. According to this proposed reaction mechanism, the cellulose degradation depends on both the concentration of water and on the concentration of protons.

The next step towards the formation of GVL is the isomerization of glucose to fructose. Scheme 2.3 shows the proposed mechanism by Qian for the isomerization of glucose to fructose.²⁰³ This proposed mechanism is in line with the experimental literature preceding.^{204,205} The Brønsted acid catalyzed isomerization initiates with the protonation of C2 oxygen followed by the breakage of the C-O bond and the formation of 5-membered ring structure. During this step, simultaneously the C1-O bond breaks leaving a carbocation outside the cyclic structure. This is followed by the transfer of H to C1 (1,2 hydride shift) to form a secondary carbocation, which is stabilized by the neighboring oxygen in the ring. Finally, fructose is formed by the attack of water molecule to the carbocation.



Scheme 2.3: Reaction mechanism of glucose isomerization to fructose

The fructose so-formed should then undergo dehydration to HMF. Scheme 2.4 shows the mechanism of dehydration of fructose catalyzed by acid.^{206,207} Formation of HMF easily occurs from fructose by cyclic intermediate enol formed in the tautomerization step.²⁰⁸ The proposed mechanism is initiated by the protonation of the basic hydroxyl group of fructose. The protonation then leads to dehydration, which forms the intermediate enol. Enol subsequently undergo rearrangement followed by losing another molecule of water. Further, through

deprotonation HMF is formed. Guan used DFT methods to validate that the first dehydration reaction was the limiting step, whereas the other two dehydration steps are exothermic and occurs easily.²⁰⁹ The second dehydration was initiated from the carbonium ion and occurs through hydride shift and proton transfer process. The presence of water accelerates the proton transfer, while excessive water can cause side reactions. Caratzoulas through quantum chemistry calculations stated that the rate-determining step in the entire steps was the hydride shift before the third dehydration.²¹⁰ Zhang made the use of isotope tracking and *in-situ* NMR in order to study the dehydration mechanism of fructose in DMSO. He found that, after the dehydration reactions, the C1 and C6 carbons in fructose were retained in the HMF, which was consistent with the fructose dehydration pathway proposed.²¹¹



Scheme 2.4: Acid catalyzed reaction mechanism of fructose dehydration to HMF

The HMF so-formed in the presence of acid medium subsequently undergo ring-opening to form levulinic acid (LA). A proposed rehydration mechanism for this transformed is shown in the Scheme 2.5.^{212,213} Hydration of HMF occurs through the addition of a water molecule to the C2-C3 olefinic bond of the furan ring, leading to an unstable tricarbonyl intermediate, which quickly decomposes to LA and formic acid (HCOOH) in stoichiometric amounts.²¹⁴



Scheme 2.5: Acid catalyzed reaction mechanism of rehydration of HMF to LA.

2.2 Hemicellulose to GVL

The first step of the biomass conversion process is the Brønsted acid catalyzed hydrolysis. The hydrolysis mechanism of glycosidic bonds in hemicellulose is similar to that of cellulose (Scheme 2.6).²¹⁵ During the hydrolysis, H⁺ and water together work in breaking the C-O bonds in the β -1,4-glycosidic linkage and in the pyranose ring of xylan forming xylose monomers. The steps

consists of protonation of oxygen atom, cleavage of C-O bond by subsequent attack of water molecule. This process continues until the complete cleavage of all glycosidic bonds leaving behind only monomeric C5 sugars, where the cleavage of glycosidic bond is the rate-limiting step.



Scheme 2.6: Reaction mechanism of xylan depolymerization to xylose.

Now, the so-formed C5 sugars (xylose) undergo dehydration reaction with removal of three water molecules in the presence of protons as illustrated in the Scheme 2.7. It is important to mention that, both hydrolysis and dehydration reactions are parallel reactions.²¹⁶



Scheme 2.7: Reaction mechanism of xylose to furfural.

Furfural to LA reaction mechanism can be divided into two major steps. The first step is the hydrogenation of furfural to furfuryl alcohol catalyzed by a metal complex and second one is the rehydration of so-formed furfuryl alcohol to levulinic acid. The mechanism of the latter one is illustrated in-detail in the Scheme 2.8.²¹⁷ The reaction is initiated by the protonation of the hydroxyl group of furfuryl alcohol and subsequent removal of a water molecule, which is further followed by the subsequent addition of water. Finally, the formed intermediate undergoes acid catalyzed dehydration to form en-diol, which then tautomerize to LA.



Scheme 2.8: Reaction mechanism of furfural to LA

The LA formed from both cellulose and hemicellulose undergoes hydrogenation using a metal catalyst to produce GVL. A metal complex used in the studies is an organometallic pincer
complex, Ru-MACHO-BH. A general mechanism reported for Ru-MACHO-BH for hydrogenation reactions is through the reversibility between the hydrogenation and dehydrogenation of the complex and its amido intermediate⁶¹ (Scheme 2.9). The precatalyst is thermally activated by the borane dissociation. The free dihydride complex (1) is now the active species. In the proposed mechanism described by described by Z. Wei, and H. Jiao,⁶² the first step is the hydrogenation of aldehydes into alcohol, by a simultaneous transfer of the hydride from the metal center and the proton from the nitrogen ligand resulting in the formation of the amido complex (2). Finally, the amino complex is regenerated from the amido complex by the addition of dihydrogen.



Scheme 2.9: General mechanism for the hydrogenation of aldehydes using Ru-MACHO-BH

After the hydrogenation of the carbonyl functionality of the LA, the intermediate, 4hydroxylvaleric acid (HVA) that is formed, immediately undergoes cyclization finally to obtain GVL as the end product (Scheme 3.0).



Scheme 3.0: General mechanism for the formation of GVL from LA.

The up-coming chapters deals with the production of GVL from furfural, C6 and C5 carbohydrates, cellulose, hemicellulose and from biomass waste (sawdust, wheat straw) as well as from starchy biomass such as potato flour and rice grains through the synergistic mechanism of Ru-MACHO-BH and $H_3PO_4(aq)$.

3. Direct conversion of furfural to gamma-valerolactone catalyzed by Ru-PNP complexes in acidic aqueous medium

3.1 Introduction

Modern society is in need for an energy-efficient and economical process for the sustainable production of fuels. This is as a result of current challenges such as growing energy demand due to the global population growth, dependence of non-renewable resources, high oil prices and various environmental crisis due to increased CO₂ emissions. Therefore it is important to develop an alternative sources for the production of fuels and chemicals.

The first generation fuels is mainly derived from sugarcane, corn, wheat etc. has been criticized for several reasons for e.g. the impact on food prices, biodiversity and also due to the fact that they are not cost competitive with existing fossil fuels without subsidies. On the other hand the use of lignocellulosic biomass, which are non-edible to produce the so-called second generation fuels overcomes the before mentioned drawbacks and are found to be beneficial from geopolitical and environmental perspectives. In this scenario, the use of lignocellulose for the sustainable production of fuels and chemicals appears to be the most attractive and promising feedstocks.²¹⁸⁻²²⁵

In this context, furfural has recently been highlighted as one of the top value added chemical derived from biomass.²¹⁹ The fossil based synthesis of furfural is through catalytic oxidation of 1,3-dienes, which is a non-sustainable and economically non-competitive. At present furfural is commercially produced through the acid catalyzed transformation of pentosane sugars (C-5 polysaccharide). Polysaccharides firstly undergo hydrolysis in presence of H_2SO_4 to monosaccharides, mainly xylose, which then subsequently dehydrated to furfural (Figure 3.1)



Figure 3.1: Acid catalyzed transformation of xylan to furfural

However, there exists major drawbacks for the production of furfural which includes relatively low yields resulting from the undesired side reactions. Furfural can undergo polymerization reaction through condensation forming unwanted insoluble humins, resinfication, and decomposition as well.²²⁶⁻²³⁰

Furfural is a hetero aromatic furan ring with an aldehyde functional group. The aromatic character of the ring and its polarity provide furfural a good solvent selectivity as one of the main applications. It is partially soluble in both highly polar and non-polar solvents.²²⁶ The chemical reactivity is mainly governed by two functional groups such as aldehyde group and furan ring. Hence, furfural can undergo numerous reactions like acylation, acetalisation, condensation, oxidation, reduction etc.

Furfuryl alcohol is the most important platform chemical derived from furfural with a broad spectrum of applications in the industry. The relevant chemicals that can be obtained through hydrogenation reactions are depicted in Figure 3.2.



Figure 3.2: Important applications of furfural hydrogenation reactions

Among these important chemicals, GVL is emphasized a versatile chemical with wide variety of applications. GVL is used as liquid fuel additives in food, intermediate in fine chemical synthesis, green solvent, and building block for polymers.²³¹⁻²³⁵ The production of GVL from furfural involves multistep process notably through a right combination of acid and hydrogenation catalyst (Scheme 3.1). Firstly, furfural undergoes hydrogenation to furfuryl alcohol in presence of a metal catalyst and hydrogen. Furfuryl can be subsequently transformed into levulinic acid (LA) in presence of aqueous acid media and final conversion of LA with metal catalyst and molecular hydrogen (H₂) produces GVL.²³⁶⁻²³⁹



Scheme 3.1: Route for the production of GVL from Furfural

The development of environmentally benign, cost efficient processes for the synthesis of GVL has received extensive attention, and several routes using different catalysts and hydrogen sources for the reduction of levulinic acid have been developed in recent years. Thus, hydrogenation of levulinic acid to GVL has been performed using and homogeneous metal catalysts at relatively low temperatures and pressures.²⁴⁰⁻²⁴⁴ Important among them are: Zhou employed an iridium trihydride pincer catalyst to obtain a TON of 71000 at 100 °C. But a high pressure was required (100 bar) with the addition of 1.2 equivalent of base.²⁴⁵ Another iridium catalyst reported by Fu obtained an impressive TON of 78000 under additive free conditions at 120 °C and 10 bar H₂.²⁴⁶ An iron based pincer complex reported by Song can efficiently catalyze the hydrogenation of levulinic acid and methyl levulinate into GVL achieving a high TON as well (TON= 23000).²⁴⁷ Nielsen reported the conversion of neat alkyl levulinates to γ -valerolactone with low catalyst loadings (0.05-0.01 mol%) of either PNP Ru or Ir complexes, respectively.²⁴⁸

In order to make this process economically viable, alternative process has to be developed for the direct production of GVL that doesn't involve any intermediate isolation and purification. Every single step have been separately studied and explored²⁴⁹⁻²⁵¹ however, a one pot homogeneous system that directly transform furfural to GVL under mild reaction conditions remains elusive in the literature.

The direct conversion of furfural to GVL has been mainly achieved by hydrogenation methodologies using heterogeneous catalysis. For instance, Jae reported a one-step process for the conversion of furfural to GVL using a bifunctional Sn-Al-Beta zeolite which possess Lewis and Brønsted acid sites. A GVL yield up to 60% was obtained at 180 °C in 2-butanol.²⁵² Melero utilized a Zr-Al-Beta zeolite and a one pot conversion to GVL has been achieved with 22.6% yield at 170 °C after 24 hours using 2-propanol as H-donor.²⁵³ Another example for the integrated conversion of furfural with 2-propanol to GVL over Au/ZrO2 with ZSM-5 was reported by Fan. He employed different acid catalysts in which ZSM-5 yielded 80.4% GVL at 120 °C after 24 hours with good selectivity.²⁵⁴ Recently Hu reported the direct conversion of furfural to GVL with a yield of 90.5% via consecutive hydrogenation and acid catalyzed reactions over CuAl and H-ZSM-5 in ethanol. The reaction could be run at 120 °C but a high pressure of hydrogen was required (50 bar).²⁵⁵ Heterogeneous catalysts are interesting for their easy separation and operating under continuous flow, but there are several drawbacks such as low selectivity, low activity and require harsh reaction conditions. One solution to address this is by homogeneous catalysis. There is only one example of homogeneous catalysis for the ring opening of furfural, however the reaction stops at levulinic acid with 42% yield using arene-Ru catalyst in presence of formic acid at 100 °C after 8 hours.²⁵⁶ The direct and selective conversion of furfural is challenging due to undesired side reactions in presence of acid medium.²⁵⁷⁻²⁵⁹ Moreover, to the best of our knowledge a homogeneous catalytic direct furfural hydrogenation to GVL remains elusive in the literature.

2.2 Results and Discussion

In this study I show the effective and direct conversion of furfural to GVL under mild reaction conditions using low catalyst loadings of PNP pincer complexes. PNP pincer complexes are known for their robustness and efficacy in catalyzing both dehydrogenation as well as hydrogenation reactions.²⁶⁰⁻²⁶⁴ However, they are generally known to work under either base²⁶⁵⁻²⁶⁸ or additive free conditions.²⁶⁹⁻²⁷³ Here, we show the activity of PNP pincer complex (Ru-MACHO-BH) in acidic medium (H₃PO₄) for the direct synthesis of GVL from furfural through a one-pot sequence of hydrogenation, hydrolysis, and a second hydrogenation (Scheme 3.2).



Scheme 3.2: Direct conversion of furfural to GVL

I have commenced the studies by testing the furfural conversion with the well-known PNP complexes Ru-MACHO and its ^{*i*Pr}PNP congener (Ru-1). Being a reductant, formic acid²⁷⁴⁻²⁷⁶ was initially used as the acid additive. As a note, using excess acid may lead to humins formation from furan derivatives.²⁷⁷ The yield is determined by GC using 1,4-dioxane as the internal standard.

The initial reaction with 0.2 mol% of Ru-MACHO or its ^{*i*Pr}PNP congener with 2 M formic acid under 20 bar of H₂ in 3:7 v/v EtOH/H₂O, afforded full conversion of furfural. However, the reaction stopped at LA after 18 hours at 100 °C (Appendix A, Table A1). Increasing the H₂ pressure to 30 bar and using water as the sole solvent, led to no significant changes (Appendix A, Table A1). Gratifyingly, when employing Ru-MACHO-BH in 3:7 v/v EtOH/H₂O led to full conversion of furfural within 18 hours with 34% of GVL (Table 2.1, Entry 1). Some unreacted LA was still detected. Increasing the amount of formic acid concentration to 4 M improved the GVL yield to 46% (Entry 2). Changing the EtOH/H₂O ratio to 1:1 resulted in no significant change in the yield (Entry 3). To probe for the effect of catalyst loading on the production of GVL from furfural we tested the reaction with different catalyst loading of Ru-MACHO-BH ranging from 0.2 to 2 mol% with 4 M formic acid under similar reaction conditions (Entries 3-6). Merely 10% yield was obtained with 2 mol% catalyst loading, while with 1 and 0.5 mol% the yields were 27% and 48%, respectively. With the higher catalyst loading, furfuryl alcohol was observed as the major product along with a formation of methanol. These observations suggest that the formic acid itself is hydrogenated to methanol, which was confirmed by a blank reaction performed with Ru-MACHO-BH and formic acid under similar reaction conditions in the absence of furfural (Appendix A, Table A2 and Figure A9). Therefore, in order to selectively obtain GVL 0.2 mol% catalyst loading was found optimal. I then studied the effect of formic acid concentration on the yield of GVL. Thus, when increasing the acid concentration from 2 to 8 M in the presence of 0.2 mol% Ru-MACHO-BH, the initial reaction rates dropped significantly. Thus, the reaction yielded only LA with 8 M formic acid compared to the 34% of GVL when using 2 M formic acid. This suggests higher acid concentration has a negative effect on the catalyst activity might be due to the degradation of catalyst in presence of high acid concentration. (Appendix A, Table A2).

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	Furfural	Ru-MACHO-BH : <u>OOH, EtOH/H₂O</u> par H ₂ , 100 °C, 18 h	GVL GVL H N Ph ₂ Ru-MACH	—РРh ₂ й—СО Н ВН ₃ НО-ВН
Entry	Ru-MACHO-BH (mol%)	HCOOH [M]	EtOH/H ₂ O v/v ratio	GVL yield [%] ^[a]
1	0.2	2	3:7	34
2	0.2	4	3:7	46
3	0.2	4	1:1	48
4	0.5	4	1:1	48
5	1	4	1:1	27
6	2	4	1:1	10
7	-	4	1:1	0

Standard reaction conditions: Furfural (0.90 mmol), 30 bar H_2 at 100 °C in 18 hours. ^[a]Determined by GC-FID using 1,4-dioxane as the internal standard.

Table 3.1: Furfural hydrogenation to GVL using formic acid

Replacing formic acid to the other acid additives oxalic acid or PTSA resulted in either no conversion of furfural or in LA as the sole product (Appendix A, Table A4). Interestingly, with $H_3PO_4(aq)$ the catalytic hydrogenation of furfural exhibited surprisingly good GVL yield of 72% with 0.5 mol% catalyst loading in 1:1 v/v EtOH/H₂O after 18 hours (Table 2.2, Entry 1). Increasing the catalyst loading to 2 mol% results in a gradual decrease in the GVL yield using 3.8 M $H_3PO_4(aq)$ (Entries 1-3) . Under similar conditions albeit with using ethanol as the sole solvent, the reaction afforded 80% yield of GVL when using 0.5 mol% of the Ru-MACHO-BH. The considerably lower yields observed in the presence of EtOH/H₂O mixtures may be due to humins formation, which

is more favoured in presence of water. Thus, further optimizations were carried out in EtOH. Using 1 mol% catalyst loading under similar reaction, in EtOH the reaction achieved good yield of 68% and 83% of GVL respectively with 1.9 M and 3.8 M $H_3PO_4(aq)$ (Entry 5 and 6). The performance of other PNP Ru complexes, such as Ru MACHO and its iPrPNP congener (Ru-1), was evaluated as well. Both the catalysts work in presence of $H_3PO_4(aq)$ towards hydrogenating furfural to GVL, but their activities are inferior to Ru-MACHO-BH (Entry 6 vs Entries 8 and 9).

$ \begin{array}{c} \text{Ru-PNP} \\ \text{Ru-PNP} \\ \text{H}_{3}\text{PO}_{4}, \text{EtOH/H}_{2}\text{O} \\ \text{Optimum} \\ \text{Optimm} \\ \text{Optimum} \\ $					
	Furfural	30 bar H ₂ , 80	GVL		
Entry	Catalyst (mol%)	H ₃ PO ₄ [M]	EtOH/H ₂ O v/v ratio	Time [h]	GVL yield [%] ^[a]
1	Ru-MACHO-BH (0.5)	3.8	1:1	18	72
2	Ru-MACHO-BH (1)	3.8	1:1	18	73
3	Ru-MACHO-BH (2)	3.8	1:1	18	63
4	Ru-MACHO-BH (1)	1.9	1:1	18	56
5	Ru-MACHO-BH (1)	1.9	EtOH	18	68
6	Ru-MACHO-BH (1)	3.8	EtOH	18	83
7 ^[b]	Ru-MACHO-BH (1)	3.8	EtOH	18	84
8	Ru-MACHO (1)	3.8	EtOH	18	58
9	Ru-1 (1)	3.8	EtOH	18	75

Standard reaction conditions: Furfural (0.90 mmol), 85 w/w% H_3PO_4 , EtOH (1 mL), 30 bar H_2 . ^[a]Determined by GC-FID using 1,4-dioxane as the internal standard. ^[b]120 °C.

Table 3.2: Furfural hydrogenation to GVL using phosphoric acid.

I then evaluated the influence of various catalytic parameters such as catalyst loading, temperature, concentration of acid and reaction time on the GVL yield. For the catalytic reactions with low catalyst loading (0.2 mol%) and low concentrations of $H_3PO_4(aq)$, the hydrogenated intermediate LA was also observed along with the GVL. With higher catalyst loadings (0.5 or 1 mol%), full conversion of furfural was achieved with high yields of 80% and 83% of GVL, respectively, with 3.8 M $H_3PO_4(aq)$ in ethanol at 100 °C under 30 bar of H_2 in 18 hours. With decrease in the catalyst loading to 0.2 mol% and under similar reaction condition a comparatively low yield of 67% was obtained (Figure 3.3a). Secondly, the effect of temperature was tested on the reaction kinetics by performing the reactions at different temperatures (120 °C and 80 °C). Thus, 80% yield was obtained using 1 mol% catalyst loading and 3.8 M $H_3PO_4(aq)$ after 7 hours compared to 84% after 18 hours. At lower temperature (80 °C) I observe no GVL, which suggests

that Ru-MACHO-BH requires a minimum temperature to be catalytically active for hydrogenation (Figure 3.3b). It is noteworthy to mention the effect of acid concentration on the yield of GVL. It is observed that the optimal concentration of $3.8 \text{ M H}_3\text{PO}_4(aq)$ is required for the maximum GVL yield using 1 mol% catalyst loading at 100 °C under 30 bar of H₂ after 18 hours. A high (7.9 M) and low (1.9 M) concentration resulted in a decreased yield showing that an optimum acid concentration is detrimental for catalytic activity (Figure 3.3c).



Standard reaction conditions: Furfural (0.90 mmol), 85 w/w% H_3PO_4 , EtOH (1 mL), 30 bar H_2 . Yields determined by GC-FID using 1,4-dioxane as the internal standard.



The catalytic system was also evaluated at shorter reaction times. Thus, using 1 mol% catalyst loading and 3.8 M of $H_3PO_4(aq)$ the reaction afforded full conversion with 84% GVL after 7 hours. The remaining loss of yield is likely due to formation of humins. Further lowering the reaction time to 5 hours a low yield was obtained (68%) where the unreacted LA as the major product (Figure 3.3d).

In-depth studies on the effect of concentration along with different catalyst loading was studied with lower reaction time (7 hours). I observe that further increase or decrease in acid concentration led to a low yield, which follows the same trend as observed with the longer reaction time (18 hour). Hence, with 0.5 and 0.2 mol% catalyst loading with 3.8 M H₃PO₄(aq) 64% and 9% yields, respectively, were obtained (Table 3.3, Entries 1 and 3). The low yield suggests an incomplete reaction, with furfuryl alcohol and LA as the major products. Moreover, the effect of concentration of furfural in EtOH was investigated with 1 mol% of Ru-MACHO-BH by using 0.90 mmol of furfural and 30 bar H₂ at 100 °C in EtOH volumes ranging from 0.5-2 mL using 3.8 M H₃PO₄(aq). A drop in the yield of GVL was observed affording 64% and 54%, respectively, with 0.5 and 2 mL of EtOH (Table 3.3, Entries 5 and 6), showing that a concentrated solution is slightly detrimental for catalytic activity. The effect of catalyst loading along with acid. Same trend is observed at longer reaction time (18 hours) and high reaction temperature (120 °C).

Entry	Catalyst (mol%)	H_3PO_4 [M]	EtOH/H ₂ O v/v ratio	Time [h]	GVL yield [%] ^[a]
1	Ru-MACHO-BH (0.2)	3.8	EtOH	7	9.2
2	Ru-MACHO-BH (0.2)	5.7	EtOH	7	27
3	Ru-MACHO-BH (0.5)	3.8	EtOH	7	64
4	Ru-MACHO-BH (0.5)	5.7	EtOH	7	48
5 ^[b]	Ru-MACHO-BH (1)	7.5	EtOH	7	64
6 ^[c]	Ru-MACHO-BH (1)	1.9	EtOH	7	54
7 ^[d]	Ru-MACHO-BH (1)	3.8	EtOH	18	83

Standard reaction conditions: Furfural (0.90 mmol), 85 w/w% H_3PO_4 , EtOH (1 mL), 30 bar H_2 . ^[a]Determined by GC-FID using 1,4-dioxane as the internal standard. ^[b]2 mL of EtOH, ^[c]0.5 mL of EtOH, ^[d]10.2 mmol Furfural in 10 mL EtOH.

Table 3.3: Furfural hydrogenation to GVL using H₃PO₄

I then scaled up to 1 g of furfural using 1 mol% of Ru-MACHO-BH with 3.8 M $H_3PO_4(aq)$ at 100 °C and 30 bar H_2 (Entry 7). After 18 hours, 46% of GVL was isolated after the treatment with sodium carbonate to remove phosphoric acid followed by extraction with ethyl acetate. The isolated yield has to be improved further with other extraction method such as distillation to avoid the loss of yield during solvent extraction. However, the GC yield of 83% represents that the reaction is reproducible in larger scale as well.

A general mechanism reported for Ru-MACHO-BH for hydrogenation reactions is through the reversibility between the hydrogenation and dehydrogenation of the complex and its amido intermediate²⁷⁸ (Scheme 3.3). The precatalyst is thermally activated by the borane dissociation. The free dihydride complex (1) is now the active species. In the proposed mechanism described by described by Z. Wei, and H. Jiao,²⁷⁹ the first step is the hydrogenation of aldehydes into

alcohol, by a simultaneous transfer of the hydride from the metal center and the proton from the nitrogen ligand resulting in the formation of the amido complex (2). Finally, the amino complex is regenerated from the amido complex by the addition of dihydrogen.



Scheme 3.3: General mechanism for the hydrogenation of aldehydes using Ru-MACHO-BH

Preliminary NMR studies were also conducted to corroborate the stability of Ru-MACHO-BH in presence of phosphoric acid. ¹H NMR and ³¹P NMR of the catalyst were recorded with phosphoric acid (Appendix A, Figure A10-A13). The usual triplet of Ru-H in ¹H NMR suggests that the catalyst is stable in phosphoric acid even after 24 hours. However, I could not perform an in-depth mechanistic studies on the synergistic behavior of catalyst and acid during my PhD studies. I believe the mechanistic studies would be extremely important to understand the undisclosed or unexplored behavior of PNP catalyst in acid, opening an undiscovered plethora of transformations.

2.3 Summary

I demonstrate an efficient route for the direct conversion of biomass derived furfural to GVL under mild and sustainable reaction conditions. Using low loadings of Ru-MACHO-BH in presence of H₃PO₄(aq) allows the unprecedented homogeneously catalyzed transformation of furfural to GVL in 84% yield at 100 °C after 7 hours. To the best of my knowledge, this work represent the first homogeneous catalytic system that convert biomass derived furfural directly to GVL.

The influence on GVL yield of various catalytic parameters such as catalyst loading, temperature, substrate/acid concentration, reaction time was also evaluated. The GVL yield here represents the maximum optimized yield that I could obtain and cannot be further improved due to the formation of humin byproducts that cannot otherwise avoided under acidic reaction conditions. Moreover, the system is comparable and reproducible even in large scale (up to 1g).

Finally, my findings corroborate the novel catalytic power of the synergistic interplay between a PNP pincer catalyst and a Brønsted acid that opens new opportunities within homogenous

catalytic hydrogenation. Based on the results discussed, the right combination of a PNP catalyst and a Brønsted acid is crucial as the catalysts are intolerant to high acidic environment which can otherwise undergo catalyst degradation or deactivation. Therefore it is important to study the synergistic mechanism between Ru-PNP and phosphoric acid to have a better understanding of this unexplored field within pincer chemistry. Unfortunately, during my PhD I couldn't explore the in-depth mechanistic studies which would be in future carried out in Nielsen's lab.

Based on these results it is possible to envision other potential biomass substrates or even real biomass as a feedstocks for such transformations. For example, moving a one step backward to C6 or C5 sugars or two steps backward to polysaccharides (cellulose and hemicellulose) and/or finally utilizing real biomass waste as feedstocks (see Chapter 4 and 5).

4. One-pot catalytic conversion of carbohydrates directly to GVL

4.1 Introduction

Within the context of bio-based economy, lignocellulosic biomass as a renewable feedstock for fuels, chemicals and materials has been increased in recent years as an alternative to fossil fuel resources.²⁸⁰⁻²⁸³ Biofuels from lignocellulosic biomass are promising replacements for the energy sources and green chemicals, mainly from the most abundant biomass-derived sugars.²⁸⁴⁻²⁸⁶ With viable catalytic process, a wide variety of platform chemicals can be produced from sugars, among which GVL is an interesting molecule as already discussed in the previous chapters.

The primary strategy for GVL production from carbohydrates involves complex integrated process. The main distinct steps consists of the transformation of carbohydrates to levulinic acid (LA) with acid catalysts followed by subsequent hydrogenation to GVL in presence of a hydrogenation catalyst.²⁸⁷⁻²⁸⁹ From C5 sugars such as xylose, first undergoes acid dehydration to form furfural (Scheme 4.1). Furfural, further follows the same mechanistic pathway to eventually produce GVL as mentioned in the previous chapter. C6 sugars (glucose and fructose) undergoes a pathway, different in terms of the products obtained after dehydration. Acid dehydration results in HMF instead, with C6 sugars. HMF further undergoes rehydration to form LA. Finally, a hydrogenation followed by cyclization leads to GVL. Moreover, it is important to mention that the glucose should first isomerize to fructose before it forms HMF via dehydration (Scheme 4.1).



Scheme 4.1: Reaction pathway of xylose, glucose and fructose towards GVL

However, these reaction pathways come with several pitfalls (Scheme 4.1, blue arrows) For example, in acidic medium xylose or glucose can undergo retro-aldol condensation forming glyceraldehyde and lactic acid. Alternatively, they can be hydrogenated to xylitol or sorbitol, respectively. Furthermore, the formation of insoluble humins from furan derivatives is favored significantly with the use of excess acid. In addition, formic acid formed in the reaction medium can undergo decomposition into CO_2 and H_2 or CO and H_2O or MeOH.

Commercially, LA production is mainly performed in water medium,^{290,291} therefore an energy intensive upstream process is required to separate LA or its esters from the water before it undergo hydrogenation reaction.^{292,293} For example, firstly C6 sugars (glucose and fructose) undergo hydrolysis to LA by H₂SO₄ in water.²⁹⁴ This is followed by pH adjustment of the mixture and filtering to remove insoluble humin byproducts before the hydrogenation to be taken place. In contrary, one-step, direct conversion of carbohydrates to GVL is more economically viable as it does not require an intermediate isolation or purification.

Considering this, few pioneering researches have been developed on the direct production of carbohydrates from C6 and C5 sugars to GVL. The production of GVL from C5 sugars mainly from xylose also involves a multi-step process. Nevertheless, every single step have been separately studied and explored, a one pot homogeneous system that directly transform xylose to GVL under mild reaction conditions remains elusive in the literature. Melero reported a heterogeneous system, which converts xylose to GVL in isopropanol over bifunctional Brønsted and Lewis Zr-Al-beta zeolite.²⁹⁵ A yield of 35% GVL was obtained at 190 °C after 48 hours. A similar catalytic system with Brønsted and Lewis acid zeolites were used by Roman-Leshkov and achieved 78% GVL yield.²⁹⁶ Recently, Zhang reported a chitosan-supported ruthenium catalyst with ZSM-5 zeolite for the direct transformation of xylose to GVL with 37% yield at 170 °C after 30 hours.²⁹⁷ To the best of our knowledge, the direct synthesis of GVL from has not been reported to date.

With glucose and fructose there exists few reports on the direction synthesis of GVL. Heers developed a one-step conversion of glucose and fructose over Ru/C in combination with trifluoroacetic acid (TFA) and using either H₂ or formic as the hydrogen source.²⁹⁸ GVL yield of 52% from fructose was obtained at 180 °C after 16 hours. When using H₂ as hydrogen donor, 62% GVL yield was achieved with fructose at 180 °C under high pressure of H₂ (94 bar). A pre-formed homogeneous system of RuCl₃ and tris(3-sulfonatophenyl)phosphane (TPPTS) in combination with TFA gave 23% GVL yield from glucose.²⁹⁸ Braca reported the use of Ru-carbonyls (Ru(CO)₄l₂) along with HI catalytic system for the conversion of D-glucose and D-fructose to GVL in aqueous medium. GVL yields up to 40% were achieved at 200 °C.²⁹⁹ Later, employing Shvo-catalyst system in combination with H₂SO₄, were able to achieve moderate yield of GVL (55%) from fructose at a low temperature of 130 °C using GVL as a solvent.³⁰⁰ Li reported the direct transformation of fructose to GVL over Ru/TiO₂ catalyst in combination with H₃PW₁₂O₄₀ in water/γ-butyrolactone mixture.³⁰¹ GVL yield for inulin and fructose reached 70.5 and 67.6% respectively at 130-150 °C under 40 bar H₂ after 6 hours. Recently, Dong studied the production of GVL from carbohydrates

over RuZrO₂ coupling with heteropoly acid based SO₃H-functionalized ionic liquid.³⁰² GVL yield of 63% was obtained with fructose using RuZrO₂ and [MIMPS]₄SiW (1-methyl-3-(3-sulfopropylimidazolium)silicotungstate) at 180 °C, first in 10 bar N₂ for 3 hours (dehydration), and then in 40 bar H₂ for 10 hours. This chapter focuses on the combined action of homogeneous hydrogenation catalyst (Ru-MACHO-BH) and a Brønsted acid (H₃PO₄) as dehydration catalyst for the direct conversion of monomeric C6 and C5 sugars (xylose, glucose and fructose) to GVL.

4.2 Results and discussion

With the previous knowledge on the furfural hydrogenation to GVL, I decided to take one step back with the reaction and test the monosaccharides with the same combination of a hydrogenation catalyst (Ru-MACHO-BH) and Brønsted acid (H₃PO₄). My initial work concentrated on testing the conversion of xylose to GVL. Thus, with 0.5 mol% of Ru-MACHO-BH and 3.8 M H₃PO₄(aq) under 30 bar of H₂ in EtOH, the conversion towards GVL was 44% after 48 hours at 125°C (Table 4.1, Entry 1). The influence on catalyst loading was tested with lowering the catalyst loading to 0.2 mol% (Entry 2). However, there was no significant changes in the yield, thus yielding 48% of GVL with other parameters kept unchanged. Noticeably, insoluble humins was observed in the reaction medium. As discussed in the previous chapter, humins are usually reported to produce from the polymerization of furanics in acidic medium which cannot be completely avoided but can be minimized by optimization of various reaction conditions. Control experiments without Ru-MACHO-BH led only the dehydration of xylose to furfural and significant humins as expected.

The effect of different alcohol solvent such EtOH, MeOH and isopropanol (IPA) was investigated with both 0.5 mol% and 0.2 mol% catalyst loading 3.8 M H₃PO₄(aq) under 30 bar of H₂ at 125 °C. With 0.5 mol%, the reaction afforded almost same yield in EtOH and IPA media whereas a minor drop to 38% yield was observed in MeOH (Appendix B, Table A1). This effect is nullified with low catalyst loading (0.2 mol%), where the GVL yield obtained in all the alcohol solvent media was almost the same (Appendix B, Table A1). The longer reaction time had no significant effect on the yield as well. Hence, under identical conditions in different alcohol solvent and longer reaction time (96 hours) same GVL yield was observed (Appendix B, Table A2).



Entry	Ru-MACHO-BH (mol%)	H ₃ PO ₄ [M]	EtOH/H ₂ O v/v ratio	GVL yield [%] ^[a]
1	0.5	3.8	EtOH	44
2	0.2	3.8	EtOH	48
3	0.5	5.7	EtOH	45
4	0.2	3.8	1:1	44
5	0.5	3.8	1:1	45
6	0.2	5.7	1:1	52
7	0.5	5.7	1:1	60

Standard reaction conditions: Xylose (0.65 mmol), 85 w/w% H_3PO_4 , EtOH (1 mL), 30 bar H_2 in 48 hours. ^[a]Determined by GC-FID using 1,4-dioxane as the internal standard.

Table 4.1: One-pot direct conversion of xylose to GVL.

Increasing the acid concentration to 5.7 M H₃PO₄(aq), led to 45% yield in EtOH, which again led to no notable difference after 48 hours (Entry 3). Nevertheless, the concentration effect of acid was evident when the reaction was carried out in 1:1 v/v EtOH/H₂O. Thus, using 0.2 mol% and 0.5 mol% of Ru-MACHO-BH and 3.8 M H₃PO₄(aq) under 30 bar of H₂ at 125 °C in 1:1 v/v EtOH/H₂O, the yields of GVL were 45% and 44% respectively (Entries 4 and 5). 52% yield was achieved with increasing the acid concentration to 5.7 M H₃PO₄(aq) using 0.2 mol% catalyst loading in 1:1 v/v EtOH/H₂O (Entry 6). Further increase in the catalyst loading (0.5 mol%) along with the acid concentration caused a sharp increase in GVL yield to 60% (Entry 7). Lowering the reaction time to 18 hours gave low yield of GVL (Appendix B, Table A3).

The resulting enhancement in the GVL yield from using 3.8 M to 5.7 M $H_3PO_4(aq)$ implied the dehydration of xylose to furfural is favoured with increase in acid concentration. However, further increasing the acid concentration a gradual drop in the GVL was observed. Thus, 50% and 45% yield was achieved using 7.5 and 10.9 M $H_3PO_4(aq)$ respectively after 48 hours under similar conditions of pressure and temperature suggesting catalyst inhibition or even degradation (Figure 4.1a).



Standard reaction conditions: a) Ru-MACHO-BH (0.5 mol%) and xylose (0.65 mmol) using different concentration of 85 w/w% $H_3PO_4(aq)$ in 1:1 EtOH/ H_2O mixture (1 mL), 30 bar H_2 at 125 °C after 48 hours. b) Ru-MACHO-BH (0.5 mol%) with different concentrations of xylose using 5.7 M $H_3PO_4(aq)$ in 1:1 EtOH/ H_2O mixture (1 mL), 30 bar H_2 at 125 °C after 48 hours. Yields determined by GC-FID using 1,4-dioxane as the internal standard.

Figure 4.1: One-pot direct conversion of xylose to GVL: a) Effect of phosphoric acid concentration. b) Effect of xylose concentration.

Next, I test the effect of concentration of xylose in 1:1 v/v EtOH/H₂O was investigated with 0.5 mol% of Ru-MACHO-BH by using 5.7 M H₃PO₄(aq) and 30 bar H₂ at 125 °C in varying concentration ranging from 0.1-0.6 M. The reaction afforded 73% GVL with 0.07 M and dropped to 45% with higher xylose concentration showing that optimal substrate concentration is required for the maximum GVL yield and higher substrate concentration is detrimental for catalytic activity (Figure 4.1b).

I then explored the catalytic activity for the transformation of glucose and fructose. Studies were commenced by employing the optimized reactions found in case of xylose. Thus using 0.5 mol% Ru-MACHO-BH using 5.7 M H₃PO₄(aq) and 30 bar H₂ at 125 °C in 1:1 v/v EtOH/H₂O GVL yield of 16% and 29% respectively from glucose and fructose (Table 4.2, Entries 3 and 4). Under identical reaction conditions fructose produce higher GVL yield than glucose. The lower activity of glucose can be explained by the proposed mechanism that glucose first isomerized to fructose and then followed the same conversion pathway as fructose.²³ The rate determination step for the dehydration of glucose can be the isomerization step, which would make the glucose conversion having a different apparent activation energy than for fructose dehydration.²³ It is important to mention that no subsequent hydrogenation products of GVL such as 2-MTHF and 1,4-PDO were not detected. Also, no intermediates from hydrogenation of LA to GVL was observed in the system. Except for LA and GVL, in certain cases formic acid together with methanol, sorbitol were also observed in the reaction medium. Formic acid and humins are the two main byproducts from the acid catalyzed dehydration of sugars. Sorbitol is the hydrogenation product of glucose. Furthermore, the amount of formic acid often almost decreased to zero after the reaction, which

can be attributed to the decomposition of formic acid to methanol considering the presence of metal catalyst in presence of H_2 .

The acid concentration is crucial for the LA formation from sugars. Thus different $H_3PO_4(aq)$ concentrations were tested to convert glucose and fructose to GVL. It has been observed that a low and high acid concentration has a negative effect on the GVL yield confirming that an optimal acidity is favourable for LA production. Thus, lowering the $H_3PO_4(aq)$ concentration to 3.8 M resulted in 21% and 25% yields with glucose and fructose respectively (Entries 1 and 2). However, with higher concentration of 7.9 M $H_3PO_4(aq)$, the yield diminished significantly to 13% in case of glucose and 24% with fructose (Entries 5 and 6). Presence of LA was still observed in the reaction media indicating incompleteness of the reactions which explains the low yield indicating that the activity of Ru-MACHO-BH was supressed due to the presence of excess acid.



Entry	Glucose [M]	Fructose [M]	H ₃ PO ₄ [M]	GVL yield [%] ^[a]
1	0.6		3.8	21
2		0.6	3.8	25
3	0.6		5.7	16
4		0.6	5.7	29
5	0.6		7.9	13
6		0.6	7.9	24

Standard reaction conditions: Ru-MACHO-BH (0.5 mol%), glucose and fructose (0.65 mmol), 85 w/w% H_3PO_4 in 1:1 v/v EtOH/ H_2O (1 mL), 30 bar H_2 after 48 hours. ^[a]Determined by GC-FID using 1,4-dioxane as the internal standard.

Table 4.2: One-pot direct conversion of glucose and fructose to GVL.

The effect on substrate concentration was investigated here as well, with 0.5 mol% catalyst loading by using 5.7 M $H_3PO_4(aq)$ and 30 bar H_2 at 125 °C in 1:1 v/v EtOH/ H_2O in glucose and fructose concentration ranging from 0.1-1.3 M (Figure 4.2). The reaction afforded 31% with 0.1

M glucose concentration and the yield drop gradually with increase in concentration, resulting a low yield of 10% GVL with 1.3 M, showing that a higher concentrated solution is detrimental for catalytic activity. The same effect is observed in case of fructose as well. A low substrate concentration was found necessary to have good yield of GVL. In fact under identical reaction conditions, yield of 34% is achieved with lower concentration (0.1 M) and dropped to 21% with 1.3 M concentration of fructose.



Standard reaction conditions: Ru-MACHO-BH (0.5 mol%), 5.7 M $H_3PO_4(aq)$ in 1:1 v/v EtOH/ H_2O (1 mL), 30 bar H_2 after 48 hours.

Figure 4.2: Concentration effect of glucose and fructose on the yield of GVL.

4.3 Summary

I demonstrated a one-pot direct approach for the catalytic production of GVL from carbohydrates (xylose, glucose and fructose) using Ru-MACHO-BH in combination with Brønsted acid (H₃PO₄) in EtOH/H₂O with H₂ as the hydrogen source. Specifically, GVL yields of 73%, 31% and 34% were obtained for xylose, glucose and fructose respectively. A bit lower activity of glucose when compared to glucose can be explained with the proposed conversion pathway, in which the rate determining step for the dehydration process being the isomerization of glucose to fructose. Since no other products from LA was detected, the selectivity towards GVL was 100% based on the conversion of LA. And is important to mention that the GVL so-formed cannot be further hydrogenated in the present system. The byproducts possibly be formed in the reaction mixture other than humins were not identified with the current analytical method that we have in-house.

This process may find important applications for the production of GVL from biomass-derived carbohydrates without any intermediate isolation and purification. Further optimization of the

reaction conditions may eventually make the approach industrially viable for these type of transformation.

As I already mentioned in the previous chapter, the striking activity of Ru-MACHO-BH with a Brønsted is very interesting. Such combinations has not been previously reported with Noyori-type pincer catalysts. Therefore, my findings set the first example of Noyori-type pincer catalysts that shows activity with Brønsted acid. However, the behavior of catalyst with acid is something yet to be studied in detail especially, the mechanism with intermediate isolation and possibly some theoretical modelling as well. This combination of PNP pincer catalyst and Brønsted acid can potentially be utilized for the transformations of other relevant molecules which are otherwise unexplored.

With the ground-breaking results already obtained with carbohydrates, the next possibilities was to take a step back and transfer this system to real biomass waste feedstocks. The next chapter is based on above said transformations.

5. Direct conversion of biomass waste feedstock to GVL using PNP complex in acidic aqueous medium

5.1 Introduction

Biomass comprises around 12.83% of renewable energy source for the environment and its utilization is expected to span for future decades.³⁰³ Bulk quantities of biomass wastes are generated from the consumption of agricultural products, wood processing, and cultivation. The residues from theses constitutes waste and can be potential used as a feedstock for fuels and energy. Biomass waste can be utilized for energy recovering using different incineration methods such as pyrolysis, steam reforming, gasification, hydrolysis as well as hydrothermal treatment.³⁰⁴ Compared to fossil fuels biomass conversion has several advantages, for e.g. zero-emission of CO₂, low emission of SOx and NOx.³⁰⁵ However, biomass have the possibility of potentially providing a negative carbon footprint,³⁰⁶ which can only be reached if it is used for producing value-added compounds.³⁰⁷ Hence, there is a fundamental need to improve our treatment of biomass sources.

Among various biomass, lignocellulose and starch have gained much attention due to their wide abundance and the many value-added biomass-derived platform chemicals that originate from polysaccharides (cellulose, hemicellulose, amylose, and amylopectin). As already discussed in the previous chapters one of the most important platform molecules is γ-valerolactone (GVL), which has a wide array of applications in chemical, pharmaceutical industries.³⁰⁸

As discussed in the previous chapters, cellulose and hemicellulose make up approximately 75-85 wt% of lignocellulose,³⁰⁹ while amylose and amylopectin constitute the entire content of starch.³¹⁰ Thus, GVL production from lignocellulosic feedstock can be divided into two specific multistep cascade processes (Scheme 5.1a). In the first path, hemicellulose (20-35 wt%) is first hydrolyzed to xylose and dehydrated to form furfural, both steps mediated by acid. A subsequent hydrogenation leads to furfuryl alcohol, which is then rehydrated by acid to levulinic acid (LA). Finally, a hydrogenation followed by cyclization leads to GVL. In the second path, acid mediates the hydrolysis of cellulose (30-50 wt%) to glucose followed by the isomerization to fructose, dehydration to (5-hydroxymethyl furfural) HMF, and then rehydration to LA. LA is then converted to GVL in the same way as in the 'hemicellulose pathway'. However, these reaction pathways come with several pitfalls. For example, in acidic medium xylose or glucose can undergo retroaldol condensation forming dihydroxyacetone and lactic acid. Alternatively, they can be hydrogenated to xylitol or sorbitol, respectively.³¹¹ Furthermore, the formation of insoluble humins from furan derivatives is favored significantly with the use of excess acid.³¹² In addition, formic acid formed in the reaction medium can undergo decomposition into CO₂ and H₂ or CO and H₂O. Hydrogenation of formic acid can also produce MeOH in the reaction medium.

Likewise, GVL production from starch includes two cascade processes, one from amylose and another from amylopectin (Scheme 5.1b). Both undergo hydrolysis to glucose monomer and follows same pathway as that of cellulose.



Scheme 5.1: a) General stepwise mechanism for the conversion of biomass into GVL (blue arrow indicates the major pitfalls), b) General stepwise mechanism for the conversion of starch (amylose and amylopectin) into GVL. c) Direct conversion of sawdust, straw, rice grains, potato flour and polysaccharides into GVL using Ru-MACHO-BH and phosphoric acid under mild reaction conditions.

Owing to the complexity of lignocellulosic biomass and its chemical resistance towards energy and cost effective selective transformation to GVL from real biomass remains a huge challenge. Thus, a catalytic system for a one-pot transformation of biomass to GVL must tolerate multiple different substrates and operate under very distinct acid- and hydrogenation-mediated steps simultaneously. In addition, all these highly differentiated steps must be carried out with high conversion and selectivity to reach reasonable yields of GVL. For example, we have previously shown that HMF is a more potent substrate for hydrogenation than furfural is,³¹³ and yet must the opposite selectivity take place here for a successful and high-yielding production of GVL from biomass.

Conducting these processes in stepwise manners requires financially unviable, energy intensive, and waste-producing separation, intermediate isolation, and purification. The processes become even less viable when using sacrificial H-donor agents such as isopropanol or formic acid. On the contrary, obtaining GVL directly from real biomass in a one-pot cascade manner using H₂ as hydrogen source is highly attractive. A major goal is therefore to find a combination of an acid and hydrogenation catalyst that not only function together, but also perform in a cooperative manner such that *all* the described reaction steps proceed highly effectively and selectively.

The direct conversion of real biomass to GVL using H₂ as hydrogen source has not been achieved before. Even the direct production of GVL from polysaccharides and C6- as well as C5-carbohydrates are scarcely reported. So far there exists only one example for the direct conversion of real biomass to GVL. Thus, Huang demonstrated a one-pot conversion of poplar to GVL using a transfer hydrogenation method with mixed $Al_2(SO_4)_3$ and Ru/ZrO_2 catalyst and a sacrificial H-donor (iPrOH) leading to a yield of 12.2 wt% GVL using 800 W microwave heating to 180 °C for 60 min.³¹⁴ The same authors also converted cellulose to GVL using the same conditions for 70 min, leading to a GVL yield of 51.2%. Heeres used Ru/C with trifluoroacetic acid (TFA) at 180 °C under 94 bar H₂ for 8 h to convert cellulose to GVL in 29% yield.³¹⁵ The use of the homogeneous water soluble ruthenium catalyst RuCl₃ and tris(3-sulfonatophenyl)phosphane (TPPS) in combination with TFA gave a lower GVL yield of 23%. Zhang developed a chitosan-Ru/PPh₃ catalyst system that enables a one-pot catalytic transformation of hemicellulose to GVL with a yield of merely 30% GVL using formic acid as H-donor in ethanol heated to 170 °C for 30 hours.³¹⁶ Li investigated a one-step direct strategy importantly for the transformation of cellulose and commercial starch over combined H₃PW₁₂O₄₀ and Ru/TiO₂ catalysts.³¹⁷ They obtained 40.5% and 48.3% of GVL from cellulose and starch respectively at 150 °C under 40 bar H₂ in GBL-H₂O solvent. To the best of our knowledge, there exist no direct procedures for transforming real biomass to GVL using H_2 as hydrogen source. Likewise, there are no examples of using homogeneous catalysis for producing GVL directly from any of the substrates of real biomass and polysaccharides.

It is worth noting the excellent performance of PNP complex in hydrogenation catalysis in presence of a Brønsted acid, which has never been explored before. Nevertheless, there exist few examples of the use of pincer complexes, all of which are lutidine-based, that work under acidic conditions for hydrogenative purposes.³¹⁸⁻³²⁰ Leitner reported a Ru triphos complex that also shows activity under highly acidic conditions.³²¹ However, there are no reports on using Noyori-type PNP pincer complexes as catalysts in the presence of Brønsted acid.

This represents the first example of homogeneously catalyzed direct production of GVL from raw woody- and starchy biomasses in excellent yields by using a combination of Ru-MACHO-BH and H₃PO₄(aq) (Scheme 5.1b). This combination allows to integrate the myriad of cascade events of hydrolysis/isomerization/dehydration/rehydration/hydrogenation/lactonization in such a way that the system performs highly efficiently and selectively under mild reaction conditions. In addition to the raw biomass feedstock, polysaccharides such as cellulose and hemicellulose as substrates were investigated as well to obtain insight to the underlying mechanisms and performances of the two main reaction pathways for the woody biomass.

5.2 Results and Discussion

5.2.1 Direct hydrogenation of real biomass waste

To verify the applicability of one-pot direct approach, two types of woody biomass such as beechwood sawdust and wheat straw were employed as feedstocks for the direct protonolysis/hydrogenation using Ru-MACHO-BH and $H_3PO_4(aq)$. Initial investigations with furanics revealed that the combination of Ru-MACHO-BH and $H_3PO_4(aq)$ is catalytically active for the transformation to GVL, therefore I decided to test the real biomass for such transformation.

I commenced the studies with beechwood sawdust. Hence, we first investigated the effect of $H_3PO_4(aq)$ concentration while maintaining the catalyst loading as well as H_2 pressure and reaction temperature constant at 0.5 mol%, 30 bar, and 140 °C, respectively. Gratifyingly, employing 7.5 M $H_3PO_4(aq)$ led to an encouraging 15 wt% yield of GVL after 96 hours (Table 5.1, Entry 1), which was improved to 23 wt% by increasing the concentration of $H_3PO_4(aq)$ to 9.3 M (Entry 3). Shortening or extending the reaction time to 24 or 168 hours, respectively, did not significantly change the yield (Entries 2 and 4). Further increasing the $H_3PO_4(aq)$ concentration to 10.1 M improved the yield to 25 wt%, which decreased again upon longer reaction times (Appendix, Table A1). With 10.9 M $H_3PO_4(aq)$, the optimal yield of 26 wt% was obtained after 24 hours (Entry 7). Considering that the theoretical weight of GVL from beech wood is limited to 46 wt% (assuming completely dry biomass and that only hemicellulose and cellulose are converted to GVL), the yield is 57%. The moisture content for sawdust was determined by thermogravimetric analysis (TGA), which accounts to 4.5 wt% (Appendix, Figure A12).

Both shortening and extending the reaction time resulted in lower yields (Entries 6 and 8). Moreover, after 18 hours, we still detected the levulinic acid intermediate, which was fully converted after 24 hours. It is noteworthy to mention that no hydrodeoxygenation products, such as hydrocarbons, were observed under these reaction conditions, both in the liquid and gas phases (Appendix, Figure A13). Also, a blank reaction was performed to confirm the so-formed stability of GVL under acidic aqueous environment. Thus, GVL was used as a substrate and applying identical conditions (Ru-MACHO-BH, 10.9 M $H_3PO_4(aq)$, 30 bar H_2 , 140 °C), the reaction was left for 72 hours. The reaction mixture was analyzed both in the liquid and gas phases. It was

observed that GVL was quite stable under these conditions, hence no decomposition products was observed (Appendix. Figure A11 and A14). Finally, the reaction was carried out in an EtOH/H₂O mixture to study the solvent effect. With 1:1 v/v EtOH/H₂O, we observe a lower GVL yield of 14 wt% under otherwise optimized conditions (Entry 9).

To demonstrate the power of our system, the same reaction conditions were employed with other biomass substrates such as wheat straw. Thus, employing 8.4 M of $H_3PO_4(aq)$ a 12 wt% yield of GVL is obtained after 48 hours (Entry 10). By increasing the acid concentration to 9.3 M, the same yield is observed within 24 hours (Entry 11). The maximum yield of GVL (18 wt%) is observed using 10.9 M of $H_3PO_4(aq)$ for 48 hours (Entry 13). This yield accounts for 56% of the theoretical limit of 32 wt%. The moisture content for wheat straw was determined by TGA as well. By examining the TGA profile, the moisture content was calculated to be 5.39 wt% (Appendix, Figure A12). Further continuing the reaction to 72 hours a slight decrease in the yield was observed (Entry 14). Employing 11.8 M of acid led no improvement in the yield when run for 96 hours (Entry 15). Under the optimized conditions we then tested the reaction in 1:1 v/v EtOH/H₂O. Again, a decrease in the yield was observed (Entry 16). Obviously, the source and the texture of the lignocellulose had a significant influence on the yield of GVL. However, these results validate the versatility of the catalytic system towards different biomass waste valorization to GVL with approximately 90% per step selectivity considering the six-step multistep process.

Next, I tried to scale up the process up to 1g of beechwood sawdust as well as wheat straw. Thus using approximately 20 mg of Ru-MACHO-BH, 10.9 M $H_3PO_4(aq)$ at 140 °C under 30 bar H_2 . After 48 hours, a yield of 8 wt% and 3 wt% of GVL was obtained from sawdust and straw respectively (Appendix, Table A1). I speculate that the diminished yield during the scale up process could be because of the lack of proper equipment for larger scale.



Biomass	Entry	H ₃ PO ₄ [M]	Time [h]	GVL yield ^a [wt% (mol%)]	
		Beechw	ood sawdust		
Lignocellulosic content	wt%	1	7.5	96	15 (33)
Hemicellulose	37	2	9.3	24	22 (48)
Cellulose	42	3	9.3	96	23 (50)
Lignin	19	4	9.3	168	20 (43)
		5	10.1	96	19 (41)
		6	10.9	18	21 (46)
		7	10.9	24	26 (57)
		8	10.9	96	18 (39)
		9 ^b	10.9	24	14 (30)
		Whe	eat straw		
Lignocellulosic content	wt%	10	8.4	48	12 (38)
Hemicellulose	25	11	9.3	24	12 (38)
Cellulose	33	12	10.9	24	12 (38)
Lignin	17	13	10.9	48	18 (56)
		14	10.9	72	16 (50)
		15	11.8	96	17 (53)
		16 ^b	10.9	24	11 (34)

Standard reaction conditions: Beech wood (91 mg, corresponding to 0.22 mmol hemicellulose and 0.21 mmol cellulose³²²) and wheat straw (91 mg, corresponding to 0.16 mmol hemicellulose and 0.15 mmol cellulose³²³), Ru-MACHO-BH (1.65 mg, 0.0028 mmol), 85 w/w% H₃PO₄(aq) in H₂O (1 mL) at 140 $^{\circ}$ C and 30 bar H₂, ^a Determined by GC-FID. Yields are calculated with respect to dry biomass. ^b1:1 v/v EtOH/H₂O (1 mL).

Table 5.1: Direct conversion of sawdust and straw to GVL

I also performed benchmark reactions with the starch sources rice grains and potato flour. Again, the same reaction conditions which found optimal for the woody biomass were used with these substrates and only varied on the time to achieve completion of each reaction. Thus, yields of 8 wt% and 9 wt% were obtained from rice grains and potato flour, respectively, after 24 hours (Entries 1 and 3). Levulinic acid was still detected in both the reaction media, indicating that the reactions are incomplete and explaining the low yields. Indeed, extending the reaction time to 72 hours consumed all the levulinic acid and the GVL yields increased to 16 wt% and 20 wt% from rice grains and potato flour with, respectively (Entries 2 and 4). These results indicates that the catalytic system is very efficient in hydrolyzing not only the $\alpha(1-4)$ glycosidic linkages, but also the $\alpha(1-6)$ linkages between glucose units of amylopectin, which is the major component of starch.



Potato flour

Biomass		Entry	H ₃ PO ₄ [M]	Time [h]	GVL yield ^a [wt% (mol%)]
			Rice grains	5	
Starch content	wt%	1	10.9	24	8 (14)
Amylose	35	2	10.9	72	16 (30)
Amylopectin	65				
			Potato flou	r	
Starch content	wt%	3	10.9	24	9 (17)
Amylose	17.8	4	10.9	72	20 (36)
Amylopectin	82.2				

Standard reaction conditions: Rce grains (91 mg, corresponding to 0.50 mmol relative to the glucose monomers³²⁴), Potato flour (91 mg corresponding to 0.50 mmol relative to the glucose monomers³²⁴) Ru-MACHO-BH (1.65 mg, 0.0028 mmol), 85 w/w% H₃PO₄(aq) in H₂O (1 mL) at 140 ⁰C and 30 bar H₂, ^a Determined by GC-FID. Yields are calculated with respect to dry biomass.

Table 5.2: Direct conversion of rice grain and potato flour to GVL

It is important to mention the formation of humins in the reaction mixture. As already discussed in the previous chapter, humins are unavoidable byproduct that is formed as a result of the polymerization of furanics in the acidic media. The yield reported here are GC yield using 1,4dioxane as the internal standard. The product is also confirmed by ¹H NMR analysis. Other byproducts formed in the reaction medium is not identified due to the limitations in the instruments and other practicalities.

5.2.2 Direct hydrogenation of polysaccharides

To elaborate on the results with real biomass, pure cellulose and hemicellulose were investigated as model substrates using the combination of Ru-MACHO-BH and H₃PO₄(aq) system. I commenced with hemicellulose evaluating the performance of the catalytic system with hemicellulose. In general, hemicellulose requires significantly milder conditions than cellulose. Corn core xylan and beechwood xylan were employed as two different xylan types of xylan from different biomass. A reaction temperature of 125 °C was found necessary to reach effective acid-mediated substrate turnover. A low of 9% yield of GVL was achieved from xylan from corn core using 0.5 mol% Ru-MACHO-BH and 7.5 M H₃PO₄(aq) in H₂O after 48 hours (Table 5.3, Entry 1). On the other hand, the yield of GVL produced from beechwood at higher temperature (140 °C) with 5.7 M H₃PO₄(aq) was 13% (Entry 2). With increase in the acid concentration to 8.4 M, the yield further diminished to yield to 5% (Entry 3). From these observations I speculate that whether the diminished activity and low yield is as a result of humins formation, which is favored under higher acid concentration and higher temperature when water is employed as the only solvent.

I then carried out the reaction in 1:1 v/v EtOH/H₂O mixture. Thus using 5.7 M acid in 1:1 v/v EtOH/H₂O led to significant increase in the yield to 64% (Entry 4). However, further increasing the acid concentration to 7.5 M is somewhat detrimental on the yield, with merely 57% of GVL obtained (Entry 6). This can be explained by the formation of humins observed in higher acid concentration. Using 5.7 M H₃PO₄(aq) in 1:1 v/v EtOH/H₂O at 140 °C yielded 33% (Entry 8). Further increase in the acid concentration, a diminished activity was observed with merely 5% yield (Entry 10). In cases of significant low yields, I observe a lot of humins in the reaction mixture, hence I speculate higher acid concentration has a negative effect on the yield of GVL.

To compare the results to that of corn core xylan with $EtOH/H_2O$, I performed the reaction with beechwood xylan under similar conditions. Thus, using 5.7 M $H_3PO_4(aq)$ in 1:1 v/v $EtOH/H_2O$ at 125 °C yielded 28% of GVL after 48 hours (Entry 5). The concentration effect of substrate was also evaluated at this point, using 0.1 M concentration of xylan, the yield of GVL is found to be doubled (Appendix, Table A2). Almost similar yield was obtained with 140 °C (Entry 10). Hence it is a balance between low concentration and a slight increase in the temperature. Using 7.5 M acid, 87% yield of GVL was observed already at 125 °C (Entry 7).



Xylan sour		ource (M)	H₃PO₄	Solvent	P/T	GVL yield ^a
Entry	Corn core	Beechwood	[M]	Solvent	[bar]/[°C]	[%]
1	0.6		7.5	H ₂ O	30/125	9
2		0.6	5.7	H ₂ O	30/140	13
3		0.6	8.4	H ₂ O	30/140	5
4	0.6		5.7	$EtOH/H_2O^b$	30/125	64
5		0.6	5.7	$EtOH/H_2O^b$	30/125	28
6	0.6		7.5	$EtOH/H_2O^b$	30/125	57
7		0.6	7.5	$EtOH/H_2O^b$	30/125	87
8	0.6		5.7	$EtOH/H_2O^b$	30/140	33
9	0.6		8.4	$EtOH/H_2O^b$	30/140	5
10		0.6	5.7	EtOH/H ₂ O ^b	30/140	43

Reaction conditions: Ru-MACHO-BH (0.5 mol%), xylan from corn core (76.2% xylose monomers) or xylan from beech wood (95% xylose monomers), 85 w/w% H_3PO_4 , EtOH (1 mL), 30 bar H_2 , at 125 °C in 48 hours Catalyst loading and yield are relative to moles of xylose monomers contained in xylan. ^a Determined by GC-FID using 1,4-dioxane as the internal standard. ^b 1:1 v/v EtOH/ H_2O (1 mL).

Table 5.3: Direct conversion of hemicellulose to GVL.

By evaluating the influence of various catalytic parameters, it is clear that the influence of temperature, acid concentration and solvent follows the same trend even though the yield of GVL obtained for both type of xylan are different. This could be because of the difference in the xylose monomer content present in both xylan.

Next, cellulose was used as a feedstock. My studies with cellulose commenced with low concentration of acid and using water as the sole solvent. Thus, using 0.5 mol% Ru-MACHO-BH and 5.7 M H₃PO₄(aq) afforded 20% yield of GVL (Table 5.4, Entry 1). Increasing the reaction time to 96 hours, 24% and 30% yield, respectively, of GVL was obtained using 5.7 M and 7.5 M of H₃PO₄(aq) at 125 °C (Entries 2 and 3). Control experiments without Ru-MACHO-BH led to no GVL, rather the reaction stops at levulinic acid, which is in line with the general acid catalyzed mechanism for the conversion of cellulose to levulinic acid.³²⁵ It was also observed that the humins formation in this case was significantly higher.

The effect of temperature was also studied as high temperature is known to be very detrimental for the acid mediated hydrolysis of cellulose.³²⁶ Thus, at 140 °C with 5.7 M H₃PO₄(aq) 33% of GVL was obtained after 96 hours (Entry 4), a 9% improvement from 125 °C. Using 7.5 M of H₃PO₄(aq) provided 30% of GVL after 48 hours (Entry 5), which further yielded 47% after 96 hours (Entry 6). This suggests a higher rate of degradation of the cellulose to levulinic acid at higher temperature and acid concentration, suggesting that the conversion of cellulose to levulinic acid in water is a limiting factor, while the hydrogenation step seemingly proceeds more efficiently. (An overall dependence on the temperature and concentration of acid is depicted in the Figure 5.1 as well).



Standard reaction conditions: Microcrystalline cellulose (0.6 M), 85 w/w% H_3PO_4 , H_2O (1mL), 30 bar H_2 , 96 hours. Determined by GC-FID. Catalyst loading and yield are relative to moles of glucose monomers contained in cellulose.

Figure 5.1: Effect of temperature and acid concentration on the direct conversion of cellulose to GVL.

Hence the effect of concentration of both acid and substrate was investigated using different $H_3PO_4(aq)$ concentrations ranging from 5.7 M to 7.5 M with 0.1 M cellulose instead of the 0.6 M used so far. Comparing Entries 7 and 4, it is evident that lowering the cellulose concentration is beneficial. Effect of substrate concentration on the yield of GVL along with the increase in acid concentration is given in (Appendix, Table A3). Increasing acid concentration and reaction time to the previously optimized 7.5 M $H_3PO_4(aq)$ and 96 hours provided 50% yield of GVL (Entry 8). It is worth noting the excellent stability and high activity of Ru-MACHO-BH even in higher acid concentration, which is reflected in the full conversion of so-formed levulinic acid to GVL. The reaction was then scaled up to 1.4 g of cellulose using 0.5 mol% of Ru-MACHO-BH at 140 °C and 30 bar H_2 (Entry 9). After 72 hours, a yield of 43% of GVL was obtained, demonstrating the reproducibility of the system at a larger scale.

			Ru-MACHO-BH H ₃ PO ₄ , EtOH/H ₂ O 30 bar H ₂ , 125-140 ⁰ C			Ph ₂ ·CO
	Cellul			GVL	Ph ₂ Bł	H ₃
				I	Ru-MACHO-	-BH
Entry	Cellulose	H_3PO_4	Solvent	P/T	Time	GVL yield ^a
	[M]	[M]		[bar]/[°C]	[h]	[%]
1	0.6	5.7	H ₂ O	30/125	48	20
2	0.6	5.7	H ₂ O	30/125	96	24
3	0.6	7.5	H ₂ O	30/125	96	30
4	0.6	5.7	H ₂ O	30/140	96	33
5	0.6	7.5	H ₂ O	30/140	48	30
6	0.6	7.5	H ₂ O	30/140	96	47
7	0.1	5.7	H ₂ O	30/140	48	37
8	0.1	7.5	H ₂ O	30/140	96	50
9 ^c	0.5	7.5	H ₂ O	30/140	72	43
10	0.6	5.7	EtOH/H ₂ O ^b	30/125	48	7
11	0.6	7.5	EtOH/H ₂ O ^b	30/125	48	12

Reaction conditions: Microcrystalline cellulose (0.6 and 0.1 mmol based on glucose monomers), 85 w/w% H_3PO_4 , Ru-MACHO-BH (0.5 mol%), H_2O (1 mL), 30 bar H_2 , at 140 °C. ^a Determined by GC-FID using 1,4-dioxane as the internal standard. Catalyst loading and yield are relative to moles of glucose monomers contained in cellulose. ^b 1:1 v/v EtOH/H₂O (1 mL). ^c Microcrystalline cellulose (7.8 mmol), H_2O (15 mL).

Table 5.4: Direct conversion of cellulose to GVL

In order to investigate the influence of EtOH as a solvent on the yield of GVL, I performed the reaction with cellulose in a 1:1 v/v EtOH/H₂O medium. Thus, employing 0.5 mol% Ru-MACHO-BH and 5.7 M of phosphoric acid under 30 bar H₂ pressure in EtOH/H₂O, afforded only 7% GVL after 48 hours at 125 °C (Entry 10). Increasing the acid concentration to 7.5 M led to significant increase in the yield to 12% (Entry 11). Under identical conditions, the reaction with water as the sole solvent produce significantly higher GVL.

5.3 Summary

In this chapter I have presented a one-pot direct catalytic process for the direct production of GVL from different real biomass using a homogeneous catalyst Ru-MACHO-BH and H₃PO₄(aq) with excellent yields under mild and sustainable reaction conditions. The exceptional activity of Ru-MACHO-BH along with a Brønsted acid (H₃PO₄) enabled direct conversion of real biomass such as, wheat straw, rice grains, potato flour and sawdust into GVL with 16-26 wt% at 140 °C under 30 bar H₂. This versatile protocol can be transferred for the unprecedented transformation of hemicellulose and cellulose to GVL. And representing the first example of direct transformation of lignocellulosic and starchy biomass to GVL using H₂ as a reductant. This ground breaking method requires no chemical pretreatment or separation of the raw biomass and thus tremendous energy savings can be potentially gained compared to the existing approaches for production of GVL and thereby simplifies the whole process viable for industries.

Based on these results, it is high likely that the other PNP catalysts possibly shows activity. The future step to bring this project to a very broader scope is to try other PNP catalysts especially with Fe or Mn PNP complexes. Similarly, it is also possible to envision different other acids, broader scope of acceptable feedstock such as, poplar, bamboo, crab shell (chitin), rice husk, coffee grounds, real agricultural waste material, etc. Products other than GVL is also potentially important. For e.g., I observe 1,4-pentanediol as one of the products along with GVL from cellulose while using the Ru-PNP iPr congener as the catalyst. In some cases, sorbitol is formed which can be considered yet another potential byproduct formed along with GVL.

The superior efficiency of this catalyst for direct hydrogenation of lignocellulose is speculated to originate from the synergistic effect between Ru-MACHO-BH and Brønsted acid combining cascade hydrogenation/protonolysis. The activity of Ru-PNP complex in acidic media is also noteworthy as is not been explored before. However, the mechanistic studies on the behavior of Ru-MACHO-BH with Brønsted acid is not investigated in this chapter due to the time limitation. Further investigations on this project especially the mechanistic investigations will be carried out in the future in Nielsen's lab. I strongly believe, this new discovery of the activity of Noyori-type pincer complexes with acid will certainly paves the way to explore otherwise unexplored plethora of transformations.

There still exists certain unknown factors about the catalytic system such as the knowledge on the time-dependent substrate conversion to known the reaction kinetics, other potential side products, the bottlenecks and finally the catalyst composition over time (stability). Once a complete idea about the catalytic system is known and optimized a continuous flow process can be envisioned eventually. Such a setup will greatly improve the industrial potential of my system.

6. New Ru-CNC pincer complex: synthesis characterization and catalysis

6.1 Introduction

Pincer complexes have been synthesized since 1970s, since then new designs, tuning and modifications continue to emerge.³²⁷ The tridentate skeleton imparts thermal stability and the electronic and steric properties can be tuned upon the modification of ligand parameters.³²⁸ Arduengo-type carbenes have been gained much attention as alternative to phosphines in homogeneous catalysts and offers several advantages.³²⁹⁻³³³ Carbenes show a high trans effect than N or P donor ligands, tuning the electronics around the metal and thereby modifying the catalytic properties.³³⁴ While chelate and pincer-type phosphine and amine ligands are well known, their carbene analogues are less reported. One reason could be they are usually obtained from ligand precursors that need to be activated through deprotonation by base, prior to the coordination to the metal. However, with the ready accessibility of imidazolium pyridine salts, they emerged a new class of CNC type ligands that lead to a variety of pincer complexes.^{335,336} Figure 6.1 shows examples of reported CNC ligand architecture.³³⁷⁻³³⁹



Figure 6.1: Examples of reported CNC architecture.

Danopolous reported the biscarbene based CNC ruthenium complex (Figure 6.2).³⁴⁰ Deprotonation of 2,6-bis(arylimidazolium)pyridine dibromide with KN(SiMe₃)₂ gave thermally stable 2,6-bis(arylimidazol-2-ylidene)pyridine, which further underwent complexation with [RuCl₂(PPh₃)₃] to obtain neutral CNC complex. The complex was utilized for catalytic activity in transfer hydrogenation of carbonyl compounds. Later, Peris synthesized similar ruthenium dibromide biscarbene complex (Ru(CNC)(CO)Br₂) by direct complexation of 2,6-bis(1-n-butylimidazolium-3-yl)pyridine bromide with [(COD)RuCl₂]n in refluxing EtOH/Et₃N. Et₃N acts as a good base for the deprotonation and EtOH upon oxidation to acetaldehyde and decarbonylation serves as a source of CO ligand.³⁴¹ The complex has proved to be effective in the transfer hydrogenation of ketones.



Figure 6.2: CNC Ruthenium Pincer Complexes

Suarez reported Ru biscarbene CNC complexes.³³⁶ The complex adapted a fac-geometry due to the flexibility of the extended arms, contrary to the previously reported mer-coordinated CNC complexes. The complex is synthesized by the treatment of bis-imidazolium salt with silver oxide, followed by transmetallation with [RuHCl(CO)(PPh₃)₃] leading to catalytic active species in imine hydrogenation in presence of *t*BuOK. In contrast, Pidko describe the formation of a mer-complex with the six-membered chelating bis-imidazolium CNC ligand with bulky mesityl substituents when reacted with [RuHCl(CO)(PPh₃)₃] using 2-tert-butylimino-2-diethylamino-1,3-dimethyl-perhydro-1,3,2-dazaphosphorine (BEMP) as base in the presence of LiBr.³⁴²nAlthough examples of lutidine derived CNC complexes are known, amino-based Ru-CNC complexes are not reported so far. Herein, I present the synthesis of amino-based Ru-CNC complex and some interesting catalytic properties they offer.

6.3 Results and discussion

Synthesis of Ru-CNC complex was initiated with the ligand synthesis. The amino-based CNC ligand synthesis requires multi-step process (See Appendix E, ligand synthesis). The Ag-NHC complex was prepared based on the N-heterocyclic carbene transfer to metal.³⁴³ Reaction with Ag-NHC with Ru precursor, RuHClCO(PPh₃)₃ in THF at 55 °C undergo transmetallation to give the amino-based Ru-CNC complex (Scheme 6.1).



Scheme 6.1: Synthetic route of Ru-CNC complex

The complex has been characterized by various spectroscopic methods. It is found to be stable in ambient atmosphere. The ¹H and ³¹P NMR is measured in CD₂Cl₂ (Figure 6.3). The ³¹P{¹H} NMR spectrum of the complex shows a singlet at 47.34 ppm. ¹H NMR reflect the non-equivalence of the two halves of the CNC ligand and the hydrido ligand gives rise two hydride peaks, a doublet at –13.8 ppm with J_{HP} = 24 Hz and at –7.7 ppm with J_{HP} = 24 Hz. The less intense hydride peak at -7.7 ppm represents the mer isomer of the complex in solution with PPh₃ trans to hydride. This is in line with the previous reported examples.³⁴⁴ The methylene protons of the CNC ligand



Figure 6.3: ³¹P{¹H} and ¹H NMR (CD₂Cl₂, 400 MHz) spectra of Ru-CNC complex.

produce four different doublet signals in the range 0.64–1.45 ppm. These data are consistent with the fac-coordination of the CNC ligand in which one of the NHC fragment is placed trans to the hydrido and the other trans to PPh₃.³⁴⁵⁻³⁴⁸ The IR spectrum of the complex is shown in Figure 6.4. The strong absorption band at 1924 cm⁻¹ represents the CO stretching mode and the band at 1973 cm⁻¹ can be assigned to Ru-H stretching. The N-H stretching mode appears at 3080 cm⁻¹.



Figure 6.4: IR spectrum of Ru-CNC complex.

Further confirmation of the structure of Ru-CNC was obtained from single-crystal X-ray diffraction (Figure 6.5). Crystals were obtained through vapor diffusion in toluene/hexane solvent

system. The complex crystallizes in I2/a space group and the solid state structure consists of a distorted octahedral structure in which the CNC pincer coordinated in a fac configuration. Table 6.1 summarizes the selected bond distances and angles for the complex. The Ru-H bond length of 1.56 (3) Å is within the expected bond lengths of Ru-H complexes.³⁴² The C-O bond distance of 1.156 (6) Å is in agreement with the triple bond character. In addition, the Ru-C distances of 2.118 (5) Å and 2.082 (8) Å which is trans to NH and trans to PPh₃ respectively. The bite angle of C13-Ru-C4 = 87.9 (2)°, while the CO is placed trans to C13 and the hydride trans to the NH of the pincer system. Elemental analysis also confirmed the right composition of the complex so formed. (Appendix E).



Figure 6.5: X-ray crystal structure of Ru-CNC (50% probability ellipsoids, solvent molecules emitted for clarity).

Atom	Atom	Length / Å	Atom	Atom	Atom	Angle/°
Ru	Н	1.56 (3)	н	Ru	Р	79 (2)
Ru	Р	2.348 (2)	н	Ru	Ν	175 (2)
Ru	Ν	2.288 (4)	Р	Ru	Ν	105.3 (1)
Ru	C4	2.118 (5)	C13	Ru	C4	87.9 (2)
Ru	C13	2.082 (8)	C13	Ru	C(O)	174.2 (2)
Ru	C(O)	1.871 (5)	C4	Ru	C(O)	87.0 (2)
0	C(Ru)	1.156 (6)	Ν	Ru	C(O)	92.4 (2)
			Ν	Ru	C13	89.9 (2)
			Ν	Ru	C4	84.9 (2)
			0	С	Ru	177.2 (4)

Table 6.1: Selected bond lengths and bond angles of Ru-CNC.

The catalytic activity of the complex is tested for various substrates and the studies are unoptimized and very preliminary. Initially, the activity was examined in the transfer hydrogenation of model ketone substrates (Appendix E). In the presence of ^tBuOK, the complex (0.5 mol%) catalyze the transfer hydrogenation of benzophenone at 80 °C using ⁱPrOH as the Hdonor. After 6 hours, full conversion of benzophenone to its corresponding alcohol is observed. Control experiments without any base additive led to no conversion of benzophenone, suggesting that the presence of a strong base seems to be necessary for the reaction to occur. I then turned my attention towards exploring the catalytic activity for the hydrogenation/transfer hydrogenation of C=C functional groups. For example, 1-hexene was used as a substrate, and employing 0.5 mol% catalyst loading in presence of ^tBuOK, the reaction afforded full conversion towards hexane under 15 bar of H₂ at 60 °C in tetrahydrofuran. Under the same reaction condition, instead of base, strong Brønsted acid was tested for its catalytic activity. Interestingly, using 5 equivalents of HCl(aq), the reaction afforded full conversion towards hexane. This suggests that metal-hydrido complex can deliver its hydrogen even under acidic conditions. Lowering the hydrogen pressure to 1 bar led no conversion of 1-hexene in acid as well as base additive. I have further examined the activity in transfer hydrogenation of 1-hexene by hydrogen transfer from isopropyl alcohol (ⁱPrOH) in the presence of ^tBuOK and HCl. No conversion was observed in this case as well, suggesting that a minimum pressure of hydrogen is necessary to show catalytic activity.

Attempts have been taken to test the biomass derived levulinic acid hydrogenation. Thus using 0.2 mol% catalyst loading without any additive afforded 58% yield of GVL under 20 bar of H₂ at 100 °C after 16 hours in water. At the same time ethyl levulinate was also tested for the transfer hydrogenation reaction using EtOH as H donor. Surprisingly, the reaction works both in acid and base additive. 30% and 23% GVL was observed using ^tBuOK and H₃PO₄(aq) respectively at 100 °C after 18 hours. Although the reaction conditions have not yet been optimized, it is obvious that these results are very promising and the catalyst shows very versatile behavior. However, the mechanistic studies and further optimization studies are yet to be carried out.

Observing these results, I hypothesis that this scenario opens for carrying out hydrodeoxygenation (HDO) transformations in acid, to mediate for example a complete carbonyl hydrogenation of series of cascade reaction of 1) hydrogenation, 2) dehydration, and 3) a second hydrogenation. The preliminary data discussed above supports my hypothesis. In short, the data shows that an alkene and a polyol containing both primary and secondary alcohols undergo HDO to the corresponding hydrocarbons using my novel CNC-Ru catalyst. However, I only have proof of reactivity at this stage. Optimizations as well as high-yielding reactions with model substrates are missing at this stage and are yet to be carried out. Such a transformation will be a game changing for biomass waste utilization. In this context, I have carried out some literature studies on biomass HDO reactions. HDO reactions of biomass is mainly limited to heterogeneous catalysis that employs harsher reaction conditions (high pressure, >50 bar H₂; high temperature, >250 °C). The model biomass substrates such as phenolic monomers or sorbitol are utilized for such transformations.³⁴⁸⁻³⁵³ A platinum based heterogeneous catalyst (Pt/NbOPO₄) is reported to
convert real biomass to hydrocarbons 28.1 wt% but still employing harsh reaction conditions (190 °C and 50 bar H₂).³⁵⁴ Homogeneous catalyzed HDO reactions on biomass derived substrates are scarcely reported. For example, 2,5-hexadione or glycerol is used as a substrate and generally poor yields are obtained (<40%) even at very harsh conditions.³⁵⁵⁻³⁵⁸ Therefore, research in this field is highly necessary to improve the current state-of-the-art catalytic system to much more mild and sustainable way.

6.4 Summary and outlook

In summary, I have synthesized novel amino-based Ru-CNC complex by replacing the phosphorous arms with N-Heterocyclic carbenes. I have characterized the complex with various spectroscopic methods such as NMR, IR, X-ray and elemental analysis. This complex represents the first amino-based Ru-CNC pincer and the complex adapts a fac-geometry of the CNC ligand in which one of the NHC fragment is placed trans to the hydrido and the other trans to PPh₃. It is important to mention here that this project on catalyst development and catalytic studies are at the very beginning stage, therefore they is room for future work. Further characterization such as HRMS, electrochemical studies are yet to be carried out for the complex. There is also possibility of fine sterics/electronic tuning the complex and study the structure-activity relationship. For example, the aromatic unit can be varied through inductive and mesomeric effect which will affect the Ru-H hydricity. Steric influence can be studied by tuning the wingtip substituents. In addition, the counter ions can be exchanged with other anions and study its effects as well.

The catalytic studies of the complex discussed in this Chapter is very preliminary and unoptimized results. This results show that the complex can catalyze an alkene and a polyol with primary and secondary into their corresponding hydrocarbons. The conditions employed for such transformations ranges from 65-140 °C, 15-30 bar H₂ and typically with HCl (aq). It is important to note that the complex is catalytically active for hydrogenation reactions under acidic conditions. Hence, analyzing these results, I hypothesis that this complex can be utilized for hydrodeoxygenation reactions (HDO) combining couple of dehydration and hydrogenation reactions to yield hydrocarbons. Studying the previously reported literatures on such reaction type shed light on the fact that new sustainable methods has to be developed. Biomass HDO reactions are mostly limited to heterogeneous systems and that to employing harsh reaction conditions. Therefore, developing mild and sustainable catalytic process for biomass transformation to hydrocarbons will be highly potential for biomass waste utilization. However, I have results only at this stage of reactivity. Optimization of the catalytic system with model substrates are also missing. Further development of the catalytic system and mechanistic studies will be carried out in Nielsen's lab in the future.

7. Main conclusions and perspectives

In conclusion, I have disclosed the activity of Ru-PNP complexes in combination with a Brønsted acid (H_3PO_4) within sustainable catalysis for various transformations. In this thesis, I have demonstrated that such a breakthrough method is first-in-class to upgrade biomass while employs game-changing mild and potentially sustainable conditions.

In Chapter 3, I have showed for the first time that the Ru-PNP pincer catalyst does catalyze hydrogenation reactions in presence of acid medium (H₃PO₄). Surprisingly, I figured out that this system efficiently transforms biomass derived substrate, furfural directly to GVL. This leads to further optimization of the reaction through the evaluation of various catalytic parameters. Using low loading of loadings of Ru-MACHO-BH in presence of H₃PO₄(aq), achieved good yield of GVL directly without any intermediates (levulinic acid) isolation or separation. This ground-breaking method obviously resulted in the possibility for spin-off projects.

In Chapter 4 is constructed by taking a one step back in the reaction chain and attempting with carbohydrates. To my delight, the reaction worked efficiently with good yields of GVL. Thus, one-pot direct approach for the catalytic production of GVL from carbohydrates (xylose, glucose and fructose) using the same combination of Ru-MACHO-BH and $H_3PO_4(aq)$ in EtOH/ H_2O under mild reaction conditions. Specifically, GVL yields of 73%, 31% and 34% were obtained for xylose, glucose and fructose respectively. Since no other products from LA was detected, the selectivity towards GVL was 100% based on the conversion of LA. And is important to mention that the GVL so-formed cannot be further hydrogenated in the present system.

As an out-turn of the findings from Chapter 3 and 4, Chapter 5 demonstrates a one-pot direct catalytic process for the direct production of GVL from different real biomass using a homogeneous catalyst Ru-MACHO-BH and $H_3PO_4(aq)$ with excellent yields under game-changing mild and sustainable conditions. This protocol represents the first example of direct transformation of lignocellulosic and starchy biomass to GVL using H_2 as a reductant. The yields of GVL obtained are 26 wt% from beechwood sawdust, 17 wt% from wheat straw, which represents approximately 55% of the maximum theoretical yield. In case of starchy biomass, the yields are 16 wt% and 20 wt% from rice grains and potato flour respectively. No chemical pretreatment or separation of the biomass feedstock or isolation of the intermediates is required and thus tremendous energy savings can be potentially gained in comparison to the existing thermochemical or hydrolysis approaches for production of fuels and chemicals from biomass.

Based on these results, it is high likely that the other PNP catalysts possibly shows activity. The future step to bring this project to a very broader scope is to try other PNP catalysts especially with Fe- or Mn-PNP complexes. I also envision using acceptable feedstock, such as paper tissue, coffee grounds, nut shells, peels from banana, potato, etc. Products other than GVL is also potentially important. For e.g., I observe 1,4-pentanediol as one of the products along with GVL from cellulose while using the Ru-PNP iPr congener as the catalyst. In some cases, sorbitol is

formed which can be considered yet another potential byproduct formed along with GVL. These observations has to be explored more in the future.

At this stage of the project, the major challenge is understanding the mechanism of the process and thereby identifying the potential bottlenecks. This will allow me to improve the selectivity and long-term stability of the system. Through identifying the intermediates and obtaining data of the reaction kinetics by monitoring the biomass conversion over time, further optimization on the reaction conditions is possible. With successful implementation of a reaction set-up, for example an automated liquid and sampling Parr reactor may help solve the current challenges. This can take this project to the next level with endless possibilities of new discoveries of potential products from biomass having different application and optimizing the reaction conditions to maximize the product. Hence, my scientific results can be considered as new sustainable path forward for the production of bulk-chemicals and fuels. In addition, I will be able to develop a continuous-flow system in which the biowaste feedstock is fed in a constant flow in one end of a reactor containing the catalytic system, and the GVL comes out in the other end. Such a setup will greatly improve the industrial potential of my system.

The superior efficiency of the catalytic system for direct hydrogenation of lignocellulose is speculated to originate from the synergistic effect between Ru-MACHO-BH and Brønsted acid combining cascade hydrogenation/protonolysis. The activity of Ru-PNP complex in acidic media is also noteworthy as is not been explored before. However, the mechanistic studies on the behavior of Ru-MACHO-BH with Brønsted acid is not investigated yet due to the time limitation. Further investigations on this project especially the mechanistic investigations will be carried out in the future in Nielsen's lab.

I strongly believe, this new discovery of the activity of Noyori-type pincer complexes with acid will certainly paves the way to explore otherwise unexplored plethora of transformations. For example, I envision that combining PNP pincer catalyst with a Brønsted acid can be used as a solution to hydrogenation carboxylic acid, that are otherwise notoriously difficult substrate to hydrogenate. This system can be utilized to hydrogenate formic acid to methanol and thereby having a great potential in CO₂ valorization as well.

In Chapter 6, I present a novel Ru-CNC complex, its synthesis and characterization. Although examples of lutidine derived CNC complexes are known, amino-based Ru-CNC complexes are not reported so far. Thereby representing the first amino based Ru-CNC complex. This is achieved by replacing the phosphorous arms with N-heterocyclic carbenes. I have characterized the complex with various spectroscopic methods such as NMR, IR, X-ray and elemental analysis. The complex adapts a fac-geometry of the CNC ligand in which one of the NHC fragment is placed trans to the hydrido and the other trans to PPh₃. It is important to mention here that this project on catalyst development and catalytic studies are at the very beginning stage, therefore they is room for future work. Further characterization such as HRMS, electrochemical studies are yet to be carried out for the complex. There is also possibility of tuning the sterics and electronic parameters and study the structure-activity relationship. For example, the aromatic unit can be varied through

inductive and mesomeric effect which will effect the Ru-H hydricity. Steric influence can be studied by tuning the wingtip substituents. In addition, the couter ions can be exchanged with other anions and study its effects as well.

Through some catalytic reactions with some model substrates, it was found that the complex is active in highly acidic conditions. The studies are in the very beginning stage. However, my preliminary data supports towards the transformation of some of the model substrates. Hence, I hypothesis that this scenario opens for carrying out hydrodeoxygenation (HDO) transformations in acid. For example, alkene and a polyol containing both primary and secondary alcohols undergo HDO to the corresponding hydrocarbons using my novel CNC-Ru catalyst under strong acidic conditions. Optimizations of the catalytic system with model substrates are yet to be carried out. Developing a mild process for converting biomass to hydrocarbons using H₂ again for biomass waste utilization is attractive.

This interesting property of the complex can be utilized for activation of several molecules in acid medium. For example for hydrogenating CO₂ to formic acid, thereby allowing CO₂ hydrogenation directly to methanol possibly through a prior esterification process. Therefore I see a great potential on the new catalyst and I believe this can further opens to several projects with great potential and finding creative solutions within homogeneous catalysis.

Appendix A: Supplementary Information for chapter 3

1. General Information

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Furfural (99%), H_3PO_4 (85 w/w%), Ru-MACHO-BH are commercially available and used without further purification. H_2 gas ($H_2O \leq 3$ ppm; $O_2 \leq 2$ ppm) was purchased from Air Liquide. All reactions dealing with air or moisture-sensitive compounds were performed using standard Schlenk techniques or in an argon-filled glovebox. GC-FID were recorded on an Agilent 19091J-413 HP-5 5% Phenyl methyl siloxane capillary column using 1,4-dioxane as internal standard. The ¹H NMR spectra were recorded on a Bruker Advance III 400 MHz spectrometer and were referenced on the solvent peak.

For the hydrogenation screening experiment, in a glove box, substrate (0.65 mmol) and catalyst (0.2-1 mol%) were weighed in a glass vial equipped with a magnetic stir bar and sealed with a Teflon-lined cap. Upon bringing the glass vial outside the glove box, dissolved 1 mL of solvent (H₂O/EtOH) followed by corresponding amount of acid. Subsequently, the vial was placed in a seven-well reactor with a needle placed through the rubber stopper of the vials for the gas flow. The autoclave was sealed tightly and flushed with argon/hydrogen (three times) and finally required hydrogen pressure (30 bar) was loaded into the autoclave and desired temperature was also applied. The reactor was cooled to room temperature before the hydrogen was released and the sample was prepared for GC analysis with 1,4- dioxane as the internal standard.



Figure A1: High pressure autoclave used in this study



Figure A2: Calibration curve for GVL using 1,4-dioxane as the internal standard

2. Catalytic reactions for hydrogenation of furfural to GVL

	Ca <u>HCOO</u> 30 bar, Furfural	atalyst ∖H, EtOH/H₂Q , 100 °C, 18 h	√0 GVL	Ru-MACHO		l P [/] P [/] Pr₂ ů—CO I
Entry	Catalyst (mol%)	нсоон [M]	EtOH/H ₂ O (v/v) ratio	P/T [bar]/[°C]	Product	GVL yield ^[a] [%]
1	Ru-MACHO (0.2)	2	1:1	30/100	LA	-
2	Ru-MACHO (0.2)	2	7:3	30/100	LA	-
3	Ru-1 (0.2)	2	7:3	20/100	LA	-
4	Ru-1 (0.2)	2	H ₂ O	20/100	LA	-
5	Ru-1 (0.2)	2	7:3	30/100	LA	-

Table A1: Reaction conditions: furfural (0.90 mmol), EtOH/H₂O (1 mL) at 100 °C for 18 h. ^[a] Determined by GC-FID using 1,4-dioxane as internal standard.



Entry	Ru-MACHO-BH [mol%]	нсоон [M]	Products	GVL yield ^[a] [%]
1 ^[b]	2	4	MeOH	0
2	-	4	-	0
3	0.2	2	GVL	34
4	0.2	4	GVL	48
5	2	4	furfuryl alcohol, GVL	10
6	0.2	8	LA	0
7	2	8	furfuryl alcohol, GVL	37

Table A2: Reaction conditions: furfural (0.90 mmol), 1:1 EtOH/H₂O (1 mL), 30 bar H₂ at 100 °C for 18 hours. ^[a] Determined by GC-FID using 1,4-dioxane as internal standard. ^[b] Without FAL.

Furfu	O Yl alcohol	Ru-MACHO-BH HCOOH, EtOH/H ₂ O 30 bar, 100 °C, 18 h	√0 ≠0 GVL	H N P P H Ph ₂ H	PPh ₂ —CO 3H ₃
				Ru-MACHO)-BH
	Entry	Ru-MACHO-BH [mol%]	G	VL yield ^[a] [%]	
	1	0.2		48	
	2	1		17	

Table A3: Reaction conditions: furfuryl alcohol (0.90 mmol), HCOOH (4 M), 1:1 EtOH/H₂O (1 mL), 30 bar H₂ at 100 °C for 18 hours. ^[a] Determined by GC-FID using 1,4-dioxane as internal standard.



Table A4: Reaction conditions: furfural (0.90 mmol), Acid additive (4 mmol), 1:1 EtOH/H₂O (1 mL), 30 bar H₂ at 100 °C for 18 hours. ^[a] Determined by GC-FID using 1,4-dioxane as internal standard.

	Furfural	Ru-MACHO-BH H ₃ PO ₄ , EtOH/H ₂ O 30 bar, 120 °C	→ GVL	≥0 H N P Ph₂ Ph₂ Ru-MA	Н
Entry	Ru-MACHO-BH [mol%]	H₃PO₄(aq) [M]	Time [h]	Products	GVL yield ^[a] [%]
1	1	3.8	7	GVL	80
2	0.5	3.8	7	GVL, LA	46
3	1	3.8	18	GVL	84
4 ^[b]	1	7.5	18	GVL	41
5 ^[c]	1	1.9	18	GVL	60

Table A5: Reaction conditions: furfural (0.90 mmol), EtOH (1 mL), 30 bar H₂ at 120 °C. ^[a] Determined by GC-FID using 1,4-dioxane as internal standard. ^[b] 0.5 mL of EtOH, ^[c] 2 mL of EtOH.



Table A6: Reaction conditions: furfural (0.90 mmol), EtOH (1 mL), 30 bar H_2 at 100 °C for 5 hours. ^[a] Determined by GC-FID using 1,4-dioxane as internal standard.



Area Percent Report

Sorted By	:	Signa	1		
Calib. Data Modified	:	12/8/	2006	12:33:15	PM
Multiplier	:	1.000	0		
Dilution	:	1.000	0		
Use Multiplier & Dilut	tion	Factor w	ith	ISTDs	

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
			I			
1	1.256	BB	0.0100	268.28110	0.24542	?
2	1.330	BV S	0.0207	2.82523e4	25.84459	?
3	1.386	BV X	0.0157	4.93722	0.00452	?
4	1.413	VV X	8.40e-3	23.56898	0.02156	2
5	1.436	VBS	0.0109	7.27989e4	66.59479	?
6	1.638	BV	0.0257	46.64048	0.04267	2
	1.660	VV VD	0.0180	26.36352	0.02412	2
8	2 012	DD	0.0182	15 73760	0.00432	- 2
10	2.012	BB	0.0214	3/03 01392	3 19615	2
11	2 847	BB	0.0198	2 00222	0.00183	2
12	3.050	BV	0.0342	6.86157	0.00628	C14
13	3.202	VB	0.0531	76.25008	0.06975	?
14	3.540	BB	0.0265	1,94312	0.00178	C15
15	3.976	BB	0.0257	2.25746	0.00207	C16
16	4.165	BB	0.0309	10.32347	0.00944	?
17	4.407	BB	0.0308	3.91556	0.00358	?
18	4.602	BB	0.0291	3.89039	0.00356	?
19	4.848	BV	0.0414	13.97369	0.01278	?
20	4.919	VB	0.0302	4.19565	0.00384	?
21	5.190	BB	0.0368	64.86580	0.05934	?
22	5.477	BB	0.0553	3301.24219	3.01990	?
23	5.933	BB	0.0321	26.95572	0.02466	?
24	6.912	BB	0.0311	6.41667	0.00587	?
25	7.045	BB	0.0341	723.48901	0.66183	?
26	7.342	BB	0.0364	73.86584	0.06757	?
27	8.472	BB	0.0374	13.21048	0.01208	?
28	8.787	BB	0.0618	10,96173	0.01003	?
29	8.941	BV	0.0297	3.45419	0.00316	?
30	9.008	VB	0.0376	12.45941	0.01140	?
31	11.650	BB	0.0404	4.49463	0.00411	?
32	14.375	BB	0.0367	4.55242	0.00416	?
33	16.265	BB	0.0380	4.33731	0.00397	?
34	16.388	BB	0.0420	4,90215	0.00448	?

Figure A3: GC-FID of the crude reaction of furfural (0.90 mmol) with 1 mol% Ru-MACHO-BH using 3.8 M $H_3PO_4(aq)$ and EtOH (1 mL), 30 bar H_2 at 100 °C after 5 hours using 1,4-dioxane as internal standard.



Figure A4: ¹H NMR (DMSO- d_6 , 400 MHz) of the crude reaction of furfural (0.90 mmol) with 1 mol% Ru-MACHO-BH and 3.8 M H₃PO₄(aq) in EtOH (1 mL), 30 bar H₂ at 100 °C after 5 hours.



Figure A5: GC-FID of the crude reaction of furfural (0.90 mmol) with 0.5 mol% Ru-MACHO-BH using 3.8 M H₃PO₄(aq) and EtOH (1 mL), 30 bar H₂ at 100 °C after 18 hours using 1,4-dioxane as internal standard.

1.05905

9.15407

0.00000

3.98981

5.63802

12.06982

2.91982

3.18205

8.66576

0.0196 3543.93848

0.0578 3693.07202

0.0205

0.0247

0.0000

0.0280

0.0297

0.0599

0.0294

0.0307

0.0330

3.31095

0.00099

0.00000 C15

0.00373 C16 0.00527 ?

0.01128 ?

3.45028 ?

0.00297 ?

0.00810 ?

0.00273

?

? 0.00855 C14

?

9

10

11

12

13

14

15

16

17

18

19

2.286 BB

2.848 BB

3.040 BB

3.978 BB

4.603 BB

4.853 BB

5.218 BB

5.486 BB

6.362 BB

6.913 BB

3.466



Figure A6: ¹H NMR (DMSO- d_6 , 400 MHz) of the crude reaction of furfural (0.90 mmol) with 0.5 mol% Ru-MACHO-BH and 3.8 M H₃PO₄(aq) in EtOH (1 mL), 30 bar H₂ at 100 °C after 18 hours.



Figure A7: GC-FID of the crude reaction of furfural (0.90 mmol) with 0.5 mol% Ru-MACHO-BH using 3.8 M $H_3PO_4(aq)$ and 1:1 v/v EtOH/ H_2O (1 mL), 30 bar H_2 at 100 °C for 18 hours using 1,4-dioxane as internal standard.



Figure A8: ¹H NMR (DMSO-d6, 400 MHz) of the crude reaction of furfural (0.90 mmol) with 0.5 mol% Ru-MACHO-BH and 3.8 M $H_3PO_4(aq)$ in 1:1 v/v EtOH/ H_2O (1 mL), 30 bar H_2 at 100 °C for 18 hours.



Figure A9: ¹H NMR (DMSO-d6, 400 MHz) of the blank reaction with Ru-MACHO-BH and 3.8 M HCOOH in 1:1 v/v EtOH/H₂O (1 mL) in absence of furfural, 30 bar H₂ at 100 °C for 18 hours.



Figure A10: ¹H NMR (EtOH-d6, 400MHz) of Ru-MACHO-BH in phosphoric acid after 1 hour.



Figure A11: ³¹P NMR (EtOH-d6, 400MHz) of Ru-MACHO-BH in phosphoric acid after 1 hour.







Figure A13: ³¹P NMR (EtOH-d6, 400MHz) of Ru-MACHO-BH in phosphoric acid after 18 hours

Appendix B: Supplementary Information for chapter 4

1. General Information

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Furfural (99%), H_3PO_4 (85 w/w%), Ru-MACHO-BH are commercially available and used without further purification. H_2 gas ($H_2O \le 3$ ppm; $O_2 \le 2$ ppm) was purchased from Air Liquide. All reactions dealing with air or moisture-sensitive compounds were performed using standard Schlenk techniques or in an argon-filled glovebox. GC-FID were recorded on an Agilent 19091J-413 HP-5 5% Phenyl methyl siloxane capillary column using 1,4-dioxane as internal standard. The ¹H NMR spectra were recorded on a Bruker Advance III 400 MHz spectrometer and were referenced on the solvent peak.

For the hydrogenation screening experiment, in a glove box, substrate (0.65 mmol) and catalyst (0.5 mol%) were weighed in a glass vial equipped with a magnetic stir bar and sealed with a Teflon-lined cap. Upon bringing the glass vial outside the glove box, dissolved 1 mL of solvent (H₂O/EtOH) followed by corresponding amount of acid. Subsequently, the vial was placed in a seven-well reactor with a needle placed through the rubber stopper of the vials for the gas flow. The autoclave was sealed tightly and flushed with argon/hydrogen (three times) and finally required hydrogen pressure (30 bar) was loaded into the autoclave and desired temperature was also applied. The reactor was cooled to room temperature before the hydrogen was released and the sample was prepared for GC analysis with 1,4- dioxane as the internal standard.



Figure A1: Calibration curve for GVL using 1,4-dioxane as the internal standard

2. Catalytic experiments for hydrogenation of xylose to GVL

	Ru-MACH HOOOH 0H 30 bar H Xylose	О-ВН <u>DH/H2</u> О → Ощ ₂ , 125 ⁰ С	GVL H	$H = PPh_2$ $= Ru = CO$ $H = BH_3$ $= CHO-BH$
Entry	Ru-MACHO-BH [mol%]	H ₃ PO ₄ [M]	Solvent	GVL Yield ^a [%]
1	0.5	3.8	IPA	43
2	0.5	3.8	MeOH	38
3	0.5	5.7	MeOH	45
4	0.2	3.8	IPA	47
5	0.2	3.8	MeOH	47

Standard reaction conditions: Xylose (0.65 mmol), 85 w/w% H_3PO_4 , alcohol (1 mL), 30 bar H_2 in 48 hours. ^[a]Determined by GC-FID using 1,4-dioxane as the internal standard.

Table A1: Direct conversion of xylose to GVL in different alcohol media.

но но но ху	Ru-MAC OH OH 30 bar H ₂ , $\frac{H_3PO_2}{OH}$	CHO-BH <u>₄, EtOH →</u> 125 ⁰ C, 96 hours	GVL	H PPh ₂ Ph ₂ H Ph ₂ H Ph ₂ H BH ₃ Ru-MACHO-BH
Entry	Ru-MACHO-BH [mol%]	Solvent	Time (h)	GVL Yield ^a [%]
1	0.5	EtOH	96	44%
2	0.5	IPA	96	41%
3	0.2	EtOH	96	46%

Standard reaction conditions: Xylose (0.65 mmol), 3.8 M $H_3PO_4(aq)$, alcohol (1 mL), 30 bar H_2 in 48 hours. ^[a]Determined by GC-FID using 1,4-dioxane as the internal standard.

Table A2: Direct conversion of xylose to GVL with longer reaction time.



Standard reaction conditions: 3.8 M $H_3PO_4(aq)$, 1:1 EtOH/ H_2O (1 mL), 30 bar H_2 in 18 hours. ^[a]Determined by GC-FID using 1,4-dioxane as the internal standard.

Table A3: Direct conversion of xylose to GVL with shorter reaction time.



Area Percent Report

Sorted By : Signal Calib. Data Modified : 12/8/2006 12:33:15 PM Multiplier : 1.0000 Dilution : 1.0000 Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A,

Peak	RetTime	Туре	e Width	Area	Area	Name
#	[min]		[min]	[pA*s]	8	I
1	1.257	BB	7.25e-3	24.22780	0.03133	?
2	1.315	BV S	7.77e-3	5316.80273	6.87569	?
3	1.370	BV X	7.47e-3	2.32947	0.00301	?
4	1.393	VV X	0.0141	83.79234	0.10836	?
5	1.414	VV X	8.36e-3	24.28563	0.03141	?
6	1.435	VBS	0.0102	6.77674e4	87.63684	?
7	1.709	BB	0.0143	2.55260	0.00330	?
8	1.776	BB	0.0117	9.05608	0.01171	?
9	2.007	BB	0.0139	37.99453	0.04913	?
10	2.221	BV	0.0151	6.83144e-1	0.00088	?
11	2.281	VB	0.0177	2557.00781	3.30672	?
12	2.993		0.0000	0.00000	0.00000	C14
13	3.466		0.0000	0.00000	0.00000	C15
14	3.577	BB	0.0277	3.27026	0.00423	?
15	3.926		0.0000	0.00000	0.00000	C16
16	4.604	BB	0.0311	16.18981	0.02094	?
17	5.433	BB	0.0399	1439.08240	1.86102	?
18	6.936	BB	0.0363	8.08529	0.01046	?

Figure A2: GC-FID of the crude mixture of the reaction of xylose (0.65 mmol) with Ru-MACHO-BH (0.5 mol%) using 5.7 M $H_3PO_4(aq)$ and under 30 bar H_2 at 125 °C in 1:1 v/v EtOH/H₂O after 48 hours.



Figure A3: ¹H NMR (dmso-d₆, 400 MHz) of the crude reaction of 0.6 mmol xylose (0.65 mmol) and Ru-MACHO-BH (0.5 mol%) using 5.7 M $H_3PO_4(aq)$ under 30 bar H_2 at 125 °C in 1:1 v/v EtOH/H₂O mixture after 48 hours.



Figure A4: GC-FID of the reaction mixture of the reaction of xylose (0.1 mmol) and Ru-MACHO-BH (0.5 mol%) using 5.7 M H₃PO₄(aq) under 30 bar H₂ at 125 °C in 1:1 v/v EtOH/H₂O mixture after 48 hours.



Area Percent Report

Sorted By Calib. Data Modified Multiplier Dilution	:	Sign 12/8 1.00	al /2006 00	12:33:15	PM
DITUCTON	•	1.00	00		
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Signal 1: FID1 A,

Peak	RetTime	Type	Width	Area	Area	Name
#	[min]		[min]	[pA*s]	8	
1	1.259	BB	8.90e-3	2.86774	0.00384	?
2	1.315	BV S	7.71e-3	5080.50244	6.80246	?
3	1.370	BV X	7.31e-3	2.04384	0.00274	?
4	1.393	VV X	0.0141	61.48492	0.08232	?
5	1.414	VV X	8.05e-3	21.36893	0.02861	?
6	1.436	VB S	0.0105	6.61445e4	88.56311	?
7	1.707	BB	0.0137	3.35637	0.00449	?
8	2.011	BB	0.0145	3.99035	0.00534	?
9	2.216	BB	0.0156	5.09153	0.00682	?
10	2.284	BB	0.0184	3242.40674	4.34137	?
11	2.993		0.0000	0.00000	0.00000	C14
12	3.466		0.0000	0.00000	0.00000	C15
13	3.926		0.0000	0.00000	0.00000	C16
14	5.301	BB	0.0248	1.83525	0.00246	?
15	5.378	BB	0.0338	113.39149	0.15182	?
16	5.880	BB	0.0340	3.44956	0.00462	?

Figure A5: GC-FID of the reaction mixture of glucose (0.1 mmol) and Ru-MACHO-BH (0.5 mol%) using 5.7 M $H_3PO_4(aq)$ under 30 bar H_2 at 125 °C in 1:1 v/v EtOH/ H_2O mixture after 48 hours.



Area Percent Report

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Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs
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Signal 1: FID1 A,

Peak	RetTime	Type	Width	Area	Area	Name
#	[min]		[min]	[pA*s]	8	
1	1.255	BV S	6.43e-3	698.01837	0.95828	?
2	1.314	VV S	7.67e-3	4462.77783	6.12679	?
3	1.370	BV X	8.24e-3	2.49964	0.00343	?
4	1.392	VV X	0.0133	69.36193	0.09522	?
5	1.413	VV X	8.36e-3	20.82538	0.02859	?
6	1.435	VBS	9.95e-3	6.39320e4	87.76988	?
7	1.705	BB	0.0121	12.34311	0.01695	?
8	2.011	BB	0.0144	2.31383	0.00318	?
9	2.215	BB	0.0155	6.15900	0.00846	?
10	2.281	BB	0.0175	2825.18774	3.87860	?
11	2.993		0.0000	0.00000	0.00000	C14
12	3.466		0.0000	0.00000	0.00000	C15
13	3.926		0.0000	0.00000	0.00000	C16
14	5.297	BB	0.0249	3.10943	0.00427	?
15	5.407	BB	0.0344	754.19977	1.03541	?
16	5.866	BB	0.0317	10.75708	0.01477	?
17	6.004	BB	0.0338	8.02883	0.01102	?

Figure A6: GC-FID of the crude reaction mixture of fructose (0.1 mmol) and Ru-MACHO-BH (0.5 mol%) using 5.7 M $H_3PO_4(aq)$ under 30 bar H_2 at 125 °C in 1:1 v/v EtOH/ H_2O mixture after 48 hours.



Figure A7: ¹H NMR (dmso-d₆, 400 MHz) of the crude reaction of fructose (0.1 mmol) and Ru-MACHO-BH (0.5 mol%) using 5.7 M $H_3PO_4(aq)$ under 30 bar H_2 at 125 °C in 1:1 v/v EtOH/ H_2O mixture after 48 hours.

Appendix A4: Supplementary information for chapter 5

1. General information

Most chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Ru-MACHO-BH, Microcrystalline cellulose, Xylan (corn core and beech wood) are commercially available and used without further purification. Real biomass like sawdust from beech wood and wheat straw are dried in oven before use. Potato flour and rice grains are dried under vacuum overnight before use. H₂ gas (H₂O \leq 3 ppm; O₂ \leq 2 ppm) was purchased from Air Liquide. All reactions dealing with air or moisture-sensitive compounds were performed using standard Schlenk techniques or in an argon-filled glovebox. GC-FID were recorded on an Agilent 19091J-413 HP-5 5% Phenyl methyl siloxane capillary column using 1,4-dioxane as the internal standard. The ¹H and ¹³C NMR spectra were recorded on a Bruker Advance III 400 MHz spectrometer. The batches for gas analysis, the gas phase was carefully collected in a gas bag and analyzed by MicroGC. TGA was fulfilled under N₂ atmosphere (30 mL min⁻¹) using a METTLER TOLEDO thermal analyzer in the temperature interval 25-300 °C with a constant heating rate of 10 °C min⁻¹.

2. General procedure for catalysis

For a typical hydrogenation screening experiment, in a glove box, substrate (0.1-0.65 mmol) and catalyst (0.5 mol%) were weighed in a glass vial equipped with a magnetic stir bar and sealed with a Teflon-lined cap. Biomass such as sawdust and straw was dried in the oven (140 °C) overnight. Potato flour and rice grains dried under vacuum overnight before use. Upon bringing the glass vial outside the glove box, dissolved 1 mL of solvent (H₂O) followed by corresponding amount of acid (3.8 M-10.9 M mmol). Subsequently, the vial was placed in the reactor with a needle placed through the rubber stopper of the vial for the gas flow. At a time one reaction was run in order to avoid cross contamination. The autoclave was sealed tightly and flushed with argon/hydrogen (three times) and finally required hydrogen pressure (30 bar) was loaded into the autoclave. The reactor was then slowly heated to the desired temperature under stirring and held at the desired temperature for desired time. After the reaction is finished, the reactor was cooled to room temperature before the gas was released and the sample was prepared for GC analysis with 1,4-dioxane as the internal standard.



Figure A1: Calibration curve for GVL using 1,4-dioxane as the internal standard.

3. Catalytic reactions



Biomass	Entry	H₃PO₄ [M]	Time [h]	GVL yield ^a [wt% (mol%)]	
		Beechw	ood sawdust		
Lignocellulosic content	wt%	1	10.1	24	25 (54)
Hemicellulose	37	2	10.1	38	21 (46)
Cellulose	42	3 ^b	10.9	48	8 (17)
Lignin	19				
		Whe	eat straw		
Lignocellulosic content	wt%	4 ^c	10.9	48	3 (9)
Hemicellulose	25				
Cellulose	33				
Lignin	17				

Standard reaction conditions: Beech wood (91 mg, corresponding to 0.22 mmol hemicellulose and 0.21 mmol cellulose ¹⁹) and Ru-MACHO-BH (1.65 mg, 0.0028 mmol), 85 w/w% $H_3PO_4(aq)$ in H_2O (1 mL) at 140 ^{0}C and 30 bar $H_{2,a}$ Determined by GC-FID. Yields are calculated with respect to dry biomass. ^b Beechwood (1g), Ru-MACHO-BH (20 mg), H_2O (15 mL). ^c Wheat straw (1g), Ru-MACHO-BH (20 mg), H_2O (15 mL).

Table A1: Direct conversion of biomass feedstock to GVL



Entry	Catalyst (mol%)	Substrate (mmol)	H₃PO₄ (mmol)	Solvent	GVL Yieldª (%)
1	Ru-MACHO-BH (0.5)	Xylan (corn core) 0.6	4	EtOH	52
4	Ru-MACHO-BH (0.5)	Xylan (beech wood) 0.1	6	EtOH/H₂O	38
5	Ru-MACHO-BH (0.5)	Xylan (beech wood) 0.6	6	EtOH/H₂O	28

Reaction conditions: Xylan from corn core (76.2% xylose monomers). Xylan from beech wood (95%), 85 w/w% H_3PO_4 , 1:1 v/v EtOH/ H_2O mixture (1 mL), 30 bar H_2 , at 125 °C in 48 hours. Catalyst loading and yield are relative to moles of xylose monomers contained in xylan. ^aDetermined by GC-FID using 1,4-dioxane as the internal standard.

Table A2: Direct conversion of xylan to GVL



Entry	Catalyst (mol%)	Cellulose (mmol)	H₃PO₄ (M)	Time (h)	GVL Yield ^a (%)
1	Ru-MACHO-BH (0.5)	0.1	5.7	48	37
2	Ru-MACHO-BH (0.5)	0.1	6.5	48	41
3	Ru-MACHO-BH (0.5)	0.1	6.5	72	47
4	Ru-MACHO-BH (0.5)	0.1	6.5	96	48
5	Ru-MACHO-BH (0.5)	0.1	7.5	96	50

Reaction conditions: Microcrystalline cellulose, 85 w/w% H_3PO_4 , H_2O (1 mL), 30 bar H_2 , at 140 °C. ^aDetermined by GC-FID using 1,4-dioxane as the internal standard. Catalyst loading and yield are relative to moles of glucose monomers contained in cellulose.

Table A3: Direct conversion of cellulose to GVL at 140 °C with different acid concentration.



Area Percent Report

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Dilution	:	1.00	000		
Use Multiplier & Dilut	ion	Factor	with	ISTDs	

Signal 1: FID1 A,

Peak	RetTime	Type	Width	Area	Area	Name
#	[min]		[min]	[pA*s]	8	
1	1.377	BB	8.47e-3	201.97957	1.40650	?
2	1.502	BB	9.87e-3	3.96411e-1	0.00276	?
3	1.549	BV	9.28e-3	2.71882	0.01893	?
4	1.577	VBS	0.0103	1.34929e4	93.95897	?
- 5	2.450	HB	0.0176	502.00952	3.49578	?
6	2.993		0.0000	0.00000	0.00000	C14
7	3.466		0.0000	0.00000	0.00000	C15
8	3.926		0.0000	0.00000	0.00000	C16
9	5.602	MM	0.0464	160.41508	1.11706	?

Figure A2: GC-FID of the reaction mixture of beechwood sawdust (91 mg) with 10.9 M of H_3PO_4 and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 24 hours.



Figure A3: ¹H NMR (D₂O, 400 MHz) of the crude reaction of beechwood sawdust (91 mg) with 10.9 M of H_3PO_4 and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 24 hours.



Area Percent Report

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Dilution	:	1.0000		
Use Multiplier & Dilut	tion	Factor with	ISTDs	

Signal 1: FID1 A,

Peak	RetTime	Type	Width	Area	Area	Name
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2	1.370	BV	0.0120	1.65894	0.00138	?
3	1.414	BV	0.0117	20.32687	0.01688	?
4	1.435	VB S	0.0261	1.15164e5	95.63568	?
5	2.286	BH	0.0252	2457.04810	2.04041	?
6	2.993		0.0000	0.00000	0.00000	C14
7	3.466		0.0000	0.00000	0.00000	C15
8	3.926		0.0000	0.00000	0.00000	C16
9	5.400	MM	0.0419	482.59518	0.40076	?

Figure A4: GC-FID of the reaction mixture of wheat straw (91 mg) with 10.9 M of H_3PO_4 and Ru-MACHO BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 48 hours.


Figure A5: ¹H NMR (dmso-d₆, 400 MHz) of the crude reaction of wheat straw (91 mg) with 10.9 M of H_3PO_4 and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 48 hours.



Figure A6: GC-FID of the reaction mixture of rice grains (91 mg) with 10.9 M of H_3PO_4 and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 72 hours.



Area Percent Report

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Use Multiplier & Dilut	tion	Factor with	ISTDs	

Signal 1: FID1 A,

Peak	RetTime	T	pe	Width	Area	Area	Name
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1	1.255	BB		0.0100	10.00459	0.00536	?
2	1.316	BB		0.0147	3.70818	0.00199	?
3	1.368	BB		7.96e-3	2.03438	0.00109	?
4	1.411	BV		8.68e-3	36.07652	0.01932	?
5	1.432	VB	S	0.0190	1.79040e5	95.89713	?
6	1.526	BB	х	9.07e-3	7,12259	0.00381	?
7	1.630	BB	Х	9.42e-3	2.87165e-1	0.00015	?
8	1.724	BB		0.0369	3.21941	0.00172	?
9	2.021	BB		0.0176	3.45120	0.00185	?
10	2.294	HH		0.0217	6137.80908	3.28753	?
11	2.993			0.0000	0.00000	0.00000	C14
12	3.466			0.0000	0.00000	0.00000	C15
13	3.926			0.0000	0.00000	0.00000	C16
14	5.434	HH		0.0439	1424.71912	0.76311	?
15	5.900	HH		0.0656	31.61740	0.01693	?
Total	.s :				1.86700e5		

Figure A7: GC-FID of the reaction mixture of potato flour (91 mg) with 10.9 M of H_3PO_4 and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 72 hours.



Area Percent Report

Sorted By Calib. Data Modified	:	Sign 12/8	nal 3/2006	5 12 : 33:15	PM
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Dilution	:	1.00	000		
Use Multiplier & Dilu	ation	Factor	with	ISTDs	

Signal 1: FID1 A,

Peak	RetTime	Type	Width	Area	Area	Name	
#	[min]		[min]	[pA*s]	00		
1	1.256	BB	6.81e-3	67.07451	0.08230	?	
2	1.314	BV S	8.03e-3	5192.20654	6.37053	?	
3	1.371	BV X	7.34e-3	2.04072	0.00250	?	
4	1.393	VV X	0.0144	46.74556	0.05735	?	
5	1.414	VV X	8.01e-3	22.86432	0.02805	?	
6	1.435	VBS	0.0110	7.19634e4	88.29481	?	
7	1.705	BB	0.0120	19.52512	0.02396	?	
8	1.776	BB	0.0122	6.01460	0.00738	?	
9	2.008	BB	0.0143	25.60098	0.03141	?	
10	2.216	BB	0.0155	6.97473	0.00856	?	
11	2.282	BB	0.0180	2797.69287	3.43260	?	
12	2.993		0.0000	0.00000	0.00000	C14	
13	3.466		0.0000	0.00000	0.00000	C15	
14	3.578	BB	0.0269	2.47971	0.00304	?	
15	3.926		0.0000	0.00000	0.00000	C16	
16	4.604	BB	0.0300	12.75125	0.01565	?	
17	4.782	BB	0.0295	5.19553	0.00637	?	
18	5.305	BB	0.0224	1.40013	0.00172	?	
19	5.428	BB	0.037	7 1286.333	01 1.578	325 ?	
20	5.879	BB	0.028	9 3.587	93 0.004	140 ?	
21	6 014	BB	0.027	3 2 805	56 0.003	844 2	
21	6 022		0.027	5 4 757	25 0.005	54.5	
22	6.932		0.027	3 4.757	25 0.000	240 D	
23	6.968	VB	0.038	3 1.130	25 0.009	148 f	
24	7.372	BB	0.033	8 6.224	08 0.00	764 ?	
25	7.910	BB	0.034	3 20.136	74 0.024	171 ?	

Figure A8: GC-FID of the reaction mixture of xylan from corn core (0.6 mmol) with 5.7 M of H_3PO_4 and Ru-MACHO-BH (0.5 mol%) under 30 bar H_2 and 125 °C in 1:1 v/v EtOH/ H_2O mixture for 48 hours.



Figure A9: ¹H NMR (dmso-d₆, 400 MHz) of the crude reaction of 0.6 mmol Xylan from corn core (0.6 mmol) with 5.7 M of H_3PO_4 and Ru-MACHO-BH (0.5 mol%) under 30 bar H_2 and 125 °C in 1:1 v/v EtOH/ H_2O mixture for 48 hours.



Figure A10: GC-FID of the reaction mixture of cellulose (0.6 mmol) with 7.5 M of $H_3PO_4(aq)$ and Ru-MACHO-BH (0.5 mol%) under 30 bar H_2 and 140 °C in water for 96 hours.



Figure A11: GC-FID of the reaction mixture of GVL with 10.9 M of $H_3PO_4(aq)$ and Ru-MACHO-BH under 30 bar H_2 and 140 °C in water after 72 hours hours.

Moisture determination by TGA analysis



Figure A12: TGA profile for moisture content analysis based on thermal degradation of sawdust and straw.

Gas phase analysis by MicroGC

External Standard Report

Page 1 of 2 (13)

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External Standard Report

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Totals			
		8750365	8.1

Channel 2, 10m PPQ Heated Injector, Backflush Results				
Pk #	Name	Retention Time	Area	Concentration
2	CO2	0.5	160760958	78.5
	C2H4			0.0 BDL
	C2H6			0.0 BDL
3	H2O	0.7	186150748	2729.0
	C4H10			0.0 BDL
12	Acetone	4.3	624	0.0
20	iPrOH	5.3	222	0.0
Totals				
			346912552	2807.6

Channel 3, 10m MS5A Heated Injector Results				
Pk #	Name	Retention Time	Area	Concentration
1	H2	0.4	454464004	59.8
2	O2 (ref)	0.5	7356593	7.7
3	N2	0.7	22241869	30.9
4	СО	1.5	15	0.0
Totals				
			484062481	98.4

Figure A13: MicroGC report of hydrogenation of beechwood sawdust (Table 1, Entry 7 in the main text)

External Standard Report

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External Standard Report

Page 2 of 2 (6)

Method Name: C:\Users\Administrator\Agilent\Method\20190717_Luca_Final.met Data: C:\Users\Administrator\Agilent\Result\146_sakk-108_2021-11-15 11-58-38 (GMT +01-00).dat.rslt\146_sakk-108_2021-11-15 12-15-04 (GMT +01-00)-Rep3.dat User: SYSTEM (SYSTEM) SYSTEM (SYSTEM) Acquired: 11/15/2021 12:15:52 PM (GMT +01:00) Printed: 11/15/2021 12:23:26 PM (GMT +01:00)				
Totals			21417504	19.9
Channel 2, 10m PPQ Heated Injector, Backflush Results Pk #	Name	Retention Time	Area	Concentration
2	CO2	0.5	582417	0.3
	C2H4			0.0 BDL
3	C2H6 H2O	0.7	670108	0.0 BDL
5	C4H10	0.7	070108	0.0 BDL
	Acetone			0.0 BDL
10	iPrOH	5.4	9466	0.0
Totals			1261991	10.1
Channel 3, 10m MS5A Heated Injector Results <i>Pk #</i> 1 2 5	<u>Name</u> H2 O2 (ref) N2 CO	<i>Retention Time</i> 0.4 0.5 1.5	<i>Area</i> 36056238 18194089 1399	<u>Concentration</u> 4.7 19.0 0.0 BDL 0.0
Totals				
			54251726	23.8

Figure A14: MicroGC report of the blank reaction using GVL as the substrate with Ru-MACHO-BH and $H_3PO_4(aq)$ under 30 bar H_2 at 140 °C in water after 72 hours.

Appendix E: Supplementary information for chapter 6

1. General information

Water and dioxygen sensitive reaction were performed under inert atmosphere using Schlenk technique or in a glove box. All solvents (anhydrous) and reagents were purchased from commercial suppliers and used as supplied until otherwise stated. The ligand was prepared using literature procedures.³⁶⁰ The ¹H, ¹³C{¹H} and ³¹P spectra were recorded on a Bruker Advance III 400 MHz spectrometer and were referenced on the solvent peak. The chemical shifts are described in ppm (parts per million) downfield shift from SiMe₄ and are reported as relative integral, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet), coupling constant (J/Hz). The attenuated total internal reflection (ATR) Fourier transform infrared (FTIR) spectrometer was equipped with a Ge on KBr beam splitter, HgCDTe detector and a single-reflection Ge ATR accessory. Single crystal X-ray diffraction was performed on a SuperNova dual source CCD diffractometer t 120 K using Mo Kα radiation. Elemental analysis were acquired from micro analytical laboratory at the department of chemistry, University of Copenhagen on a Thermo Fischer Flash EA 1112 analyzer.

2. Ligand synthesis

Synthesis of L1



An amount of 3.5 g (13 mmol) of bis (2-chloroethly) amine hydrogen chloride was added to 40 mL of DCM to form a suspension. 25 mL of aqueous solution of 1 M NaOH were added and stirred at room temperature for 2 hours. The DCM layer was separated, dried oven anhydrous sodium sulphate and concentrated to obtain the final product as slight yellowish oil. ¹H NMR (400 MHz, Chloroform-d) δ 7.26 – 7.08 (m, 5H), 3.71 – 3.61 (s, 1H), 3.48 – 3.36 (t, J = 7.0 Hz, 2H), 2.96 – 2.73



Figure A1: ¹H NMR (CDCl₃, 400 MHz) of L1





1-isopropyl imidazole (1.6 g, 14.5 mmol) was added to a 1,4-dioxane solution (14 mL) of **L1** (1.3 g, 5.6 mmol) and the resulting mixture was stirred and refluxed for 18 hours. After the reaction, the mixture was concentrated under rotary evaporator and extracted with water thrice, the aqueous layer washed with hexane and DCM thrice. The volatiles were removed under reduced pressure to obtain **L2** as whitish yellow powder. ¹H NMR (400 MHz, D₂O) 1.44 (12H, s), 2.97 (4H, t), 3.56 (2H, s), 4.18 (4H, t), 4.49 (q, 2H), 6.96 (m, 2H), 7.24 (m, 5H), 7.48 (m, 2H), 8.51 (s, 2H).



Figure A2: ¹H NMR (D₂O, 400 MHz) of L2

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Synthesis of L3
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To an ethanol solution of **L2** (5.5 mmol, 1 eq.) was added Pd/C 10% (3 eq.) and NH_4HCO_2 (15 eq.) were added and a reflux-adapter was attached. The reaction mixture was evacuated and purged with N_2 at least thrice, and the mixture was heated to 60 °C for 4 hours. The mixture was allowed to cool to room temperature and filtered through a celite pad and washed with ethanol and the combined organic phase was concentrated in vacuum. ¹H NMR (400 MHz, D₂O) 1.44 (12H, d), 3.0 (4H, t), 4.20 (4H, t), 4.54 (2H, q), 7.40 (2H, s), 7.50 (2H, s), 8.76 (2H, s).



Figure A3: ¹H NMR (D₂O, 400 MHz) of L3

Synthesis of L4



To a DCM solution of L3 (2.7 mmol) was added Ag₂O (3.3 mmol) and the mixture stirred in the dark for 18 hours. After the reaction, the mixture was filtered through celite pad and the volatiles removed from the filtrate under reduced pressure to obtain L4 as orange foam. ¹H NMR (400 MHz, CD₂Cl₂), 1.39 (12H, d), 2.95 (4H, t), 4.10 (4H, t), 4.66 (2H, q), 6.98 (2H, d), 7.12 (2H, d).



Figure A4: ¹H NMR (CD₂Cl₂, 400 MHz) of L4



Figure A5: ¹³C NMR (CDCl₃, 400 MHz) of L4

Synthesis of Ru-CNC complex



A mixture of silver complex, L4 (100 mg, 0.17 mmol) and RuHClCO(PPh₃)₃ (134 mg, 0.14 mmol) in THF 8 mL was heated at 55 °C for 24 hours. The resulting solution was filtered and brought to dryness and extracted with MeOH (2×5 mL). Solvent was evaporated and the obtained solid was recrystallized from MeOH/toluene. Brownish yellow solid (Yield = 45%). ¹H NMR (400 MHz, CD₂Cl₂): -13.8 (1H, d), -7.8 (1H, d), 0.64 (3H, d), 0.94 (3H, d), 1.23 (3H, d), 1.4 (3H, d), 5.04 (1H, h), 5.53 (1H, h), 6.88 (1H, d), 7.04 (1H, d), 7.11 (1H,d), 7.15 (1H, d), 7.30 (m, 15H). ³¹P{¹H} NMR (CD₂Cl₂, 400 MHz): 47.3.

Elemental Analysis for C₃₅H₄₃N₅POClRu

Calculated: C: 58.61; H: 6.04; N: 9.76

Found: C: 57.08; H: 6.36; N: 8.83

Catalytic studies

General procedure for catalysis

For a typical hydrogenation screening experiment, the autoclave vessel was loaded with desired amount of catalyst, substrate, solvents and additives. The autoclave was sealed tightly and flushed with argon/hydrogen (three times) and finally required hydrogen pressure was loaded into the autoclave. The autoclave was then slowly heated to the desired temperature under stirring and held at the desired temperature for desired time. After the reaction is finished, the reactor was cooled to room temperature before the sample was prepared for NMR analysis.



Figure A6: ¹H NMR (dmso-d₆, 400 MHz) of the crude reaction of transfer hydrogenation of benzophenone (0.5 mmol) with 0.05 mmol of ^tBuOK and Ru-CNC (0.5 mol%) using iPrOH (3 mL) and 80 °C after 6 hours.



Figure A7: ¹H NMR (CDCl3, 400 MHz) of the crude reaction of hydrogenation of 1-hexene (0.5 mmol) with 5 equivalents of HCl(aq) and Ru-CNC (0.5 mol%) in THF under 15 bar H₂ and 65 °C after 18 hours.



Figure A8: ¹H NMR (dmso-d₆, 400 MHz) of the crude reaction of the hydrogenation of levulinic acid (0.5 mmol) and Ru-CNC (0.2 mol%) in H₂O under 20 bar H₂ and 100 °C after 16 hours.

Appendix F-Paper 1

Manuscript in preparation

This work is based on the finding from Chapter 3 on the direct conversion of furfural to GVL using the combination of Ru-PNP complexes and phosphoric acid. As already discussed, this work highlights the potential valorization of biomass derived furfural to platform chemical. This is done is performed at the department of Chemistry (DTU).

Homogeneous catalysis for the direct conversion of furfural to gamma-valerolactone

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Abstract

Developing efficient processes for the valorizations of biomass-derived substrates is crucial for a sustainable production of chemicals and fuels to cope up with the increased energy demands. Herein we report the first example of homogeneous catalyzed direct conversion of furfural to GVL under mild and sustainable reaction conditions. A combination of Ru-MACHO-BH and a Brønsted acid (H₃PO₄) allows for the direct transformation of furfural to GVL with 83% yield at 100 0 C and under 30 bar of H₂ in ethanol.

Introduction

In the view of depleting fossil fuels and increasing environmental problems, modern society is in need of a sustainable, economical production of fuels and chemicals.^[1] One solution is to develop new alternative methods utilizing renewable biomass, which has attracted recent interest. Lignocellulosic biomass is potentially an ideal carbon-neutral resource in a sustainable economy and is therefore highly attractive from geopolitical and environmental perspectives.^[2] In this scenario, furfural has recently been emphasized as one of the top value-added chemicals produced in the so-called lignocellulosic biorefineries.^[3] Industrially, furfural is produced by acid-catalyzed dehydration of C5 sugars, such as xylose, by H_2SO_4 .^[4] The polysaccharide are first hydrolyzed to monosaccharides (mainly xylose), which were subsequently dehydrated to furfural. Many valuable chemicals can be synthesized as upgraded products from furan derivatives. Among them, γ -valerolactone (GVL) is an important chemical with wide range of applications. GVL is used as liquid fuel additives in food, intermediate in fine chemical synthesis, green solvent, and building block for polymers.^[5]



Scheme 1. This work: Direct conversion of furfural to GVL using Ru-PNP complexes in presence of $H_3PO_4(aq)$).

The production of GVL from furfural involves a multistep process involving hydrolysis and hydrogenation. Firstly, furfural must undergo hydrogenation to furfuryl alcohol. Furfuryl alcohol is subsequently transformed to levulinic acid (LA) in presence of aqueous acid media, and finally LA is converted to GVL through the formation of 4-hydroxyvaleric acid in a second hydrogenation step (Scheme 1).^[6] In the literature, each step has been separately studied and explored.^[7] In order to carry out this process in an economically viable fashion, a direct production of GVL from furfural that does not involve any intermediate isolation and purification should be developed.

The direct conversion of furfural to GVL has been mainly achieved using heterogeneous catalysis. Jae reported a one-step process using a bifunctional Sn-Al-Beta zeolite, which possess Lewis and Brønsted acid sites, in 2-butanol at 180 °C to obtain up to 60% of GVL.^[8] Melero utilized a Zr-Al-Beta zeolite and employing harsh reaction conditions, a low yield of 22.6% GVL was achieved at 170 °C after 24 hours using 2-propanol as H-donor.^[9] Employing Au/ZrO₂ combined with ZSM-5 and 2-propanol, Fan synthesized 80.4% GVL from furfural at 120 °C after 24 hours.^[10] Recently, Hu reported the direct conversion of furfural to GVL with a yield of 90.5% via consecutive hydrogenation and acid catalyzed reactions over CuAl and H-ZSM-5 in ethanol. The reaction could be run at 120 °C but a high pressure of H₂ was required (50 bar).^[11] Heterogeneous catalysts are interesting for their easy separation and operating under continuous flow, but there are several drawbacks such as low selectivity, low activity and typically the requirement of harsh reaction conditions. One solution to address these issued is by homogeneous catalysis. Moreover, to the best of our knowledge a homogeneous catalytic direct furfural hydrogenation to GVL remains elusive in the literature.

There are many examples for homogeneous catalysts for the production of GVL from LA.^[12] Zhou employed an iridium trihydride pincer catalyst to obtain a TON of 71000 at 100 °C employing a high H₂ pressure was required (100 bar) with the addition of 1.2 equivalent of base (KOH).^[13] Another iridium catalyst reported by Fu obtained an impressive TON of 78000 under additive free conditions at 120 °C and 10 bar H₂.^[14] An iron based pincer complex reported by Song can

efficiently catalyze the hydrogenation of LA and methyl levulinate into GVL achieving a high TON as well (TON 23000).^[15] Nielsen reported the conversion of neat alkyl levulinates to γ-valerolactone with low catalyst loadings (0.05-0.01 mol%) of either PNP Ru or Ir complexes, respectively.^[16] There is only one example of homogeneous catalysis for the ring opening of furfural, in which the reaction stops at LA with 42% yield using an arene-Ru catalyst in presence of formic acid.^[17] The direct and selective conversion of furfural is challenging due to undesired side reactions in presence of acid.^[18]

Results and Discussion

Herein, we show the effective and direct conversion of furfural to GVL under mild reaction conditions using low catalyst loadings of PNP pincer complex. PNP pincer complexes are known for their robustness and efficacy in catalyzing both dehydrogenation as well as hydrogenation reactions.^[19] However, they are generally known to work under either base^[20] or additive free conditions. ^[21] Very recently, we demonstrated that Ru-MACHO-BH is also an active hydrogenation catalyst under acidic conditions.^[22] Here, we show the activity of PNP pincer complex (Ru-MACHO-BH) in acidic medium (H₃PO₄) for the direct synthesis of GVL from furfural through a one-pot sequence of hydrogenation, hydrolysis, and a second hydrogenation (Scheme 1).

We commenced the studies by testing the furfural conversion with the well-known PNP complexes Ru-MACHO and its ^{iPr}PNP congener (Ru-1). Being a reductant, formic acid^[23] was initially used as the acid additive. As a note, using excess acid may lead to humins formation from furan derivatives.^[24] Thus, with 0.2 mol% of Ru-MACHO or its ^{iPr}PNP congener with 2 M formic acid under 20 bar of H_2 in 3:7 v/v EtOH/ H_2O , the reaction afforded full conversion of furfural. However, the reaction stopped at LA after 18 hours at 100 °C (SI, Table S1). Increasing the H_2 pressure to 30 bar and using water as the sole solvent, led to no significant changes (SI, Table S1). Gratifyingly, when employing Ru-MACHO-BH in 3:7 v/v EtOH/H₂O led to full conversion of furfural within 18 hours with 34% of GVL (Table 1, Entry 1). Some unreacted LA was still detected. Increasing the amount of formic acid concentration to 4 M improved the GVL yield to 46% (Entry 2). Changing the EtOH/H₂O ratio to 1:1 resulted in no significant change in the yield (Entry 3). To probe for the effect of catalyst loading on the production of GVL from furfural we tested the reaction with different catalyst loading of Ru-MACHO-BH ranging from 0.2 to 2 mol% with 4 M formic acid under similar reaction conditions (Entries 3-6). Merely 10% yield was obtained with 2 mol% catalyst loading, while with 1 and 0.5 mol% the yields were 27% and 48%, respectively. With the higher catalyst loading, furfuryl alcohol was observed as the major product along with a formation of methanol. These observations suggest that the formic acid itself is hydrogenated to methanol, which was confirmed by a blank reaction performed with Ru-MACHO-BH and formic acid under similar reaction conditions in the absence of furfural (SI, Table S2, Figure S8). Therefore, in order to selectively obtain GVL 0.2 mol% catalyst loading was found optimal. We then studied the effect of formic acid concentration on the yield of GVL. Thus, when increasing the acid concentration from 2 to 8 M in the presence of 0.2 mol% Ru-MACHO-BH, the initial

reaction rates dropped significantly. Thus, the reaction yielded only LA with 8 M formic acid compared to the 34% of GVL when using 2 M formic acid. This suggests that the higher acid concentration has a negative effect on the catalyst activity which might be due to the degradation of catalyst in presence of high acid concentration. (SI, Table S2).

н

	FAL FAL Ru-M HCOO 30 bar H	IACHO-BH H, <u>EtOH/H₂O</u> H ₂ , 100 °C, 18 h	GVL GVL H N Ph2 Ph2 Ru-MACI	—РРh ₂ ù—СО Ч ВН ₃ НО-ВН
Entry	Ru-MACHO- BH (mol%)	HCOOH [M]	EtOH/H₂O v/v ratio	GVL yield [%] ^[a]
1	0.2	2	3:7	34
2	0.2	4	3:7	46
3	0.2	4	1:1	48
4	0.5	4	1:1	48
5	1	4	1:1	27
6	2	4	1:1	10

Table 1. Furfural hydrogenation to GVL using formic acid

Standard reaction conditions: Furfural (0.90 mmol), 30 bar H_2 at 100 ^{0}C in 18 hours. ^[a] Determined by GC-FID using 1,4-dioxane as internal standard.

Replacing formic acid to the other acid additives such as oxalic acid or PTSA resulted in either no conversion of furfural or in LA as the sole product (SI, Table S4). Interestingly, with $H_3PO_4(aq)$ the catalytic hydrogenation of furfural exhibited surprisingly excellent GVL yield of 72% with 0.5 mol% catalyst loading in 1:1 v/v EtOH/H₂O after 18 hours (Table 2, Entry 1). Using 3.8 M $H_3PO_4(aq)$ and gradually increasing the catalyst loading to 2 mol% results in a decrease in the GVL yield when the loading exceeds 1 mol% (Entries 1-3). Under similar conditions albeit with using ethanol as the sole solvent, the reaction afforded 80% yield of GVL when using 0.5 mol% of the Ru-MACHO-BH (Entry 6).

The considerably lower yields observed in the presence of $EtOH/H_2O$ mixtures may be due to humins formation, which is more favoured in presence of water. Thus, further optimizations were carried out in EtOH. For the catalytic reactions with low catalyst loading (0.2 mol%) and low concentrations of $H_3PO_4(aq)$, the hydrogenated intermediate LA was also observed along with the GVL (Entries 5 and 8). With higher catalyst loadings (0.5 or 1 mol%), full conversion of furfural

was achieved with high yields of 80% and 83% of GVL, respectively, with 3.8 M $H_3PO_4(aq)$ in ethanol under 30 bar of H_2 in 18 hours (Entries 6 and 7).

	Ru-PNP	
$\langle 0 \rangle \langle 0 \rangle$	H ₃ PO ₄ , EtOH/H ₂ O	$\sim^{\circ} \sim^{\circ}$
₩	30 bar H ₂ , 80-120 °C	
FAL		GVL

Entry	Ru-PNP catalyst (mol%)	H ₃ PO ₄ [M]	EtOH/H ₂ O v/v ratio	Time [h]	GVL yield [%] ^[a]
1	Ru-MACHO-BH (0.5)	3.8	1:1	18	72
2	Ru-MACHO-BH (1)	3.8	1:1	18	73
3	Ru-MACHO-BH (2)	3.8	1:1	18	63
4	Ru-MACHO-BH (1)	1.9	1:1	18	56
5	Ru-MACHO-BH (0.2)	3.8	EtOH	18	67
6	Ru-MACHO-BH (0.5)	3.8	EtOH	18	80
7	Ru-MACHO-BH (1)	3.8	EtOH	18	83
8	Ru-MACHO-BH (1)	1.9	EtOH	18	68
9	Ru-MACHO-BH (1)	3.8	EtOH	7	84
10	Ru-MACHO-BH (1)	3.8	EtOH	5	72
11 ^[b]	Ru-MACHO-BH (1)	3.8	EtOH	7	80
12 ^[b]	Ru-MACHO-BH (1)	3.8	EtOH	18	84
13 ^[c]	Ru-MACHO-BH (1)	3.8	EtOH	7	0
14	Ru-MACHO (1)	3.8	EtOH	18	58
15	Ru-1 (1)	3.8	EtOH	18	75
16 ^[d]	Ru-MACHO-BH (1)	3.8	EtOH	18	83

Table 2. Furfural hydrogenation to GVL using phosphoric acid.

Standard reaction conditions: Furfural (0.90 mmol), 85 w/w% H_3PO_4 , EtOH (1 mL), 30 bar H_2 , 100 °C. ^[a] Determined by GC-FID using 1,4-dioxane as internal standard. ^[b] 120 °C, ^[c] 80 °C, ^[d] 10.2 mmol furfural in 10 mL EtOH.

The catalytic system was also evaluated at shorter reaction times. Thus, using 1 mol% catalyst loading and 3.8 M of $H_3PO_4(aq)$ the reaction afforded full conversion with 84% GVL after 7 hours (Entry 9). The remaining loss of yield is likely due to formation of humins. Further increase or decrease in acid concentration led to a low yield, which follows the same trend as observed with the longer reaction time (18 hour). Hence, with 0.5 and 0.2 mol% catalyst loading and under identical reaction conditions, 64% and 9% yields, respectively, were obtained (SI, Table S5). The low yield suggests an incomplete reaction, with furfuryl alcohol and LA as the major products. Further lowering the reaction time to 5 hours a low yield was obtained (19%) where the unreacted LA as the major product (Entry 10).

The effect of catalyst loading along with acid concentration was also studied (SI, Table S7). The effect of concentration of furfural in EtOH was investigated with 1 mol% of Ru-MACHO-BH by using 0.90 mmol of furfural and 30 bar H₂ at 100 °C in EtOH volumes ranging from 0.5-2 mL using 3.8 M H₃PO₄(aq). A drop in the yield of GVL was observed affording 64% and 54%, respectively, with 0.5 and 2 mL of EtOH (SI, Table S5), showing that a concentrated solution is slightly detrimental for catalytic activity. Finally, we tested the effect of temperature on the reaction kinetics by performing the reactions at different temperatures (120 °C and 80 °C). Thus, 80% yield was obtained using 1 mol% catalyst loading and 3.8 M H₃PO₄(aq) after 7 hours compared to 84% after 18 hours (Entries 11 and 12). At lower temperature (80 °C) we observe no GVL, which suggests that Ru-MACHO-BH requires a minimum temperature to be catalytically active for hydrogenation (Entry 13).

The performance of other PNP Ru complexes, such as Ru-MACHO and its ^{*i*Pr}PNP congener (Ru-1), was evaluated as well. Both the catalysts work in presence of $H_3PO_4(aq)$ towards hydrogenating furfural to GVL, but their activities are inferior to Ru-MACHO-BH (Entry 7 vs Entries 14 and 15). We then scaled up to 1 g of furfural using 1 mol% of Ru-MACHO-BH with 3.8M $H_3PO_4(aq)$ at 100 °C and 30 bar H_2 (Entry 16). After 18 hours, we isolated 46% of GVL after the treatment with sodium carbonate to remove phosphoric acid followed by extraction with ethyl acetate. This GC yield here represents that the reaction is reproducible in larger scale as well.

Conclusion

We demonstrate an efficient route for the conversion of biomass derived furfural to GVL under mild and sustainable reaction conditions. Using low loadings of Ru-MACHO-BH in presence of $H_3PO_4(aq)$ allows the unprecedented homogeneously catalyzed transformation of furfural to GVL in 84% yield at 100 °C after 7 hours. The influence on GVL yield of various catalytic parameters was also evaluated. Finally, our findings corroborate the novel catalytic power of the synergistic interplay between a PNP pincer catalyst and a Brønsted acid that we recently disclosed and that opens new opportunities within homogenous catalytic hydrogenation.

Experimental Section

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Furfural (FAL, 99%), H₃PO₄ (85 w/w%), Ru-MACHO-BH are commercially available and used without further purification. H₂ gas (H₂O \leq 3 ppm; O₂ \leq 2 ppm) was purchased from a commercial supplier as well. All reactions dealing with air or moisture-sensitive compounds were performed using standard Schlenk techniques or in an argon-filled glovebox. GC-FID were recorded on an Agilent 19091J-413 HP-5 5% Phenyl methyl siloxane capillary column using 1,4-dioxane as internal standard. The ¹H spectra were recorded on a Bruker Advance III 400 MHz spectrometer and were referenced on the solvent peak.

General procedure for the hydrogenation of furfural to GVL

For the hydrogenation screening experiment, in a glove box, substrate (0.65 mmol) and catalyst (0.2-1 mol%) were weighed in a glass vial equipped with a magnetic stir bar and sealed with a Teflon-lined cap. Upon bringing the glass vial outside the glove box, dissolved 1 mL of solvent ($H_2O/EtOH$) followed by corresponding amount of acid. Subsequently, the vial was placed in a seven-well reactor with a needle placed through the rubber stopper of the vials for the gas flow. The autoclave was sealed tightly and flushed with argon/hydrogen (three times) and finally required hydrogen pressure (30 bar) was loaded into the autoclave and desired temperature was also applied. The reactor was cooled to room temperature before the hydrogen was released and the sample was prepared for GC analysis with 1,4-dioxane as internal standard.

Acknowledgements

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Keywords: biomass • furfural • hydrogenation • sustainable • catalysis

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Supplementary Information

Homogeneous catalyzed direct conversion of furfural to gammavalerolactone

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- 1. General information
- 2. Catalytic reactions for hydrogenation of furfural to GVL
- 3. GC-FID and NMR spectra of the reactions

1. General Information

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Furfural (FAL, 99%), H₃PO₄ (87 w/w%), Ru-MACHO-BH are commercially available and used without further purification. H₂ gas (H₂O \leq 3 ppm; O₂ \leq 2 ppm) was purchased from a commercial supplier as well. All reactions dealing with air or moisture-sensitive compounds were performed using standard Schlenk techniques or in an argon-filled glovebox. GC-FID were recorded on an Agilent 19091J-413 HP-5 5% Phenyl methyl siloxane capillary column using 1,4-dioxane as internal standard. The ¹H spectra were recorded on a Bruker Advance III 400 MHz spectrometer and were referenced on the solvent peak.

	Cat <u>HCOOH</u> 30 bar, Furfural	alyst <u>I, EtOH/H₂O</u> 100 ºC, 18 h	GVL H	Cl PPh2 N-Rù-CO PH2 H Ph2 Ru-MACHO	H_{Pr_2}	2
Entry	Catalyst (mol%)	нсоон [M]	EtOH/H ₂ O	P/T	Product	GVL vield ^[a]
	/ (- ···-)		v/v ratio	[bar]/[°C]		[%]
1	Ru-MACHO (0.2)	2	1:1	30/100	LA	-
2	Ru-MACHO (0.2)	2	7:3	30/100	LA	-
3	Ru-1 (0.2)	2	7:3	20/100	LA	-
4	Ru-1 (0.2)	2	H ₂ O	20/100	LA	-
5	Ru-1 (0.2)	2	7:3	30/100	LA	-

2. Catalytic reactions for hydrogenation of furfural to GVL

Table S1. Reaction conditions: Furfural (0.90 mmol), EtOH/H₂O (1 mL) at 100 °C for 18 h. ^[a] Determined by GC-FID using 1,4-dioxane as internal standard.



Ru-MACHO-BH

Entry	Ru-MACHO-BH [mol%]	HCOOH [M]	Products	GVL yield ^[a] [%]
1 ^[b]	2	4	MeOH	0
2	-	4	-	0
3	0.2	2	GVL	34
4	0.2	4	GVL	48
5	2	4	FAL, GVL	10
6	0.2	8	LA	0
7	2	8	FAL, GVL	37

Table S2. Reaction conditions: Furfural (0.90 mmol), $1:1 \text{ v/v} \text{ EtOH/H}_2\text{O}$ (1 mL), 30 bar H₂ at 100 °C for 18 h. ^[a] Determined by GC-FID using 1,4-dioxane as internal standard. ^[b] Without FAL.

0 Furfu	у ryl alcohol	Ru-MACHO-BH HCOOH, EtOH/H ₂ O 30 bar, 100 °C, 18 h	€ GVL	H N Rů CC P H Ph ₂ BH ₃
			ı	Ru-MACHO-BH
	Entry	Ru-MACHO-BH [mol%]	G	VL yield ^[a] [%]
	1	0.2		48
	2	1		17

Table S3. Reaction conditions: Furfuryl alcohol (0.90 mmol), HCOOH (4 M), 1:1 EtOH/H₂O (1 mL), 30 bar H₂ at 100 °C for 18 h. ^[a] Determined by GC-FID using 1,4-dioxane as internal standard.



Table S4. Reaction conditions: Furfural (0.90 mmol), Acid additive (4 mmol), 1:1 EtOH/H₂O (1 mL), 30 bar H₂ at 100 °C for 18 h. ^[a] Determined by GC-FID using 1,4-dioxane as internal standard.



Entry	Ru-MACHO-BH [mol%]	H ₃ PO ₄ (aq) [M]	Solvent	Products	GVL yield ^[ə] [%]
1	0.2	3.8	EtOH	GVL, LA, FAL	9.2
2	0.2	5.7	EtOH	GVL, LA	27
3	0.5	3.8	EtOH	GVL, LA	64
4	0.25	5.7	EtOH	GVL, LA	48
6	1	1.9	EtOH	GVL, LA	24
7	1	3.8	EtOH/H₂O	GVL	45
8 ^[b]	1	1.9	EtOH	GVL	54
9 ^[c]	1	7.5	EtOH	GVL	64

Table S5. Reaction conditions: Furfural (0.90 mmol), EtOH (1 mL), 30 bar H₂ at 100 °C after 7 hours. ^[a] Determined by GC-FID using 1,4-dioxane as internal standard, ^[b] 2 mL of EtOH, ^[c] 0.5 mL of EtOH.

$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array}\\ \end{array}\\ \end{array} \\ \hline \\ \end{array} \\ \hline \\ Furfural \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\$						
Entry	Ru-MACHO-BH [mol%]	H₃PO₄(aq) [M]	Time [h]	Products	GVL yield ^[a] [%]	
1	1	3.8	7	GVL	80	
2	0.5	3.8	7	GVL, LA	46	
3	1	3.8	18	GVL	84	
4 ^[b]	1	7.5	18	GVL	41	
5 ^[c]	1	1.9	18	GVL	60	

Table S6. Reaction conditions: Furfural (0.90 mmol), EtOH (1 mL), 30 bar H₂ at 120 °C. ^[a] Determined by GC-FID using 1,4-dioxane as internal standard. ^[b] 0.5 mL of EtOH, ^[c] 2 mL of EtOH.
	Ru-MAC H_3PO_4, E H_3PO_4, E 30 bar, 1 Furfural	СНО-ВН <u>tOH/H₂0</u> 00 °C. 5 h	GVL H GVL H H N Ph2 Ph2 Ru-MACI	I —PPh ₂ ù—CO I BH ₃ HO-BH
Entry	Ru-MACHO-BH [mol%]	H₃PO₄(aq) [M]	Products	GVL yield ^[a] [%]
1	0.2	3.8	GVL, LA, FUR	5
2	0.5	3.8	GVL, LA	19
3	1	1.9	GVL, LA	68

Table S7. Reaction conditions: Furfural (0.90 mmol), EtOH (1 mL), 30 bar H_2 at 100 °C for 5 hours. ^[a] Determined by GC-FID using 1,4-dioxane as internal standard.



Figure S1. Calibration curve for GVL using 1,4-dioxane as internal standard.



Sorted By	-	Signal		
Calib. Data Modified	:	12/8/2006	5 12:33:15	PM
Multiplier	:	1.0000		
Dilution	-	1.0000		
Use Multiplier & Dilut	tion	Factor with	ISTDs	

Signal 1: FID1 A,

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Area %	Name
	I	I ———	I	I	I I	
1	1.256	BB	0.0100	268.28110	0.24542	?
2	1.330	BVS	0.0207	2.82523e4	25.84459	?
3	1.386	BV X	0.0157	4.93722	0.00452	?
4	1.413	VV X	8.40e-3	23.56898	0.02156	2
5	1.436	VBS	0.0109	7.2798964	66.594/9	2
07	1.638	BV	0.0257	46.64048	0.04267	-
<i>.</i>	1 705	VV	0.0180	4 72431	0.02412	- 2
ä	2 012	BB	0.0214	15 73769	0.01440	2
10	2.286	BB	0.0189	3493 91382	3.19615	2
11	2.847	BB	0.0198	2.00222	0.00183	?
12	3.050	BV	0.0342	6.86157	0.00628	C14
13	3.202	VB	0.0531	76.25008	0.06975	?
14	3.540	BB	0.0265	1.94312	0.00178	C15
15	3.976	BB	0.0257	2.25746	0.00207	C16
16	4.165	BB	0.0309	10.32347	0.00944	?
17	4.407	BB	0.0308	3.91556	0.00358	?
18	4.602	BB	0.0291	3.89039	0.00356	?
19	4.848	BV	0.0414	13.97369	0.012/8	2
20	4.919	VB	0.0302	4.19565	0.00384	2
21	5.190	BB	0.0368	64.86580	0.05934	?
22	5.477	BB	0.0553	3301.24219	3.01990	?
23	5.933	BB	0.0321	26.95572	0.02466	?
24	6.912	BB	0.0311	6.41667	0.00587	?
25	7.045	BB	0.0341	723,48901	0.66183	?
26	7.342	BB	0.0364	73.86584	0.06757	?
27	8.472	BB	0.0374	13.21048	0.01208	?
28	8.787	BB	0.0618	10.96173	0.01003	?
29	8.941	BV	0.0297	3.45419	0.00316	?
30	9.008	VB	0.0376	12.45941	0.01140	?
31	11.650	BB	0.0404	4.49463	0.00411	?
32	14.375	BB	0.0367	4.55242	0.00416	?
33	16.265	BB	0.0380	4.33731	0.00397	?
34	16.388	BB	0.0420	4,90215	0.00448	?

Figure S2. GC-FID of the crude reaction of furfural (0.90 mmol) with 3.8 M $H_3PO_4(aq)$ with 1 mol% Ru-MACHO-BH and EtOH (1 mL), 30 bar H_2 at 100 °C for 5 hours using 1,4-dioxane as internal standard.



Figure S3. ¹H NMR (DMSO- d_6 , 400 MHz) of the crude reaction of furfural (0.90 mmol) with 1 mol% Ru-MACHO-BH and 3.8 M H₃PO₄(aq) in EtOH (1 mL), 30 bar H₂ at 100 °C for 5 hours.



Figure S4. GC-FID of the crude reaction of furfural (0.90 mmol) with 3.8 M $H_3PO_4(aq)$ with 0.5 mol% Ru-MACHO-BH and EtOH (1 mL), 30 bar H_2 at 100 °C for 18 hours using 1,4-dioxane as internal standard.



Figure S5. ¹H NMR (DMSO- d_6 , 400 MHz) of the crude reaction of furfural (0.90 mmol) with 0.5 mol% Ru-MACHO-BH and 3.8 M H₃PO₄(aq) in EtOH (1 mL), 30 bar H₂ at 100 °C for 18 hours.



19	7.345 BB	0.0332	159.66397	0.13032 ?
Figure S6. GC-FID	of the crude	reaction	of furfural	(0.90 mmol) with 3.8 M H ₃ PO ₄ (aq) with
0.5 mol% Ru-MACH	O-BH and 1:1	v/v EtOH	/H ₂ O (1 mL)), 30 bar H $_2$ at 100 °C for 18 hours using 1,4-
dioxane as internal	standard.			

1.97105

6.91165

6.70979

139.15062

0.0611 4338.80469

0.0293

0.0330

0.0305

0.0301

4.606 BB

4.815 BB

5.499 BB

6.915 BB

7.034 BB

14

15

16

17

18 19 0.00161 ?

0.00564 ?

3.54151 ?

0.00548 ? 0.11358 ?



Figure S7. ¹H NMR (DMSO-d6, 400 MHz) of the crude reaction of furfural (0.90 mmol) with 0.5 mol% Ru-MACHO-BH and 3.8 M $H_3PO_4(aq)$ in 1:1 v/v EtOH/ H_2O (1 mL), 30 bar H_2 at 100 °C for 18 hours.



Figure S8. ¹H NMR (DMSO-d6, 400 MHz) of the blank reaction with Ru-MACHO-BH and 3.8 M HCOOH in 1:1 v/v EtOH/H₂O (1 mL) in absence of furfural, 30 bar H₂ at 100 °C for 18 hours.

Appendix F-Paper 2

Manuscript in preparation

This is based on the results discussed in Chapter 5 highlighting the direct conversion of biomass feedstock to GVL under game-changing mild and sustainable reaction conditions. This will represent the state-of-the system in transforming biomass to GVL using H₂ as hydrogen source. And discloses the activity of Ru-PNP complex under acidic conditions. This work is done is carried out at the Department of Chemistry, DTU.

Homogeneous catalytic direct conversion of biomass waste feedstock to gamma-valerolactone

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Abstract: As the only sustainable hydrocarbon resource, biomass must play an essential role in the production of green fuels and chemicals. Gamma-valerolactone (GVL) holds highly promising potential as a future biomass-derived sustainable fuel and feed compound in many chemical industries. It is therefore extremely attractive to directly convert biomass to GVL, particularly if using H_2 as the hydrogen source. However, such a transformation is elusive owing to the high complexity and relatively inert nature of biomass. Herein, we describe the direct and mild catalytic conversion of woody and starchy biomasses to GVL. Our catalytic system comprises 1.8 wt% of the homogeneous catalyst Ru-MACHO-BH in an aqueous solution of H₃PO₄ (10.9 M). Applying 30 bar of H₂ at 140 °C for 24-72 hours provides GVL in excellent yields (16-26 wt%) from straw, sawdust, rice grains, and potato flour. The outcomes correspond to approximately 30-57% of the theoretically maximum yields, or an average of approximately 80-90% yield to the desired intermediate/product in each reaction step. Importantly, no chemical pretreatment nor intermediate separation or workup is required. We also investigated our protocol for the direct conversion of woody polysaccharides (cellulose and hemicellulose) to GVL. Thus, using 0.5 mol% of Ru-MACHO-BH and 5.7 M H₃PO₄(aq) at 125 ^oC under 30 bar of H₂ in EtOH/H₂O results in transformation of hemicellulose to GVL in 87% yield after 48 hours. Using the same catalyst loading, cellulose gave 50% yield of GVL with 7.5M H₃PO₄(aq) after 96 hours. Moreover, the combinations of Ru-MACHO-BH and H₃PO₄(aq) provides unprecedented insights to the previously undisclosed synergistic performance between a Noyori-type hydrogenation pincer catalyst and a Brønsted acid in cascade hydrogenation/protonolysis reactions, opening for a plethora of novel transformations.

One-Sentence Summary: A homogeneous catalytic system consisting of catalytic amounts of Ru-MACHO-BH allows for valorizing woody and starchy biomasses to GVL under mild conditions (30 bar H_2 , 140 °C, $H_3PO_4(aq)$, 24-72 hours) with yields ranging from 16-26 wt%.

It is of utmost importance to lower the anthropogenic CO_2 output and to secure a net decrease of atmospheric CO₂ levels (1). Towards this end, biomass is the only perennial resource with the possibility of providing a negative carbon footprint (2), which can only be reached if it is used for producing value-added compounds instead of simply incinerating it back to CO_2 (3). One example is biomass gasification, which allows large scale supply of fuels and energy with low-cost CO_2 capture and storage, resulting in the production of primary fuels and chemicals with the possibility of achieving zero or even negative carbon emissions (4). However, such approach inherently results in small molecule building blocks, necessitating follow-up processes to produce more advanced chemicals.. Owing to the complexity of lignocellulosic biomass and its resistance towards chemical transformations, cost and energy effective production of fuels and chemicals from biomass remains a huge challenge. Two methods have been reported so far to address this. One being the hydrolysis process, wherein the lignocellulose is separated into isolated sugars and lignin followed by chemical process (5-7). Second one is thermochemical treatment of lignocellulose for the production of upgradable intermediates, such as syngas (gasification) or bio-oils (pyrolysis) with subsequent catalytic process (8, 9). These process are generally multistep and are very less efficient in terms of cost and energy. Hence, there is a fundamental need to improve or develop efficient strategies for the treatment of biomass. Among various biomass, lignocellulose and starch have gained much attention due to their wide abundance and the many value-added biomass-derived platform chemicals that originate from polysaccharides (cellulose, hemicellulose, amylose, and amylopectin). One of the most important platform molecules is y-valerolactone (GVL), which has a wide array of applications. For example, it can be used as fuel additive/biofuel, liquid hydrocarbon diesel, bulk chemicals, green solvent, and in the syntheses of polymers or pharmaceuticals (10).

Importantly, cellulose and hemicellulose make up approximately 75-85 wt% of lignocellulose (11), while amylose and amylopectin constitute the entire content of starch (12). Thus, GVL production from lignocellulosic feedstock can be divided into two specific multistep cascade processes (Scheme 1a). In the first path, hemicellulose (20-35 wt%) is first hydrolyzed to xylose and dehydrated to form furfural, both steps mediated by acid. A subsequent hydrogenation leads to furfuryl alcohol, which is then rehydrated by acid to levulinic acid (LA). Finally, a hydrogenation followed by cyclization leads to GVL. In the second path, acid mediates the hydrolysis of cellulose (30-50 wt%) to glucose followed by the isomerization to fructose, dehydration to (5-hydroxymethyl furfural) HMF, and then rehydration to LA. LA is then converted to GVL in the same way as in the 'hemicellulose pathway'. However, these reaction pathways come with several pitfalls. For example, in acidic medium xylose or glucose can undergo retro-aldol condensation forming dihydroxyacetone and lactic acid. Alternatively, they can be hydrogenated to xylitol or sorbitol, respectively (13). Furthermore, the formation of insoluble humins from

furan derivatives is favored significantly with the use of excess acid (14). In addition, formic acid formed in the reaction medium can undergo decomposition into CO_2 and H_2 or CO and H_2O .

Likewise, GVL production from starch includes two cascade processes, one from amylose and one from amylopectin (Scheme 1b). Both undergo hydrolysis to glucose monomer and follows the same pathway as that of cellulose.

Thus, a catalytic system for a one-pot transformation of biomass to GVL must tolerate multiple different substrates and operate under very distinct acid- and hydrogenation-mediated steps simultaneously. In addition, all these highly differentiated steps must be carried out with high conversion and selectivity to reach reasonable yields of GVL. For example, we have previously shown that HMF is a more potent substrate for hydrogenation than furfural is (15), and yet must the opposite selectivity take place here for a successful and high-yielding production of GVL from biomass.

Conducting these processes in stepwise manners requires financially unviable, energy intensive, and waste-producing separation, intermediate isolation, and purification. The processes become even less viable when using sacrificial H-donor agents such as isopropanol or formic acid. On the contrary, obtaining GVL directly from real biomass in a one-pot cascade manner using H₂ as hydrogen source is highly attractive. A major goal is therefore to find a combination of an acid and hydrogenation catalyst that not only function together, but also perform in a cooperative manner such that *all* the described reaction steps proceed highly effectively and selectively.

Owing to the complexity of lignocellulosic and starchy biomass and their resistances to chemical transformation, directly converting any of them to GVL using H₂ as hydrogen source has not been achieved before. Even the direct production of GVL from polysaccharides and C6- as well as C5-carbohydrates are scarcely reported. Thus, Huang demonstrated a one-pot conversion of poplar to GVL using a transfer hydrogenation method with mixed Al₂(SO₄)₃ and Ru/ZrO₂ catalyst and a sacrificial H-donor (iPrOH) leading to a yield of 12.2 wt% GVL using 800 W microwave heating to 180 °C for 60 min (16). The same authors also converted cellulose to GVL using the same conditions for 70 min, leading to a GVL yield of 51.2%. Heeres used Ru/C with trifluoroacetic acid (TFA) at 180 °C under 94 bar H₂ for 8 h to convert cellulose to GVL in 29% yield (17). The use of soluble ruthenium the homogeneous water catalyst **RuCl**₃ and tris(3-sulfonatophenyl)phosphane (TPPS) in combination with TFA gave a lower GVL yield of 23%. Zhang developed a chitosan-Ru/PPh₃ catalyst system that enables a one-pot catalytic transformation of hemicellulose to GVL with a yield of merely 30% GVL using formic acid as H-donor in ethanol heated to 170 °C for 30 h (18). Li investigated a one-step direct strategy for the transformation of cellulose and commercial starch over combined H₃PW₁₂O₄₀ and Ru/TiO₂ catalysts (19). They obtained 40.5% and 48.3% of GVL from cellulose and starch, respectively, at 150 °C under 40 bar H₂ in GBL-H₂O solvent. To the best of our knowledge, there exist no direct

procedures for transforming biomass to GVL using H₂ as hydrogen source. Likewise, there are no examples of using homogeneous catalysis for producing GVL directly from any of the substrates of real biomass, polysaccharides, carbohydrates, or even furanics.

It is worth noting the excellent performance of PNP complex in hydrogenation catalysis in presence of a Brønsted acid, which has never been explored before. Nevertheless, there exist few examples of the use of pincer complexes, all of which are lutidine-based, that work under acidic conditions for hydrogenative purposes (20-22). Leitner reported a Ru-triphos complex that also shows activity under highly acidic conditions (23). However, there are no reports on using Noyori-type PNP pincer complexes as catalysts in the presence of Brønsted acid.

Herein, we report the first example of homogeneously catalyzed direct production of GVL from raw woody- and starchy biomasses in excellent yields by using a combination of Ru-MACHO-BH and H₃PO₄(aq) (Scheme 1b). This combination allows to integrate the myriad of cascade events of hydrolysis/isomerization/dehydration/rehydration/hydrogenation/lactonization in such a way that the system performs highly efficiently and selectively under mild reaction conditions. In addition to the raw biomass feedstock, we also investigated cellulose and hemicellulose as substrates to obtain insight to the underlying mechanisms and performances of the two main reaction pathways for the woody biomass.

(a) General mechanism from lignocellulose



(b) General mechanism from starch



Scheme 1. a) General stepwise mechanism for the conversion of biomass into GVL (blue arrow indicates the major pitfalls), b) General stepwise mechanism for the conversion of starch (amylose and amylopectin) into GVL. c) Direct conversion of sawdust, straw, rice grains, potato flour and polysaccharides into GVL using Ru-MACHO-BH and phosphoric acid under mild reaction conditions.

We commenced our studies with beechwood sawdust. Initial investigations revealed that the combination of Ru-MACHO-BH and $H_3PO_4(aq)$ is catalytically active for the transformation to GVL. Hence, we first investigated the effect of $H_3PO_4(aq)$ concentration while maintaining the catalyst

loading of as well as H₂ pressure and reaction temperature constant at 0.5 mol%, 30 bar, and 140 °C, respectively. Gratifyingly, employing 7.5 M $H_3PO_4(aq)$ led to an encouraging 15 wt% yield of GVL after 96 hours (Table 1, Entry 1), which was improved to 23 wt% by increasing the concentration of H₃PO₄(aq) to 9.3 M (Entry 3). Shortening or extending the reaction time to 24 or 168 hours, respectively, did not significantly change the yield (Entries 2 and 4). Further increasing the $H_3PO_4(aq)$ concentration to 10.1 M improved the yield to 25 wt%, which decreased again upon longer reaction times (Entry 5 versus Entries 6 and 7). With 10.9 M H₃PO₄(aq), the optimal yield of 26 wt% was obtained after 24 hours (Entry 9). Considering that the theoretical weight of GVL from beech wood is limited to 46 wt% (assuming completely dry biomass and that only hemicellulose and cellulose are converted to GVL), the yield is 57%. Both shortening and extending the reaction time resulted in lower yields (Entries 8 and 10). Moreover, after 18 hours, we still detected the levulinic acid intermediate, which was fully converted after 24 hours. It is noteworthy to mention that no hydrodeoxygenation products, such as hydrocarbons, were observed under these reaction conditions, both in the liquid and gas phases (SI, Fig. S14). Also, a blank reaction was performed to confirm the so-formed stability of GVL under acidic aqueous environment. Thus, GVL was used as a substrate and applying identical conditions (Ru-MACHO-BH, 10.9 M H₃PO₄(aq), 30 bar H₂, 140 °C), the reaction was left for 72 hours. The reaction mixture was analyzed both in the liquid and gas phases. It was observed that GVL was quite stable under these conditions, hence no decomposition products was observed (SI, Fig. S15). Finally, the reaction was carried out in an EtOH/H₂O mixture to study the solvent effect. With 1:1 v/v $EtOH/H_2O$, we observe a lower GVL yield of 14 wt% under otherwise optimized conditions (Entry 11)

To demonstrate the power of our system, the same reaction conditions were employed with other biomass substrates. Thus, employing 10.9 M of $H_3PO_4(aq)$ a 12 wt% yield of GVL is obtained from wheat straw after 24 hours (Entry 12), which is increasing to 18 wt% when extending to 48 hours (Entry 13). This yield accounts for 56% of the theoretical limit of 32 wt%. Further continuing the reaction to 72 hours a slight decrease in the yield was observed (Entry 14). These results validate the versatility of the catalytic system towards valorizing different biomass sources to GVL with approximately 90% per step selectivity of the six-step process.

To test the versatility of the catalytic system, we also performed benchmark reactions with the starch sources rice grains and potato flour. The same reaction conditions found optimal for the woody biomass were also used with these substrates and only varied on the time to achieve completion of each reaction. Thus, yields of 8 wt% and 9 wt% were obtained from rice grains and potato flour, respectively, after 24 hours (Entries 15 and 17). Levulinic acid was still detected in both the reaction media, indicating that the reactions are incomplete and explaining the low yields. Indeed, extending the reaction time to 72 hours consumed all the levulinic acid and the GVL yields increased to 16 wt% and 20 wt% from rice grains and potato flour with, respectively

(Entries 16 and 18). These results indicates that the catalytic system is very efficient in hydrolyzing not only the $\alpha(1-4)$ glycosidic linkages, but also the $\alpha(1-6)$ linkages between glucose units of amylopectin, which is the major component of starch.

Rice grains	Sawdust Straw	Ru-MACHO-Bł H ₃ PO ₄ , H ₂ O 30 bar H ₂ , 140 ⁰		р	H H H H H H H P H H CO P H B B B H B B H B B B B B B B B B B B B B
Biomass		Entry	c(H₃PO₄) [M]	Time [h]	GVL yield ^a [wt% (mol%)]
	Ве	echwood sav	/dust		
Lignocellulosic content	wt%	1	7.5	96	15 (33)
Hemicellulose	37	2	9.3	24	22 (48)
Cellulose	42	3	9.3	96	23 (50)
Lignin	19	4	9.3	168	20 (43)
		5	10.1	24	25 (54)
		6	10.1	38	21 (46)
		7	10.1	96	19 (41)
		8	10.9	18	21 (46)
		9	10.9	24	26 (57)
		10	10.9	96	18 (39)
		11 ^b	10.9	24	14 (30)
		Wheat stray	N		
Lignocellulosic content	wt%	12	10.9	24	12 (38)
Hemicellulose	25	13	10.9	48	18 (56)
Cellulose	33	14	10.9	72	16 (50)
Lignin	17				

Rice grains							
Starch content	wt%	15	10.9	24	8 (14)		
Amylose	35				. ,		
Amylopectin	65	16	10.9	72	16 (30)		
		Potato flo	our				
Starch content	wt%	17	10.9	24	9 (17)		
Amylose	17.8	18	10.9	72	20 (36)		
Amylopectin	82.2	10	10.9	, _	20 (30)		

Standard reaction conditions: Beech wood (91 mg, corresponding to 0.22 mmol hemicellulose and 0.21 mmol cellulose (24)) and wheat straw (91 mg, corresponding to 0.16 mmol hemicellulose and 0.15 mmol cellulose (25)), rice grains (91 mg, corresponding to 0.50 mmol relative to the glucose monomers (26)), Potato flour (91 mg corresponding to 0.50 mmol relative to the glucose monomers (26)), Ru-MACHO-BH (1.65 mg, 0.0028 mmol), 85 w/w% H₃PO₄(aq) in H₂O (1 mL) at 140 ^oC and 30 bar H₂, ^a Determined by GC-FID. Yields are calculated with respect to dry biomass. ^b1:1 v/v EtOH/H₂O (1 mL)

Table 1. Direct conversion of various real biomass feedstock to GVL.

To elaborate on these results, pure cellulose and hemicellulose were investigated as model substrates using the combination of Ru-MACHO-BH and $H_3PO_4(aq)$ system. We commenced with cellulose with low concentration of acid and using water as the sole solvent. Thus, using 0.5 mol% Ru-MACHO-BH and 5.7 M $H_3PO_4(aq)$ afforded 20% yield of GVL (Table 2, Entry 1). Increasing the reaction time to 96 hours, 24% and 30% yield, respectively, of GVL was obtained using 5.7 M and 7.5 M of $H_3PO_4(aq)$ at 125 °C (Entries 2 and 3). Control experiments without Ru-MACHO-BH led to no GVL, rather the reaction stops at levulinic acid, which is in line with the general acid catalyzed mechanism for the conversion of cellulose to levulinic acid (27). It was also observed that the humins formation in this case was significantly higher.

	HO		Ru-MACHO-BH H ₃ PO ₄ , EtOH/H ₂ O 30 bar H ₂ , 125-140 ⁰ C	►°<°		PPh ₂ -CO
	Ĺ	OH Cellulose	」 _n	GVL	Ph ₂ ''BI	H ₃
Entry	Cellulose	H₃PO₄	Solvent	P/T	Ru-MACHO	GVL vield ^a
	[M]	[M]		[bar]/[°C]	[h]	[%]
1	0.6	5.7	H ₂ O	30/125	48	20
2	0.6	5.7	H ₂ O	30/125	96	24
3	0.6	7.5	H ₂ O	30/125	96	30
4	0.6	5.7	H ₂ O	30/140	96	33
5	0.6	7.5	H ₂ O	30/140	48	30
6	0.6	7.5	H ₂ O	30/140	96	47
7	0.1	5.7	H ₂ O	30/140	48	37
8	0.1	7.5	H ₂ O	30/140	96	50
9 ^c	0.5	7.5	H ₂ O	30/140	72	43
10	0.6	5.7	EtOH/H ₂ O ^b	30/125	48	7
11	0.6	7.5	EtOH/H ₂ O ^b	30/125	48	12

Reaction conditions: Microcrystalline cellulose (0.6 and 0.1 mmol based on glucose monomers), 87 w/w% H₃PO₄, Ru-MACHO-BH (0.5 mol%), H₂O (1 mL), 30 bar H₂, at 140 °C. ^a Determined by GC-FID using 1,4-dioxane as the internal standard. Catalyst loading and yield are relative to moles of glucose monomers contained in cellulose. ^b 1:1 v/v EtOH/H₂O (1 mL). ^c Microcrystalline cellulose (7.8 mmol), H₂O (15 mL).

Table 2. Direct conversion of cellulose to GVL.

The effect of temperature was also studied as high temperature is known to be very detrimental for the acid mediated hydrolysis of cellulose (28). Thus, at 140 °C with 5.7 M H₃PO₄(aq) 33% of GVL was obtained after 96 hours (Entry 4), a 9% improvement from 125 °C. Using 7.5 M of H₃PO₄(aq) provided 30% of GVL after 48 hours (Entry 5), which further yielded 47% after 96 hours (Entry 6). This suggests a higher rate of degradation of the cellulose to levulinic acid at higher temperature and acid concentration, suggesting that the conversion of cellulose to levulinic acid in water is a limiting factor, while the hydrogenation step seemingly proceeds more efficiently. Hence the effect of concentration of both acid and substrate was investigated using different H₃PO₄(aq) concentrations ranging from 5.7 M to 7.5 M with 0.1 M cellulose instead of the 0.6 M used so far. Comparing Entries 7 and 4, it is evident that lowering the cellulose concentration is beneficial. Increasing acid concentration and reaction time to the previously optimized 7.5 M H₃PO₄(aq) and 96 hours provided 50% yield of GVL (Entry 8). It is worth noting the excellent stability and high activity of Ru-MACHO-BH even in higher acid concentration, which is reflected in the full conversion of so-formed levulinic acid to GVL. The reaction was then scaled up to 1.4 g of cellulose using 0.5 mol% of Ru-MACHO-BH at 140 °C and 30 bar H₂ (Entry 9). After 72 hours, a yield of 43% of GVL was obtained, demonstrating the reproducibility of the system at a larger scale. In order to investigate the influence of EtOH as a solvent on the yield of GVL, we performed the reaction with cellulose in a 1:1 v/v EtOH/H₂O medium. Thus, employing 0.5 mol% Ru-MACHO-BH and 5.7 M of phosphoric acid under 30 bar H₂ pressure in EtOH/H₂O, afforded only 7% GVL after 48 hours at 125 °C (Entry 10). Increasing the acid concentration to 7.5 M led to significant increase in the yield to 12% (Entry 11). Under identical conditions, the reaction with water as the sole solvent produce significantly higher GVL.

To investigate the influence of EtOH as a solvent on the yield of GVL, we performed the reaction with cellulose in a 1:1 v/v EtOH/H₂O medium. Thus, employing 0.5 mol% Ru-MACHO-BH and 5.7 M of phosphoric acid under 30 bar H₂ pressure in EtOH/H₂O, afforded only 7% GVL after 48 hours at 125 °C (Entry 10). Increasing the acid concentration to 7.5 M led to significant increase in the yield to 12% (Entry 11). Under identical conditions, the reaction with water as the sole solvent produce significantly higher GVL.

Next, we evaluated the performance of the catalytic system with hemicellulose. In general, hemicellulose requires significantly milder conditions than cellulose. Corn core xylan and beechwood xylan were employed as two different xylan types of xylan from different biomass. A reaction temperature of 125 °C was found necessary to reach effective acid-mediated substrate turnover. A low of 9% yield of GVL was achieved from xylan from corn core using 0.5 mol% Ru-MACHO-BH and 7.5 M H₃PO₄(aq) in H₂O after 48 hours (Table 3, Entry 1). On the other hand, the yield of GVL produced from beechwood at higher temperature (140 $^{\circ}$ C) with 5.7 M H₃PO₄(aq) was 13% (Entry 2). With increase in the acid concentration to 8.4 M, the yield further diminished to yield to 5% (Entry 3). From these observations we speculate that whether the diminished activity

and low yield is as a result of humins formation, which is favored under higher acid concentration and higher temperature when water is employed as the only solvent.



Fata /	Xylan so	Xylan source (M)		Column	P/T	GVL yield ^a
Entry	Corn core	core Beechwood [M]		[bar]/[°C]	[%]	
1	0.6		7.5	H ₂ O	30/125	9
2		0.6	5.7	H ₂ O	30/140	13
3		0.6	8.4	H ₂ O	30/140	5
4	0.6		5.7	$EtOH/H_2O^b$	30/125	64
5		0.6	5.7	EtOH/H ₂ O ^b	30/125	28
6	0.6		7.5	$EtOH/H_2O^b$	30/125	57
7		0.6	7.5	$EtOH/H_2O^b$	30/125	87
8	0.6		5.7	EtOH/H ₂ O ^b	30/140	33
9	0.6		8.4	$EtOH/H_2O^b$	30/140	5
10		0.6	5.7	EtOH/H ₂ O ^b	30/140	43

Reaction conditions: Ru-MACHO-BH (0.5 mol%), xylan from corn core (76.2% xylose monomers) or xylan from beech wood (95% xylose monomers), 85 w/w% H_3PO_4 , EtOH (1 mL), 30 bar H_2 , at 125 °C in 48 h. Catalyst loading and yield are relative to moles of xylose monomers contained in xylan. ^a Determined by GC-FID using 1,4-dioxane as the internal standard. ^b 1:1 v/v EtOH/H₂O (1 mL).

Table 3. Direct conversion of hemicellulose to GVL.

We then carried out the reaction in 1:1 v/v EtOH/H₂O mixture. Thus using 5.7 M acid in 1:1 v/v EtOH/H₂O led to significant increase in the yield to 64% (Entry 4). However, further increasing the acid concentration to 7.5 M is somewhat detrimental on the yield, with merely 57% of GVL obtained (Entry 6). This can be explained by the formation of humins observed in higher acid concentration. Using 5.7 M H₃PO₄(aq) in 1:1 v/v EtOH/H₂O at 140 °C yielded 33% (Entry 8). To compare the results to that of corn core xylan, we performed the reaction with beechwood xylan under similar conditions. Thus, using 5.7 M H₃PO₄(aq) in 1:1 v/v EtOH/H₂O at 125 °C yielded 28%

of GVL after 48 hours (Entry 5). Using 7.5 M acid, 87% yield of GVL was observed already at 125 °C (Entry 7).

Conclusion

We demonstrate for the first time the production of GVL from wide variety of biomass waste feedstocks under mild and sustainable reaction conditions in good yield. This one-pot direct approach avoids the separation of raw biomass and isolation of intermediates which simplifies the whole process viable for industries. The exceptional activity of Ru-MACHO-BH along with a Brønsted acid (H₃PO₄) enabled direct conversion of real biomass such as, wheat straw, rice, potato flour and sawdust into GVL with 16-26 wt% at 140 °C under 30 bar H₂. This versatile protocol can be transferred for the unprecedented transformation of hemicellulose and cellulose to GVL. The superior efficiency of this catalyst for direct hydrogenation of lignocellulose is found to originate from the synergistic effect between Ru-MACHO-BH and Brønsted acid combining cascade hydrogenation/protonolysis.

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Author contributions: SK and MN conceptualized this work. Methodologies, data collection and analysis was carried out by SK under the supervision of MN. SK and MN contributed to the implementation and writing of the manuscript. Review and editing done by SK and MN.

Supplementary Information

Homogeneous catalyzed direct conversion of biomass waste feedstock to gamma-valerolactone

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Materials and Methods

General information

Most chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Ru-MACHO-BH, Microcrystalline cellulose, Xylan (corn core and beech wood) are commercially available and used without further purification. Real biomass like sawdust from beech wood and wheat straw are dried in oven before use. Potato flour and rice grains are dried under vacuum overnight before use. H₂ gas (H₂O \leq 3 ppm; O₂ \leq 2 ppm) was purchased from Air Liquide. All reactions dealing with air or moisture-sensitive compounds were performed using standard Schlenk techniques or in an argon-filled glovebox. GC-FID were recorded on an Agilent 19091J-413 HP-5 5% Phenyl methyl siloxane capillary column using 1,4dioxane as the internal standard. The ¹H and ¹³C NMR spectra were recorded on a Bruker Advance III 400 MHz spectrometer. The batches for gas analysis, the gas phase was carefully collected in a gas bag and analyzed by MicroGC. TGA was fulfilled under N₂ atmosphere (30 mL min⁻¹) using a METTLER TOLEDO thermal analyzer in the temperature interval 25-300 °C with a constant heating rate of 10 °C min⁻¹.

General procedure for catalysis

For a typical hydrogenation experiment, in a glove box, substrate (0.1-0.65 mmol) and catalyst (0.5 mol%) were weighed in a glass vial equipped with a magnetic stir bar and sealed with a Teflon-lined cap. Upon bringing the glass vial outside the glove box, dissolved 1 mL of solvent (H₂O) followed by corresponding amount of acid (4-12 mmol). Subsequently, the vial was placed in a seven-well reactor with a needle placed through the rubber stopper of the vials for the gas flow. The autoclave was sealed tightly and flushed with argon/hydrogen (three times) and finally required hydrogen pressure (30 bar) was loaded into the autoclave and desired temperature was also applied. The reactor was cooled to room temperature before the hydrogen was released and the sample was prepared for GC analysis with 1,4- dioxane as the internal standard.

Catalytic Experiments



Biomass		Entry	H ₃ PO ₄ [M]	Time [h]	GVL yield ^a [wt% (mol%)]				
	Beechwood sawdust								
Lignocellulosic cont	ent wt%	1 ^b	10.9	48	8 (17)				
Hemicellulose	37								
Cellulose	42								
Lignin	19								
		Whe	at straw						
Lignocellulosic cont	ent wt%	2	9.3	24	12 (38)				
Hemicellulose	25	3	10.9	24	12 (38)				
Cellulose	33	4	11.8	96	17 (53)				
Lignin	17	5 ^c	10.9	24	11 (34)				
		6 ^d	10.9	48	3 (9)				

Standard reaction conditions: Beech wood (1g, corresponding to 0.22 mmol hemicellulose and 0.21 mmol cellulose¹⁹) and wheat straw (91 mg, corresponding to 0.16 mmol hemicellulose and 0.15 mmol cellulose²⁰), Ru-MACHO-BH (1.65 mg, 0.0028 mmol), 85 w/w% H₃PO₄(aq) in H₂O (1 mL) at 140 $^{\circ}$ C and 30 bar H₂, ^a Determined by GC-FID. Yields are calculated with respect to dry biomass. ^b Beechwood (1g), Ru-MACHO-BH (20 mg), H₂O (15 mL).^c1:1 v/v EtOH/H₂O (1 mL). ^d Wheat straw (1g), Ru-MACHO-BH (20 mg), H₂O (15 mL).

Table S1: Direct conversion of sawdust and straw to GVL.



Entry	Catalyst	Cellulose	H ₃ PO ₄	Time	GVL
	(mol%)	(mmol)	(M)	(h)	Yield ^a (%)
1	Ru-MACHO-BH (0.5)	0.1	5.7	48	37
2	Ru-MACHO-BH (0.5)	0.1	6.5	48	41
3	Ru-MACHO-BH (0.5)	0.1	6.5	72	47
4	Ru-MACHO-BH (0.5)	0.1	6.5	96	48
5	Ru-MACHO-BH (0.5)	0.1	7.5	96	50

Reaction conditions: Microcrystalline cellulose, 85 w/w% H_3PO_4 , H_2O (1 mL), 30 bar H_2 , at 140 °C. ^aDetermined by GC-FID using 1,4-dioxane as the internal standard. Catalyst loading and yield are relative to moles of glucose monomers contained in cellulose.

Table S2: Direct conversion of cellulose to GVL at 140 °C with different acid concentration.



Fig. S1. Effect of temperature and acid concentration on the direct conversion of cellulose to GVL. Standard reaction conditions: Microcrystalline cellulose (0.6 M), 85 w/w% H_3PO_4 , H_2O (1mL), 30 bar H_2 , 96 hours. Determined by GC-FID. Catalyst loading and yield are relative to moles of glucose monomers contained in cellulose.

[]	Ru-MACHO-BH	
	H ₃ PO ₄ , EtOH/H ₂ O	0~0~
HO OH O O	30 bar H ₂ , 125-140 ⁰ C	
L J _n Hemicellulose		GVL

Entry	Catalyst (mol%)	Substrate (M)	H₃PO₄ (M)	Solvent	GVL Yield ª (%)
1	Ru-MACHO-BH (0.5)	Xylan (corn core) 0.6	3.8	EtOH	52
4	Ru-MACHO-BH (0.5)	Xylan (beech wood) 0.1	5.7	EtOH/H ₂ O	38
5	Ru-MACHO-BH (0.5)	Xylan (beech wood) 0.6	5.7	EtOH/H ₂ O	28

Reaction conditions: Xylan from corn core (76.2% xylose monomers). Xylan from beech wood (95%), 85 w/w% H_3PO_4 , 1:1 v/v EtOH/ H_2O mixture (1 mL), 30 bar H_2 , at 125 °C in 48 hours. Catalyst loading and yield are relative to moles of xylose monomers contained in xylan. ^aDetermined by GC-FID using 1,4-dioxane as the internal standard.

Table S3: Direct conversion of xylan to GVL



Fig. S2. Calibration curve for GVL using 1,4-dioxane as the internal standard.



Fig. S3. GC-FID of the reaction mixture of beechwood sawdust (91 mg) with 10.9 M of $H_3PO_4(aq)$ and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 24 hours.



Fig. S4. ¹H NMR (D₂O, 400 MHz) of the crude reaction of beechwood sawdust (91 mg) with 10.9 M of $H_3PO_4(aq)$ and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 24 hours.



Signal 1: FID1 A,

Peak	RetTime	Type	Width	Area	Area	Name
#	[min]		[min]	[pA*s]	8	
1	1.257	BB S	0.0122	2293.85376	1.90489	?
2	1.370	BV	0.0120	1.65894	0.00138	?
3	1.414	BV	0.0117	20.32687	0.01688	?
4	1.435	VBS	0.0261	1.15164e5	95.63568	?
5	2.286	BH	0.0252	2457.04810	2.04041	?
6	2.993		0.0000	0.00000	0.00000	C14
7	3.466		0.0000	0.00000	0.00000	C15
8	3.926		0.0000	0.00000	0.00000	C16
9	5.400	MM	0.0419	482.59518	0.40076	?

Fig. S5. GC-FID of the reaction mixture of wheat straw (91 mg) with 10.9 M of $H_3PO_4(aq)$ and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 48 hours.



Fig. S6. ¹H NMR (dmso-d₆, 400 MHz) of the crude reaction of wheat straw (91 mg) with 10.9 M of $H_3PO_4(aq)$ and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 48 hours.



Fig. S7. GC-FID of the reaction mixture of rice grains (91 mg) with 10.9 M of H_3PO_4 and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 72 hours.



Area Percent Report

Sorted By	:	Signal			
Calib. Data Modified	:	12/8/2006	5 12:33:15	ΡM	
Multiplier	:	1.0000			
Dilution	:	1.0000			
Use Multiplier & Dilut	ion	Factor with	ISTDs		

Signal 1: FID1 A,

Peak	RetTime	T	pe	Width	Area	Area	Name
#	[min]			[min]	[pA*s]	망	
1	1.255	BB		0.0100	10.00459	0.00536	?
2	1.316	BB		0.0147	3.70818	0.00199	?
3	1.368	BB		7.96e-3	2.03438	0.00109	?
4	1.411	BV		8.68e-3	36.07652	0.01932	?
5	1.432	VB	S	0.0190	1.79040e5	95.89713	?
6	1.526	BB	Х	9.07e-3	7.12259	0.00381	?
7	1.630	BB	Х	9.42e-3	2.87165e-1	0.00015	?
8	1.724	BB		0.0369	3.21941	0.00172	?
9	2.021	BB		0.0176	3.45120	0.00185	?
10	2.294	HH		0.0217	6137.80908	3.28753	?
11	2.993			0.0000	0.00000	0.00000	C14
12	3.466			0.0000	0.00000	0.00000	C15
13	3.926			0.0000	0.00000	0.00000	C16
14	5.434	HH		0.0439	1424.71912	0.76311	?
15	5.900	HH		0.0656	31.61740	0.01693	?
Total	s:				1.86700e5		

Fig. S8. GC-FID of the reaction mixture of potato flour (91 mg) with 10.9 M of H_3PO_4 and Ru-MACHO-BH (1.65 mg) under 30 bar H_2 and 140 °C in water for 72 hours.


Area Percent Report

Sorted By :	Signal
Calib. Data Modified :	12/8/2006 12:33:15 PM
Multiplier :	1.0000
Dilution :	1.0000
Use Multiplier & Diluti	on Factor with ISTDs

Signal 1: FID1 A,

Peak #	RetTime [min]	Туре	Width [min]	Area [pA*s]	Area %	Name	
1	1 256	BB	6 810-3	67 07451	0.08230	2	
2	1 314	BVS	8 030-3	5192 20654	6 37053	2	
3	1.371	BVX	7.340-3	2.04072	0.00250	2	
4	1.393	WV X	0.0144	46.74556	0.05735	2	
5	1.414	VV X	8.01e-3	22.86432	0.02805	?	
6	1,435	VBS	0.0110	7,19634e4	88,29481	?	
7	1.705	BB	0.0120	19,52512	0.02396	?	
8	1.776	BB	0.0122	6.01460	0.00738	?	
9	2.008	BB	0.0143	25.60098	0.03141	?	
10	2.216	BB	0.0155	6.97473	0.00856	?	
11	2.282	BB	0.0180	2797.69287	3.43260	?	
12	2.993		0.0000	0.00000	0.00000	C14	
13	3.466		0.0000	0.00000	0.00000	C15	
14	3.578	BB	0.0269	2.47971	0.00304	?	
15	3.926		0.0000	0.00000	0.00000	C16	
16	4.604	BB	0.0300	12.75125	0.01565	?	
17	4.782	BB	0.0295	5.19553	0.00637	?	
18	5.305	BB	0.0224	1.40013	0.00172	?	
10	5 420	םם (0 0277	1206 22201	1 57025	2	
13) D.420		0.0377	1200.33301	1.57623) f	
20	0 0.879	BB	0.0289	3.00/93	0.00440		
21	6.014	BB	0.0273	2.60000	0.00344		
22	6.932	BV	0.0275	4./5/25	0.00584		
23	6.968	N NB	0.0383	7.73025	0.00948	· · ·	
24	1.372	BB	0.0338	6.22408	0.00764	12	
- 25	7.910	BB	0.0343	20.13674	0.02471	. ?	

Fig. S9. GC-FID of the reaction mixture of xylan from corn core (0.6 mmol) with 5.7 M of H_3PO_4 and Ru-MACHO-BH (0.5 mol%) under 30 bar H_2 and 125 °C in 1:1 v/v EtOH/ H_2O mixture for 48 hours.



Fig. S10. ¹H NMR (dmso-d₆, 400 MHz) of the crude reaction of 0.6 mmol Xylan from corn core (0.6 mmol) with 5.7 M of H₃PO₄ and Ru-MACHO-BH (0.5 mol%) under 30 bar H₂ and 125 °C in 1:1 v/v EtOH/H₂O mixture for 48 hours.



Fig. S11. GC-FID of the reaction mixture of cellulose (0.6 mmol) with 7.5 M of $H_3PO_4(aq)$ and Ru-MACHO-BH (0.5 mol%) under 30 bar H_2 and 140 °C in water for 96 hours.



Fig. S12. GC-FID of the reaction mixture of GVL with 10.9 M of $H_3PO_4(aq)$ and Ru-MACHO-BH under 30 bar H_2 and 140 °C in water after 72 hours hours.

Moisture determination by TGA analysis



Fig. S13. TGA profile for moisture content analysis based on thermal degradation of sawdust and straw.

Gas phase analysis by MicroGC

External Standard Report

Page 1 of 2 (13)

Method Name:	C:\Users\Administrator\Agilent\Method\20190717_Luca_Final.met
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+01-00).dat.rslt\1	48_sakk-109_2021-11-15 14-33-40 (GMT +01-00)-Rep7.dat
User:	SYSTEM (SYSTEM)
Acquired:	11/15/2021 2:34:28 PM (GMT +01:00)
Printed:	11/15/2021 2:42:09 PM (GMT +01:00)



External Standard Report

Page 2 of 2 (22)

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+01-00).dat.rslt\	148_sakk-109_2021-11-15 15-07-19 (GMT +01-00)-Rep11.dat
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Printed:	11/15/2021 3:15:40 PM (GMT +01:00)

Totals			
		8750365	8.1

Channel 2, 10m PPQ Heated Injector, Backflush Results				
Pk #	Name	Retention Time	Area	Concentration
2	CO2	0.5	160760958	78.5
	C2H4			0.0 BDL
	C2H6			0.0 BDL
3	H2O	0.7	186150748	2729.0
	C4H10			0.0 BDL
12	Acetone	4.3	624	0.0
20	iPrOH	5.3	222	0.0
Totals				
			346912552	2807.6

Channel 3, 10m MS5A Heated Injector Results	Nama	Detention Time	4	Concentration
FK #	Name	Kelention Time	Area	Concentration
1	H2	0.4	454464004	59.8
2	O2 (ref)	0.5	7356593	7.7
3	N2	0.7	22241869	30.9
4	CO	1.5	15	0.0
Totals				
			484062481	98.4

Fig. S14. MicroGC report of hydrogenation of beechwood sawdust (Table 1, Entry 7 in the main text)

External Standard Report

 Method Name:
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 C:\Users\Administrator\Agilent\Result\146_sakk-108_2021-11-15 11-58-38 (GMT

 +01-00).dat.rslt\146_sakk-108_2021-11-15 12-15-04 (GMT +01-00)-Rep3.dat

 User:
 SYSTEM (SYSTEM)

 Acquired:
 11/15/2021 12:15:52 PM (GMT +01:00)

 Printed:
 11/15/2021 12:23:26 PM (GMT +01:00)



External Standard Report

Page 2 of 2 (6)

Method Name: C:\l Data: C:\l +01-00).dat.rslt\146_sa User: SYS Acquired: 11/1 Printed: 11/1	Jsers\Administrator\Agilent\Met Jsers\Administrator\Agilent\Res kk-108_2021-11-15 12-15-04 (GN TEM (SYSTEM) 5/2021 12:15:52 PM (GMT +01: 5/2021 12:23:26 PM (GMT +01:	hod\20190717_Luca alt\146_sakk-108_20 4T +01-00)-Rep3.da 00) 00)	_Final.met 21-11-15 11-58-38 (C t	IMT
Totals			21417504	10.0
Channel 2, 10m PPQ Heated Injector, Backflush Results Pk #	Name	Retention Time	Area	Concentration
2	CO2	0.5	582417	0.3
	C2H4			0.0 BDL
	C2H6			0.0 BDL
3	H2O	0.7	670108	9.8
	C4H10			0.0 BDL
	Acetone			0.0 BDL
10	iPrOH	5.4	9466	0.0
Totals			1261991	10.1
Channel 3, 10m MS5A Heated Injector Results	N			
Pk #	Name	Retention Time	Area	Concentration
1	H2	0.4	36056238	4.7
2	O2 (ref)	0.5	18194089	19.0
5	N2 CO	1.5	1399	0.0 BDL 0.0
Tel				
I otals			54251726	23.8

Fig. S15. MicroGC report of the blank reaction using GVL as the substrate with Ru-MACHO-BH and $H_3PO_4(aq)$ under 30 bar H_2 at 140 °C in water after 72 hours.

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