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Lactate-Based Ionic Liquid Catalyzed Reductive Amination/ Cyclization of Keto Acids under Mild Conditions: A Metal-Free Route to Synthesize Lactams

Cailing Wu,[a, b] Hongye Zhang,[a] Bo Yu,[a] Yu Chen,[a, b] Zhengang Ke,[a, b] Shien Guo,[a, b] Zhimin Liu*[a,b]

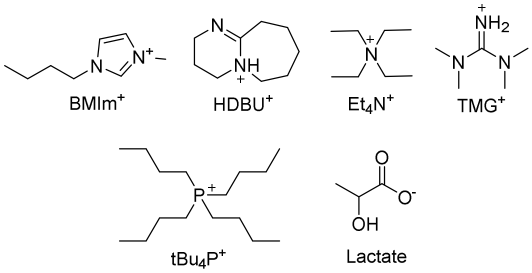
[a]*Beijing National Laboratory for Molecular Sciences, Key Laboratory of Colloid, Interface and Thermodynamics, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

[b]*University of Chinese Academy of Sciences, Beijing 100049, China.*

ABSTRACT: Task-specific ionic liquids (ILs) have shown promising applications in catalysis. Herein we present lactate-based IL (e.g., 1-butyl-3-methylimidazolium lactate, [BMIm][Lac]) catalyzed reductive amination/cyclization of keto acids using triethoxysilane as a reducing agent, which provides a metal-free route to synthesis of lactams under mild conditions, even at room temperature. [BMIm][Lac] combining with $(EtO)_3SiH$ afforded a series of five and six-membered lactams in good to excellent yields at 80°C within 1 h, showing comparable performance to the best metal-based catalyst reported to date. The mechanism investigation indicated that the ILs (e.g., [BMIm][Lac]) served as a multifunctional catalyst, which could activate hydrosilanes and simultaneously catalyzed the cyclization of LA with amines.

KEYWORDS: biomass, levulinic acid, reductive amination, ionic liquid, lactams, conversion

Biomass-based routes to synthesis of chemicals or fuels have been paid much attention with the demands of green and sustainable development.[1-3] Due to the complicated chemical structures of the naturally raw materials such as cellulose, lignin, etc., biomass platform compounds are instead used as feedstocks for the synthesis of chemicals. Levulinic acid (LA), as one of the most promising platform compounds,[4] can be produced from cellulose, starch, or C6 sugars via acid-catalyzed hydrolysis,[5-8] which has been applied in the production of many value-added chemicals including γ–valerolactone, 1,4-pentanediol, 2-methyltetrahydrofuran, N-alkyl-5-methyl-2-pyrrolidones.[9-11]Reductive amination/cyclization of LA is a promising route to synthesize N-alkyl-5-methyl-2-pyrrolidones that are important structural motifs with wide applications in pharmaceutical, agrochemical and material industries.[12,13] Various metal-based catalysts have been explored for the LA reductive amination to produce lactams or pyrrolidines using different reducing agent. [14-21] For example, indium acetate（In(OAc) $_3$) was shown to be very effective for LA reductive amination to lactams using $PhSiH_3$ as a reducing agent at 120°C. However, no metal-free catalyst has been reported for LA reductive amination/cyclization to lactams in a literature survey to date.

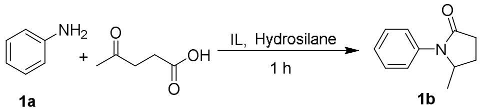


Scheme 1. Chemical structures of the lactate anion and cations of the lactate-based ILs.

Ionic liquids (ILs), composed entirely of ions, exhibit unique features such as high thermal and chemical stability, negligible vapor pressure, excellent solvent power, and tunable properties, ect..[22-24] In particular, ILs can be designed with specific task via choice or functionalization of cations or anions, and thus have been widely applied in many areas, such as chemical reactions,[22] material synthesis,[25,26] separation and fractionation.[27] Specially, ILs has been extensively used in biomass processing and chemical transformation,[28-31] for instance, degradation of cellulose, conversion of sugars to 5-hydroxymethylfurfural (HMF), as well as enzymatic hydrolysis of IL-pretreated cellulose. Lactic acid is an environmentally friendly bio-based chemical derived from carbohydrates or glycerol via chemical and fermentation routes.[32-35] Lactate-based ILs are considered to be non-toxic and pharmaceutically acceptable, and have been used as green solvents for organic synthesis.[36-38]

Herein, we reported a series of lactate-based ILs with different cations as illustrated in Scheme 1. They were found to be capable of efficiently catalyzing the reductive amination of LA using hydrosilane without any metal catalysts or addictives under mild conditions, even at room temperature. All the lactate-based ILs showed very high performances for the LA reductive amination. Using 1-butyl-3-methylimidazolium lactate ([BMIm][Lac]) as the catalyst, combined with $(EtO)_3SiH$, a series of lactams were obtained in excellent yields in most cases. The combination of the IL with $(EtO)_3SiH$ showed better performance than the best metal-based catalyst reported to date.[21,39] The mechanism investigation indicated that the ILs (e.g., [BMIm][Lac]) served as a multifunctional catalyst, which could activate hydrosilane and simultaneously catalysed the cyclization of LA and amine.

Table 1. IL-catalyzed reductive amination of levulinic acid with hydrosilanes.[a]



Entry	Catalyst	Silane/equiv.	Tem./^{o}C	Yield^b
1	--	$(EtO)_3SiH/2$	80	0
2	[BMIm][Lac]	$(EtO)_3SiH/2$	80	95
3	[HDBU][Lac]	$(EtO)_3SiH/2$	80	96
4	[tBu_4P][Lac]	$(EtO)_3SiH/2$	80	93
5	[TMG][Lac]	$(EtO)_3SiH/2$	80	93
6	[Et_4N][Lac]	$(EtO)_3SiH/2$	80	91
7	[BMIm]Cl	$(EtO)_3SiH/2$	80	11
8	[BMIm]Br	$(EtO)_3SiH/2$	80	7
9	[BMIm]I	$(EtO)_3SiH/2$	80	3
10	[BMIm]BF_4	$(EtO)_3SiH/2$	80	3
11	[BSO_3MIm]Cl	$(EtO)_3SiH/2$	80	8
12	[BMIm](CF_3SO_3)	$(EtO)_3SiH/2$	80	4
13	[BMIm][OAc]	$(EtO)_3SiH/2$	80	15
14	[BMIm][Lac]	$(EtO)_3SiH/2$	50	79
15	[BMIm][Lac]	$(EtO)_3SiH/2$	30	44/75^c/91^d
16	[BMIm][Lac]	$(EtO)_3SiH/1.5$	80	73
17	[BMIm][Lac]	$(EtO)_3SiH/1$	80	51
18	[BMIm][Lac]	$Ph_2SiH_2/2$	80	50
19	[BMIm][Lac]	$Et_2SiH_2/2$	80	0
20	[BMIm][Lac]	$Me(OMe)_2SiH/2$	80	68
21	[BMIm][Lac]	$PhSiH_3/2$	80	58
22	[BMIm][Lac]	PMHS/2	80	5
23	$In(OAc)_3$^{e}	$PhSiH_3/2$	80	95
24	$AlCl_3.6H_2O$^{f}	$PhSiH_3/2$	80	51

[a] Reaction conditions: IL (0.2 mmol), aniline(1 mmol), LA (1 mmol); [b] Determined by GC analysis using dodecane as the internal standard; [c]Reaction time: 3 h; [d] Reaction time: 6h; [e] 1 mol%; [f] 5 mol%. [g][HDBU][Lac]: 1,8-diazabicyclo[5.4.0]undec-7-enelactate; [TMG][Lac]: tetramethylguanidine lactate.

The lactate-based ILs as illustrated in Scheme 1 were synthesized via the neutralization of lactic acid with corresponding bases. The formation of these ILs were confirmed by ^1H and ^{13}C NMR analysis (see Supporting Information). In our initial experiments, the reductive amination of LA with aniline (**1a**) was performed to explore the optimal reaction conditions, and the results are listed in Table 1. The reaction did not proceed without any catalyst (Table 1, entry 1). To our delight, all the tested lactate-based ILs with different cations were very effective for this reaction, affording 5-methyl-1-phenylpyrrolidin-2-one (**1b**) in excellent yields using triethoxysilane ($(EtO)_3SiH$) as a reducing agent at 80°C within 1 h (Table 1, entries 2-6). To explore other reaction conditions, [BMIm][Lac] was selected as the catalyst. For comparasion, other imidazole-based ILs including [BMIm]Cl, [BMIm]Br, [BMIm]I, [BMIm]BF_4, [BSO_3MIm]Cl, [BMIm](CF_3SO_3), [Bmim][OAc] were examined, and they were found to exhibit inferior activity compared to the lactate-based ILs (Table 1, entries 7-13). These findings indicated that the lactate-based ILs were effecient catalysts of this reaction, and the lactate anion played the key role in catalyzing the reaction. The influence of temperature was investigated. As listed in Table 1 (entries 2, 14, 15), the reaction could proceed even at room temperature, producing **1b** in a yield of 44% within 1h. Prolonging the reaction time to 3 h and 6 h, the **1b** yield increased to 75% and 91%, respectively. Notably, 5-methyl-1-phenyl-1,5-dihydro-pyrrol-2-one (**B**) and/or 5-methyl-1-phenyl-1,3-dihydro-pyrrol-2-one (**B'**) were detected in the reaction solutions performed at 30 °C and 50 °C within 1 h, while it was not detectable in the reaction solution of 80 °C. This suggested that **B** and/or **B'** were intermediates of the final product, and they could convert to **1b** rapidly at high temperature (e.g., 80 °C) under the experimental conditions.

The amount of $(EtO)_3SiH$ was found to have an influence on the **1b** yield remarkably (Table 1, entries 2, 16, 17), which decreased to 51% as the amount decreased to 1 equiv.. These resultes indicated that 2 equiv. of $(EtO)_3SiH$ was required to get a high **1b** yield. In addition, other hydrosilanes including phenylsilane ($PhSiH_3$), poly-(methylhydrosiloxane) (PMHS), diphenylsilane (Ph_2SiH_2), diethylsilane (Et_2SiH_2) and methyldimethoxysilane ($Me(OMe)_2SiH$) were also examined in the reductive amination of LA with **1a** (Table 1, entries 18-22). As shown in Table 1, $PhSiH_3$, Ph_2SiH_2 and $Me(OMe)_2SiH$ were also effective for this reaction, however, displaying much lower activity compared to $(EtO)_3SiH$. Thus, $(EtO)_3SiH$ was selected as the reducing agent for the reductive amination/cyclization of LA.

It was reported that $In(OAc)_3$ and $AlCl_3.6H_2O$ were efficient catalysts for the reductive amination of LA with amines.[21,39] In the case of $In(OAc)_3$ as the catalyst, solvents (e.g., toluene) were required, and in the case of $AlCl_3.6H_2O$, extra $PhSiH_3$ was required to get a comparable product yield. In this work, using [BMIm][Lac] as the catalyst, since it is soluble in the reactants and products, no solvent is required, which make the reaction process simpler. In addition, $PhSiH_3$ was the most appropriate hydrosilane as $In(OAc)_3$ and $AlCl_3.6H_2O$ acted as the catalyst, while $(EtO)_3SiH$ was the best one in the case of [BMIm][Lac] as the catalyst. As known, $PhSiH_3$ is much more expensive than $(EtO)_3SiH$.[40] Therefore, the combination of [BMIm][Lac] and $(EtO)_3SiH$ had obvious advantages for the amination of LA compared to that of $In(OAc)_3$ or $AlCl_3.6H_2O$ with $PhSiH_3$. In this work, the activities of [BMIm][Lac], $In(OAc)_3$ and $AlCl_3.6H_2O$ for the reductive amination of LA with **1a** were compared under the listed conditions (Table 1, entries 23, 24). Obviously, [BMIm][Lac] (20 mol%) combined with $(EtO)_3SiH$ showed similar activity to $In(OAc)_3$ (1mol%, with phenylsilane) under the same other conditions.

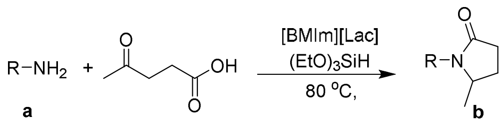
In addition, the IL [BMIm][Lac] could be readily separated from the reaction solution, and it can be reused for five times without obvious decrease in the yield of **1b** (Figure S1a). This indicated that the IL was stable and recyclable for this reaction.

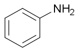
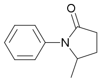
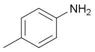
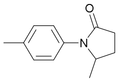
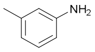
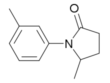
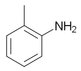
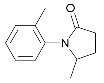
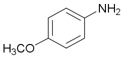
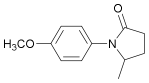
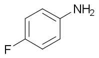
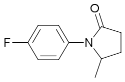
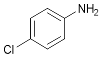
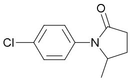
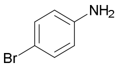
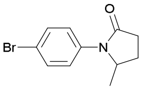
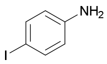
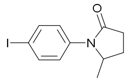
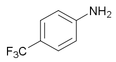
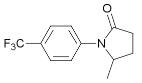
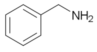
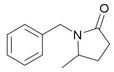
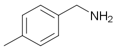
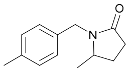
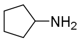
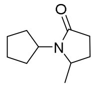
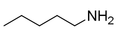
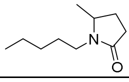
Taking the optimal conditions in hand, various substituted primary anilines were explored to react with LA catalyzed by [BMIm][Lac] in the presence of $(EtO)_3SiH$, and the results are summarized in Table 2. Obviously, most of primary anilines with electron-donating or electron-withdrawing groups including methyl, methoxy, fluoro, chloro, bromo and iodine were tolerated, affording the corresponding products in excellent yields (Table 2, entries 1-9). For the isomers of methyl-substituted anilines, the substitution position of methyl group in the benzene ring considerably impacted the reactivity of the amines with LA, and their reactivity follows the order: *p*-methyl aniline > *m*-methyl aniline > *o*-methyl aniline (Entries 2-4). Prolonging reaction time (i.e., 2h) led to the increase in the product yields (Table 2, entries 3, 4). Notably, the *para*-substituted anilines with electron-donating groups, such as methyl- and methoxy-substituted anilines showed similar reactivity to aniline **1a**, affording the corresponding products in excellent yields (Table 2, entries 1, 2, 5). For the anilines substituted by electron-withdrawing groups, such as fluoro-, chloro-, bromo- and iodine-, they showed declined reactivity compared to aniline, whereas excellent product yields were obtained as the reaction time was prolonged to 2h (Table 2, entries 6-9). However, *p*-trifluoromethyl aniline suffered from relatively low reactivity (Table 2, entry 10), probably due to the strong electron-withdrawing effect of the substitute. In addition, benzylic amines and aliphatic amines were also examined, which showed very high reactivity under the experimental conditions (Table 2, entries 11-14). The above results showed that the [BMIm][Lac]/$(EtO)_3SiH$ system was very effective for the reductive amination of LA to produce corresponding N-alkyl-5-methyl-2-pyrrolidones.

In order to demonstrate the potential of the [BMIm][Lac]/$(EtO)_3SiH$ system, the reductive amination/cyclization of 4-acetylbutyric acid with aniline derivatives were conducted, and the results are shown in Scheme 2. It was clear that 4-acetylbutyric acid could react with different substituted anilines, affording the corresponding N-alkyl-6-methyl-2-piperidinones in excellent yields. Notably, prolonged reaction time (e.g., 2 h) was required for 4-acetylbutyric acid to react with anilines compared to that for LA.

To gain deep insight into the role of the IL in catalysing the reaction, the interaction of [BMIm][Lac] with $(EtO)_3SiH$ was examined by NMR analysis. From the ^1H NMR spectra of

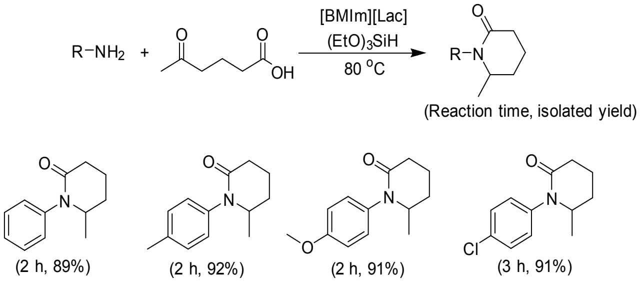
Table 2. Reductive amination of levulinic acid with various amines using triethoxysilane.[a]



Entry	Amine	Product	Yield [%][b]
1			95[c] (93)
2			91 (90)
3			74/91[d] (87)
4			56/72[d](65)
5			95 (93)
6			91[d] (89)
7			93[d] (90)
8			92[d](90)
9			89[d] (83)
10			36[e] (30)
11			92 (85)
12			91 (83)
13			96(90)
14			94(88)

[a] Reaction conditions: [BMIm][Lac] (0.2 mmol), amine (1 mmol), LA (1 mmol), $(EtO)_3SiH$ (2 mmol), 1 h; [b] Determined by ^1H NMR using mesitylene as the internal standard, followed by isolated yield in parenthesis; [c] Yield determined by GC analysis using dodecane as the internal standard; [d] Reaction time: 2h; [e] Reaction time: 3 h.

Scheme 2. Reductive amination of 4-acetylbutyric acid with various amines using triethoxysilane.[a]



[a]Reaction conditions: IL (0.2 mmol), aniline (1 mmol), 4-acetylbutyric acid (1 mmol), $(EtO)_3SiH$ (2 mmol).

[BMIm][Lac], $(EtO)_3SiH$ and the mixture of [BMIm][Lac] and $(EtO)_3SiH$ (Figure 1), it was observed that the ^1H NMR signal belonging to H atom (1) from $[BMIm]^+$ shifted upfield, and the signals to H atom (4) from $(Lac)^-$ shifted downfield. And the signals to H atoms (b, c) from $(EtO)_3SiH$ shifted downfield from 3.86 and 1.25 ppm to 3.64 and 1.18 ppm, respectively. All these shifts demonstrated that [BMIm][Lac] activated the Si-H bond and make it possible involve in the reaction.

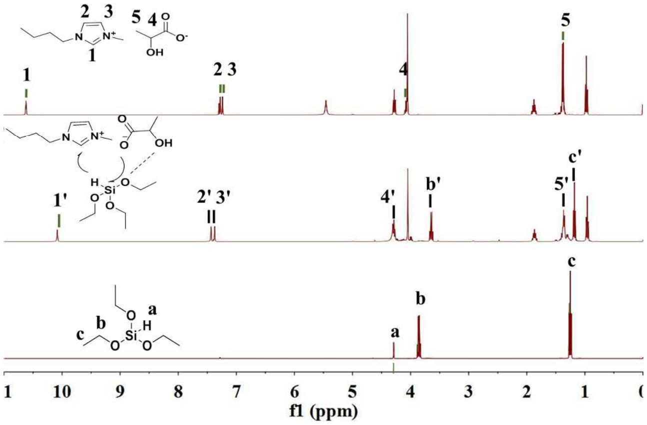
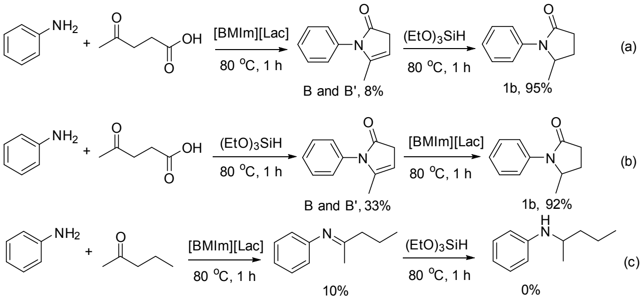


Figure 1. ^1H NMR spectra of pure [BMIm][Lac], the mixture of [BMIm][Lac] (0.1 mmol) and $(EtO)_3SiH$ (0.1 mmol) and pure $(EtO)_3SiH$; ($CDCl_3$, 298 K).

In preliminary experiments, intermediate **B** was detected in the reaction solutions performed at 30 °C and 50 °C, respectively. In order to further reaveal the reaction pathway of the reductive amination reaction of LA with aniline, control experiments as illustrated in Scheme 3 were carried out. As reported, amine could react with ketone to form imine.[41] However, in this work no imine intermediate 4-(phenylimino) pentanoic acid (A) was detected in the reaction solutions of aniline and LA in the presence of [BMIm][Lac] or $(EtO)_3SiH$. Instead, cyclized intermediate **B** or **B'** was detected in yields of 8% and 33%, respectively, under the experimental conditions (Scheme 3a, b). To explored whether A can be formed from aniline and LA or not, the reaction of aniline and 2-pentanone as a control reaction was performed in the presence of [BMIm][Lac] and $(EtO)_3SiH$, and N-phenylpentan-2-imine was obtained in a yield of 10% (Scheme 3c). In this reaction, no N-(pentan-2-yl) aniline was detected, suggesting that the imine could not be hydrogenated by $(EtO)_3SiH$ in the presence [BMIm][Lac], which was identical to our previous results,[42] while different from that reported before.[15,17,21] Based on this control experiment, it can be deduced that **A** may be formed from aniline and LA, and further rapidly convert to B under the experimental conditions.

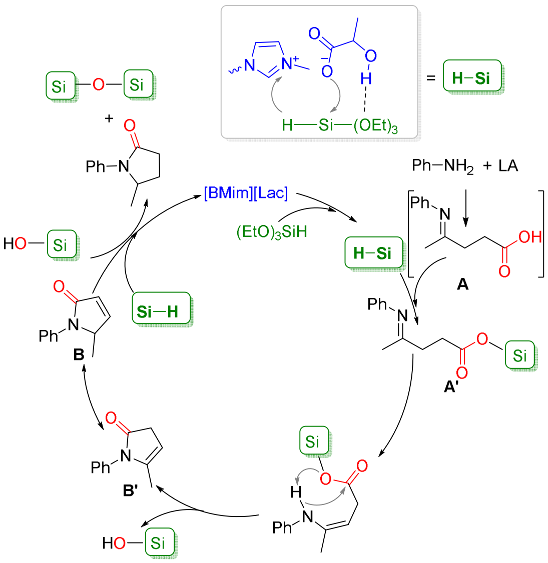
Scheme 3. Control experiments of reductive amination of LA with aniline using (EtO) $_3$SiH.



Reaction conditions: aniline (1.0 mmol); [a] and [b] LA (1.0 mmol), $(EtO)_3SiH$ (2.0 mmol), [BMIm][Lac] (0.2 mmol); [c] 2-pentanone (1.0 mmol), [BMIm][Lac] (0.2 mmol).

Notably, the control experiments Scheme 3**a**, **b** indicate that both [BMIm][Lac] and $(EtO)_3SiH$ was able to individually promote the formation of **B**, and $(EtO)_3SiH$ showed better performance than [BMIm][Lac]. These results imply that in the presence of the IL and $(EtO)_3SiH$ (i.e., in our reaction system), the formation of **B** may undergo the generation of silyl ether (**A'**) by the reaction of aniline with LA and the IL-activated $(EtO)_3SiH$, followed by the release of siloxane.[21] This may explained why 2 equiv. $(EtO)_3SiH$ was required to get a high yield within 1h. As $(EtO)_3SiH$ was added into the reaction solution of LA, aniline and [BMIm][Lac], intermediate **B** disappeared and **1b** was obtained in a high yield of 95% at 80 °C after 1 h. Similarly, the addition of [BMIm][Lac] into the reaction solution of LA, aniline and $(EtO)_3SiH$ afforded a **1b** yield of 92% without detectable **B** at 80 °C after 1 h. These findings suggested that $(EtO)_3SiH$ as a reducing agent involved the formation of **1b** via the reduction of **B**, while the IL catalyzed the reaction. From the above results, it can be concluded that the combination of $(EtO)_3SiH$ and [BMIm][Lac] made the reaction proceed rapidly.

On the basis of the above results, a possible reaction pathway for [BMIm][Lac]-catalyzed reductive amination/cyclization of LA using $(EtO)_3SiH$ as a reductant was proposed as illustrated in Scheme 4. First, the condensation between aniline and LA occurs to form a ketimine A, which rapidly reacts with the IL-activiated hydrosilane to form silyl ether.[43-45] Subsequently, the cyclization of the silyl ether occured, resulting in the formation of **B** or **B'**, which is finally reduced to pyrrolidone by $(EtO)_3SiH$ catalyzed by the IL.



Scheme 4. Possible reaction pathway of reductive amination/cyclization of LA

In conclusion, lactate-based ILs were found to be very effective for catalyzing reductive amination/cyclization of keto acids using (EtO)$_3$SiH as a reductant under mild conditions, even at room temperature, which provides a metal-free approach to synthesize lactams. Using [BMIm][Lac] as the catalyst, various lactams were obtained in good to excellent yields at 80 °C within 1-3 h. This approach to synthesize lactams may find promising applications.

ASSOCIATED CONTENT

Supporting Information

General experimental procedures, yields determination and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: liuzm@iccas.ac.cn

Notes

The authors declare no competing financial interests.

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