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Towards the Efficient Development of Homogeneous Catalytic Transformation to γ-Valerolactone from Biomass-Derived Platform Chemicals

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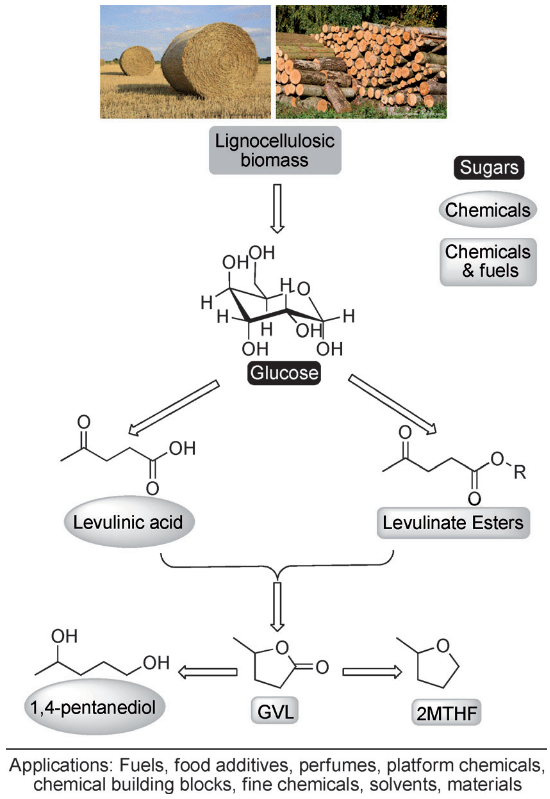
Recent efforts focused on the production of selected chemicals from biomass as an effective approach to replace fossil feedstocks. Among them, transformation of the biogenic platform molecule levulinic acid to γ-valerolactone has been an extensively studied reaction. Although this transformation can be achieved by heterogeneous catalysis, there exists also a strong interest for effective homogeneous catalysis that can operate selectively under milder and sustainable conditions. Herein, we report the utilization of various triphos-analogue ligands that in the presence of Ru(acac)$_3$ (acac = acetylacetonate) lead to highly efficient γ-valerolactone production (yield up to 95 %). Excellent catalyst turnover numbers (up to 75 855) and turnover frequencies (up to 1382 h^{-1}) were accomplished.

Introduction

The depletion of fossil fuels with increasing amount of atmospheric carbon dioxide over the last century encourages chemical researchers in academia and industry to look for more benign transformations of viable renewable resources.[1–3] In this aspect, plant biomass is considered as economical and energy-efficient resource for the sustainable production of biofuels and various utility chemicals.[1,3] In general, such transformations generate significantly less greenhouse-gas emission than their fossil-fuel counterpart.[2] The carbohydrates resulting from lignocellulosic biomass consist of the largest fraction of global biomass feedstocks. Here, catalysis is playing a crucial role in the development of new technologies for producing energy, alternative fuel, as well as basic and fine chemicals from biomass.[1,4–5]

Although the first-generation biofuels, which are usually derived from starch, vegetable oil, or animal fat, have been successfully implemented, still more efficient processes need to be developed to reduce the current world's dependence on petroleum. In this respect, especially new technologies using (nonedible) lignocellulosic biomass must be developed, and γ-valerolactone (GVL) has been acknowledged as an interesting renewable platform molecule with potential impact for the production of both energy or carbon-based consumer products (Scheme 1).[6]

GVL can easily be stored and moved globally in large quantities because of its low melting point, high boiling/flash point and water miscibility to assist biodegradation. The emission characteristics can simply be minimized by the low vapor pressure of GVL.[6] The sweet "nontoxic" smell can be utilized for easy recognition of leaks and spills. Owing to such attractive physical and chemical properties, GVL is considered as a sustainable liquid for global storage and transportation.



Scheme 1. Lignocellulosic biomass roadmap for the production and application of GVL. 2MTHF = 2-methyltetrahydrofuran

Hence, a cost-effective and environmentally benign synthesis of GVL from levulinic acid/ester has attracted substantial at-

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tention both in homogeneous and heterogeneous catalysis.[4a,7–8] Levulinic acid is now considered amongst the top 12 chemical building blocks from biomass because of the versatile applications and synthetic utility of GVL as depicted in Scheme 1.[3a,b] So far, the hydrogenation of levulinic acid to GVL was accomplished by heterogeneous catalysts (e.g., ruthenium or platinum catalysts supported on carbon, aluminum oxide, or titanium dioxide).[7] Although this approach offers the advantage of easy catalyst recycling, high pressure and/or temperatures are necessary to obtain high conversion. Moreover, such processes are usually associated with the formation of over-hydrogenated 2-methyltetrahydrofuran, which has safety issues as the latter product can readily be converted into the corresponding hazardous peroxide.[8f] These problems prompted researchers to look into analogous homogeneous catalytic pathways.[4a,8] Already in 1982, Yoshikawa et al. reported the catalytic hydrogenation of levulinic acid using $RuCl_2(PPh_3)_2$ as the catalyst at 180 °C.[8a] Almost 25 years later in 2008, Horváth et al. observed that $Ru(acac)_3$ (acac = acetylacetonate) ligated with PBu_3, tris(3-sulfonatophenylphosphine) (TPPTS) provides good to moderate yields of GVL at 80 bar hydrogen pressure and high temperature (200 °C).[8b] More recently, Guo and Fu et al. developed a $RuCl_3/PPh_3$-based catalytic system for levulinic acid hydrogenation using formic acid as hydrogen source (no external hydrogen gas applied). Again, high temperature (200 °C) and 10 mol % base were necessary to obtain sufficient conversion to achieve high yield of GVL.[8c] In 2010, Leitner and co-workers improved these earlier methods by using $Ru(acac)_3$ as the catalyst, P*n*Oct_3 as the ligand and NH_4PF_6 as an additive at 100 bar hydrogen pressure and 160 °C.[8d] The following year, a biphasic $RuCl_3$–TPPTS system was developed by Heeres et al. in which the catalytic system can be recycled but the product yield dropped by approximately 30 % after the first catalytic run.[8e] Although these catalysts (see below) allowed for high yields of the desired product, still the turnover numbers (TON, moles of products/moles of catalyst) need to be improved. The maximum TON does not exceed 1560 if using the reported homogeneous ruthenium-based catalyst (Supporting Information, Scheme S1).[8a–e] In this aspect, the work of Zhou et al. is noteworthy. By using sophisticated iridium pincer complexes, excellent catalyst TONs (71 000) were achieved at 100 °C. However, addition of 120 mol % of base eventually limits its practical potential.[8f] In 2013, a high TON of 78 000 was achieved by using half-sandwich iridium complex at 120 °C; reported again by Guo and Fu et al. (Scheme S1).[8g]

Herein, we report three ruthenium–triphos-based efficient catalytic systems, which yielded GVL in excellent yield (up to 95 %) with very high TON (75 855) under relatively mild reaction conditions (140 °C) on a preparative scale (substrate loading as high as 185 mmol) and under solvent-free (neat) conditions. In essence, we believe these catalyst systems constitute an important step towards a practical GVL production in a sustainable manner under homogeneous conditions (Scheme S1).

Results and Discussion

The initial optimizations were performed in the presence of $Ru(acac)_3$ as the catalyst and *p*-toluenesulfonic acid (PTSA) as an additive by using methyl levulinate as the model substrate. Unlike most of the relevant reports under homogeneous conditions (Scheme S1),[4a,8] here only a catalytic amount of the additive (1.75 equivalents with respect to the catalyst) was used. In the absence of both acid and ligand, only 19 % yield of GVL was obtained. The addition of PTSA increased the yield merely to 21 % (Figure 1, Table S1).

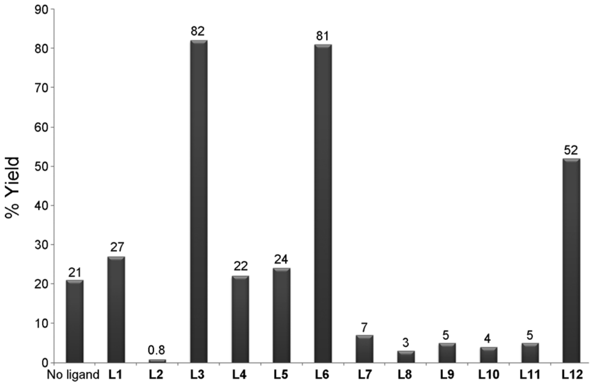
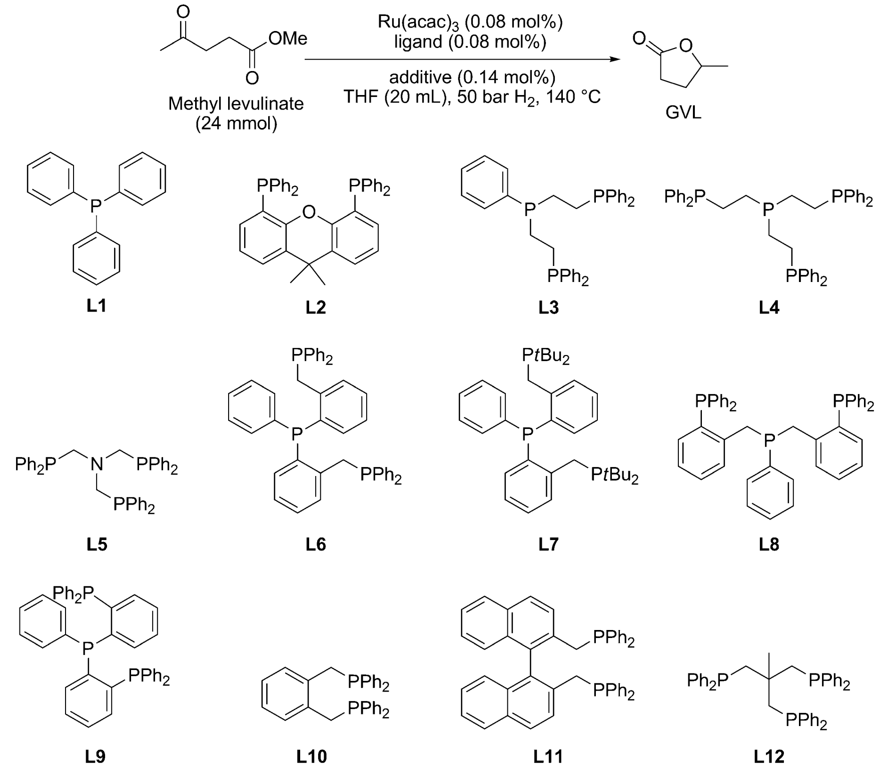


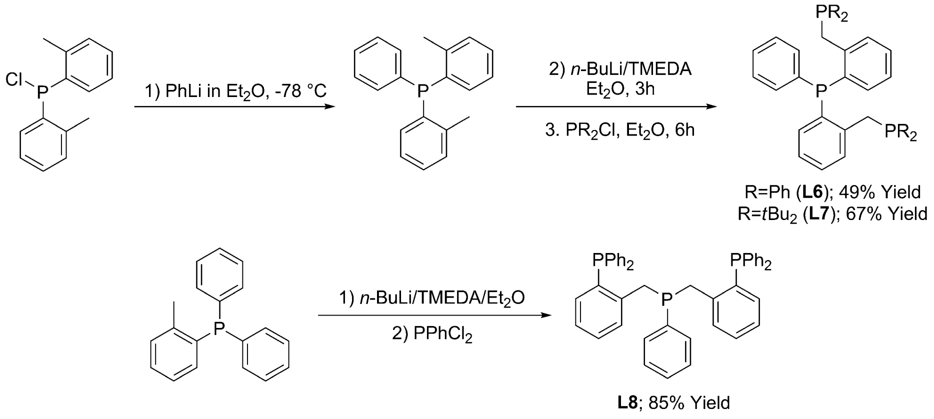
Figure 1. Hydrogenation reaction of methyl levulinate under variation of ligands (reaction conditions: 0.08 mol % $Ru(acac)_3$, 0.08 mol % ligand, 0.14 mol % additive, substrate, 24 mmol, 50 bar H_2, solvent: THF, 140 °C, 22 h). For details, see Table S1.

Next, various mono-, bi-, and tridentate phosphine-based ligands were added to the model reaction (Scheme 2, Figure 1). The product yield was slightly improved (up to 27 %) in the presence of monodentate PPh_3 (**L 1**) but only traces of activity was noted in the case of bidentate Xantphos (**L 2**) as the ligand. To our delight, the commercially available triphos, bis(2-diphenylphosphinoethyl)phenylphosphine (**L 3**) led to 82 % yield under identical reaction conditions. Notably, another commercially available tridentate ligand (tris[2-(diphenylphosphino)ethyl]phosphine, **L 4**) gave rise to 35 % of GVL. Next, according to the literature we prepared tris((diphenylphosphino)-methyl)amine (**L 5**); however, subsequent catalytic tests revealed low activity (24 % of GVL). These initial results prompted us to explore the structural aspects of the triphos backbone of **L 3** in more detail (Figure 1, Scheme 2). Hence, three newly designed triphos analogue ligands {[(phenylphosphinediyl)bis-(2,1-phenylene)]bis(methylene)}bis-(diphenylphosphine) (**L 6**), {[(phenylphosphinediyl)bis(2,1-phenylene)]bis(methylene)}bis-(di-*tert*-butylphosphine) (**L 7**) and {[(phenylphosphinediyl)bis-(methylene)]bis(2,1-phenylene)}bis-(diphenylphosphine) (**L 8**) were prepared and fully characterized. The synthetic routes of these ligands (**L 6**–**L 8**) are depicted in Scheme 3 and the detailed procedures are described in the Supporting Information.

Interestingly, **L 6** and **L 7** revealed significantly different catalytic performances. In the presence of **L 6**, 81 % of GVL was obtained, but **L 7** gave only 7 % of the desired product under



Scheme 2. List of ligands utilized during initial optimization of the reaction conditions.



Scheme 3. Synthetic routes for ligands **L6**–**L8**. TMEDA = *N*,*N*,*N*′,*N*′-Tetramethylethylenediamine.

identical reaction conditions (Figure 1). This clearly indicates the positive influence of the phenyl-substituted phosphine ligand. To our surprise, the ligand **L8**, which contains analogous features to **L6**, exhibited very poor reactivity (only 3% GVL yield). Similarly, [(phenylphosphinediyl)di-2,1-phenylene]-bis(diphenylphosphine) (**L9**), 1,2-bis(diphenylphosphinomethyl)benzene (**L10**), and 2,2′-bis[(diphenylphosphino)methyl]-1,1′-binaphthalene (**L11**) yielded only 4–5% of GVL, respectively (Figure 1, Scheme 2, Table S1). The reactivity comparison between the positive catalytic influence of **L3** and **L6** and the negative influence of **L7**–**L9** indicates a constructive role of the "methylenic diphenylphosphino" (–CH$_2$–PPh$_2$) moiety at the triphos backbone in this hydrogenation chemistry. Interestingly, the commercially available triphos derivative, 1,1,1-tris(diphenylphosphinomethyl)ethane (**L12**) gave 52% of GVL under identical conditions. Such a positive influence of methylenic diphenylphosphino (–CH$_2$–PPh$_2$) moiety of **L3**, **L4**, and **L6** could be attributed to the stable catalytically active species formation during the reaction, because ruthenium nanoparticles were observed at the end of the reactions using **L5**, **L7**–**L9** as the ligands (entries 18–20, Table S1) under such reducing environment.[8a–e,9]

Next, we explored the influence of additives as it was rationalized in earlier reports.[8] For this study, the combination of ligand **L3** with Ru(acac)$_3$ was considered. In the absence of any acid as an additive, only 30% of GVL was obtained. To our surprise, very poor activity (6% yield) was observed in the presence of the similar Brønsted acid, methanesulfonic acid (MSA) as an additive. Addition of inorganic acids such as phosphoric acid (H_3PO_4) and phosphotungstic acid ($H_3PW_{12}O_{40}$) yielded 58 and 15% of GVL, respectively, under optimized reaction conditions. Interestingly, substantial yield of GVL (62%) was achieved by using scandium triflate. However, only traces of activity (≈<1%) were observed by using sodium triflate. This implies the necessity of either acid or a suitable cation in this process. In conclusion, the initially tested PTSA was established as the best additive in the presence of ligand **L3**.

Nevertheless, the strong influence of the additive encouraged us to further optimize the catalytic system with **L4**, which contains a methylenic diphenylphosphino (–CH$_2$–PPh$_2$) moiety at the triphos backbone. If 5 equivalents of PTSA were used (instead of the usual 1.75 equiv.) with **L4**, the GVL yield increased drastically to 77% from 35%. Finally, the yield with **L4** as the ligand rose to 82% if using scandium triflate as an additive. However, the use of other additive/ligand combinations usually resulted in the formation of black ruthenium nanoparticles after the reaction and, hence, lower activity was detected (entries 1–20, Table S1). Thus, PTSA was found to be

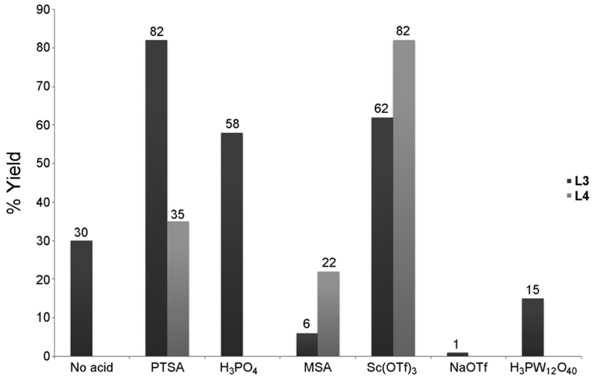


Figure 2. Influence of additives in the hydrogenation of methyl levulinate using **L3** and **L4** (reaction conditions: 0.08 mol% $Ru(acac)_3$, 0.08 mol% ligand, 0.14 mol% additive, substrate 24 mmol, 50 bar, 22 h). For details see Table S1.

the only additive that commonly operates for **L3**, **L4**, and **L6**. In essence, these studies demonstrate the crucial role of acids in this catalysis. Similar critical influences of acids in relation to the hydrogenation chemistry has also earlier been mentioned in the literature.[8a–e,9] (Figure 2)

After initial optimization, similar overall catalyst productivities (TON) of 980, 983, and 970 were measured by using **L3**, **L4**, and **L6**, respectively, if using 0.08 mol% of catalyst and methyl levulinate as the substrate (Figure 3). However, at lower catalyst loadings these ligands behave differently. For example, catalyst TONs of 3650, 2850, and 3050 were obtained at 0.025 mol% catalyst systems with **L3**, **L4**, and **L6**, respectively (Figure 3, Table 1, entries 1–3). Here, the ligand **L6** appeared to significantly accelerate the reaction (only 6 h reaction time) relative to the other two ligands (reaction time 22 h for **L3** and **L4**) under identical reaction conditions. At this stage, further influence of temperature and pressure on this catalytic system was assessed by using 0.025 mol% of catalyst and **L3** as the ligand. However, the combination of earlier observed 140 °C temperature and 50 bar H_2 pressure were found to have a most pronounced effect on the reactivity and selectivity (entries 24–28, Table S1) in this catalysis.

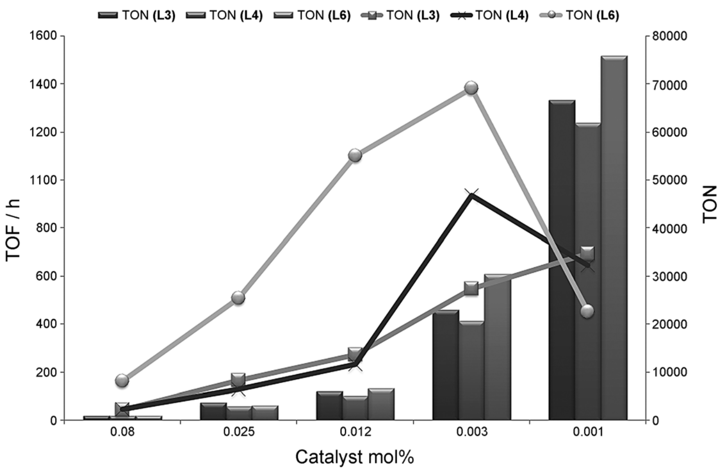


Figure 3. Respective catalyst TONs and turnover frequencies (TOF) of ligands **L3**, **L4**, and **L6** versus catalyst concentration.

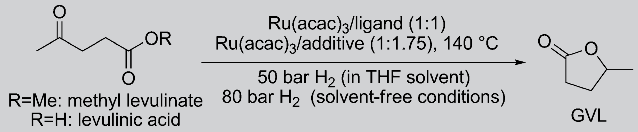
Next, we performed the benchmark reaction under solvent-free conditions to showcase the efficacy of our catalytic systems. Using 0.012 mol% of catalyst, the catalyst TON with **L3**, **L4**, and **L6** were 6000, 5100 and 6600, respectively (Table 1, entries 4–6). Here again, the **L6** ligand operated very fast (6 h) that is, with high turnover frequency (TOF) of 1100 h^{-1}, relative to **L3** (TOF = 273 h^{-1}) and L4 (TOF = 232 h^{-1}, Figure 3). The respective gas consumption profile reveals that the reaction with **L6** was even faster (almost completed) during the initial 3 h (Supporting Information, Figure S1).[10] These results encouraged us to decrease the catalyst loading furthermore to 0.003 mol%. Gratifyingly, catalyst TON of 23 000, 20 600, and 30 400 were obtained by using **L3**, **L4**, and **L6**-based catalytic systems, respectively (Figure 3, Table 1, entries 7–9). Notably, 95% yield with TON = 30 400 was achieved after 22 h using the **L6**-based catalytic system. Moreover, the ligand **L6** operated much faster with very high catalyst TOF of 1382 h^{-1}, whereas **L3** and **L4** exhibited TOFs of 548 h^{-1} (42 h reaction time) and 936 h^{-1} (22 h reaction time), respectively.[11] Finally, we performed the hydrogenation reaction in the presence of only 0.001 mol% catalyst, at which loading, interestingly, all three catalytic systems needed longer time to proceed. Here, **L3** and **L4** yielded catalyst TONs of 66 666 (TOF = 694 h^{-1}) and 61 866 (TOF = 644 h^{-1}) after 4 days, however, very high catalyst TON of 75 855 (TOF = 452 h^{-1}) was accomplished using **L6** after 7 days (Figure 3, Table 1, entries 10–12). To the best of our knowledge, such high TONs using ruthenium-based catalytic systems have not been reported yet.

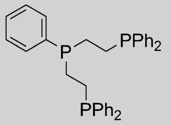
To our surprise, though **L6** was able to provide highest catalyst TON using 0.001 mol% of catalyst, the corresponding TOF was affected by the longer reaction time. Likewise, adding two equivalents of ligand failed to realize a faster reaction as only 24% GVL yield was obtained (Table 1, entry 13); presumably as a result of blocking of active catalytic sites. As shown in Figure 3, only the catalyst system consisting of ligand **L3** was completely stable irrespective of the catalyst loading as TOF always has an increasing trend.[12]

Levulinic acid was finally tested as the substrate by using these three optimized catalytic systems (using 0.001 mol% of catalyst) under similar reaction conditions (Table 1, entries 11–13). Interestingly, ligand **L4** (TON = 73 142) was found to be highly active here compared to **L3** (TON = 59 265) and **L6** (TON = 12 000). The unexpected lower activity of **L6** can be attributed to its bad solubility in levulinic acid, which was also reflected by its poor yield and ruthenium black formation after the reaction.

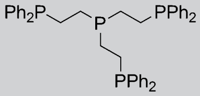
Interestingly, we observe that TOFs increase at lower catalyst loadings, attributed to the inhibition of THF solvent at higher catalyst loadings (Figure 3). This result prompted us to explore the further solvent effects on our system because TOFs were increased on exclusion of solvent. Thus we performed the fol-

Table 1. Hydrogenation of methyl levulinate and levulinic acid.[a]

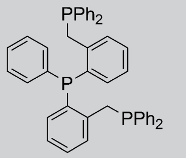




L3



L4



L6

Entry	R (substrate [mmol])	Ru(acac)$_3$ [mol %]	Ligand	Additive	Time [h]	Yield [%] (TON)
1[b]	Me (80)	0.025	**L 3**	PTSA	22	91 (3650) 88 (3530)[c]
2[b]	Me (80)	0.025	**L 4**	Sc(OTf)$_3$	22	71 (2850)
3[b]	Me (80)	0.025	**L 6**	PTSA	6	76 (3050)
4	Me (160)	0.012	**L 3**	PTSA	22	75 (6000)
5	Me (160)	0.012	**L 4**	Sc(OTf)$_3$	22	65 (5100)
6	Me (160)	0.012	**L 6**	PTSA	6	82 (6600)
7	Me (160)	0.003	**L 3**	PTSA	42	72 (23 000)
8	Me (160)	0.003	**L 4**	Sc(OTf)$_3$	22	65 (20 600)
9	Me (160)	0.003	**L 6**	PTSA	22	95 (30 400) 89 (28 478)[c]
10	Me (185)	0.001	**L 3**	PTSA	96	67 (66 666)
11	Me (185)	0.001	**L 4**	Sc(OTf)$_3$	96	62 (61 866)
12	Me (185)	0.001	**L 6**	PTSA	168	76 (75 855) 74 (74 000)[c]
13[d]	Me (185)	0.001	**L 6**	PTSA	168	24 (24 000)
14	H (68)	0.001	**L 3**	PTSA	96	59 (59 265)
15	H (68)	0.001	**L 4**	Sc(OTf)$_3$	96	73 (73 142) 71 (71 111)[c]
16[e]	H (68)	0.001	**L 6**	PTSA	168	12 (12 000)

[a] Reaction conditions: A 100 mL stainless-steel autoclave or 25 mL Hastelloy-c autoclave was charged with the catalyst Ru(acac)$_3$, the ligand **L 3**, **L 4**, or **L 6** (1 mole equivalent with respect to catalyst) and the additive (1.75 mole equivalent with respect to catalyst) under argon atmosphere, unless noted otherwise. The required amount of substrate and/or THF was then added under argon atmosphere, unless noted otherwise. The reaction was then performed at 140 °C after the addition of hydrogen at 80 bar. Finally, yield and TON were determined by GC with respect to isooctane as an internal standard against authenticated samples. TON is expressed in [$\text{mmol}_{\text{GLV}}\,\text{mmol}_{\text{catalyst}}^{-1}$]. All the reactions were repeated at least twice to ensure reproducibility and yields or TONs reported in this study are averages of at least two runs. See Table S1 and the Experimental Section in the Supporting Information for more details. [b] Performed in THF (20 mL) under 50 bar of H_2. [c] Yield and TON of isolated GVL. [d] 2 Equivalents of **L 6**. [e] Ruthenium black was observed after the reaction.

lowing control experiments with **L 3** as the ligand: 1) Using solvent-free conditions at higher catalyst loadings, and 2) using THF as the solvent at lower catalyst loadings.[12,13] Additionally, these reactions were also performed by using γ-butyrolactone as the solvent.[14] At a higher catalyst loading (0.025 mol %), TOFs of 166, 223, and 234 h^{-1} were observed using THF as the solvent, under neat conditions, and γ-butyrolactone as the solvent, respectively, (Table S2, Figure S2). However, the THF inhibition effect was more pronounced at lower catalyst loadings (0.003 mol %). Here, TOFs (yields) of 119 h^{-1} (15 %), 548 h^{-1} (72 %), and 875 h^{-1} (87 %) were observed if using THF as the solvent, under neat conditions, and γ-butyrolactone as the solvent, respectively (Table S2, Figure S2). To our surprise, these reactions now proceeded with quantitative yields and at lesser time (i.e., even higher TOF) with γ-butyrolactone as the solvent (Figure S2). These results were also reflected by the corresponding TOFs and gas consumption profile (Figure S3). Therefore, these control experiments provided further evidence for the inhibition effect by THF (presumably by blocking of active catalytic sites through coordination) and the higher TOF under solvent-free conditions.

Conclusion

The present report demonstrates the facile production of γ-valerolactone from a most popular and versatile biogenic platform chemical, methyl levulinate and levulinic acid. Excellent yields (up to 95 %), high catalyst turnover numbers (up to 75 855), and high turnover frequencies (up to 1382 h^{-1}) were obtained by using three different highly selective and flexible multifunctional ruthenium-based catalytic systems. Herein, three different analogous triphos ligands have been identified to be highly effective in this transformation and the newly synthesized ligand **L 6** led to highest catalyst turnover numbers and catalyst turnover frequencies in the present study. The advantages of these processes include utilization and very low loading of ruthenium catalyst, use of catalytic amounts of additive, solvent-free conditions, practical substrate scale under comparatively low hydrogen pressure. This report also includes the design and syntheses of three new triphos-analogue ligand structures, which demonstrate the influential role of “methylenic diphenylphosphino” ($-CH_2-PPh_2$) moiety at triphos backbone in hydrogenation chemistry. In essence, these reactions constitute a further step towards a practical γ-valerolactone production using homogeneous catalysis.

Experimental Section

Catalytic reactions

General procedure: An autoclave (100 mL stainless-steel or 25 mL Hastelloy-c) was charged with equimolar amounts of catalyst, Ru(acac)$_3$ and respective phosphine-based ligands along with additives, unless noted otherwise. Then, the autoclave was evacuated and back-filled with argon three times. Under high stream of argon, the substrate (methyl levulinate or levulinic acid) and/or THF were added. Then, the autoclave was pressured with H_2 (50 or 80 bar) and heated at 140 °C for the specified reaction time. Afterwards, the autoclave was cooled to RT, the pressure was released, and the reaction mixture was stirred with isooctane as an internal standard. The mixture was then filtered through Celite and subject to GC analysis for the determination of yield and conversion. GVL was isolated by vacuum distillation and subsequently characterized by NMR spectroscopy. The very detailed experimental procedures are also described in the Supporting Information.

Acknowledgements

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Keywords: biomass · homogeneous catalysis · ligand effects · ruthenium · oxygen heterocycles

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[10] The gas consumption profile also reveals that the ligand **L3** has a slow but steady reaction rate throughout the reaction time, whereas the rate decreases after 8 h in the case of **L4** after a good start. For details see Figure S1.

[11] The longer reaction time (42 h) only in the case of **L3** can be attributed to the initial slow rate of the reaction.

[12] The (always) steady reaction rate in the case of **L3** is reflected in its constant increasing trend of TOFs. See Figure 3 and Figure S1.

[13] The ligand **L3** was selected for this study because of its always increasing trend of TOF; see Figure 3.

[14] γ-Butyrolactone was selected as an additional solvent because of its similarity of chemical and physical properties with the product, γ-valerolactone.

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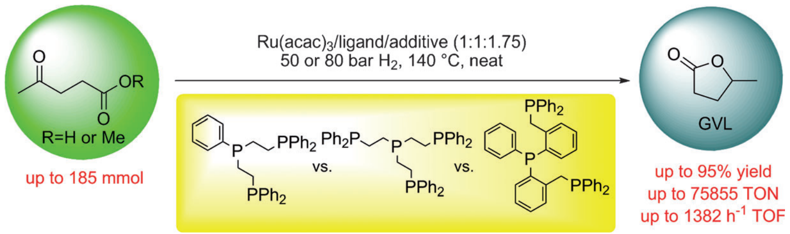
Towards the Efficient Development of Homogeneous Catalytic Transformation to γ-Valerolactone from Biomass-Derived Platform Chemicals



Practically sustainable in every way: The practical production of γ-valerolactone (GVL) is described from the biomass-derived platform chemicals methyl levulinate and levulinic acid using three different ruthenium–triphos-based catalyst systems under optimized reaction conditions. acac = Acetylacetonate, TON = turnover number, TOF = turnover frequency.