

Choline-based biodegradable ionic liquid catalyst for Mannich-type reaction

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Abstract. A three-component Mannich-type reaction of aromatic aldehydes, ketones, and amines was catalyzed by a novel choline-based acidic ionic liquid. The proposed catalyst was a Lewis-Brønsted dual acid catalyst as well as water-tolerant. The β -amino carbonyl compounds were obtained at room temperature in reasonable to good yields ranging from 63 to 98%. After the reaction, the catalyst could be recycled and reused for 5 times without obvious decrease of the yield. Further, the catalyst was environment-friendly with a significant biodegradation rate.

Keywords. Mannich-type reaction; choline; Lewis-Brønsted acid; catalysis; biodegradation.

1. Introduction

The Mannich-type reaction is a basic C-C bond forming multi-component reaction (MCR) which involves an amino alkylation of an acidic proton beside a carbonyl functional group by formaldehyde and a primary or secondary amine or ammonia.¹ The products of Mannich reaction, β -amino carbonyl compound, are synthetic intermediates of huge value. It is widely employed in the organic synthesis of natural compounds, medicine and biologically active compounds.² Today, it has shown broad applicability in other areas such as pesticides, explosives, dyes and paints. Most Mannich reactions are catalyzed by Lewis acid or Brønsted acid.³ In recent years, the researchers continued to study new synthetic methods and new catalysts including TMG,⁴ Sm(OTf)₃,⁵ Fe(HSO₄)₃/SiO₂,⁶ triphenylphosphine,⁷ nano-Mn(HSO₄)₂,⁸ Zeolite⁹ were reported.

Choline-based ionic liquids are widely applied in many areas such as the sustainable chemistry,¹⁰ synthetic chemistry¹¹ and catalysis,¹² due to the excellent physical, chemical properties, environmental friendliness and low prices. Abbott *et al.*, proposed a novel deep eutectic ionic liquid based on choline chloride, and it showed a significant function in catalysis.¹³ On the basis of the research of choline-based ionic liquids,

Satasia *et al.*, designed a new sulfate-functionalized cholinium cation and catalyzed formamide synthesis by grindstone chemistry.¹⁴ Apart from Brønsted acid¹⁵ or Lewis-Brønsted acid, choline-based ionic liquids¹⁶ were also designed and synthesized. It has been proved that all of them have significant catalytic activity and are friendlier for the environment than conventional ionic liquids which have catalyzed many reactions like Biginelli reaction,¹⁵ Mannich reaction,¹⁶ Kabachnik–Fields reaction,¹⁷ *etc.*

In continuation of our work on MCRs,¹⁸ and considering the importance of combined catalytic systems, the choline-based functional Lewis-Brønsted dual acid ionic liquid catalyst (Figure 1) was discovered and used as the catalyst in the Mannich-type reaction under mild reaction conditions. Its use as a novel catalyst for the synthesis of β -amino carbonyl compound *via* Mannich-type reaction has also been explored.

2. Experimental

2.1 Materials and methods

All the reagents and chemicals (AR grade) were procured from Sinopharm Chemical Reagent Co. Ltd. and used as received. The sludge used in the biodegradation rate test was supplied by Nanjing Sewage Treatment Plant, China.

The Elemental analyses were done using a Perkin-Elmer CHN analyzer. The IR spectra (KBr pellet) were

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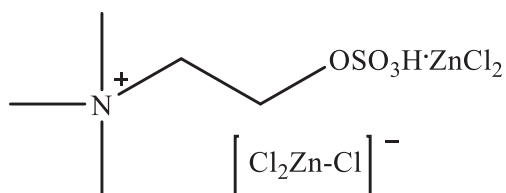


Figure 1. Structure of Lewis-Brønsted choline-based ionic liquid.

recorded on a Bruker WERTEX80 spectrometer and expressed in cm^{-1} . ^1H NMR spectra were recorded on a Bruker DRX300 (300 MHz) and Bruker Ultrashield (400 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker DRX300 (75 MHz) and Bruker Ultrashield (101 MHz) spectrometer. Mass spectra were obtained with an automated Fininigan TSQ Quantum Ultra AM (Thermal) LC/MS spectrometer. Thermal stability measurements were conducted using a NET-ZSCH STA 449F5 system.

2.2 Synthesis of Lewis-Brønsted choline-based Ionic liquid ($[\text{Ch-OSO}_3\text{H}]\text{Cl}\cdot 2\text{ZnCl}_2$)

The intermediate $[\text{Ch-OSO}_3\text{H}]\text{Cl}$ (**1**) was synthesized according to the reported methods,¹⁴ dried under vacuum to afford the white powder. The characterization data for the intermediate are as follows: $[\text{Ch-OSO}_3\text{H}]\text{Cl}$ (**1**): IR / cm^{-1} : 3417, 3043, 2987, 1483, 1405, 1231, 1038, 985, 761, 628, 571 cm^{-1} . ^1H NMR (300 MHz, D_2O): δ 3.06 (s, 9H), 3.60–3.63 (t, 2H), 4.33–4.37 (m, 2H).

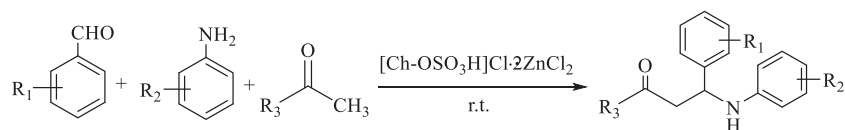
A mixture of the above intermediate $[\text{Ch-OSO}_3\text{H}]\text{Cl}$ (2.197 g; 10 mmol) and ZnCl_2 (2.726 g; 20 mmol) was rapidly grinded for 5 min; then, the uniform mixture was heated for 2 h at 100°C to afford the target ionic liquid $[\text{Ch-OSO}_3\text{H}]\text{Cl}\cdot 2\text{ZnCl}_2$ (**2**). The characterization data for the compound are as follows: $[\text{Ch-OSO}_3\text{H}]\text{Cl}\cdot 2\text{ZnCl}_2$ (**2**): Analysis: Calculated (%) for $\text{C}_5\text{H}_{14}\text{Cl}_5\text{NO}_4\text{SZn}_2$ (486.767): C, 12.34; H, 2.90; N, 2.88. Found (%): C, 12.05; H, 2.89; N, 2.83. IR / cm^{-1} : 3357, 2975, 2889, 1650, 1384, 1089, 881, 662 cm^{-1} . ^1H NMR (300 MHz, D_2O): δ 3.13 (s, 9H), 3.65–3.67 (t, 2H), 4.40 (s, 2H) ^{13}C NMR (101 MHz, D_2O): δ 51.05, 59.12, 61.91.

2.3 General procedure for the Mannich-type reaction catalyzed by $[\text{Ch-OSO}_3\text{H}]\text{Cl}\cdot 2\text{ZnCl}_2$

In a typical experiment (Scheme 1), to a round-bottomed flask charged with aromatic aldehyde (10 mmol), aromatic amine (10 mmol) and aromatic ketones (10 mmol) in 2–3 mL 85% aqueous ethanol was added $[\text{Ch-OSO}_3\text{H}]\text{Cl}\cdot 2\text{ZnCl}_2$ (0.49 g; 1 mmol) under stirring. The mixture was then stirred for a length of time at room temperature. After completion of the condensation (monitored by TLC), the solid crude product was filtered and recrystallized from 95% ethanol to afford pure β -amino carbonyl derivatives. The products obtained were identified by ^1H NMR, and physical data (M.p.) with those reported in the literature. $[\text{Ch-OSO}_3\text{H}]\text{Cl}\cdot 2\text{ZnCl}_2$ could be recovered from the filtrate and reused directly for the next run without any treatment. The characterization data for the new compounds are given below.

2.3a 1-Phenyl-3-(p-hydroxyphenyl)-3-(m-trifluoromethylphenylamino)-1-propanone (Table 3, entry 13): White solid, M.p. $157\text{--}158^\circ\text{C}$; Analysis: Calculated (%) for $\text{C}_{22}\text{H}_{18}\text{F}_3\text{NO}_2$ (385.379): C, 68.57; H, 4.71; N, 3.63. Found (%): C, 68.33; H, 4.72; N, 3.58. MS (m/z): 386.1308 ($[\text{M} + \text{H}]^+$). ^1H NMR (400 MHz, CDCl_3) δ 7.94–7.86 (m, 2H), 7.58 (t, 1H), 7.46 (t, 2H), 7.16 (t, 1H), 6.88 (d, 1H), 6.79 (dd, 3H), 6.67 (dd, 1H), 4.99–4.92 (m, 1H), 4.80 (s, 2H), 3.60–3.22 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 197.26, 153.84, 146.07, 135.55, 133.23, 132.57, 128.72, 128.46, 127.74, 127.18, 126.57, 118.97, 115.41, 114.67, 113.01, 109.32, 53.08, 45.11.

2.3b 1-Phenyl-3-(p-methylphenyl)-3-(m-trifluoromethylphenylamino)-1-propanone (Table 3, entry 14): White solid, M.p. $111\text{--}112^\circ\text{C}$; Analysis: Calculated (%) for $\text{C}_{23}\text{H}_{20}\text{F}_3\text{NO}$ (383.406): C, 72.05; H, 5.26; N, 3.65. Found (%): C, 71.85; H, 5.28; N, 3.60. MS (m/z): 384.1520 ($[\text{M} + \text{H}]^+$). ^1H NMR (400 MHz, CDCl_3) δ 7.91 (dd, 2H), 7.60–7.50 (m, 2H), 7.45 (t, 2H), 7.31 (d, 2H), 7.16–7.12 (m, 3H), 6.89 (d, 1H), 6.80 (s, 1H), 6.68 (dd, 1H), 4.98 (dd, 1H), 3.53–3.40 (m, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 197.12, 146.28,



Scheme 1. Process of Mannich-type reaction.

137.99, 136.24, 135.54, 132.53, 130.43, 128.60, 128.49, 127.72, 127.18, 125.12, 120.08, 115.34, 113.10, 109.35, 53.36, 45.14, 20.04.

3. Results and Discussion

3.1 Synthesis and characterization

The intermediate [Ch-OSO₃H]Cl was synthesized according to the reported methods; then a mixture of [Ch-OSO₃H]Cl and ZnCl₂ was rapidly grinded for 5 min, and heated for 2 h at 100°C to afford the target ionic liquid [Ch-OSO₃H]Cl·2ZnCl₂. In the FTIR spectrum for [Ch-OSO₃H]Cl·2ZnCl₂, (Figure S2 in Supplementary Information), the peaks of O-H bond (3300–3500 cm⁻¹), C-H bond (2880–2990 cm⁻¹), C-O bond (1000–1100 cm⁻¹) were well-retained. However, the Zn-Cl vibration peak in ZnCl₂ is at 503 cm⁻¹, whereas the Zn-Cl vibration peak in [Ch-OSO₃H]Cl·2ZnCl₂ appears at 663 cm⁻¹. The peak was enhanced and position shifted from 503 cm⁻¹ to 663 cm⁻¹, which indicated that the significant catalytic effect of [Ch-OSO₃H]Cl·2ZnCl₂ is due to the complexation between [Ch-OSO₃H]Cl and ZnCl₂.

In order to understand the phase transition and decomposition behavior of [Ch-OSO₃H]Cl and [Ch-OSO₃H]Cl·2ZnCl₂, DSC and TGA study were carried out. The results are shown in Figure 2. It can be seen that [Ch-OSO₃H]Cl and [Ch-OSO₃H]Cl·2ZnCl₂ have high thermal stability. The addition of zinc chloride did not change significantly the thermal stability. The high thermal stability suggests that both of them can be used in a wide temperature range. In DSC for [Ch-OSO₃H]Cl, endothermic peaks appeared

at 254.3°C and 341.6°C. The peak at 254.3°C was due to the phase transition. [Ch-OSO₃H]Cl had changed from solid into molten state. The melting enthalpy was 58.93 J/g. Another peak was due to the decomposition, the decomposing enthalpy was 509.5 J/g. The decomposing enthalpy of [Ch-OSO₃H]Cl·2ZnCl₂ was 509.5 J/g. The endothermic peak was at 344.6°C.

One-pot Mannich-type model reaction with benzaldehyde, aniline and acetophenone was established in the presence of [Ch-OSO₃H]Cl·2ZnCl₂ and the reaction time was monitored by TLC (Table 1).

It showed that the three-component Mannich-type reaction could be accomplished smoothly in aqueous ethanol at room temperature. Satisfactory results were obtained in 80–85% ethanol medium (entries 5, 6). But, when pure water or ethanol were used as medium (entries 1, 7), the reaction was suppressed. The yield rose with the addition of ethanol in water, and the yield reached maximum when the content of ethanol is 85%. It is noteworthy that the proposed catalyst [Ch-OSO₃H]Cl·2ZnCl₂ could retain its activity in the aqueous media. In aqueous media, most of the traditional Lewis acid catalysts may react with water first. It greatly affects the activity of catalyst, leading to lower yields of the target product. This work indicated that [Ch-OSO₃H]Cl·2ZnCl₂ overcame the fear of water when compared with many traditional Lewis acid catalysts.^{19–21}

In order to evaluate the catalytic activity of [Ch-OSO₃H]Cl·2ZnCl₂, different catalysts were explored in the model reaction (Table 2) in aqueous ethanol medium at the room temperature. It is inferred from Table 2 that [Ch-OSO₃H]Cl catalyzed more effectively than choline chloride and results in substantial increase of yield (entries 1, 2), which confirmed that the replacement of hydroxyl to sulfonic acid group could increase the catalytic activity. Besides, it could be inferred that ZnCl₂ showed some catalytic activity and introducing

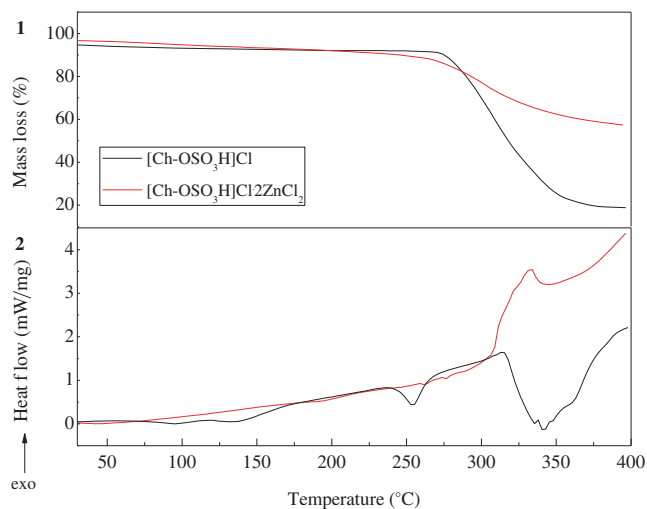


Figure 2. TGA (1)—DSC (2) scans of [Ch-OSO₃H]Cl and [Ch-OSO₃H]Cl·2ZnCl₂.

Table 1. The effects of different solvent systems to the Mannich reaction.^a

Entry	Solvent	Time (min)	Yield (%) ^b
1	H ₂ O	10	<10
2	50% ethanol	8	59
3	65% ethanol	8	76
4	75% ethanol	8	86
5	80% ethanol	8	93
6	85% ethanol	8	98
7	C ₂ H ₅ OH	8	<10

^aReaction conditions: benzaldehyde (10 mmol), aniline (10 mmol) and acetophenone (10 mmol), catalyst (1 mmol), solvent (2 mL), r.t. ^bIsolated yield.

Table 2. The activity of different catalysts for Mannich reaction.^a

Entry	Catalyst	Yield (%)
1	Choline Chloride	51
2	[Ch-OSO ₃ H]Cl	71
3	ZnCl ₂	55
4	ChCl·2ZnCl ₂	68
5 ^b	ChCl·2ZnCl ₂	71
6	[Ch-OSO ₃ H]Cl and ZnCl ₂	61
7	[Ch-OSO ₃ H]Cl·2ZnCl ₂	98

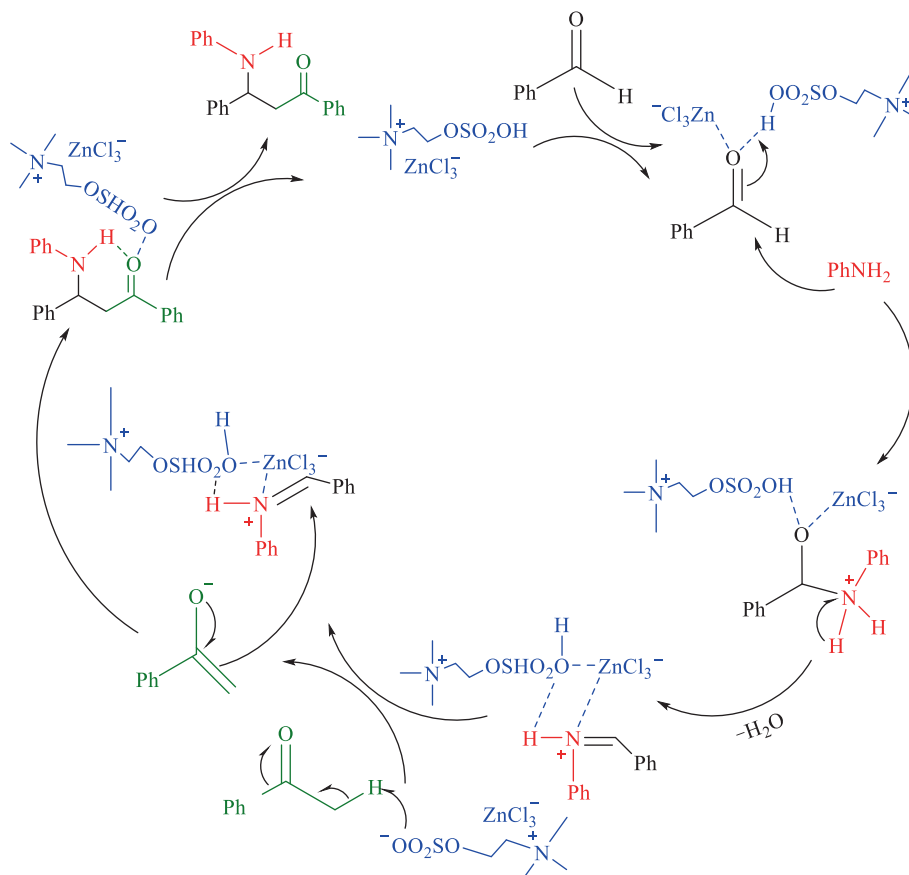
^aReaction conditions: benzaldehyde (10 mmol), aniline (10 mmol) and acetophenone (10 mmol), catalyst (1mmol), 85% ethanol (2 mL), 8 h, r.t. ^bIn H₂O.

ZnCl₂ would benefit the reaction (entry 3). However, the performance of individual use of the Lewis acid and Brønsted acid was unsatisfactory (entries 2, 3).

Based on the above results, we considered a combination of the Lewis acid and Brønsted acid. Initially, [Ch-OSO₃H]Cl and ZnCl₂ were mixed directly with a molar ratio of 1:2, and the mixture was simply used in the reaction without any pre-treatment (entry 6). But the catalytic effects were still unsatisfactory. However, if the pre-treatment process was optimized to grind them

and heated under 100°C for 2 h, the Lewis-Brønsted dual acid ionic liquid ([Ch-OSO₃H]Cl·2ZnCl₂) was generated which showed significant catalytic effect on Mannich reaction (entry 7). Choline chloride and zinc chloride were treated in the same way, and used as the catalyst for Mannich reaction in 85% aqueous ethanol (entry 4), and in pure water (entry 5). It was found that the catalytic activity of ChCl·2ZnCl₂ for Mannich reaction was far less than [Ch-OSO₃H]Cl·2ZnCl₂. Thus, it proved that a combination of Lewis and Brønsted acid under heated condition and sulfonic acid group played a significant role in promoting the catalytic activity of the catalyst.

Abott *et al.*, pointed out that actual species presented in ChCl·2ZnCl₂ which acted as Lewis acid catalyst, could be [ZnCl₃]⁻, [ZnCl₅]⁻ and [ZnCl₇]⁻.¹⁰ Liu and coworkers reported [HO₃S-(CH₂)₄-min]Cl-xZnCl₂ was Brønsted-Lewis acidic ionic liquid. Anion in the ionic liquid could be [ZnCl₃]⁻, [Zn₂Cl₅]⁻, [Zn₄Cl₉]⁻.²² The forms of anion existing in such structures are semi-empirical. These species may attract a proton from acetophenone to give anionic enolate species. Moreover, [Ch-OSO₃H]Cl·2ZnCl₂ can form an acceptor-donor complex with the aldehyde and the imine in the first stage. Therefore, addition of the enolate

**Scheme 2.** The mechanism of [Ch-OSO₃H]Cl·2ZnCl₂-catalyzed Mannich-type reaction.

form of acetophenone could be facilitated. When [Ch-OSO₃H]Cl and ZnCl₂ were mixed directly without any pre-treatment, they did not have such a catalytic effect.

On the basis of these assumptions, the experimental results and reported studies, the mechanism can be inferred. The mechanism of [Ch-OSO₃H]Cl·2ZnCl₂ catalysis of Mannich-type reaction involving benzaldehyde, aniline and acetophenone as substrate is shown in Scheme 2.

With the best reaction conditions in hand, some controlled experiments were explored with various aromatic aldehydes, aromatic amines and ketones as the substrate. The results presented in Table 3 shows that all the one-pot three-component Mannich-type reactions were accomplished in the optimal conditions, catalyzed by [Ch-OSO₃H]Cl·2ZnCl₂. It could be easily seen that no matter whether the electron donating group or the electron withdrawing group on the aromatic ring, reasonable to good yield could be obtained.

3.2 Reusability of the catalyst

In order to investigate the recycling of the catalyst, several repeat experiments were made with the recovered catalyst. The reaction was run with hydroxybenzaldehyde, p-toluidine and acetophenone as raw materials, [Ch-OSO₃H]Cl·2ZnCl₂ as the catalyst, 85% aqueous ethanol as the solvent. After the reaction, the mixture was filtered, washed several times with 85% aqueous ethanol. The filtrate containing the [Ch-OSO₃H]Cl·2ZnCl₂ was subsequently used as the catalyst - solvent system in the next run of the reaction.

The yield in the 5 cycles were 96, 96, 94, 93 and 92%. In the 5th cycle, the yield was slightly lower, which may be due to the unavoidable loss in the recovery process. But on the whole, the recovered catalyst still showed a significant catalytic activity on the reaction.

3.3 The biodegradation rate of the catalyst [Ch-OSO₃H]Cl·2ZnCl₂

Lastly, the biodegradation of [Ch-OSO₃H]Cl·2ZnCl₂ was investigated with the sludge of Nanjing sewage treatment plant. Sodium lauryl sulfate (SDS) was used as a reference. The standards were according to OECD301D.²³ The results are shown in Figure 3.

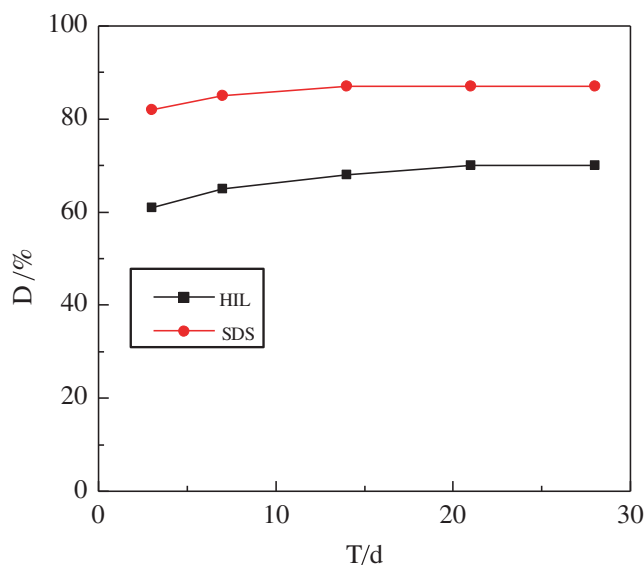


Figure 3. The biodegradation of the catalyst [Ch-OSO₃H]Cl·2ZnCl₂. Plot of D (%) vs time in days).

Table 3. [Ch-OSO₃H]Cl·2ZnCl₂-catalyzed three-component Mannich-type reaction.^a

Entry	R ₁	R ₂	R ₃	Yield/% ^b	M.p. (°C)
1	H	H	ph	98	153–154
2	H	4-Me	ph	86	163–164
3	4-Me	4-Me	ph	65	148–149
4	4-Me	4-Cl	ph	76	150–151
5	4-OCH ₃	H	ph	93	106–107
6	4-OCH ₃	4-Me	ph	84	157–158
7	4-F	4-Cl	ph	95	126–127
8	4-Cl	H	ph	87	117–118
9	4-Cl	4-Me	ph	91	152–153
10	4-Cl	4-Cl	ph	92	126–127
11	4-OH	H	ph	80	180–181
12	4-OH	4-Me	ph	96	171–172
13	4-OH	3-CF ₃	ph	63	157–158
14	4-CH ₃	3-CF ₃	ph	73	111–112
15	H	H	4-MeC ₆ H ₄	86	138–139

^aReaction conditions: benzaldehyde (10 mmol), aniline (10 mmol) and acetophenone (10 mmol), catalyst (1 mmol), 85% ethanol (2–3 mL), 6–12 h, r.t. ^bIsolated yield; products were confirmed by ¹H NMR, MS.

It was worth to note that the biodegradation rate of the catalyst can reach 70% after 3 weeks and remained stable subsequently. It was confirmed that [Ch-OSO₃H]Cl·2ZnCl₂ should be an easily biodegradable catalyst if compared with SDS, and this highlight was superior to our previous works.

4. Conclusions

In summary, a new biodegradable Lewis-Brønsted dual acid ionic liquid was discovered and used as the catalyst for the Mannich reaction of aromatic aldehydes, ketones and amines. The easily biodegradable catalyst could be recycled and reused. The procedure offers several advantages including high efficiency, good yield, and operational simplicity.

Supplementary Information (SI)

All additional information pertaining to characterization of the catalyst using elemental analysis (Table S1), IR spectra (Figures S1 and S3), ¹H NMR, ¹³C MNR spectra (Figures S2, S4 and S5), and characterization of the new compounds using elemental analysis (Tables S2 and S3), MS (Figure S6 and S9), ¹H NMR, ¹³C MNR spectra (Figures S7, S8, S10 and S11) are given in the supporting information, available at www.ias.ac.in/chemsci.

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