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A Homogeneous Nickel Catalyst for Reductive Amination of γ-Keto Acids using Hydrogen

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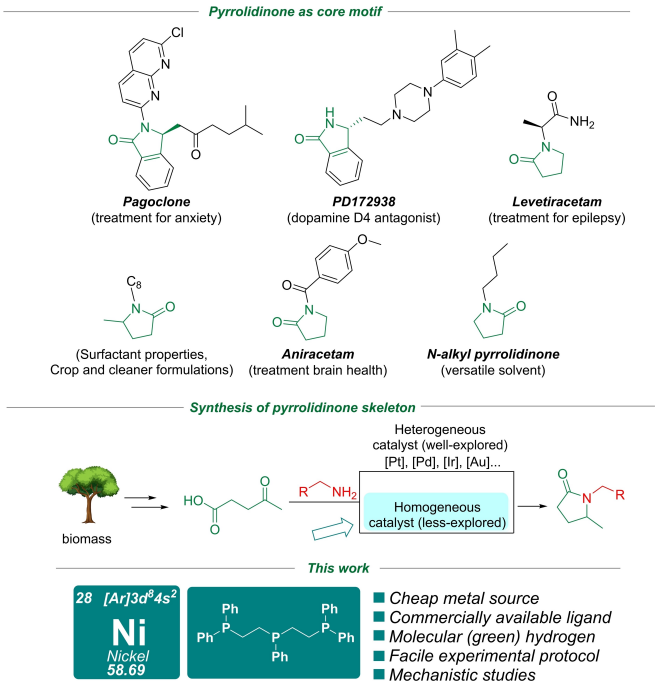
The reductive amination of levulinic and 2-acetyl benzoic acids with hydrogen and various amines proceeds efficiently in the presence of a homogeneous Ni/triphos-catalyst. The reaction rate of the overall process is significantly enhanced using 3,3,3-trifluoroethanol (TFE) as solvent. The optimized synthetic protocol allows for a straightforward access of >20 examples of *N*-functionalized pyrrolidinones in high yields (75% and >99%). Upscaling to 10 mmol-scale is demonstrated and mechanistic in situ studies revealed the presence of alkoxy- and hydroxylactams as crucial intermediates.

Introduction

The conversion of biomass or biomass derived molecules into valuable fine chemicals and fuels can play an important role to achieve a sustainable chemical industry.[1] As an example, catalytic conversion of lignocellulosic biomass has gained considerable attention for the production of bio-based platform molecules.[2] More specifically, levulinic acid (LA) can be produced from untreated biomass or from mono- or poly-saccharides via acid-catalyzed dehydration in high yield.[3] LA is considered one of the most versatile bio-based key intermediates from which many important chemicals might be produced via various transformations.[4] In fact, monomers of nylons,[5] polyesters,[6] and many more have been synthesized from LA.[7] Due to its bifunctionality stemming from the presence of both an acid and keto group LA is also a valuable substrate for the synthesis of tremendously important compound classes like oxygen- and nitrogen-based heterocycles[8] in general and in particular γ-valerolactone, α-angelicalactone and its isomers, and eventually *N*-functionalized pyrrolidinones.[9]

Compounds comprising the latter structural motif find applications as psycho-active drugs like Pagoclone and Levetiracetam or solvents and surfactants (cf. Scheme 1).[10] The first reductive amination (RA) of LA has already been reported back in 1947 by Frank and coworkers using Raney-Ni under harsh conditions (70–140 bar of H_2, 140 °C) producing 1,5-dimethyl-2-pyrrolidinone in moderate yield.[11] After this original work, many heterogenous catalysts have been developed and applied for the synthesis of pyrrolidinones from LA via RA. More specifically, Shimizu and co-workers have developed a Pt-MoO_x/TiO_2 catalyst for RA of LA operating under solvent-free conditions with very high TON.[12] Han and coworkers also reported a Pt-based catalyst on TiO_2 nanosheets which was successfully applied for the synthesis of *N*-substituted pyrrolidinones.[13] A highly dispersed cobalt catalyst has recently been reported for the synthesis of *N*-heterocycles from bio-based keto acids by some of us.[14] In addition, a comparative study regarding the performance of Ir, Pt, Pd, Ru and Rh on polyvinylpyrrolidone (PVP) was conducted by Nagaoka and



Scheme 1. Applications of selected pyrrolidinones and synthesis of this heterocycle via LA.

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coworkers, showing that Ir-PVP catalysts allow usage of nitroarenes, nitriles and amines as *N*-sources.[15]

Notably, most examples of catalysts for reductive amination of levulinic acid to *N*-heterocycles make use of supported noble metals such as Pd,[16] Au/Pd,[17] Ru,[18] and Ir.[19] However, due to their availability and price there is a recent trend towards 3d-metal based heterogeneous catalysts particularly those based on Ni,[20,21] including FeNi alloys,[22] and Cu.[23]

Compared to all these works utilizing heterogeneous catalysts, systems using homogeneous catalysts for such transformations remain somewhat underdeveloped despite the advantages that such systems could offer, e.g. defined catalytic intermediates, convenient analytical handles, improved TONs and facilitated access to rational design of catalysts. Here, the first example was disclosed by Fu and coworkers in 2011 using Ru-phosphine based complexes and formic acid as hydrogen donor.[24] More recently, silanes have been employed as hydrogen donors by Garcia and coworkers using a homogeneous Mn-based catalyst.[25] Silanes were also applied by Darcel and coworkers for the conversion of LA to both pyrrolidines and pyrrolidinones in the presence of a molecularly defined Fe-catalyst.[26] Utilization of molecular hydrogen as green reducing agent for the synthesis of pyrrolidinones was independently reported by Shi and coworkers using Co-based catalysts and Zhang and coworkers using Ir-centered complexes.[27] An enantioselective synthesis of 5-methyl pyrrolidinone was achieved by the de Vries group exploiting Ru-catalysts with chiral phosphines.[28] Other examples for the conversion of LA to *N*-heterocycles include transfer hydrogenations with formic acid as hydrogen source,[29] catalyst-free approaches,[30] borane-catalysis,[31] modification of chitosan,[32] dehydrogenation of amine boranes,[33] and Co-NHC catalysts.[34] Especially the disclosed works by Shi, Garcia and Darcel paved the way for use of cheap, non-noble metals for homogeneous reductive amination of LA. We hope to advance the state of the art with the herein presented study by combining the features of Shi's and Garcia's systems using a non-noble metal like nickel and achievement of 100% atom economy by using molecular hydrogen instead of formic acid.

Results and Discussion

Inspired by Shi's work on Co-catalyzed transformation of LA, we decided to use another non-noble alternative for reductive amination of LA using molecular hydrogen as reductant. Hence, reaction optimization was initiated by using nickel and commercial $[Ni(H_2O)_6](BF_4)_2$ as metal precursor and several multidentate phosphine ligands with different electronic properties and bite angles (Figure 1). To allow for an efficient screening of potential catalysts, all the experiments were performed by premixing the Ni-salt and phosphine in 3,3,3-trifluoroethanol (TFE) followed by the addition of LA and amine. TFE was chosen as a solvent for initial experiments due to its potentially favorable combination of gas solubility, high polarity and low nucleophilicity.[35] Interestingly, in all experiments considerable conversion of LA could be detected after 24 h at 100 °C and 60 bar H_2 to at least the unsaturated intermediate **Ia**. As expected, no hydrogenation occurs without ligand or nickel (Table S1 entries 25 and 26). Employment of **L1** led to formation of 9% of **2a**. Elongation of the aliphatic backbone shifted the selectivity of the reaction towards formation of γ-valerolactone (GVL). Catalyst systems employing ligands **L2–L7** showed pronounced hydrogenation activity of LA furnishing GVL in up 58% yield (Table S1). Use of Xanthphos (**L8**) did not result in an active catalyst system. Only formation of unsaturated lactams could be detected. Surprisingly, bite angle-modulated ligands of the Xanthphos-family (**L9–L14**) had no beneficial effect and the system remained inactive. The use of Xanthphos-derived ligands bearing electron-rich aromatic substituents (**L15**, **L16**, **L19**) led to the formation of the desired product **2a** in the range of 69% to 80% yield (Table S1). Interestingly, the electron-donating substituent needs to be located at the phenyl-ring of the ligand. Use of **L17** with *t*Bu-groups attached to the xanthene-core did not lead to formation of **2a**. An exception to this rule is constituted by **L20**. Although the ligand possesses methoxy-groups at the right position, no formation of **2a** could be detected. Introduction of pyridyl-residues disactivates the system (cf. **L19** and **L21**). Tri- and tetradentate ligands **L22**, **L23**, and **L24** formed active catalysts. Tetraphos **L22** led to low formation of the desired product **2a**, while tripodal triphos **L23** allowed significantly higher conversion to **2a** (86%). In the latter case 3% of GVL was also formed. High conversion and high selectivity were achieved upon usage of linear triphos (**L24**, 80% yield of **2a**, no GVL detected). The presence of electron-donating residues on the phosphino-part leads to higher yield of **2a**. The same effect can be observed for ligands with more than two donor sites. Due to its high conversion, high selectivity, and commercial availability, **L24** was chosen over ligands **L15**, **L16** and **L19** from the Xanthphos-class for further development of the catalytic system. **L24** was also preferred over **L23**, since the latter allowed the formation of GVL in minor amounts, which requires a greater effort to be made during the purification procedure. Due to the reasons stated above, **L24** is the ligand of choice for the following examinations.

Next, alternative Ni-salts were tested in the benchmark reaction, highlighting the significant dependency of catalytic performance on the counter anion of the metal salt. In the presence of halide anions, the yield of **2a** is significantly lowered. The use of NiF_2 yielded just 7% of lactam after 16 h (Figure 2 and Table S3). Formation of **2a** could be boosted to 28% for $NiCl_2$ and 35% for $NiBr_2$. Replacement of halide anions by the less coordinating triflate led to formation of 48% of the desired product. Best results are obtained with $[Ni(OAc)_2]{\cdot}4H_2O$ and $[Ni(acac)_2]$, operating in the same range as the initially tested $[Ni(H_2O)_6](BF_4)_2$. Yields were improved in the case of $[Ni(OAc)_2]{\cdot}4H_2O$ and $[Ni(H_2O)_6](BF_4)_2$ by extending the reaction time to 22 h.

Reduction of the catalyst amount to 1.25 mol% using $[Ni(OAc)_2]{\cdot}4H_2O$ led to incomplete conversion, while $[Ni(H_2O)_6](BF_4)_2$ allowed reduction of the catalyst amount down to 0.6 mol% whilst maintaining the initial activity of the system. But in some cases, the reaction times are to be prolonged to

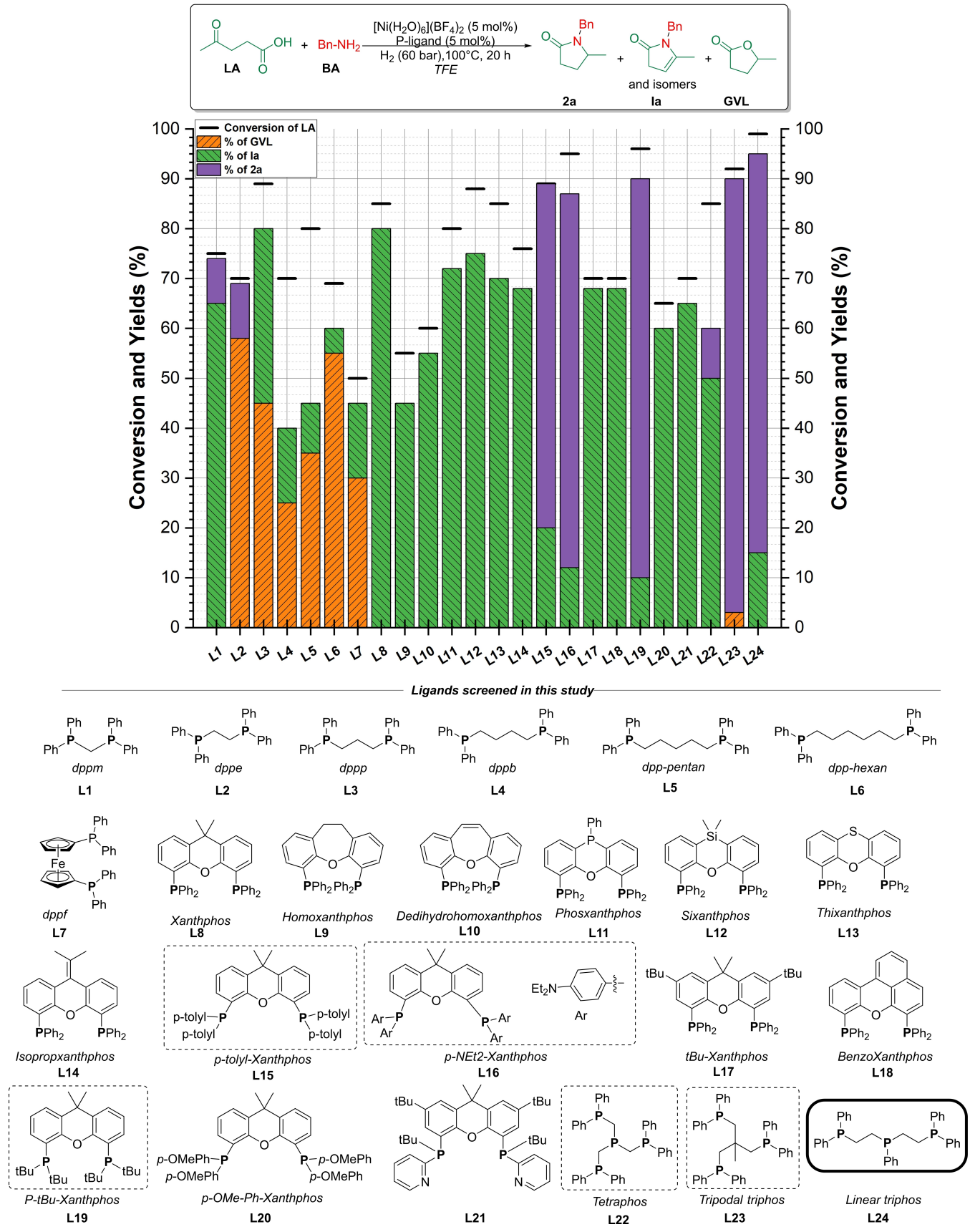


Figure 1. Ni-catalyzed reductive amination of LA with benzyl amine: Effect of ligands.

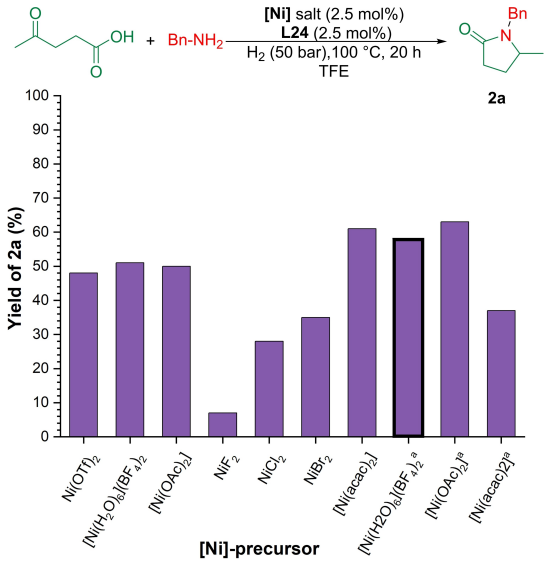


Figure 2. Effect of different Ni-precursors using **L24**. [a] 22 h instead of 16 h. The key entry is highlighted.

assure full conversion (see upscaling studies below). Thus, the catalyst loading was maintained at 2.5 mol% for exploration of the substrate scope. Considering these findings, $[Ni(H_2O)_6](BF_4)_2$ is the nickel source of choice for the following studies.

In general, the choice of an appropriate solvent heavily impacts catalytic reactions. Hence, a range of different alcohols were tested as reaction medium. Under standard conditions, significant formation of the lactam **2a** is only observed in TFE (Figure 3 and Table S5). Upon use of other alcohols or THF the desired product **2a** is not formed or only in traces. The high conversion in these solvents is explained by formation of intermediates (for detailed discussion see below).

Next, a reaction of levulinic acid and benzyl amine in the presence of both the Ni-catalyst and two equivalents of mercury in TFE at 110 °C was performed. The reaction proceeded smoothly under these conditions to give 90% yield of **2a** (Table S5, entry 3). Similarly, significant amounts of product are formed in mercury tests at 110 °C and 30 bar of hydrogen in methanol or 1,1,1,3,3,3-hexafluoroispropanol (HFIP) (Table S5, entry 4). The reaction in HFIP showed 99% conversion of levulinic acid and 90% of **2a**. In methanol, 99% of levulinic acid was converted and 75% of product accompanied by **Ia** is observed (Table S5, entry 5). The presence of 2 eq. Hg does not significantly influence the reaction outcome, thus, suggesting a homogeneous catalytic system.

The optimized system shows broad functional group tolerance in case of benzylic amines as substrates (Figure 4).

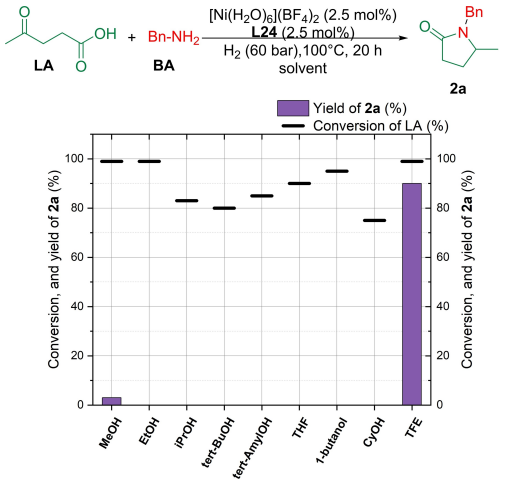


Figure 3. Reductive amination of LA: Effect of solvents using Ni/**L24**.

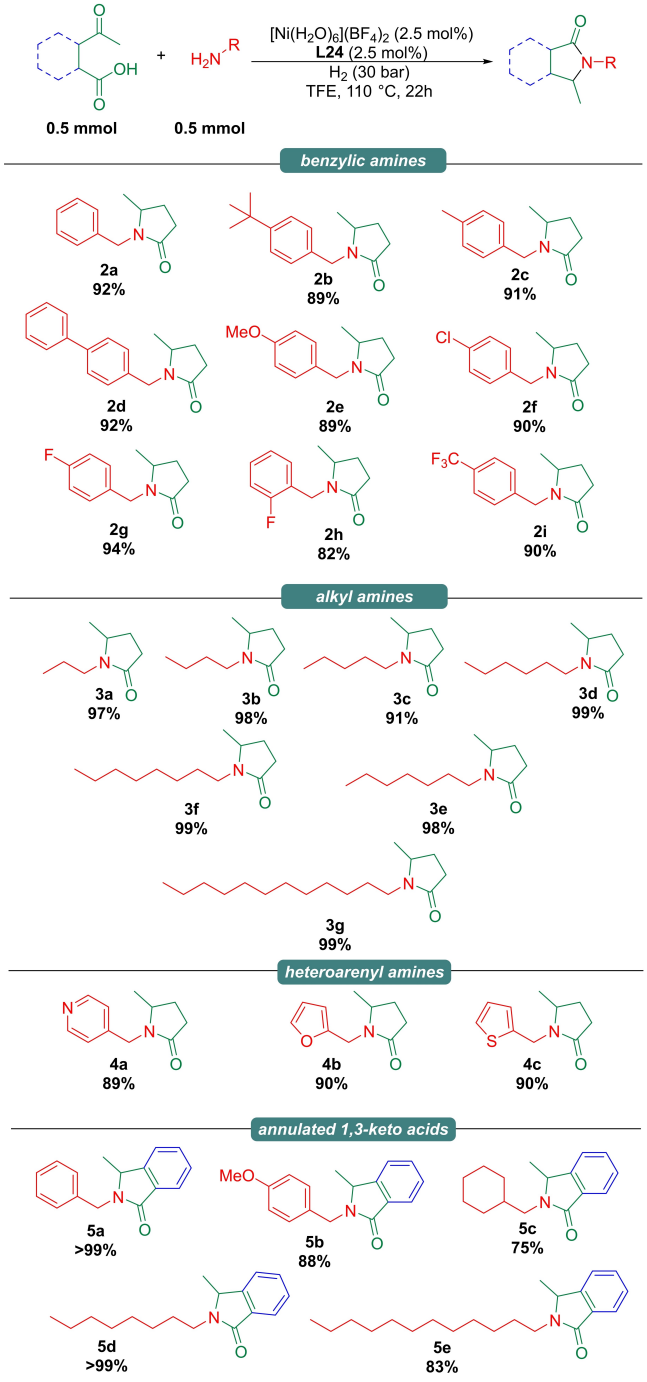


Figure 4. Reductive amination of levulinic acid and related substrates: Substrate scope.

The impact of electron-donating substituents as present in **2b**, **2c** and **2e** on the yield compared to **2a** is negligible. The same applies for electron-withdrawing substituents as present in **2f**, **2g** and **2i**. Isolated yields ranged between 89% and 94%. The presence of fluorine in *ortho*-position slightly decreased the yield of **2h** to 84%. Benzylic amines bearing heteroaryl substituents like pyridyl- (**4a**), furyl- (**4b**) or thiophenyl-groups (**4c**) led to yields of around 90%. Surprisingly, the sulfur-moiety of 2-aminomethylthiophene did not poison the catalyst, furnishing **4c** in 90% yield. Extension of the substrate scope to *n*-alkyl amines is also possible as demonstrated by the synthesis of **3a** to **3g**. The performance of the system is not significantly impacted by chain length (we attribute the slight drop in yield for **3c** to experimental error).

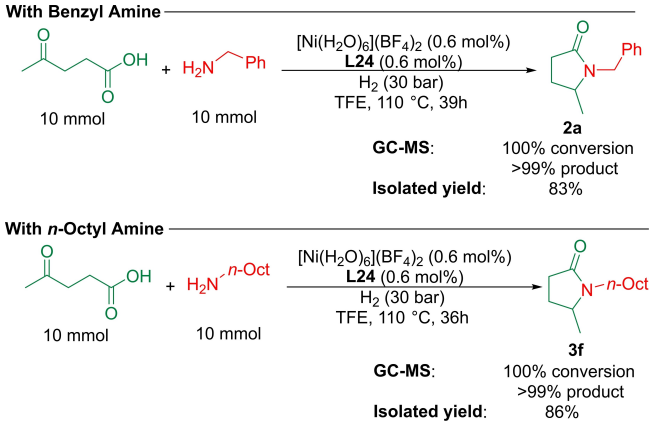
In addition to levulinic acid, the structural analogue 2-acetylbenzoic acid was readily converted to the corresponding benzopyrrolidinones in excellent yields of up to >99% as illustrated by the synthesis of **5a** to **5e**. Use of benzyl as well as aliphatic amines was equally successful. However, a slight drop in yield was observed for the derivative of cyclohexylmethylamine **5c**. Conversion of anilines led to formation of a mixture of different species. We were not able to identify them.

The synthesis of **2a** and **3f** could easily be upscaled to 10 mmol scale without changing the concentration of starting material. In case of **2a** reduction of the catalyst amount to 0.6 mol% still allowed full conversion of LA (Scheme 2). Reaction at the same temperature as the small-scale reactions (110 °C) in combination with extending reaction time to at least 36 h led to over 99% conversion and over 99% of formed product according to GC-MS. Isolation of **3f** and **2a** succeeded with 86% and 83% yield, respectively (Scheme 2). The slight drop in yield compared to the yield obtained on 0.5 mmol scale can be attributed to the different size of the silica bed used for purification of the compounds.

Control experiments of the optimized system using TFE as solvent in the absence of hydrogen confirmed the expected formation of the cyclic unsaturated lactam isomers **Ia**. Additionally, the presence of the alkoxy- and hydroxy-lactams **Ib** and **Ic**, respectively, could be detected via GC-MS (Figure 5b). Similar products were identified in the same reaction using methanol, ethanol, and *n*-butanol as solvent (Figure S2). Naturally, reaction in THF did not allow detection of the alkoxy lactam. In the absence of hydrogen, the presence of the Ni-catalyst does not alter the product distribution of the condensation reaction (cf. Figure S1). It should be noted that the presence of linear intermediates could not be confirmed for our system, which is different from the work of Han and colleagues, in which butyl levulinate and octyl amine reacted in methanol at room temperature.[13]

Interestingly, reaction of LA under hydrogen in TFE-d_1 furnished products with nominal masses up to 9 Da higher compared to the mass of condensation product or 7 Da of the hydrogenation product **2a** (Figure 5c). This unexpected degree of deuterium enrichment is not possible by incorporation of just a single D_2 molecule as it would be the case for simple exchange of H_2 for D_2. In addition, the alkoxy- and hydroxy lactam showed significant deuterium enrichment. Also, the addition of D_2O to the condensation reaction in THF after one hour at 110 °C led to enrichment of deuterium in the cyclic enamides **Ia**. Together with the reaction outcome in TFE-d_1, these findings imply the constant presence of alternating Michael-addition/retro-Michael-addition of water or the alcoholic solvent to the cyclic enamide **Ia**, thereby enriching the compound in deuterium. In addition, Ni-catalyzed isomerizations and base catalyzed deprotonation in α-position to the carbonyl group might take place.

These observations prohibit a clear determination of the reaction's mechanism by simple deuteration experiments. Nevertheless, they indicate a pronounced interplay between hydrogenation and shift of the C=C double bond via Michael-addition/retro-Michael-addition of TFE. Since the hydrogenation reaction in TFE-d_1 is not finished after 20 h (Figure 5c), which contrasts the behavior of the similar system in non-deuterated TFE, a severe influence of the alcoholic solvent beyond differences in physical constants like gas-solubility is suggested. Hydrogenation of an isomeric mixture of **Ia** in TFE, methanol, ethanol, THF and toluene at 110 °C underpinned findings of the initial solvent screening (Figure 5a and chapter 2 of the ESI). The reaction takes place only in TFE. Methanol, ethanol, THF and toluene severely inhibit the hydrogenation.



Scheme 2. Synthesis of **2a** and **3f** on 10 mmol-scale.

Conclusions

A homogeneous Ni-catalyst is presented for the general reductive amination of levulinic acid and related 2-acetyl benzoic acid. The active catalyst is easily formed in situ by reaction of $[Ni(H_2O)_6](BF_4)_2$ with commercial linear triphos (**L24**). An array of *N*-substituted 5-methyl pyrrolidinones derived from different primary benzylic, alkyl and heteroarenyl could be synthesized with yields ranging between 75% and >99%. Notably, the synthetic protocol shows a strong influence of the applied solvent.

In general, the use of TFE gave best yields and other alcoholic solvents were not suitable. Examination of the reaction mixture in absence of hydrogen revealed the co-existence of cyclic enamides **Ia**, the Michael-addition product of

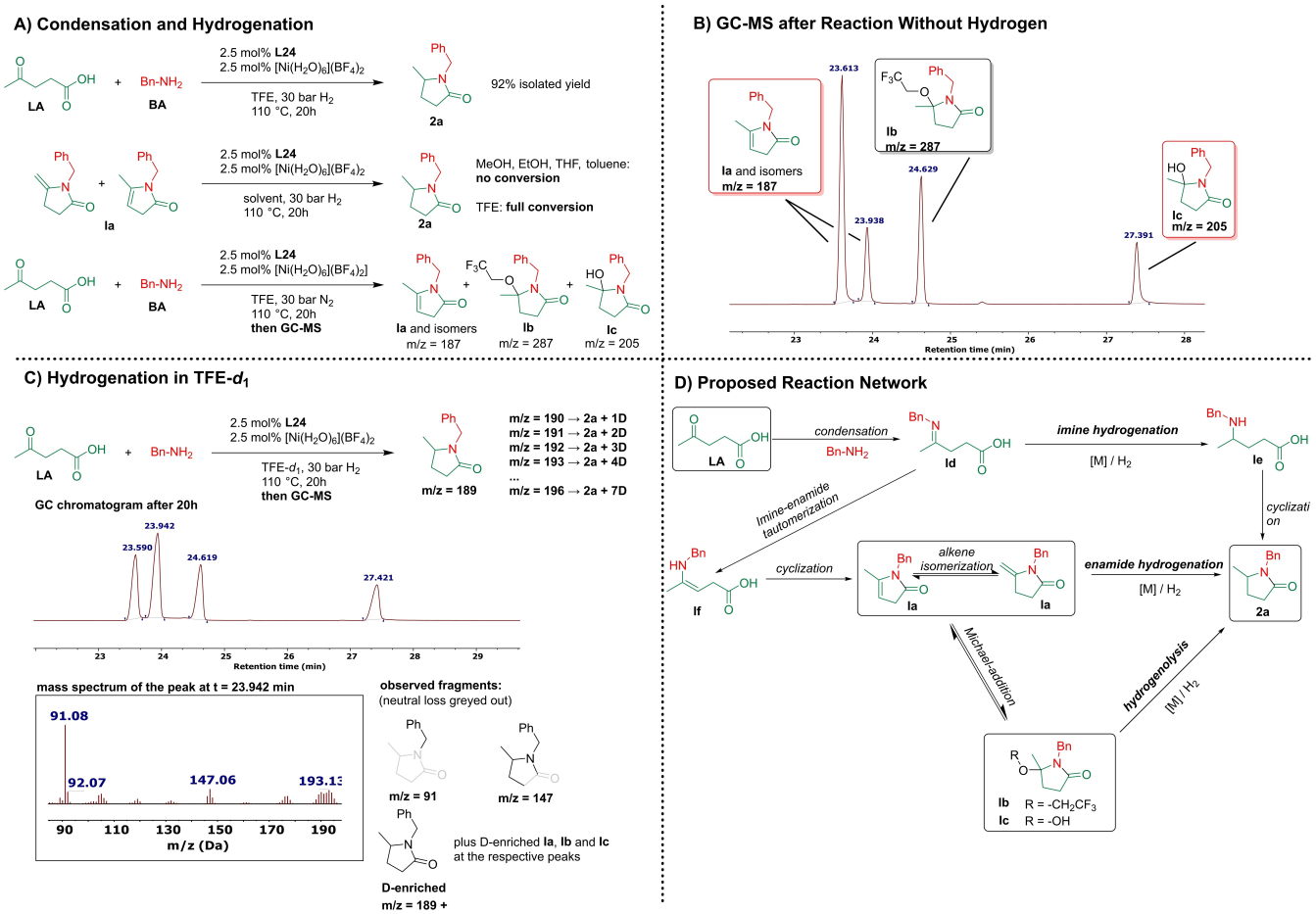


Figure 5. (a) Conversion of LA and **Ia** in presence of 30 bar of H_2 vs. conversion of LA in presence of 30 bar N_2. (b) Gas chromatogram of reaction in presence of 30 bar of N_2. (c) Hydrogenation of LA in presence of benzyl amine in TFE-d_1.with gas chromatogram of reaction mixture after 20 h plus mass trace of the peak at 23.94 min. (d) Proposed reaction network of reductive amination of LA. Identified compounds are shown in boxes (**Ia**, **Ib**, and **Ic** have been identified via GC-MS (cf. B)). Hydrogen-consuming steps are written in bold letters.

Ia and alcohol (**Ib**) as well as the hydroxy-lactam **Ic**. Deuteration studies suggest dynamic interconversion of these compounds. Hydrogenation in TFE-d_1 leads to incorporation of up to seven deuterium-atoms, hinting at constant addition of TFE-d_1 or deuterated water and extrusion of non-deuterated species.

Experimental Section

Details of experimental procedures and characterization data of the products can be found in the Supporting Information.

Supporting Information Summary

The authors have cited additional references within the Supporting Information.[12,27a,36]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Levulinic acid · Reductive amination · Nickel · Triphos · Alkoxy lactam

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