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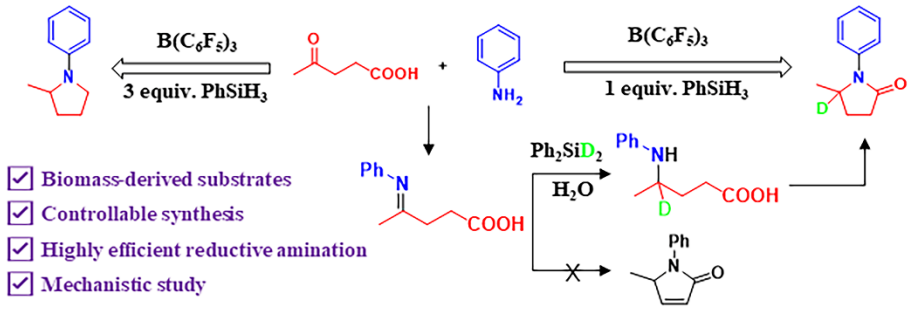
Graphical Abstract



Investigation towards the reductive amination of levulinic acid by $B(C_6F_5)_3$/hydrosilane system

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ABSTRACT

The selective transformation of the renewable biomass resources into the highly value-added platform chemicals is essentially important for sustainable chemistry. Here we report a simple and highly efficient strategy for the synthesis of *N*-heterocyclic compounds from the reductive amination of the bio-derived levulinic acid and a wide range of anilines by metal-free $B(C_6F_5)_3$/hydrosilane catalyst system. Through adjusting the amounts of hydrosilane, we can synthesize a series of pyrrolidones or pyrrolidines, respectively. Isotope-labeled NMR experiments were conducted to investigate the possible reaction pathway.

Key words: $B(C_6F_5)_3$; hydrosilane; levulinic acid; *N*-heterocyclic compounds; reductive amination

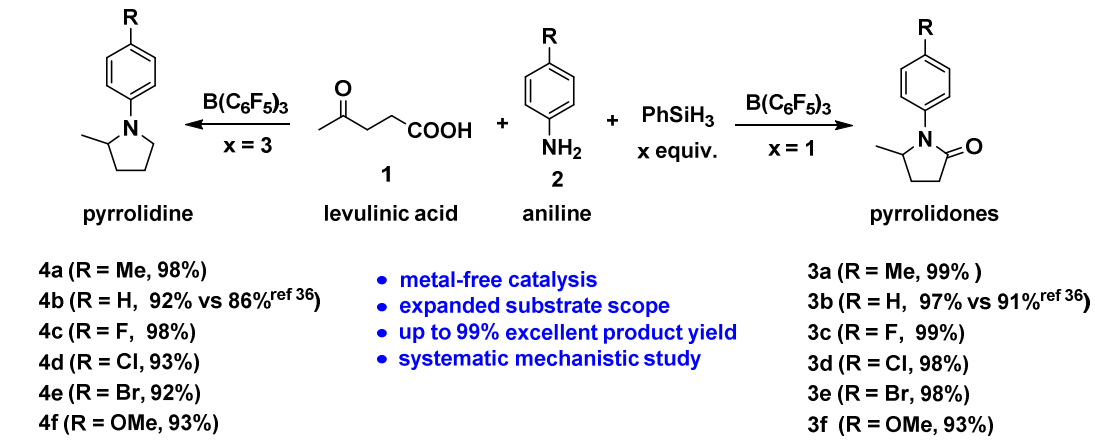
1. Introduction

The selective transformation of the renewable biomass resources into the highly value-added platform chemicals is essentially important for sustainable chemistry [1,2]. As one of the top ten platform chemicals, levulinic acid (LA) derived from the acidic hydrolysis of carbohydrates [3] has been employed for the production of many valuable fine chemicals [4,5]. Among them, N-substituted pyrrolidone derivatives have received intense attention due to their wide application in solvents, surfactants, drug racetams as well as its utilization of LA in the valorization of biomass [6]. In last decades, many catalyst based on homogeneous and heterogeneous systems have been developed to synthesize pyrrolidones from LA. Most of them utilized formic acid (formate) [7-13] or H_2 [14-22] as reducing reactants.

As an efficient and mild reducing reagent, hydrosilane has been widely applied in the reduction of unsaturated compounds [23]. Recently, it was also utilized for the reductive amination of LA to produce *N*-substituted pyrrolidones and pyrrolidines in the presence of transition-metal catalyst [24-27]. In 2016, Sakai group reported the first example for the synthesis of pyrrolidones and pyrrolidines catalyzed by $In(OAc)_3$ and InI_3, respectively [24], whereas Liu group employed $AlCl_3$/$RuCl_3$ and ionic liquid as catalysts to synthesize the *N*-substituted lactams [25, 26]. More recently, Darcel group developed an iron-based catalyst system to realize the synthesis of pyrrolidones or pyrrolidines, respectively [27].

On the other hand, $B(C_6F_5)_3$ is known as a powerful metal-free Lewis acid for the activation of hydrosilane in many organic synthesis [28] and the reduction of lignin

and lignin model compounds [29–31]. Recently, our group successfully employed the combination of $B(C_6F_5)_3$ with various hydrosilanes to achieve the highly C3-regioselective silyated indoles from the convergent disproportionation reaction of indoles [32]. Besides, the application of some classic organic reactions enabled us to achieve highly efficient cleavage of the C-C bonds in both lignin model compounds and native lignin and produce useful aromatics in high to excellent yields [33-35]. More recently, Fu et al reported one example for the transformation of the biomass-derived LA into pyrrolidones or pyrrolidines in 86% and 91% yields, respectively, during their investigation towards the $B(C_6F_5)_3$-catalyzed *N*-alkylation of amines with carbonyl acids by using silane as reducing agent [36]. However, detailed study of this reaction is still lacking. Therefore, we believed that the application of the $B(C_6F_5)_3$/hydrosilation system to the reductive amination of biomass-derived LA will not only produce the useful *N*-heterocyclic compounds, but also provide important foundation to biomass valorization. Here we reported a simple and highly efficient synthetic strategy for synthesis of pyrrolidone and pyrrolidine from the reductive amination of LA with a variety of anilines catalyzed by $B(C_6F_5)_3$/hydrosilane system. Moreover, by adjusting the amounts of hydrosilane, a series of pyrrolidone or pyrrolidine derivatives could be produced in high to excellent yields. The investigation towards the reaction pathway by ^1H NMR spectroscopy were also included into this study.



Scheme 1 Controllable synthesis of pyrrolidones or pyrrolidines. (One example was reported in reference 36 by using $B(C_6F_5)_3$/PMHS (polymethylhydro-siloxane) catalyst system)

2. Result and Discussion

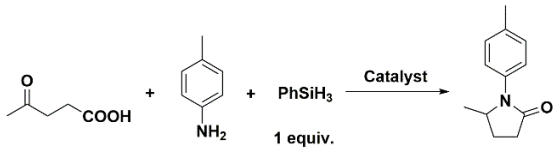
2.1 Optimization of the reaction

By using $PhSiH_3$ as hydrogen resource, we selected LA and 4-methylaniline as substrates to optimize the reaction conditions(Table 1). It turned out that after heating at 120 ºC for 6 h, only 4% yield of pyrrolidones was obtained in the absence of catalyst (Table 1, entry 1) whereas 5 mol% $B(C_6F_5)_3$ can significantly enhance the yield of **3a** to 99% (Table 1, entry 2). It should be noted that 2.5 mol% $B(C_6F_5)_3$ can produce **3a** in 99% yield but the employment of 1.25 mol% $B(C_6F_5)_3$ drastically decreased the yield of **3a** to 50% (Table 1, entries 3 and 4). For reaction performed with a lower temperature of 100 ºC or shorter reaction time of 3 h, incomplete LA conversion and lower product yield of **3a** were obtained (Table 1, entries 5 and 6). The study of the solvent effects indicated that toluene (TOL) stood out among the investigated solvents while CH_2Cl_2 or THF produced **3a** in lower yields of 89% and 92%, respectively (Table 1, entries 7 and 8). In sharp contrast, the employment of

protic solvent such as methanol only produced 7% yield of **3a**, probably due to the irreversible coordination between $B(C_6F_5)_3$ and the hydroxy group of methanol molecules (Table 1, entry 9) [37]. For comparison, several boron Lewis acid catalysts, such as $BF_3{\cdot}OEt_2$, BCl_3, BBr_3, $B(O^iPr)_3$ and BPh_3 were also evaluated for the reductive amination reactions and exhibited much lower activity than $B(C_6F_5)_3$ (Table 1, entries 10-14). Previous study indicated that the large steric hindrance and the strong electron-deficient properties enabled $B(C_6F_5)_3$ to effectively activate hydrosilane to form $(C_6F_5)_3B\cdots H\cdots Si$ active species [38], which is essentially important for the hydrosilylation of the imine intermediate generated from the reaction of LA with aniline. Since the properties of hydrosilane also have significant impact on the reaction, several hydrosilanes were screened for the reductive amination reactions. The yield of **3a** was dramatically decreased with the increasing number of bulky electron-withdrawing group on hydrosilanes: ($PhSiH_3$ (99%) > Ph_2SiH_2 (89%) >> Ph_3SiH (7%), Table S1, entries 1-3). The steric hindrance is also found to have impact on the reaction. Such as hydrosilanes with bulky substituents tend to have much lower yield of **3a** (Ph_3SiH (7%) ≈ $(OEt)_3SiH$ (4%) << Et_3SiH (83%), Table S1, entries 3-5). For more, complex hydrosilanes, the yield of **3a** is determined by the comprehensive effects of both the electron and steric hindrance of the hydrosilanes. For example, polymethylhydrosiloxane (PMHS) produced **3a** in 86% yield (Table S1, entry 6) whereas both $PhMe_2SiH$ and 1,1,3,3-tetramethyldisiloxane(TMDS) (Table S1, entries 7 and 8) showed comparable product yields as $PhSiH_3$ did. Interestingly, replacing $PhSiH_3$ with 10 bar H_2 almost quenched the reaction and furnished **3a** in less than 1%

yield (Table S1, entry 9), which indicated that the hydrosilylation reduction went through the $(C_6F_5)_3B\cdots H\cdots Si$ active species [39].

Table 1. Optimization of the reductive amination of LA with aniline.[a]



1 2a 3a

Entry	Catalyst (mol%)	Time (h)	Solvent	Temp. (°C)	Yield (%)
1	no	6	TOL	120	4
2	$B(C_6F_5)_3$ (5)	6	TOL	120	99
3	$B(C_6F_5)_3$ (2.5)	6	TOL	120	99
4	$B(C_6F_5)_3$ (1.25)	6	TOL	120	50
5	$B(C_6F_5)_3$ (2.5)	6	TOL	100	72
6	$B(C_6F_5)_3$ (2.5)	3	TOL	120	77
7	$B(C_6F_5)_3$ (2.5)	6	CH_2Cl_2	120	89
8	$B(C_6F_5)_3$ (2.5)	6	THF	120	92
9	$B(C_6F_5)_3$ (2.5)	6	CH_3OH	120	7
10	$BF_3{\cdot}OEt_2$ (2.5)	6	TOL	120	15
11	BCl_3 (2.5)	6	TOL	120	14
12	BBr_3 (2.5)	6	TOL	120	14
13	BPh_3 (2.5)	6	TOL	120	18
14	$B(O^iPr)_3$ (2.5)	6	TOL	120	22

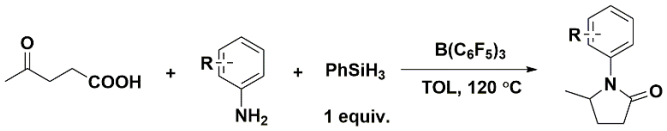
[a] Conditions: 0.25 mmol LA, 0.25 mmol aniline or 4-methylaniline, 0.25 mmol $PhSiH_3$, 1 mL TOL. Yield was determined by HPLC with standard curves.

2.2. The scope of anilines for the reductive amination of LA to pyrrolidones

With the optimized reaction conditions in hand, we examined the scope of anilines **(2)** with a variety of substituents for reaction performed with a 1:1:1 LA: anilines: $PhSiH_3$ ratio in TOL and heated at 120 °C, by using LA **(1)** as a model substrate and

$PhSiH_3$ as reducing agent (Table 2). It only took 1.5 h for simple aniline without substituents (**2b**) to reach quantitative conversion and furnish pyrrolidone **3b** in 97% yield (Table 2, entry 2), but 6 h is required for the other anilines to reach full consumption of substrates. It should be noted that this $B(C_6F_5)_3/PhSiH_3$ catalyst system can tolerate a wide range of anilines bearing *para*-substituted groups including both the electron-donating methyl group and the electron-withdrawing groups such as F, Cl, Br, furnishing corresponding pyrrolidone derivatives in high to excellent yields (**3a**, 99%; **3c**, 99%; **3d**, 98%; **3e**, 98%; **3f**, 93%) (Table 2, entries 1 and 3-6). However, the employment of aniline bearing a strong electron-withdrawing 4-CF_3 group led to a drastically decreased product yield of 74% for **3g** (Table 2, entry 7), probably due to the side reactions resulted from the strong electron-withdrawing effect of CF_3- group, which is consistent with the previous report [25]. We also examined the effectiveness of the substituent position on the reaction by using anilines with a Cl- group at varying position. Compared with **2d** possessing a para-Cl group, **2h** having a meta-Cl substituent showed comparable reactivity and produced 98% yield of **3h** whereas **2i** bearing an ortho-Cl group produced **3i** in a slightly decreased yield of 93% (Table 2, entries 8 and 9), implying that the substituent position did not have significant impact on the reaction. However, this $B(C_6F_5)_3$/hydrosilane system is not applicable to the reduction amination of aliphatic amines, such as benzylamine and *n*-octylamine (Table 2, entries 10 and 11), similar results have been observed in different catalyst systems [37].

Table 2. The scope of anilines for the reductive amination of LA to pyrrolidones.[a]



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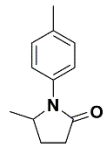
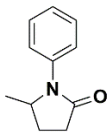
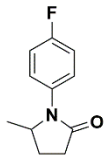


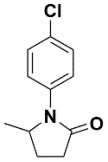
(1) **3a**, 99% (93%)



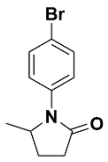
(2) **3b**, 97%[b] (89%)



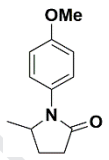
(3) **3c**, 99% (91%)



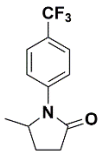
(4) **3d**, 98% (90%)



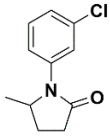
(5) **3e**, 98% (89%)



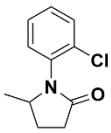
(6) **3f**, 93% (85%)



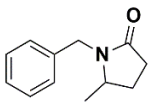
(7) **3g**, 74% (64%)



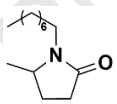
(8) **3h**, 98% (88%)



(9) **3i**, 93% (87%)



(10) **3j** trace



(11) **3k** trace

[a] Conditions: 0.25 mmol LA, 0.25 mmol aniline, 2.5 mol% $B(C_6F_5)_3$, 0.25 mmol $PhSiH_3$, 1 mL TOL, 6 h. [b] 1.5 h, 120 ºC. Yield was determined by HPLC with standard curves, isolated yield was given in parentheses.

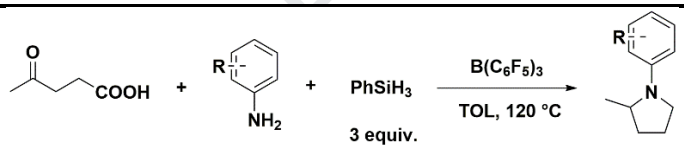
2.3. Scope of anilines for the reductive amination of LA to pyrrolidines

Previous studies showed that $B(C_6F_5)_3$/hydrosilane system was effective for the reduction of amides to amines [40, 41]. The identification of such highly efficient catalyst system for preparation of pyrrolidones from LA promoted us to investigate whether this $B(C_6F_5)_3$/hydrosilane system is applicable for the direct synthesis of pyrrolidine from LA. To our delight, by using LA and 4-methylaniline (**2a**) as substrates, the reaction performed with a 1:1:2 LA:**2a**:$PhSiH_3$ ratio afforded 56% yield of pyrrolidone **3a** and 43% yield of pyrrolidine **4a**, respectively (Table S2, entry 1). Increasing the amounts of $PhSiH_3$ to 3 equiv., we observed that the product yield

of **3a** is reaching the maximum value of 68% within 2.5 h, then gradually decreasing whereas the product yield of **4a** kept increasing to reach 98% within 24 h (Fig. S1), which clearly indicated the gradual transformation of **3a** into **4a** along with the reaction time. Therefore, we envisioned that the synthesis of either pyrrolidone or pyrrolidine derivatives could be achieved by adjusting the amounts of hydrosilane (1 or 3 equiv.), which is less than the previously reported (2 or 4 equiv.) [25-27], suggesting that the $B(C_6F_5)_3$ can efficiently activate $PhSiH_3$ for the reductive amination of LA. Next, a 1:3 LA/$PhSiH_3$ ratio was employed for the direct synthesis of pyrrolidines from LA by using the above-mentioned aniline derivatives as substrates (Table 3). Similar activity could be obtained for reactions using anilines bearing para-substituents (**2a, 2c** to **2f**), furnishing the corresponding pyrrolidines in high to excellent yields (**4a**, 98%; **4c**, 98%; **4d**, 93%; **4e**, 92%; **4f**, 93%, Table 3, entries 1 and 3-6) whereas the presence of 4-CF_3 group in **2g** almost quenched the reaction and furnished trace amounts of **4g** in up to 24 h, further confirming the effects of strong electron-withdrawing substituent on the reduction of pyrrolidone to pyrrolidine [25] (Table 3, entry 7). Compared with **4d**, the anilines substituted with Cl group at *ortho*- and *meta*- position produced the corresponding pyrrolidines in relatively lower yields (**4h** 73% and **4i**, 67%; Table 3, entries 8 and 9). Moreover, different hydrosilanes were also evaluated their effectiveness on the synthesis of pyrrolidines (Table S2). $PhSiH_3$ showed the best performance among the investigated hydrosilanes (Table S2, entries 2-7). It should be noted that neither $PhMe_2SiH$ nor TMDS could transform the pyrrolidones into pyrrolidines, thus not applicable to the

synthesis of pyrrolidines (Table S2, entries 8 and 9). Moreover, by using 4-acetobutyric acid as substrate (Scheme 2A), the reaction performed with a 1:1 LA/$PhSiH_3$ ratio and heated at 120 ºC for 6 h afforded a six-member *N*-containing heterocyclic pyrrolidone **3l** in 93% yield whereas the reaction performed with a 1:3 LA/$PhSiH_3$ ratio and heated at 120 ºC for 24 h afforded a six-member *N*-containing heterocyclic pyrrolidine **4l** in 88% yield, indicating this method was not limited to the synthesis of five-member lactam products. Switching to 2-carboxybenzaldehyde enabled us to achieve pharmaceutically important *N*-arylisoindolinone derivatives [42] **3m** and **4m** in 98% and 92% yields, respectively (Scheme 2B).

Table 3. Scope of anilines for the reductive amination of LA to pyrrolidines [a]



1 2 4

(1) **4a**, 98% (93%)

(2) **4b**, 92%[b] (83%)

(3) **4c**, 98% (88%)

(4) **4d**, 93% (85%)

(5) **4e**, 92% (83%)

(6) **4f**, 93% (82%)

(7) **4g**, trace

(8) **4h**, 73% (65%)

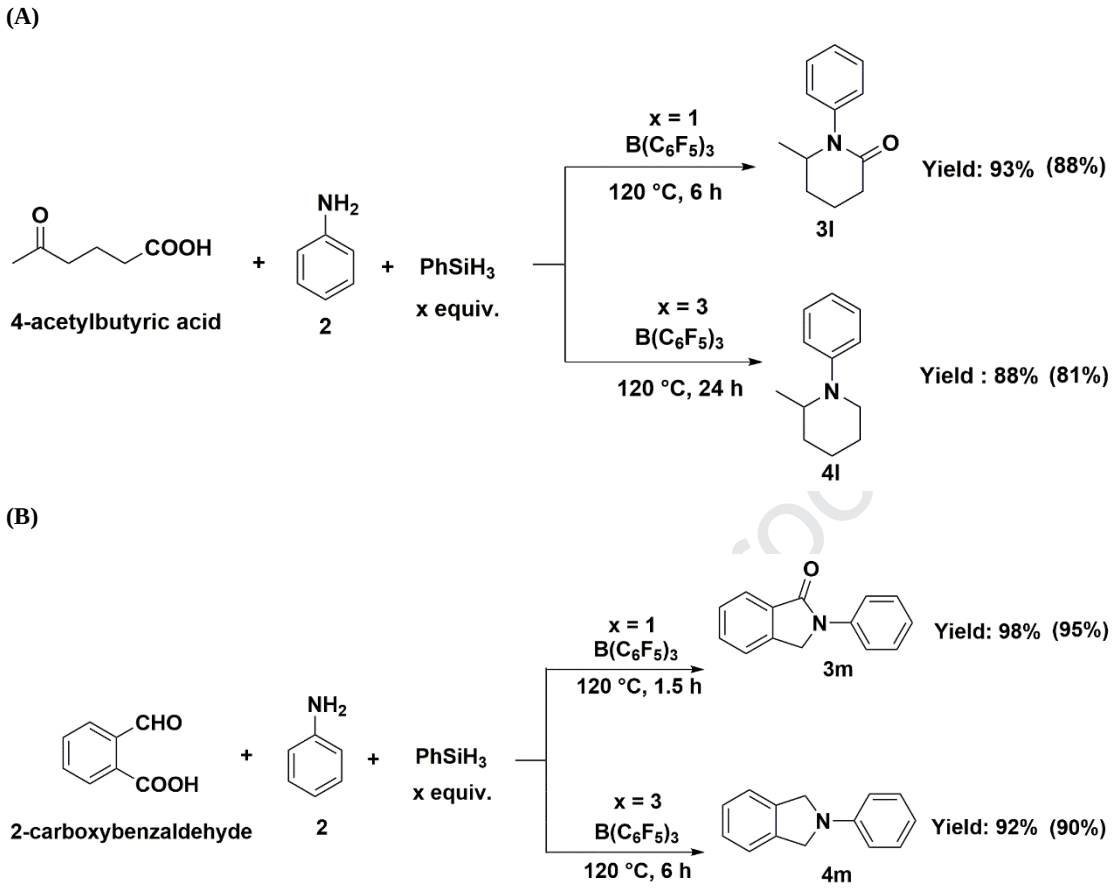
(9) **4i**, 67% (62%)

(10) **4j** trace

(11) **4k** trace

[a] Conditions: 0.25 mmol LA, 0.25 mmol aniline, 2.5 mol% $B(C_6F_5)_3$, 0.75 mmol $PhSiH_3$, 1 mL TOL, 120 ºC, 24 h.

[b] 6 h. Yield was determined by HPLC with standard curves, isolated yield was given in parentheses.



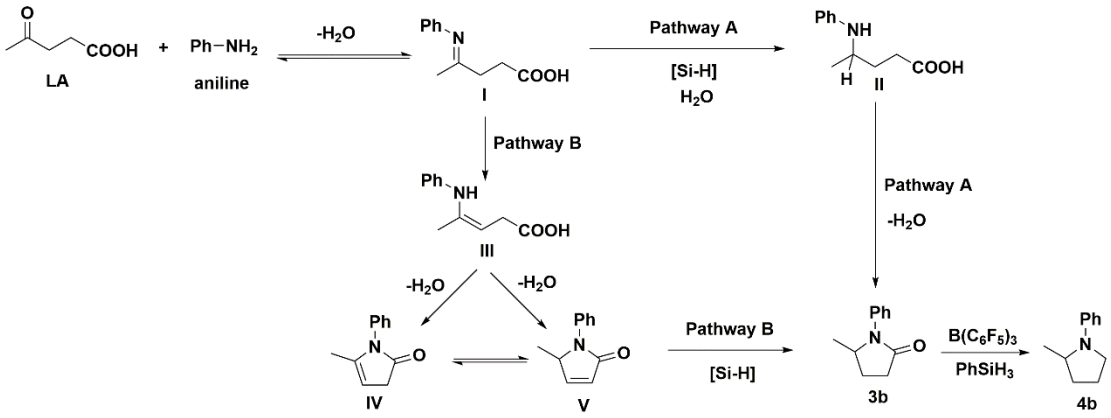
Scheme 2. Reductive amination of 4-acetylbutyric acid and 2-carboxybenzaldehyde with aniline respectively. Conditions: (A) 0.25 mmol 4-acetylbutyric acid, 0.25 mmol aniline, 2.5 mol% $B(C_6F_5)_3$, 1 mL TOL. (B) 0.25 mmol 2-carboxybenzaldehyde and aniline, 2.5 mol% $B(C_6F_5)_3$, 1 mL TOL. Yield was determined by HPLC, isolated yield was given in parentheses.

2.4 Mechanistic study

According to the previous literatures, there were two alternative pathways for the synthesis of pyrrolidone from the reductive amination of LA with aniline (Scheme 3). At first, ketimine **I** was generated from the condensation of LA and aniline, which can be directly reduced by hydrosilane to produce the cyclic pyrrolidone through pathway A [24, 27]. In the alternative pathway B [25, 26], ketimine **I** first underwent imine-enamine tautomerization [43,44] to furnish enamine **III**, which can be transformed into a five-member intermediates **IV** or **V** during the cyclization process.

There is an equilibrium between intermediates **IV** and **V**. Both **IV** and **V** can be reduced to pyrrolidone. To verify which pathway is more preferred by our system, we perform the isotope-labeled ^{1}H NMR experiments to by using the deuterium-labelled hydrosilane (Ph_2SiD_2) as reducing agent (Fig. 1). The comparison of ^{1}H NMR spectra revealed that only the H(b) of pyrrolidone product has been deuterated (Fig. S3b). If the reaction went through pathway B, the reduction would take place at the C=C double bond of **IV** or **V**, thus furnishing the deuterated H(c) or H(d). Therefore, we can safely draw the conclusion that the pathway A is adopted by the reaction. Furthermore, we turned our attention to investigate the intermediate during the reductive amination by in situ NMR experiments. As revealed by Scheme 4a and Fig. S4, LA and aniline could not generate imine **I** spontaneously or in the presence of $B(C_6F_5)_3$. We did not observe **I** during the reductive amination process, probably due to its unstable structure (Fig. S6). A 1:7 molar ratio of intermediate **II** to **3b** was observed after 30 min of reaction (Scheme 4b and Fig. S5), which was similar with that reported by Fischmeister et al. [45]. After that, the amount of intermediate **II** decreased with the reaction time. It almost disappeared at 60 min and was completely converted to **3b** after 1.5 h. However, the produced small amounts of **II** tends to be easily and rapidly transformed into **3b**, we could not isolate the intermediate **II**. The above results could further confirm our pathway. Briefly, aniline first reacted with the carbonyl group of LA to produce ketimine **I**, which is similar to the reported in previous literature [36]. The hydrosilylation reduction occurred at the C=N bond of **I**, which was subsequently hydrolyzed to yield intermediate **II**. Finally, stable

five-member pyrrolidone product **3b** would be generated through dehydration.



Scheme 3. Two alternative pathways proposed for the reductive amination of LA to pyrrolidone.

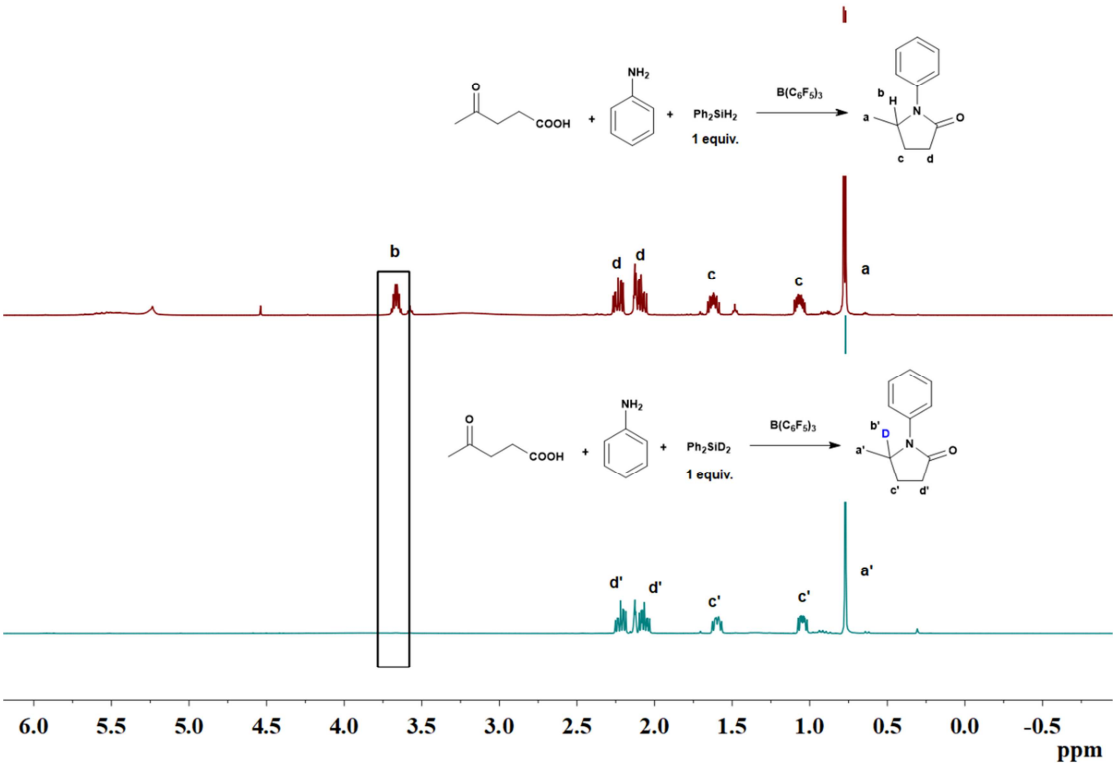
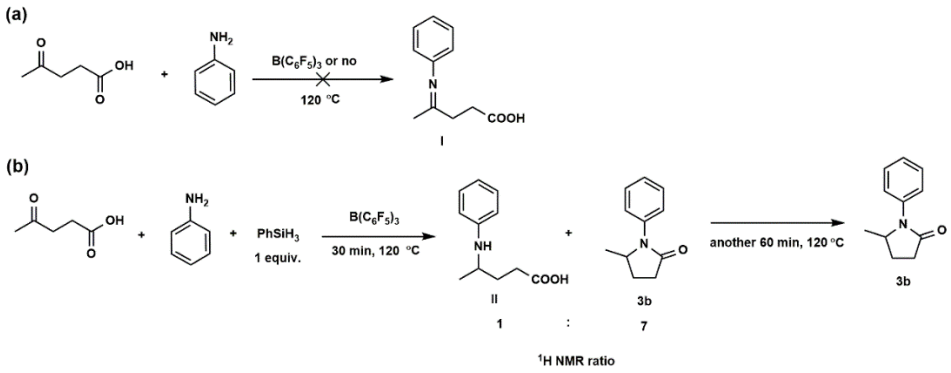


Fig. 1. Overlay of the ^{1}H NMR spectra of Ph_2SiD_2 and in-situ NMR reaction obtained for the reductive amination of LA to pyrrolidone. Conditions: (top) 0.1 mmol LA, 0.1 mmol aniline, 0.1 mmol Ph_2SiH_2, 2.5 mol% $B(C_6F_5)_3$, 0.5 mL C_7D_8, 120 ºC,1.5 h. (bottom): 0.1 mmol Ph_2SiD_2 instead of Ph_2SiH_2.



Scheme 4. Reaction intermediate in the reductive amination. Conditions: 0.125 mmol LA, 0.125 mmol aniline, 0.125 mmol $PhSiH_3$, 2.5 mol% $B(C_6F_5)_3$, 0.5 mL C_7D_8, 120 ºC.

2.5. Reuse experiment

We also investigated the reuse capability of $B(C_6F_5)_3$ for the production of pyrrolidone from the reductive amination of LA and simple aniline into pyrrolidone in Fig. 2. After full conversion of substrates was reached for the first run, the second batch of reaction mixture containing both the starting materials (LA and aniline) and reducing reactant $PhSiH_3$ were immediately added to the NMR tube. Near quantitative conversion of substrates can be maintained after three runs, but it decreased for the fourth run, probably due to the partial deactivation of the catalyst.

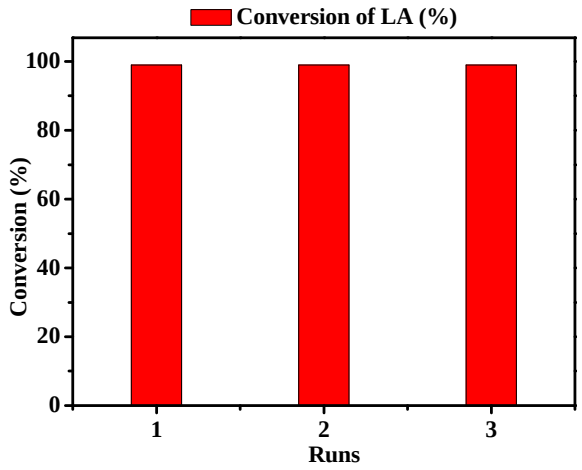


Fig. 2 Reusability of $B(C_6F_5)_3$ catalyst for the reductive amination of levulinic acid with aniline. Conditions: 0.125 mmol levulinic acid, 0.125 mmol aniline, 0.125 mmol $PhSiH_3$, 2.5 mol% $B(C_6F_5)_3$ in 0.5 mL C_7D_8, 120 ºC, 1.5 h. Conversion was determined by ^1H NMR analysis.

3. Conclusion

In summary, we employed the metal-free $B(C_6F_5)_3/PhSiH_3$ system to synthesize N-heterocyclic compounds, including pyrrolidones and pyrrolidines, from the reductive amination of biomass-derived LA with a variety of anilines. Adjusting the molar ratio of LA to hydrosilane enabled us to achieve pyrrolidones or pyrrolidines in high to excellent yields, respectively. Moreover, the combination of the detailed experimental data and isotope-labeled experiments led to the possible reaction pathway, thereby providing the much-needed insights into reaction mechanism.

4. Experimental Section

4.1 General Information

Levulinic acid (98%), methyl levulinate (98%), ethyl levulinate (98%), butyl levulinate (98%), 4-methylaniline (98%), 4-chloroaniline (98%), 4-methoxyaniline (98%), 4-fluoroaniline (98%), 4-bromoaniline (98%), 4-trifuloroaniline (98%), 3-chloroaniline (98%), 2-chloroaniline (98%), polymethylhydrosiloxane (PMHS, 98%) Ph_2SiH_2 (98%), Et_3SiH (98%), Ph_3SiH (98%), $(OEt)_3SiH$ (98%),1,1,3,3-tetramethyldisiloxane (TMDS, 98%) were provided by Energy Chemical. $PhSiH_3$ was obtained from J&K Scientific Ltd. Solvents were purchased from Adamas company. $B(C_6F_5)_3$ was prepared according to literature procedures [46].

NMR spectra were recorded on Bruker Avance II 500 (500 MHz, ^1H; 126 MHz, ^{13}C and 471 MHz, ^{19}F) instrument at room temperature. ^1H and ^{13}C spectra were referenced to internal solvent resonances and are reported as parts per million relative

to $SiMe_4$, and ^{19}F relative to $CFCl_3$. The reaction mixture was analyzed using Waters High Performance Liquid Chromatograph (HPLC) system equipped with autosampler, C18 column (Length: 150 mm, Internal diameter: 4.6 mm, 35 ºC) and UV/Vis detector (λ = 254 nm). CH_3CN: H_2O = 70: 30 was used as mobile phase with a flow rate of 1 mL/min for the analysis of the products.

4.2 Typical Procedures

The reductive amination of LA and aniline was performed in a thick wall tube with a Teflon screw cap (10 mL volume). In a typical experiment, under air atmosphere, 0.25 mmol LA, 0.25 mmol aniline, 2.5 mol% $B(C_6F_5)_3$ and 1 mL toluene were added into the reactor. One or three equiv. $PhSiH_3$ was used for the synthesis of pyrrolidone or pyrrolidine respectively. Then, the reactor was heated in oil bath for the desired time. Upon the completion of reaction, the product yield was determined by HPLC with standard curves of pure products. The pure samples were isolated by column chromatography on silica gel with the eluent (petroleum ether: ethyl acetate = 1:1) for pyrrolidones and (petroleum ether: ethyl acetate = 10:1) for pyrrolidines.

4.3 Spectral data

*1-(4-methylphenyl)-5-methylpyrrolidin-2-one (**3a**)*

Yellow solid; ^1H NMR (500 MHz, $CDCl_3$) δ 1.22 (d, *J* = 6.3 Hz, 3H), 1.73-1.80 (m, 1H), 2.36 (s, 3H), 2.38-2.42 (m, 1H), 2.52-2.59 (m, 1H), 2.62-2.67 (m, 1H), 4.24-4.30 (m, 1H), 7.21-7.26 (m, 4H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.2, 21.0, 26.8, 31.29, 55.8, 124.2, 129.6, 134.9, 135.6, 174.2 ppm.

*5-Methyl-1-phenylpyrrolidin-2-one (**3b**)*

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22 (d, *J* = 5.0 Hz, 3H), 1.74-1.81 (m, 1H), 2.35-2.42 (m, 1H), 2.52-2.59 (m, 1H), 2.63-2.69 (m, 1H), 4.30-4.34 (m, 1H), 7.21-7.24 (m, 2H), 7.37-7.42 (m, 4H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.2, 26.7, 31.4, 55.6, 124.0, 125.7, 128.9, 137.6, 174.2 ppm.

*1-(4-Fluorophenyl)-5-methylpyrrolidin-2-one (**3c**)*

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20 (d, *J* = 6.3 Hz, 3H), 1.73-1.80 (m, 1H), 2.36-2.42 (m, 1H), 2.52-2.58 (m, 1H), 2.61-2.67 (m, 1H), 4.22-4.28 (m, 1H), 7.08-7.11 (m, 2H), 7.32-7.35 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.1, 26.8, 31.2, 55.9, 115.8 (d, *J* = 22.3 Hz), 126.0 (d, *J* = 8.2 Hz), 133.5 (d, *J* = 2.9 Hz), 159.5, 161.4, 174.3 ppm. ^{19}F NMR (470 MHz, $CDCl_3$) 116.2 ppm.

*1-(4-Chlorophenyl)-5-methylpyrrolidin-2-one (**3d**)*

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20 (d, *J* = 10.5 Hz, 3H), 1.69-1.81 (m, 1H), 2.30-2.42(m, 1H), 2.47-2.67 (m, 1H), 4.22-4.32 (m, 1H), 7.34-7.37 (m, 4H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 16.0, 26.6, 31.2, 55.4, 124.9, 129.0, 130.8, 136.2, 174.2 ppm.

*1-(4-Bromophenyl)-5-methylpyrrolidin-2-one (**3e**)*

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.23 (d, *J* = 6.3 Hz, 3H), 1.74-1.81 (m, 1H), 2.36-2.43 (m, 1H), 2.52-2.59 (m, 1H), 2.63-2.69 (m, 1H), 4.27-4.33 (m, 1H), 7.31-7.32 (m, 2H), 7.51-7.53 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.0, 26.6, 31.3, 55.4, 118.7, 126.2, 132.0, 136.7, 174.2 ppm.

*1-(4-Methoxyphenyl)-5-methylpyrrolidin-2-one (**3f**)*

Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19 (d, *J* = 6.2 Hz, 3H), 1.74-1.79 (m,

1H), 2.35-2.42 (m, 1H), 2.52-2.67 (m, 2H), 3.82 (s, 1H), 4.18-4.22 (m, 1H), 6.94 (d, 8.8 Hz, 2H), 7.25 (d, *J* = 9.0 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.3, 26.9, 31.2, 55.5, 56.1, 114.3, 126.1, 130.4,157.8, 174.3 ppm.

*1-(4-(trifluoromethyl)phenyl)-5-methylpyrrolidin-2-one (**3g**)*

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.27 (d, *J* = 6.2 Hz, 3H), 1.78-1.84 (m, 1H), 2.38-2.45 (m, 1H), 2.54-2.61 (m, 1H), 2.67-2.73 (m, 1H), 4.38-4.44 (m, 1H), 7.59-7.67 (m, 4H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.9, 26.5, 31.3, 55.1, 122.7, ^{19}F NMR (470 MHz, $CDCl_3$) 126.1 (q, *J* = 3.75 Hz), 140.9, 174.3 ppm.

*1-(3-Chlorophenyl)-5-methylpyrrolidin-2-one (**3h**)*

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22 (d, *J* = 10.4 Hz, 3H), 1.70-1.81 (m, 1H), 2.31-2.43 (m, 1H), 2.47-2.70 (m, 1H), 4.24-4.35 (m, 1H), 7.15 - 7.20 (m, 1H), 7.29-7.31 (m, 2H), 7.44-7.45 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.0, 26.5, 31.3, 55.4, 121.5, 123.6, 125.5, 129.9, 134.5, 138.9, 174.2 ppm.

*1-(2-Chlorophenyl)-5-methylpyrrolidin-2-one (**3i**)*

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22 (d, *J* = 6.3 Hz, 3H), 1.76-1.84 (m, 1H), 2.40-2.46 (m, 1H), 2.56-2.60 (m, 2H), 4.18-4.22 (m, 1H), 7.20-7.22 (m, 1H), 7.27-7.31 (m, 2H), 7.46-7.48 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.2, 27.8, 30.7, 56.2, 127.6, 129.1, 130.4, 130.6, 132.9, 135.0, 175.0 ppm.

*1-Phenyl-6-methylpyrrolidin-2-one (**3l**)*

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.07 (d, *J* = 6.45 Hz, 3H), 1.71-1.76 (m, 1H), 1.82-1.87 (m, 1H), 1.97-2.01 (m, 1H), 2.08-2.12 (m, 1H), 2.53-2.56 (m, 2H), 3.90-3.94 (m, 2H), 7.16-7.18 (m, 1H), 7.27-7.30 (m, 1H), 7.38-7.42 (t, *J* = 7.75 Hz,

2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 18.3, 20.9, 30.8, 32.8, 55.7, 127.1, 128.1, 129.1, 141.6, 170.3 ppm.

*2-phenylisoindolin-1-one (**3m**)*

White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.89 (s, 2H), 7.20-7.23 (m, 1H), 7.44-7.64 (m, 5H), 7.89-7.97 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 50.7, 119.5, 122.6, 124.2, 124.5, 128.4, 129.2, 132.1, 133.3, 139.5, 140.1, 67.5 ppm.

*1-(4-methylphenyl)-5-methylpyrrolidin-2-one (**4a**)*

Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20 (d, *J* = 6.20 Hz, 3H), 1.70-1.73 (m, 1H), 1.9-2.00 (m, 1H), 2.01-2.11 (m, 2H), 2.29 (s, 3H), 3.14-3.19 (m, 1H), 3.43-3.46 (m, 1H), 3.84-3.90 (m, 1H), 6.56 (d, *J* = 8.05 Hz, 2H), 7.07 (d, *J* = 6.70 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) 19.5, 20.2, 23.4, 33.2,48.5, 53.7, 111.9, 124.2, 129.7, 145.3 ppm.

*1-phenyl-2-methylpyrrolidine (**4b**)*

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17 (d, 10.6 Hz, 3H), 1.67-1.72 (m, 1H), 1.93-2.12 (m, 3H), 3.11-3.19 (m, 1H), 3.38-3.45 (m, 1H), 3.83-3.91 (m, 1H), 6.56-6.66 (m, 3H), 7.19-7.24 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.4, 23.3, 33.2, 48.2, 53.6, 111.8, 115.14 129.2, 147.2 ppm.

*1-(4-Fluorophenyl)-2-methylpyrrolidine (**4c**)*

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20 (d, *J* = 6.3 Hz), 1.73-1.75 (m, 1H), 1.99-2.03 (m, 1H), 2.08-2.13 (m, 2H), 3.13-3.18 (m, 1H), 3.42-3.45 (m, 1H), 3.82-3.87 (m, 1H), 6.52-6.55 (m, 2H), 6.96-6.99 (m, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.4, 23.4, 33.2, 48.7, 54.1, 112.2, 112.2, 115.4, 115.6, 144.0, 153.7, 155.6

ppm. ^{19}F NMR (470 MHz, $CDCl_3$) 131.2 (m, 1F).

*1-(4-Chlorophenyl)-2-methylpyrrolidine (**4d**)*

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20 (d, *J* = 6.3 Hz), 1.72-1.75 (m, 1H), 1.99-2.12 (m, 3H), 3.15-3.20 (m, 1H), 3.40-3.44 (m, 1H), 3.86-3.91 (m, 1H), 6.46-6.63, (m, 4H), 7.12-7.15 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.2, 23.3, 33.1, 48.29, 53.8, 112.8, 119.9, 128.9, 145.8 ppm.

*1-(4-Bromophenyl)-2-methylpyrrolidine (**4e**)*

Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.18 (d, *J* = 6.2 Hz, 3H), 1.71-1.74 (m, 1H), 1.71-2.14 (m, 4H), 3.12-3.17 (m, 1H), 3.38-3.42 (m, 1H), 3.83-3.88 (m, 1H), 6.47 (d, *J* =8.5Hz, 2H), 7.30 (d, *J* = 8.9 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) 19.1, 23.3, 33.1, 48.2, 53.7, 106.9, 113.4, 131.7, 146.1 ppm.

*1-(4-Methoxyphenyl)-2-methylpyrrolidine (**4f**)*

Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20 (d, *J* = 6.15 Hz, 3H), 1.71-1.73 (m, 1H), 1.98-2.00(m, 1H), 2.07-2.11 (m, 2H), 3.13-3.18 (m, 1H), 3.42-3.46 (m, 1H), 3.80 (s, 3H), 3.81-3.84 (m, 1H), 6.59 (d, *J* = 9.0 Hz, 2H), 6.89 (d, *J* = 8.50 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.7, 23.4, 33.3, 49.0, 54.1, 56.0, 112.7, 115.1, 142.4, 150.6 ppm.

*1-(3-Chlorophenyl)-2-methylpyrrolidine (**4h**)*

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20 (d, *J* = 6.3 Hz, 3H), 1.72-1.76 (m, 1H), 1.99-2.15 (m, 3H), 3.15-3.20 (m, 1H), 3.40-3.44 (m, 1H), 3.86-3.91 (m, 1H), 6.47 (d, *J* = 10.8 Hz, 1H), 6.57 (t, *J* = 2.3 Hz, 1H), 6.63 (d, *J* = 7.8Hz, 1H), 7.14 (t, *J* = 8.2 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.1, 23.2, 33.0, 48.1, 53.7, 110.0,

111.5, 114.91, 130.0, 135.0, 148.1 ppm.

*1-(2-Chlorophenyl)-2-methylpyrrolidine (**4i**)*

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.07 (d, *J* = 6.1 Hz, 3H), 1.59-1.67 (m, 1H), 1.80-1.86 (m, 1H), 1.94-2.01 (m, 1H), 2.19-2.25 (m, 1H), 2.97-3.01 (m, 1H), 3.84-3.89 (m, 1H), 3.95-4.01 (m, 1H), 6.84-6.87 (m, 1H), 6.96-6.98 (m, 1H), 7.17-7.20 (m, 1H), 7.33-7.35 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.0, 24.0, 33.9, 52.39.54.55, 119.2, 121.1, 126.2, 126.9, 130.9, 146.5 ppm.

*1-Phenyl-6-methylpiperidin-2-one (**4l**)*

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05 (d, *J* = 6.65 Hz, 3H), 1.60-1.74 (m, 4H), 1.79-1.82 (m, 1H), 1.90-1.95 (m, 1H), 3.00-3.05 (m, 1H), 3.25-3.29 (m, 1H), 6.87 (t, *J* = 7.30 Hz, 1H), 7.00 (d, *J* = 8.10 Hz, 2H), 7.29 (t, *J* = 7.75 Hz, 2H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.0, 19.9, 27.0, 31.9, 45.2, 51.5, 117.7, 119.2, 129.0, 151.5 ppm.

*2-phenylisoindolin (**4m**)*

White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.7 (s, 4H) 6.72-6.74 (m, 2H), 6.78-6.81 (s, 1H), 7.33-7.40 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 53.7, 111.6, 116.2, 122.6, 127.2, 129.4, 138.0, 147.2 ppm.

Conflicts of interest

There are no conflicts to declare

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Appendix A. Supplementary data

The following is the Supplementary data to this article

Reference

[1] J. Zhang, S. Wu, B. Li, and H. Zhang, Advances in the Catalytic Production of Valuable Levulinic Acid Derivatives. ChemCatChem 4 (2012) 1230–1237.

[2] M.J. Climent, S. Iborra and A. Corma, Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels. Green Chem**.** 16 (2014) 516–547.

[3] R. Weingarten, W.C. Conner and G. W. Huber, Production of levulinic acid from cellulose by hydrothermal decomposition combined with aqueous phase dehydration with a solid acid catalyst. Energy Environ. Sci. 5 (2012) 7559–7574.

[4] F.D. Pileidis, M.M. Titirici, Levulinic Acid Biorefineries: New Challenges for Efficient Utilization of Biomass. ChemSusChem 9 (2016) 562–582.

[5] Z. Xue, Q. Liu, J. Wang and T. Mu, Valorization of levulinic acid over non-noble metal catalysts: challenges and opportunities. Green Chem., 20 (2018) 4391–4408.

[6] Z. Xue, D. Yu, X. Zhao and T. Mu, Upgrading of Levulinic Acid into Diverse N Containing Functional Chemicals. Green Chem., 21 (2019) 5449–5468.

[7] X. Du, L. He, S. Zhao, Y. Liu, Y. Cao, H. He, K. Fan, Hydrogen-Independent Reductive Transformation of Carbohydrate Biomass into g-Valerolactone and Pyrrolidone Derivatives with Supported Gold Catalysts. Angew. Chem. Int. Ed. 50 (2011) 7815–7819.

[8] Y. Huang, J. Dai, X. Deng, Y. Qu, Q. Guo, Y. Fu, Ruthenium-Catalyzed Conversion of Levulinic Acid to Pyrrolidines by Reductive Amination. ChemSusChem 4 (2011) 1578-1581.

[9] Y. Wei, C. Wang, X. Jiang, D. Xue, J. Li, J. Xiao, Highly efficient transformation of levulinic acid into pyrrolidinones by iridium catalysed transfer hydrogenation. Chem. Commun. 49 (2013) 5408–5410.

[10] Y. Wei, C. Wang, X. Jiang, D. Xue, Z. Liua, J. Xiao, Catalyst-free transformation of levulinic acid into pyrrolidinones with formic acid. Green

Chem. 16 (2014) 1093–1096.

[11] Z. Sun, J. Chen, T. Tu, NHC-based coordination polymers as solid molecular catalysts for reductive amination of biomass levulinic acid. Green Chem. 19 (2017) 789–794.

[12] C. Ortiz-Cervantes, M.F. Alamo, J.J. García, Synthesis of pyrrolidones and quinolines from the known biomass feedstock levulinic acid and amines. Tetrahedron Lett. 57 (2016) 766–771.

[13] A.S. Amarasekara, Y.M. Lawrence, Raney-Ni catalyzed conversion of levulinic acid to 5-methyl-2-pyrrolidone using ammonium formate as the H and N source. Tetrahedron Lett. 59 (2018) 1832–1835.

[14] W.L. Shilling, US Patent 32355562, 1996.

[15] J.D. Vidal, M.J. Climent, P. Concepcion, A. Corma, S. Iborra, M.J. Sabater, Chemicals from Biomass: Chemoselective Reductive Amination of Ethyl Levulinate with Amines. ACS Catal. 5 (2015) 5812–5821.

[16] G. Chieffi, M. Braun, D. Esposito, Continuous Reductive Amination of Biomass-Derived Molecules over Carbonized Filter Paper-Supported FeNi Alloy. ChemSusChem 8 (2015) 3590–3594.

[17] J.D. Vidal, M.J. Climent, A. Corma, P. Concepcion, S. Iborra, One-Pot Selective Catalytic Synthesis of Pyrrolidone Derivatives from Ethyl Levulinate and Nitro Compounds. ChemSusChem 10 (2017) 119–128.

[18] J. Zhang, B. Xie, L. Wang, X. Yi, C. Wang, G. Wang, Z. Dai, A. Zheng, F. Xiao, Zirconium Oxide Supported Palladium Nanoparticles as a Highly Efficient Catalyst in the Hydrogenation‐Amination of Levulinic Acid to Pyrrolidones. ChemCatChem 9 (2017) 2661–2667.

[19] S.M.A.H. Siddiki, A.S. Touchy, A. Bhosale, T. Toyao, Y. Mahara, J. Ohyama, A. Satsuma, K. Shimizu, Direct Synthesis of Lactams from Keto Acids, Nitriles, and H_2 by Heterogeneous Pt Catalysts. ChemCatChem 10 (2018) 789–795.

[20] P. Cao, T. Maa, H. Zhang, G. Yin, J. Zhao, Y. Zhang, Conversion of levulinic acid to N-substituted pyrrolidinones over a nonnoble bimetallic catalyst $Cu_{15}Pr_3/Al_2O_3$. Catal. Commun. 116 (2018) 85–90.

[21] C. Xie, J. Song, H. Wu, Y. Hu, H. Liu, Z. Zhang, P. Zhang, B. Chen, and B. Han. Ambient Reductive Amination of Levulinic Acid to Pyrrolidones over Pt Nanocatalysts on Porous TiO_2 Nanosheets. J. Am. Chem. Soc. 141 (2019)

4002−4009.

[22] A. Bellè, T. Tabanelli, G. Fiorani, A. Perosa, F. Cavani, M. Selva. A Multiphase Protocol for Selective Hydrogenation and Reductive Amination of Levulinic Acid with Integrated Catalyst Recovery. ChemSusChem 12 (2019) 3343–3354.

[23] S. Díez-González, S.P. Nolan, Copper, Silver, and Gold Complexes in Hydrosilylation Reactions. Acc. Chem. Res. 41 (2008) 349–358.

[24] Y. Ogiwara, T. Uchiyama, N. Sakai, Reductive Amination/Cyclization of Keto Acids Using a Hydrosilane for Selective Production of Lactams versus Cyclic Amines by Switching of the Indium Catalyst. Angew. Chem. Int. Ed. 55 (2016) 1864–1867.

[25] C. Wu, X. Luo, H. Zhang, X. Liu, G. Ji, Z. Liu, Z. Liu, Reductive amination/cyclization of levulinic acid to pyrrolidones versus pyrrolidines by switching the catalyst from $AlCl_3$ to $RuCl_3$ under mild conditions. Green Chem. 19 (2017) 3525–3529.

[26] C. Wu, H. Zhang, B. Yu, Y. Chen, Z. Ke, S. Guo, Z. Liu, Lactate-Based Ionic Liquid Catalyzed Reductive Amination/Cyclization of Keto Acids under Mild Conditions: A Metal-Free Route To Synthesize Lactams. ACS Catal. 7 (2017) 7772–7776.

[27] D. Wei, C. Netkaew, and C. Darcel, Iron-Catalysed Switchable Synthesis of Pyrrolidines vs Pyrrolidinones by Reductive Amination of Levulinic Acid Derivatives via Hydrosilylation. Adv. Synth. Catal. 361 (2019) 1781-1786.

[28] M. Oestreich, J. Hermeke and J. Mohr, A unified survey of Si–H and H–H bond activation catalysed by electron-deficient boranes. Chem. Soc. Rev. 44 (2015) 2202-2220.

[29] E. Feghali and T. Cantat, Unprecedented organocatalytic reduction of lignin model compounds to phenols and primary alcohols using hydrosilanes. Chem. Commun. 50 (2014) 862-865.

[30] J. Zhang, Y. Chen, and M.A. Brook, Reductive Degradation of Lignin and Model Compounds by Hydrosilanes. ACS Sustain. Chem. Eng. 2 (2014) 1983−1991.

[31] E. Feghali, G. Carrot, P. Thuéry, C. Genre and T. Cantat, Convergent Reductive Depolymerization of Wood Lignin to Isolated Phenol Derivatives by Metal-Free Catalytic Hydrosilylation. Energy Environ. Sci. 8 (2015) 2734-2743.

[32] Y. Han, S. Zhang, J. He, and Y. Zhang, $B(C_6F_5)_3$-catalyzed (Convergent)

Disproportionation Reaction of Indoles. J. Am. Chem. Soc. 139 (2017) 7399-7407.

[33] Y. Wang, Q. Wang, J. He and Y. Zhang, Highly effective C–C bond cleavage of lignin model compounds. Transformation of Lignin Model Compounds to N-substituted Aromatics *via* Beckmann Rearrangement. Green Chem. 19 (2017) 3135–3141.

[34] Y. Wang, Q. Wang, J. He and Y. Zhang, Transformation of Lignin Model Compounds to N-substituted Aromatics *via* Beckmann Rearrangement. Green Chem. 20 (2018) 3318-3326.

[35] Y. Wang, Q. Wang, J. He and Y. Zhang. Redox-neutral photocatalytic strategy for selective C–C bond cleavage of lignin and lignin models via PCET process. Sci. Bull. 64 (2019) 1658–1666.

[36] M. Fu, R. Shang, W. Cheng, Y. Fu, Boron-Catalyzed *N*-Alkylation of Amines using Carboxylic Acids. Angew. Chem. Int. Ed. 54 (2015) 9042-9046.

[37] V. Fasano, J. E. Radcliffe, and M. J. Ingleson, $B(C_6F_5)_3$‑Catalyzed Reductive Amination using Hydrosilanes. ACS Catal. 6 (2016) 1793−1798.

[38] J.M. Blackwell, E.R. Sonmor, T. Scoccitti, W.E. Piers, $B(C_6F_5)_3$-Catalyzed Hydrosilation of Imines via Silyliminium Intermediates. Org. Lett. 2 (2000) 3921–3923.

[39] M. Mirza-Aghayan, M. M. Tavana, M. Rahimifard and R. Boukherroub. Palladium on activated carbon catalyzed reductive amination of aldehydes and ketones by triethylsilane. Appl. Organomet. Chem. 28 (2014) 113–115.

[40] E. Blondiaux and T. Cantat, Efficient metal-free hydrosilylation of tertiary, secondary and primary amides to amines. Chem. Commun. 50 (2014) 9349-9352.

[41] R.C. Chadwick, V. Kardelis, P. Lim, and A. Adronov, Metal-Free Reduction of Secondary and Tertiary N ‑ Phenyl Amides by Tris(pentafluorophenyl)boron-Catalyzed Hydrosilylation. J. Org. Chem. 79 (2014) 7728−7733.

[42] Y. Tian, J. Wei, M. Wang, G. Li, F. Xu. Hantzsch ester triggered metal-free cascade approach to isoindolinones. Tetrahedron Lett. 59 (2018) 1866–1870.

[43] P.N. Basa, A. Bhowmick, L.M. Horn, and A.G. Sykes, Zinc(II) Mediated Imine-Enamine Tautomerization. Org. Lett. 14 (2012) 2698–2701.

[44] P.A. Kalmykov, I.A. Khodov, V.V. Klochkov, and M.V. Klyuev, Theoretical and experimental study of imine-enamine tautomerism of condensation products of propanal with 4-aminobenzoic acid in ethanol. Russ. Chem. Bull. 1 (2017) 0070-0075.

[45] S. Wang, H. Huang, C. Bruneau, C. Fischmeister, Formic acid as a hydrogen source for the iridium catalyzed reductive amination of levulinic acid and 2-formylbenzoic acid. Catal. Sci. Technol. 9 (2019) 4077-4082.

[46] M. Lehmann, A. Schulz, A. Villinger, Bissilylated Halonium Ions: $[Me_3Si\text{-}X\text{-}SiMe_3][B(C_6F_5)_4]$ (X=F, Cl, Br, I). Angew. Chem. Int. Ed. 48 (2009) 7444–7447.

Metal-free catalysis

Wide substrate scope

Up to 99% product yields

Systematic mechanistic study

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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