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Ionic Liquid Catalyzed Probase Method for One-pot Synthesis of *α, β*-Unsaturated Esters from Esters and Aldehydes at Mild Condition

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One-pot synthesis of*α, β*-unsaturated estersfrom unactivated esters and aldehydes using strong bases, such as sodium alkoxide and potassium tert-butoxide, were reported. However, the ionic liquids (ILs) catalyzed probase method for producing*α, β*-unsaturated esters was not reporteduntil now. In this work, series of ILs with fluoride anion were firstly prepared and used as the catalysts in combination with the probase of *N,O-Bis*(trimethylsilyl) acetamide (BSA) for *α, β*-unsaturated esters synthesis. Thisprocesscould also be promoted through the introduction of another IL with Lewis acid sites. The yield and selectivity of product could reach up to 84.2 % and 95.0 % when [Bmim]F was used in cooperation with [Bmim]Cl/$AlCl_3$ (the molar fraction of $AlCl_3$ is 0.67). Mechanism investigation through GC-MS indicate that the BSA would convert into onium amide, which acted asa strong base for α-H abstraction, with the catalysis of [Bmim]F. Meanwhile, [Bmim]Cl/$AlCl_3$ played an important role in the condensation step between enolates and aldehydes. On the basis of mechanism insights, the kinetic and thermodynamic studies were carried out in supplementary for better understanding of this new route.

Keywords: *α, β*-Unsaturated esters; Ionic liquids; Silyl enol ether; Kinetic; Thermodynamic

Introduction

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α, β-Unsaturated esters as important chemical intermediates and products are widely used in the field of polymer materials production, [1] paints and coatings preparation, [2] adhesives and textiles synthesis,[3]pharmaceutical and essences fabrication. [4]Approaches to such compounds include direct esterification,[5]Reformasky reaction,[6] Doebner method,[7] dehydrogenation,[8]Knoevenagel condensation,[9]oxidative esterification, [10]Witting reaction, [11] Horner-Wadsworth-Emmons reaction [12]and aldol condensation.[4, 13-15]The direct esterification is the simplest among these routes, while *α, β*-unsaturated acid should be prepared firstly. Itcould also be obtained from *α-halo*esters using zinc as catalyst through Reformasky reaction and from *α-cyano*estersin the presence of base *via*Knoevenagel reaction, respectively.But the zinc halides could not be recycled and the preparation of *α-cyano*esters often need poisonous cyanide reagent. Although dehydrogenation and oxidative esterification methods seem to environmental friendly and green sustainable,these technologies usually require novel metal catalysts and the catalysts are hard to recycle. Witting and Horner-Wadsworth-Emmons reactionsneedphosphine reagents, which are often toxic and environmental-unfriendly. Aldol condensation is considered as a key and efficient reaction for the construction of carbon-carbon bond to form α-hydroxyland *α, β*-unsaturatedcarbonyl compounds.[16-27]

Unactivated esters with high p*K*a value of α-H, unlike aldehydes or ketones, should be enolized during aldol condensation. Typically, alkoxide salts are able to deprotonate the *α*-H of esters, generating active enolate intermediatesthat are required for the following carbon-carbon coupling reactions.[28, 29]However, it is difficult to avoid side reactions for the solubility of these salts in common solvents as well as their nucleophilicity. Otherwise, alkali metal amides, such as lithium hexamethyldisilazide (LiHMDS), lithium diisopropylamide (LDA) andlithium tetramethylpiperidide (LiTMP), are also commonly used in organic chemistry as strongnon-nucleophilic bases. But these reaction temperature should be decreased to

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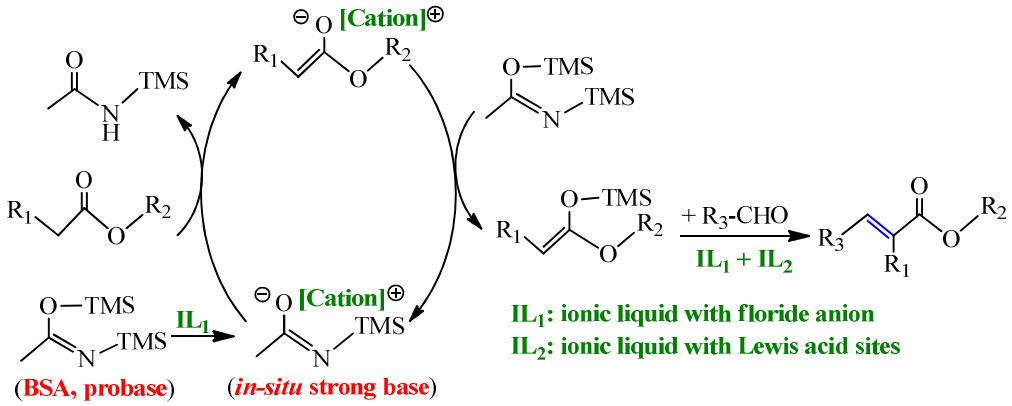
below 0℃and the operation should be also careful due to the high activityand air (or water) sensitivityof such strong bases. Followed by Kondo's researches on *in-situ*method that to produce base through fluoride anion catalysis of aminosilanes, [30, 31]Teng found the pentanidium- and bisguanidinium-salts catalyzed probase method for alkylation of lactones using silylamide. [32]Compared with the strong bases, the probase is relatively stable and it is more convenient for operation. In addition, ILs as green and environmental-protection reagents are universally applied in the replacement of traditional solvents and acidic (or basic) catalysts, result from the low vapor pressure, easy recycle and high catalytic performance in most organic reactions. [33-39]



Scheme 1 ILs catalyzed probase method for *α, β*-unsaturated esters production

Inspired from the work of Teng and Kondo, the ILscatalyzed probase strategyshown in Scheme 1 was envisioned for producing *α, β*-unsaturated esters from unactivated esters and aldehydes at mild condition, which has not been reported up to now. In present work, *N,O-bis*(trimethylsilyl) acetamide (BSA) was selected as the probase and the ILs with fluoride anion (ILs-F) were designed and selected as catalysts to catalytic decompose BSA into strong base of onium amide.The α-H deprotonation and ester enolization would occur in the presence of onium amide. Another ILs with Lewis acid sites(ILs-L) were also used in cooperation to catalyze the aldol condensation step between enolates and aldehydes. The effectof cation (for ILs-F), Lewis acidity concentration (for ILs-L) and solvent on this catalytic process were also studied. The reaction mechanism was also analyzed and investigated in

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detailsby using GC-MS. On the basis of mechanism insights, kinetic and thermodynamic studies were also carried out for better understanding of this new process.

Experimental

Materials

Dichloromethane (purity ≥ 99.5%) was supplied byXilong Chemical Co., Ltd., (China). Esters (purity ≥ 99.0%), aldehydes (purity ≥ 99.0%), AgF (purity of 99.0%) and *N,O-bis*(trimethylsilyl) acetamide (purity ≥97.0%) were purchased from *J&K* Scientific Ltd. (China). Octane (purity ≥ 99.5%) was provided by Aladdin Industrial Co.,(China). ILs (purity ≥ 99.0%) were supported by Linzhou Keneng Materials Technology Co., Ltd., (China).The solventsused for synthesis reaction should be dehydrated with calcium hydride under reflux for about 24 h and the dry solvents could be obtained after distillation. The reactants also should be dehydrated with 4 Å molecular sieves.

Preparation of ILs-F

The ILs-F were prepared fromAgF and ILs that with bromine (or chloride) anion (ILs-Br or ILs-Cl) as shown in Scheme 2. The solution of ILs-Br (or ILs-Cl, 1 eq.) was firstly fabricated in ethanol, followed by being addeddropwise the AgF (1.03 eq.) aqueous solution at room temperature under suitable stirring speed. Another 5 min stirring was kept after AgF solution was added. The formed light yellow (or white) precipitates were filtered off and the solvent was removed under high vacuum at 30℃. The obtained crude ILs-Fwere dissolved in ethanol and filtered off to remove the remaining AgF. Then the ethanol was removed under high vacuum at 30℃and the relatively high pure ILs-F were obtained. The purityand NMR spectra of each prepared IL-F wasprovided in Electronic Supporting Information.

Scheme 2 Preparation mechanism of ILs-F

Preparation of ILs-L

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In the glove box, the metal chlorides ($ZnCl_2$, CuCl, $FeCl_3$, $AlCl_3$) were weighted in suitable amount and charged into a flask. Then the flask was sealed and kept in alcohol bath under -20℃. After that, the dried [Bmim]Cl (in high vacuum at 90℃ for about 24h) in corresponding molar ratio was injected into the flask by dropping and mixed with metal chloride power under the Ar (or N_2) atmosphere. The mixture was kept stirring under -20℃ for about 4 h. The ILs with Lewis acid sites (ILs-L) [Bmim]Cl/MCl_x (M=Zn^{2+}, Cu^{+}, Fe^{3+}, Al^{3+}) could be obtained (the FT-IR spectra were provided in Electronic Supporting Information). The prepared ILs-L should be stored in the glove box or inert gas atmosphere in avoidance of hydrolysis.

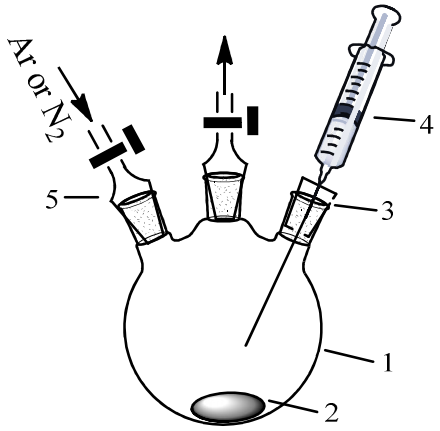

Fig.1. Theapparatus for preparing ILs-L

1-flask, 2-stir, 3-rubber plug, 4-injector, 5-glass valve

General synthesis

All synthesis reactions were carried out in a round-bottomed flask under 1 atm and the air in flask was replaced with N_2or Ar before the dehydrated solvent and reagents were added into it. The reaction mixture was kept at 283 K-298 Kwithatemperature-controlled water bath equipped with magnetic stirring. And typical reaction solution consisted of aldehyde (0.1Min solvent), ester,BSA, ILsand octane which was used as internal standard. To keep molar concentrations consistent, solutions for reactions with other reagents were prepared to have the same concentration of aldehyde (0.1M). The aldehydein suitable molar ratio to ester, octaneand ILs(for cation effect investigation, only ILs-F were used, and for other

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synthesis reaction, both ILs-F and ILs-L were used) in appreciate percentage were firstly mixed insolvent before being introduced into the flask. Then BSA was injected dropwise into former solution with syringeunder suitable stirring speed. Product samples were periodically collected and analyzed with GC-MS.

Analysis methods

^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR analysis were carried out onBrukerAVANCE instrument (600 MHz), and the spectra were collected at ambient temperature. Chemical shifts were reported in ppm relative to the residual solvent signal (D_2O: 4.79 ppm).

Product samples were analyzed and quantified in the meantime with GC-MS apparatus (QP2020,Shimadzu) equipped with a Rtx-5MS column (30 m, 0.32 mm, 0.25 μm). Products were identified by comparison to standards and MS information,carrier gas, He; temperature, 40℃ (2 min) to 300℃ at 15℃/min and hold for 5min; detector temperature, 250℃; injector temperature, 300℃.The concentration of each reactant and product wereobtained by using octane as internal standard. The mass correction factor of each substance relative to octane was determined from mixtures of standard sample that diluted withCH_2Cl_2. For others that without standard sample, it was estimated by using effective carbon number method, [40, 41]respectively.

All the FT-IR samplesof ILs-L were spread into liquid films on KBr window. The spectra were recorded on a Nicolet Fourier transform infrared spectrophotometer at room temperature. The pyridine probing IR for Lewis acidicconcentration measurement was similar to former operation, the samples were prepared by mixing pyridine, which was dried with solid KOH and distilled over 4Å molecular sieves,with ILs-L in the volume ratio of 1:5in glove box.

Results and discussion

Cation effect of ILs-F

To investigate this ILs catalyzed probase method,the

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condensationofbenzaldehydewith methyl acetate to methyl cinnamate was selected as the model reaction. According to the research results of Kondo and Teng, [32, 42, 43] the cation of *in-situ* formed strong base onium amide would affect the reaction results. Thusthe cation effect of ILs-F was firstly explored. The ILs-F with different cations wereprepared as described in experimental section and the structure was confirmed through ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR, which were illustrated in Electronic Supporting Information. And the synthetic results using ILs-F with different cation were shown in Fig.2.

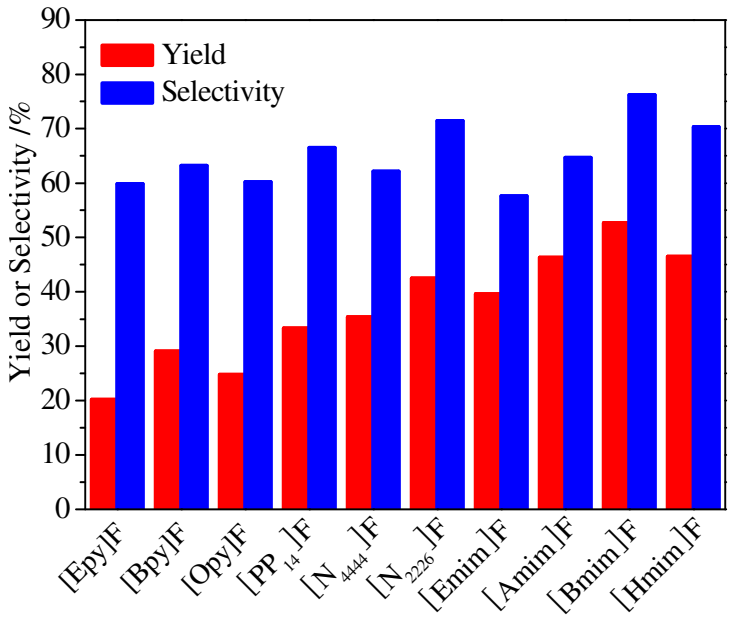

Fig. 2. Catalytic performance of ILs-F with different cations

Reaction condition: benzaldehyde (0.2 mmol, 0.1 M in CH_2Cl_2), the molar ratio of methyl acetate to BSA and benzaldehyde was 2:2:1, [Bmim]F: 20 mol.%, reaction temperature: 20℃, reaction time: 4 h.

As mentioned above, the cation has good influence on the yield and selectivity of methyl cinnamate. The resultsshowed the [Bmim]F has the best performance. In addition, it could be discovered that the chain length in the cation could directly affect the results. The data of pyridine- and imidazole-type ILs-F obviously indicate that with the increase of chain length, the catalyticperformance attains to the peak and then reduces down. It was considered that the Si-O bond in BSA could be broken with the catalysis of fluoride anion in ILs-F, followed by generating acetamide anion,then

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onium amide base would form through the interaction between acetamide anionand cation that fromILs-F according to the reported results. [32, 42, 43]Although the catalytic function focuses on the fluoride anion, the molecular voidage of ILs-F would increase with the extension of chain length, which would be beneficial for the capacity of BSA molecules in ILs-F clusters. Therefore, the catalytic decomposition of BSA into strong base acetamide anion could be promoted in some degree, leading to be conducive to the enolization of methyl acetate. [44, 45]The onium amide base, in thisreaction, plays a role of strong base to abstract the α-H of esters, producing the enolate for the next aldol condensation step.So the increasing chain length would also enhance the steric hindrance of the α-H abstraction step. Moreover, for imidazole-type ILs-F, the 2-C of imidazole ring would transform to carbene due to the active 2-H. The raw material benzaldehyde could react with the carbene, leading to reduce of the product selectivity. But the prolonged chain length could also impede this process. Therefore, the suitable chain length would promote the formation of onium amide base and enolization of esters.

Effect of ILs-L

On the basis of the cation effect analysis, [Bmim] was confirmed as the optimum one.According to Scheme 1, the benzaldehyde would condense with 1-methoxy-1-trimethylsilyloxyethene (enolate of methyl acetate) to produce methyl cinnamate, which is also called Mukaiyama reaction. And as it known to all, Lewis acid catalysts could promote Mukaiyama reaction. When [Bmim]Clwas mixed with Lewis acidic metal chloride in suitable molar ratio, the ILs-L([Bmim]Cl/MCl_x) would exhibit Lewis acidity. Based on the research results of Kou, [46]when the molar fraction of metal chloride (CuCl, $FeCl_3$, $ZnCl_2$ and $AlCl_3$) in [Bmim]Cl/MCl_x attaches to 0.67, the ILs-L would present strong Lewis acidity. So a series of ILs-L ([Bmim]Cl/MCl_x), with metal chloride molar fraction of 0.67, were prepared and applied in combinationwith [Bmim]F for catalytic condensation of methyl acetate with benzaldehyde. And the experimental results were shown as Fig. 3.It

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indicatesthatwith the addition of ILs-L, the yield and selectivity of methyl cinnamatecould be enhanced obviously. And the increasing tendency could be ranked as [Bmim]Cl/CuCl<[Bmim]Cl/$FeCl_3$<[Bmim]Cl/$ZnCl_2$<[Bmim]Cl/$AlCl_3$. Then the pyridine probing IR was conducted for acidic concentration measurement, which were described in Fig. 4. It shows that these four types of ILs-L all have Lewis acid sites, [Bmim]Cl/CuCl and [Bmim]Cl/$AlCl_3$ also haveBrΦnsted acid sites. By comparing the IR spectra, the Lewis acidconcentration could also be ranked as [Bmim]Cl/CuCl< [Bmim]Cl/$FeCl_3$<[Bmim]Cl/$ZnCl_2$<[Bmim]Cl/$AlCl_3$, which is in accordance with the activity order. So it can be considered that the catalytic performance of ILs-L is related to the amount of Lewis acid sites.

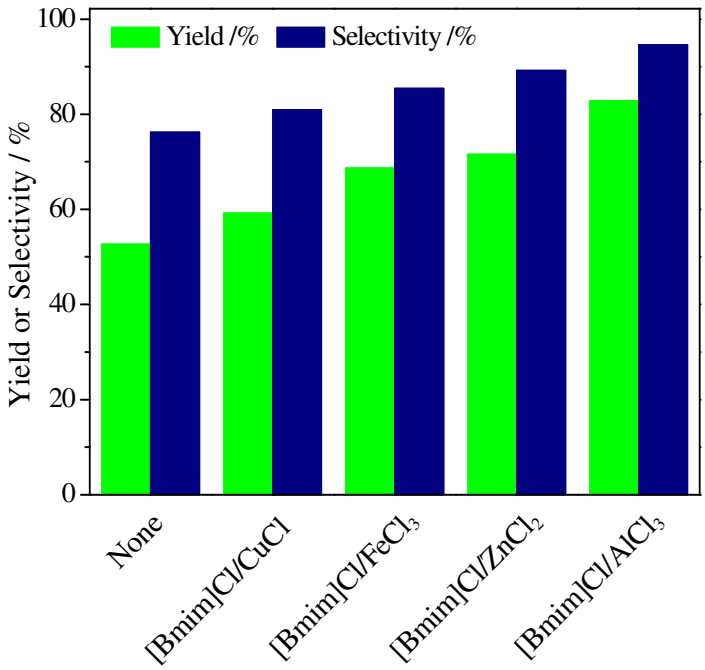

Fig. 3. Catalytic performance of different ILs-L

Reaction condition: benzaldehyde (0.2 mmol, 0.1 M in CH_2Cl_2), the molar ratio of methyl acetate to BSA and benzaldehyde was 2:2:1, [Bmim]F: 20 mol.%, ILs-L: 20 mol.% (molar fraction of MCl_x in ILs-L was 0.67), reaction temperature: 20℃, reaction time: 4 h.

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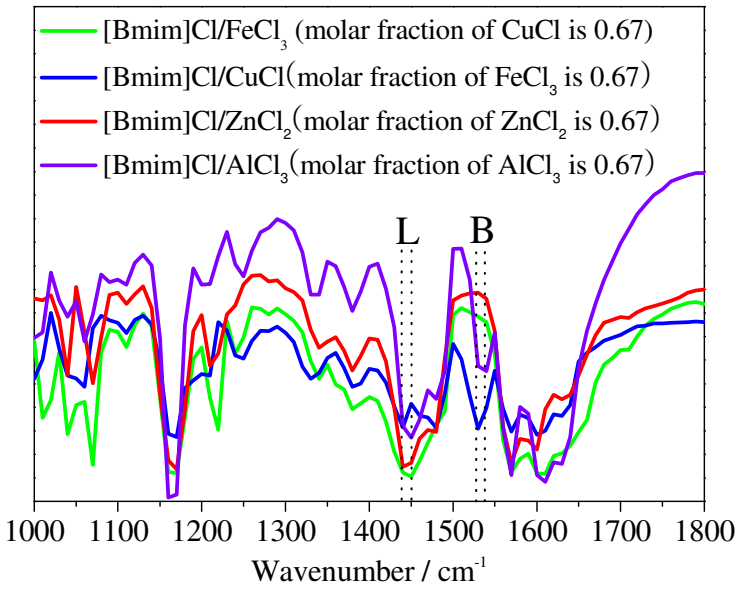

Fig. 4. Pyridine probing IR for acidity measurement

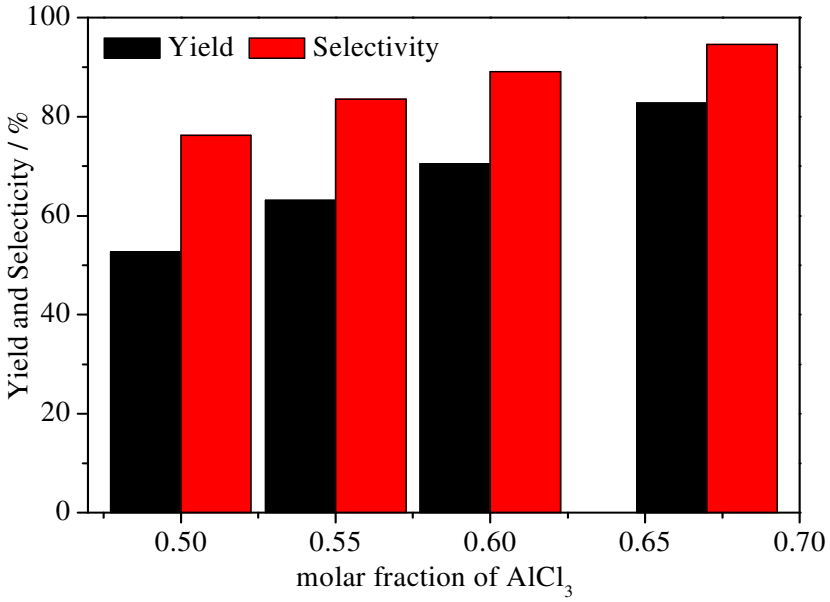

Fig. 5. Catalytic performance of [Bmim]Cl/$AlCl_3$ with different molar fraction of $AlCl_3$

Reaction condition: benzaldehyde (0.2 mmol, 0.1 M in CH_2Cl_2), the molar ratio of methyl acetate to BSA and benzaldehyde was 2:2:1, [Bmim]F: 20 mol. %, [Bmim]Cl/$AlCl_3$ (molar fraction of $AlCl_3$ changes from 0.50 to 0.67): 20 mol. %, reaction temperature: 20℃, reaction time: 4 h.

The effect of molar fraction of$AlCl_3$ was also investigated and the results were presented in Fig. 5. As it can been seen, with the increasing molar fraction of $AlCl_3$, the yield and selectivity ofmethyl cinnamate alsorise apparently. According to pyridine probing measurement results published by Kou and listed in Table 1, [46] with the molar fraction of $AlCl_3$ changing from 0.5 to 0.67, the predominant anionic

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species in [Bmim]Cl/$AlCl_3$ varies from $[AlCl_4]^-$ to $[Al_2Cl_7]^-$. The experimental results indicate that the $[Al_2Cl_7]^-$species play the important role on catalytic condensation between 1-methoxy-1-trimethylsilyloxyethene and benzaldehyde, while $[AlCl_4]^-$ shows no activity. In fact, when the molar fraction is 0.5, the [Bmim]Cl/$AlCl_3$ is neutral, but when it reaches to 0.67, [Bmim]Cl/$AlCl_3$ possesses strong Lewis acidity, which would be beneficial for the condensation step.Therefore, the [Bmim]Cl/$AlCl_3$, in which the molar fraction of $AlCl_3$ is 0.67, could be used in cooperation well with [Bmim]F for one-pot synthesis of methyl cinnamate from methyl acetate and benzaldehyde at mild condition.

Table 1 The effect of molar fraction of$AlCl_3$ on anionic species

Molar fraction of $AlCl_3$ in [Bmim]Cl/$AlCl_3$	Predominant anionic species
0.5	$[AlCl_4]^-$
0.55	$[AlCl_4]^-$ and $[Al_2Cl_7]^-$
0.6	$[AlCl_4]^-$ and $[Al_2Cl_7]^-$
0.67	$[Al_2Cl_7]^-$

Effect of solvent

In addition, the effect of solvent on the methyl cinnamate synthesis was also researched. It has been well known to all that the polar solvent would be benefit for polarity of α-(C-H) bond and α-H abstraction of carbonyl compounds. Thus, series polar solvents were selected for our reaction system. Interestingly, the influence of most polar solvent of THF and acetonitrile as shown in Table 2 are not as well as CH_2Cl_2 and CH_2Cl-CH_2Cl. Our experimental results show that the [Bmim]F and [Bmim]Cl/$AlCl_3$ has better solubility in CH_2Cl_2 and CH_2Cl-CH_2Cl than others. So it could be considered that in solvent of CH_2Cl_2 or CH_2Cl-CH_2Cl, the reaction could be treated as homogeneous catalysis systems, while it was liquid-liquid heterogeneous catalysts in others. Otherwise the onium enolate complexes should transfer from IL phase into the organic phase, which is also inefficient for the whole catalytic procedure. In addition, the polarity of CH_2Cl_2 is also suitable for α-proton abstraction,

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which could be supported by the research work of Atsushi and Downey. [47, 48]So it can be concluded that the solvent selected for the ILs catalyzed probase method should be polar and could as far as possible dissolve the [Bmim]F and [Bmim]Cl/$AlCl_3$ as well.

Table 2 Effect of solvent on synthetic results

Entry	Solvent	Yield /%	Selectivity /%
1	CH_2Cl_2	82.8	94.6
2	THF	70.4	92.1
3	CH_2Cl-CH_2Cl	75.5	93.2
4	toluene	52.7	75.4
5	acetonitrile	61.2	80.7

Reaction condition: benzaldehyde (0.2 mmol, 0.1 M in solvent), the molar ratio of methyl acetate to BSA and benzaldehyde was 2:2:1, [Bmim]F: 20 mol.%, [Bmim]Cl/$AlCl_3$ (the molar fraction of $AlCl_3$ was 0.67): 20 mol.%, reaction temperature: 20℃, reaction time: 4 h.

Mechanism analysis and kinetic studies

On the basis of impact analysis of cation, ILs-L, and solvent, the mechanism of one-pot synthesis of methyl cinnamate from methyl acetate and benzaldehyde using [Bmim]F in combination with [Bmim]Cl/$AlCl_3$ was investigated. In the light of the intermediates that detected with GC-MS (for MS information, ESI), the main reaction mechanism was illustrated as Scheme 3. The BSA firstly converted into strong base onium amide with the catalysis of [Bmim]F, then the α-H of methyl acetate was abstracted by such onium amide, generating *N*-trimethylsilyl acetamideand onium enolate. The onium amide could be *in-situ* recycled when onium enolate transformed into 1-methoxy-1-trimethylsilyloxyethene, followed by condensing with benzaldehyde to *β-O*-(trimethylsilyl) methyl phenylpropionatewith the catalysis of [Bmim]Cl/$AlCl_3$. The intermediate of *β-O*-(trimethylsilyl) methyl phenylpropionate could be further converted into methyl cinnamateand hydroxytrimethylsilanewith the catalysis of [Bmim]F. The GC-MS testing results also revealed that hydroxytrimethylsilaneand methyl cinnamate would convert into hexamethyl

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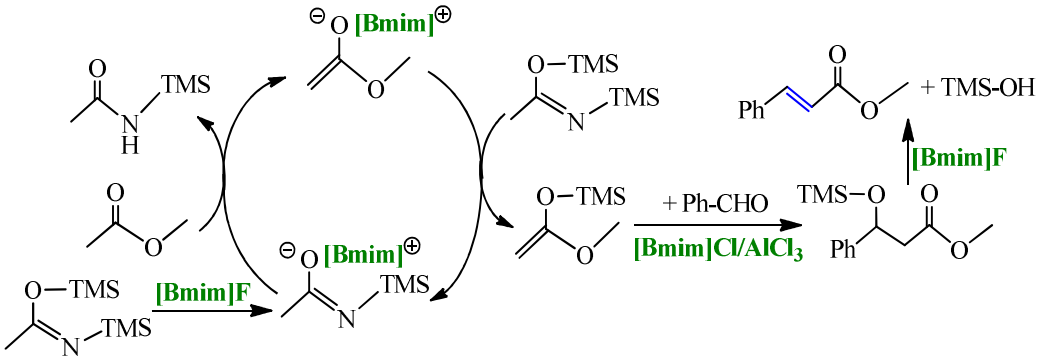
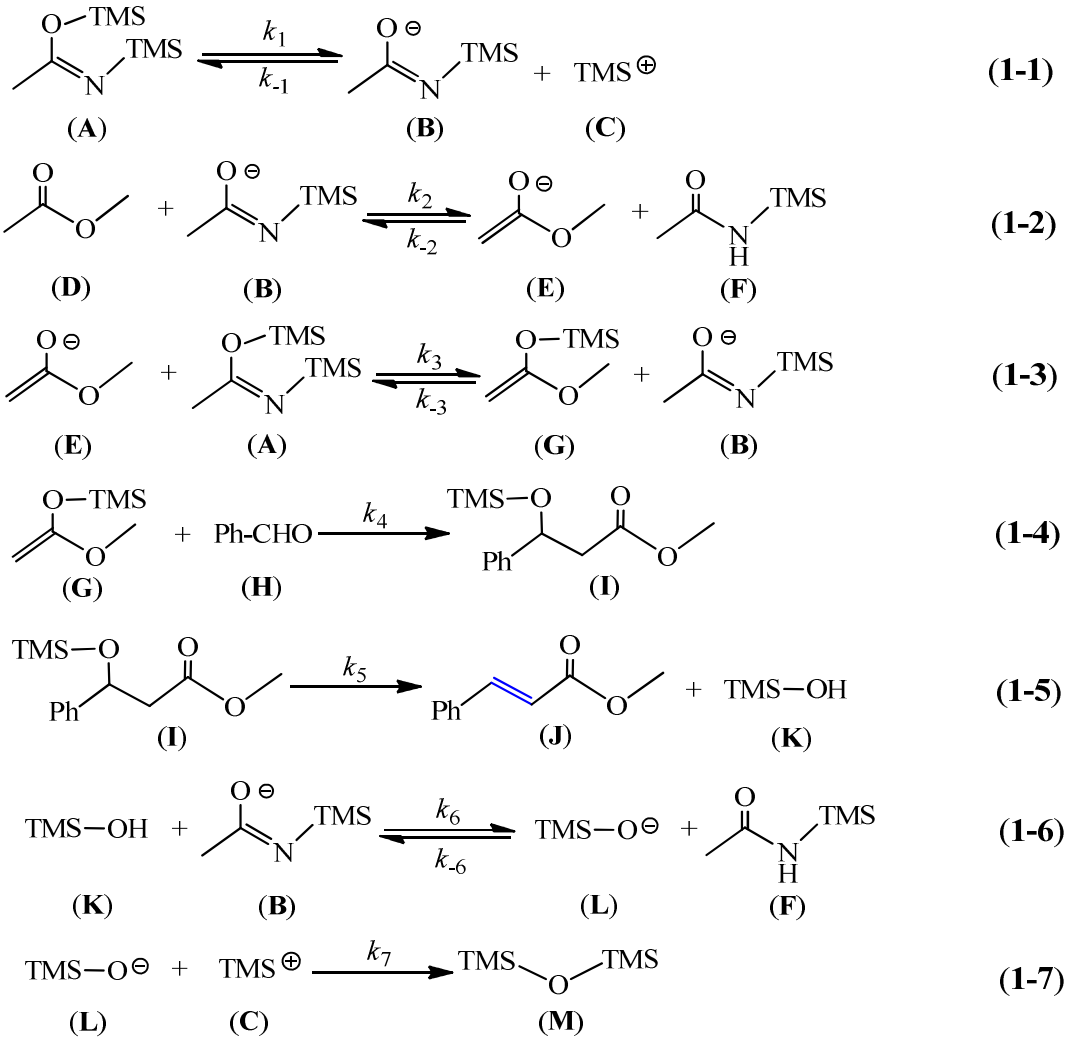
disiloxaneand trimethylsilyl cinnamaterespectively with prolonging reaction time.



Scheme 3 Mechanismanalysis for synthesis of methyl cinnamate catalyzed with [Bmim]F and [Bmim]Cl/$AlCl_3$ (the molar fraction of $AlCl_3$ is 0.67) using BSA as probase



Scheme 4 Mechanism-based kinetic model forone-pot synthesis of methyl cinnamate from methyl acetate and benzaldehyde catalyzed with [Bmim]F and [Bmim]Cl/$AlCl_3$ (the molar fraction of $AlCl_3$ is 0.67), using BSA as probase

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According to above mechanism analysis, the reaction in 3h at 283 K-298 K was selected for kinetic studies, resulting from the ignorable side reactions. And the elementary reactions from (**1-1**) to (**1-7**) were listed in Scheme 4. The reaction steps of (**1-1**), (**1-2**)and (**1-3**)were set as reversible and keep equilibrium due to the slow rate of (**1-5**). And reaction (**1-6**) was also considered as equilibrium due to the high activity of amide anion and [TMS-O]$^-$.According to the reaction steady-equilibrium principle, the equilibrium equations of (**1-2**),(**1-3**) and (**1-8**) could be obtained as formulas (***1***), (***2***), (***3***) and (***4***).

$$k_1 C_A C_D = k_{-1} C_B C_C \quad (1)$$

$$k_2 C_B C_D = k_{-2} C_E C_F \quad (2)$$

$$k_3 C_A C_E = k_{-3} C_B C_G \quad (3)$$

$$k_6 C_B C_K = k_{-6} C_F C_L \quad (4)$$

So the concentration of substrates ***C***,***G***and***L***could beexpressed asformula(***5***) and (***6***),respectively.

$$C_G = \frac{k_2 k_3 C_A C_D}{k_{-2} k_{-3} C_F} \quad (5)$$

$$C_C C_L = \frac{k_1 k_6 C_A C_K}{k_{-1} k_{-6} C_F} \quad (6)$$

Then the kinetic equations could be listed as (***7***) to (***14***) based on the model.

$$\frac{dC_A}{dt} = -k_4 C_G C_H - k_7 C_C C_L = -\frac{k_2 k_3 k_4 C_A C_D C_H}{k_{-2} k_{-3} C_F} - \frac{k_1 k_6 k_7}{k_{-1} k_{-6} C_F} \quad (7)$$

$$\frac{dC_D}{dt} = -k_4 C_G C_H = -\frac{k_2 k_3 k_4 C_A C_D C_H}{k_{-2} k_{-3} C_F} \quad (8)$$

$$\frac{dC_F}{dt} = -k_4 C_G C_H - k_7 C_C C_L = -\frac{k_2 k_3 k_4 C_A C_D C_H}{k_{-2} k_{-3} C_F} - \frac{k_1 k_6 k_7 C_A C_K}{k_{-1} k_{-6} C_F} \quad (9)$$

$$\frac{dC_H}{dt} = -k_4 C_G C_H = -\frac{k_2 k_3 k_4 C_A C_D C_H}{k_{-2} k_{-3} C_F} \quad (10)$$

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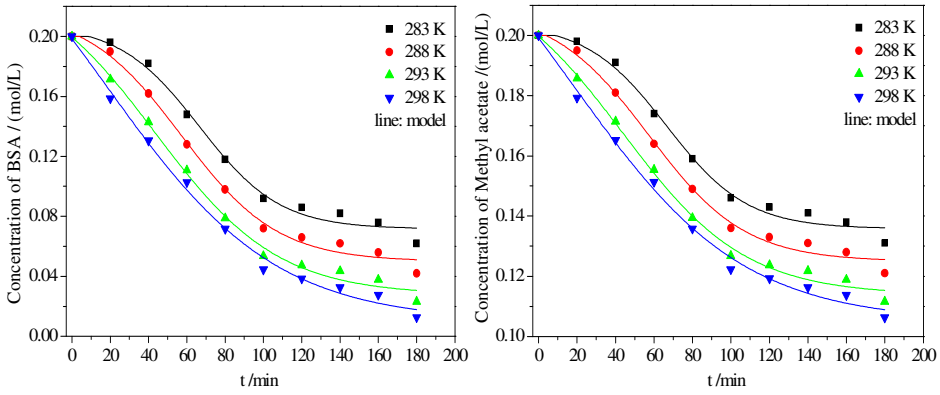
$$\frac{dC_I}{dt} = k_4 C_G C_H - k_5 C_I = \frac{k_2 k_3 k_4 C_A C_D C_H}{k_{-2} k_{-3} C_F} - k_5 C_I \quad (11)$$

$$\frac{dC_J}{dt} = k_5 C_I \quad (12)$$

$$\frac{dC_K}{dt} = k_5 C_I - k_7 C_C C_L = k_5 C_I - \frac{k_1 k_6 k_7 C_A C_K}{k_{-1} k_{-6} C_F} \quad (13)$$

$$\frac{dC_K}{dt} = k_7 C_C C_L = \frac{k_1 k_6 k_7 C_A C_K}{k_{-1} k_{-6} C_F} \quad (14)$$

Computational simulationfor the mechanism-based kinetic model was conducted by using Rung-Kutta method on matlab software. [14, 40]The temperature and concentration distribution under our reaction conditions could not been considered into account. And the obtained results were also compared with experimental concentration for the effect of reaction temperature and time, which were shown in Fig. 6. The experimental concentration of *β*-*O*-(trimethylsilyl) methyl phenylpropionateand hydroxytrimethylsilanewas also compared with the calculated data, which were presented in Fig. 7. The pre-exponential factor and activation energy of each elementary reaction were presented in Table 3.



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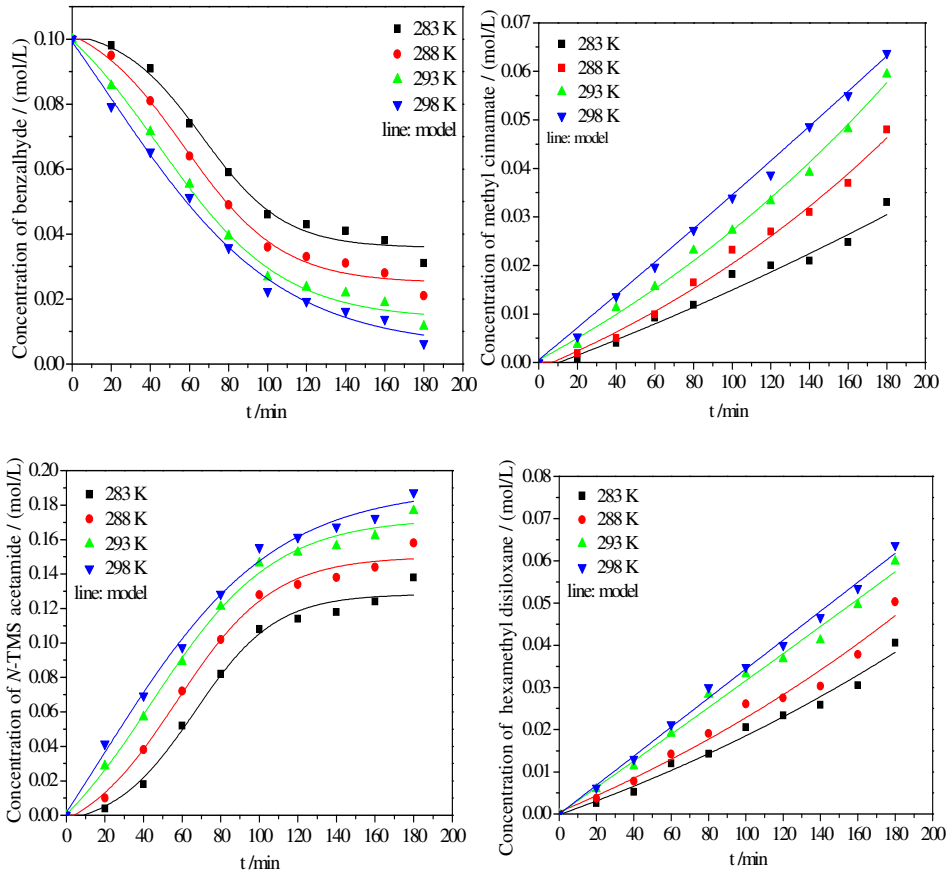

Fig. 6. Computational simulation results of kinetic model

From Fig. 6, it could be seen that the concentration of probase BSA, rawmaterials of methyl acetate and benzaldehyde drop fast in100 min, after that, the tendency becomes slow. While the concentration of methyl cinnamateand hexamethyl disiloxane increase with reaction temperature and time. And the concentration of *N*-trimethylsilyl acetamide enhances fast in 100 min, then tend to stable. Fig. 7 shows the error of the kinetic model, for *β*-*O*-(trimethylsilyl)methyl phenylpropionateand hydroxytrimethylsilane, the deviation between the calculated data and experimental concentration are all around acceptable 5 %. So the kinetic model should be believable at the temperatures from 283 K to 298 K and reaction times in180 min.

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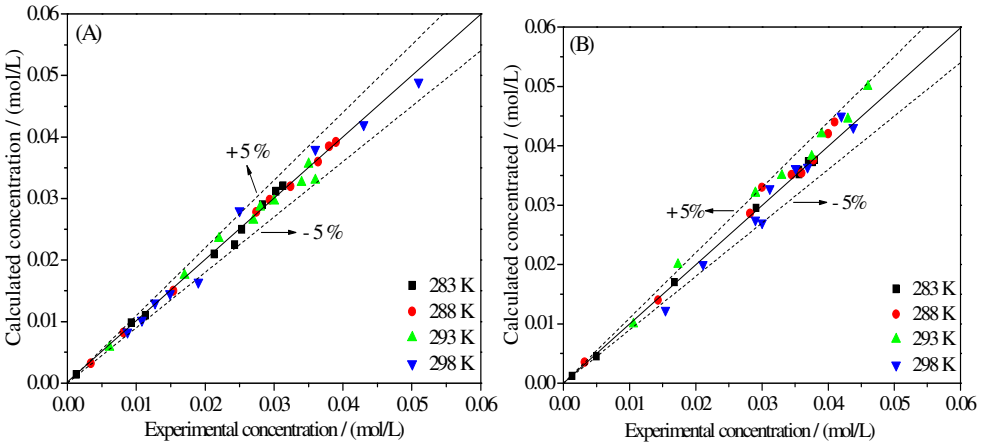

Fig. 7. Comparison of the experimental concentration with calculateddata: (A) *β-O*-(trimethylsilyl) methyl phenylpropionate, (B) hydroxytrimethylsilane

The pre-exponential factor and activation energy of each elementary reaction were listed in Table 3. For all equilibrium reactions, the activation energy of all forward reactions are lower than that of reverse, therefore, it is advantageous for the direction of methyl cinnamate formation. The activation energy of decomposition of BSA into amide anion is relatively low (23 ± 1.2 kJ/mol), which indicates the [Bmim]F has good catalytic performance. While the decomposition of *β-O*-(trimethylsilyl) methyl phenylpropionate into methyl cinnamate is more difficult than BSA with the catalysis of [Bmim]F.It is a common sense that the acidity of α-proton in unsubstituted ester is weaker than that in ketone, *β*-dicarbonyl compounds or esters that substituted with electron-accepting groups. So it is difficult for deprotonating α-proton of methyl acetate, and the activation energy is relatively high(33 ± 1.7kJ/mol) by comparison with others.But it still indicates the *in-situ* generated strong base onium amide is efficient for theα-proton abstraction process. The activation energy of 1-methoxy-1-trimethylsilyloxyethene formation, namely the recycle of onium amide, is low (18 ± 0.9 kJ/mol), which means this process is easy to proceed and the α-proton abstraction procedure could be also promoted. As for the condensation step between 1-methoxy-1-trimethylsilyloxyethene and benzaldehyde, the activation energy is the highest of all (43 ± 2.2 kJ/mol). Thus,it is treated as the rate-controllingstep. However, the energy barrier of hexamethyl disiloxane formation

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is the lowest among all steps.

Table 3 Pre-exponential factor and activation energy of each elementary reaction

Reaction step	Reaction Name	A	Ea / (kJ/mol)
(A) ⟶ (B) + (C)	BSA decomposition	2.8×10^{3}	23± 1.2
(B) + (C) ⟶ (A)	-	1.2×10^{4}	28 ± 1.4
(D) + (B) ⟶ (E) + (F)	deprotonation	6.2×10^{4}	33 ± 1.7
(E) + (F) ⟶ (D) + (B)	-	1.4×10^{5}	36 ± 1.8
(E) + (A) ⟶ (G) + (B)	trimethylsilylation	8.1×10^{2}	18 ± 0.9
(G) + (B) ⟶ (E) + (A)	-	5.3×10^{3}	25 ± 1.3
(G) + (H) ⟶ (I)	condensation	1.4×10^{6}	43 ± 2.2
(I) ⟶ (J) + (K)	product formation	2.0×10^{4}	30 ± 1.5
(K) + (B) ⟶ (L) + (F)	-	1.4×10^{3}	20 ± 1.0
(L) + (F) ⟶ (K) + (B)		1.3×10^{5}	35 ± 1.8
(L) + (C) ⟶ (M)		2.1×10^{2}	5 ± 0.3

The sensitivity analysis of significant reaction steps including BSA decomposition, ester deprotonation, enolate trimethylsilylation, condensation and product formation were carried out and the results were depicted in Fig. 8. It could be obviously discovered the condensation step was the most sensitive to reaction temperature, while the enolate trimethylsilylation was the adverse. The sequence could be ranked as condensation＞ester deprotonation＞product formation＞BSA decomposition＞enolate trimethylsilylation. And it is in accordance with the energy barrier of these reaction steps.

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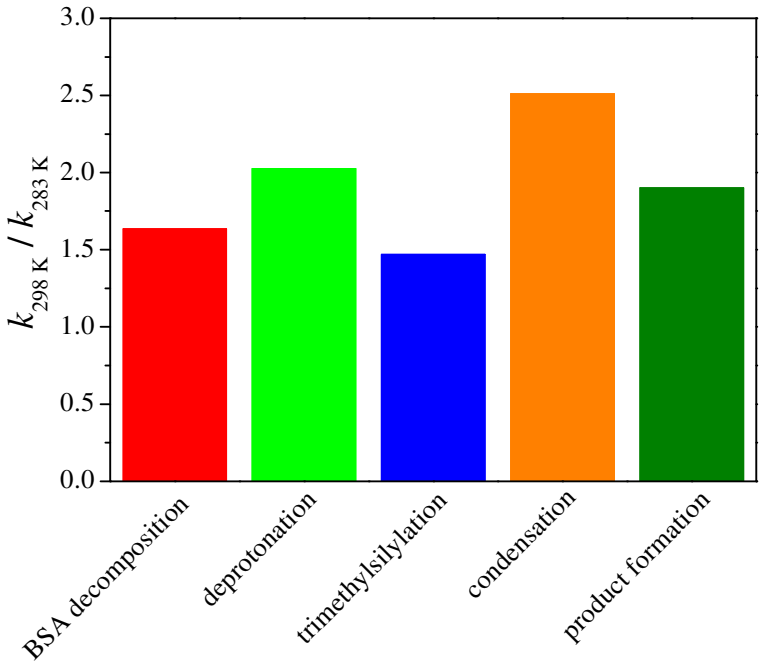

Fig. 8. Temperature sensitivity analysis for significant reaction steps

On the grounds of above kinetic studies, the equilibrium constant of each reversible reaction was calculated with reaction rate constant at different temperature, which was presented in Table 4. It could be believed that the rate constants of the forward reactionsare all higher than that of reverse, which are all benefit for the production of methyl cinnamate. By comparing these constants at different temperature, the order can be ranked as $\boldsymbol{K}_6 > \boldsymbol{K}_3 > \boldsymbol{K}_1 > \boldsymbol{K}_2$, which means the protonation of onium acetamide proceeds more thoroughly than other steps.

Table 4 Equilibrium constant of each reversible reaction under different temperature

ln $\boldsymbol{K}$	ln$\boldsymbol{K}_1$	ln$\boldsymbol{K}_2$	ln$\boldsymbol{K}_3$	ln$\boldsymbol{K}_6$
T/K				
283	0.693	0.471	1.089	1.851
288	0.656	0.449	1.038	1.740
293	0.620	0.427	0.988	1.633
298	0.586	0.407	0.939	1.530

The enthalpy change ($\Delta \boldsymbol{H}$) is one of the most important thermodynamic

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parameters of reversible reactions. Thus, the enthalpy change of each reversible reaction, exhibited in Table 5, was also calculated from equilibrium constant under different temperatures through Van't Hoff formula that expressed as formula (15). And the Van't Hoff plot over reaction temperature was shown in Fig. 9.The results were also creditableowing to the acceptable error listed in Table 5.

$$\ln K = -\frac{\Delta H}{RT} + C \tag{15}$$

As shown in Table 5, it could be obtained that all the reversible reactions are exothermal. The enthalpy change of the firstthree equilibrium reactions are close to each other and the reason could be concluded as follows. The thermal effects of these reactions are small, so the absolute value of enthalpy change are all small, which is in agreement with the fact of room-temperature reaction.By comparing the absolute value of enthalpy change with each other, the order could be ranked as $\Delta \boldsymbol{H}_6 > \Delta \boldsymbol{H}_3 > \Delta \boldsymbol{H}_1 > \Delta \boldsymbol{H}_2$.The interaction between$TMS^+and[TMS\text{-}O]^-$ is the highest, which indicatesthis reaction is the most sensitive to reaction temperature among the reversible reactions. However, as noted above, the absolute value of enthalpy change are all relatively low. It reveals that the reaction temperature has little influence on these equilibrium constants and the previous assumption of steady-equilibrium is reasonable. These equilibrium reactions are very important for the formation of methyl cinnamate. Therefore, the thermodynamic studies on equilibrium reactions involving equilibrium constant and enthalpy change could make for understanding this new catalytic process.

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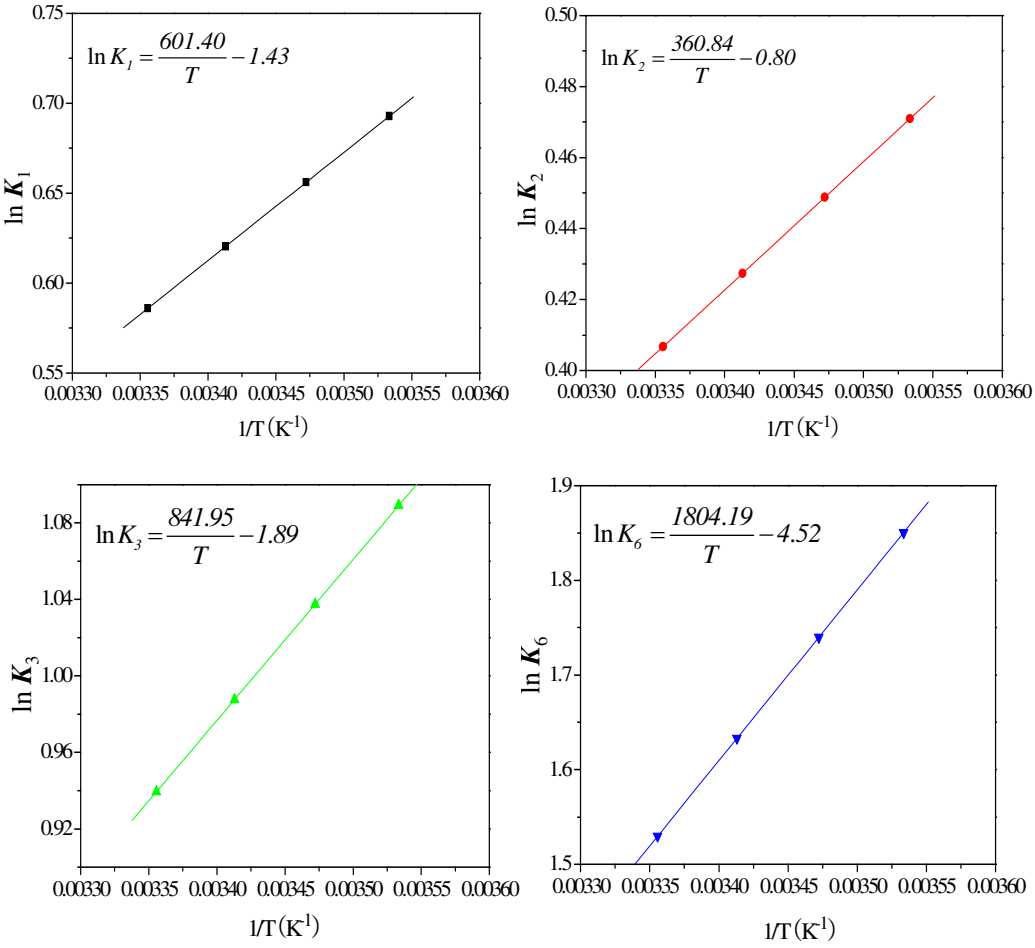

Fig. 9. Van't Hoff plot for enthalpy change of each reversible reaction

Table 5 Enthalpy change of each equilibrium reaction

Equilibrium reaction	△***H***/ (kJ/mol)	***C***	R^2
(A) $\overset{K_1}{\rightleftharpoons}$ (B) + (C)	-5.00	-1.43	0.99
(D) + (B) $\overset{K_2}{\rightleftharpoons}$ (E) + (F)	-3.00	-0.80	0.99
(E) + (A) $\overset{K_3}{\rightleftharpoons}$ (G) + (B)	-7.00	-1.89	0.99
(K) + (B) $\overset{K_6}{\rightleftharpoons}$ (L) + (F)	-15.00	-4.52	0.99

Substrates extension

In addition to methyl cinnamate, other unsubstituted acetateand propionates esters for this one-pot condensation reaction in our ILs catalyzed system were also evaluated, and the experimental results were presented in Table 6. A

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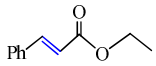
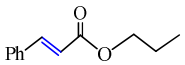
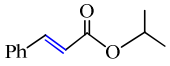
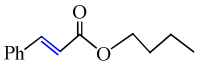
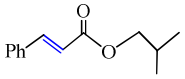
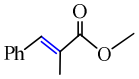
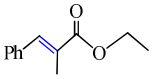
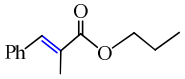
comparisonbetween benzaldehyde and acetate derivatives shows a decrease in yield with the increasing length of carbon chain that combined with the oxygen atom in ester bond. This observed decreasing tendency could be related to the increasing difficulty in enolization of esters. The substituted methyl group of the α-carbon atom and the length of carbon chain that combined with the oxygen atom in ester bond could contribute to the steric hindrance and difficulty in polarizing carbonyl groups, sequentially affecting the acidification and abstraction of the α-proton. The addition of electron-donating group in benzaldehydes could promote the yield, while the electron-withdrawing group decreases the yield.This results prove the catalytic performance of ILs-L. However, thetrend is not very sharp, which shows a cooperative effect between the strong basicity of onium amide and Lewis acidity of [Bmim]Cl/$AlCl_3$ (the molar fraction of $AlCl_3$ is 0.67). The enolate anion generated from the deprotonation of esters with onium amide could also condense with benzaldehydes directly, during which the substituted electron-withdrawing group is more advantageous.

Table 6 One-pot synthesis of methyl cinnamate from esters and benzaldehyde catalyzed with [Bmim] F and [Bmim]Cl/$AlCl_3$[a]

Entry	product	Yield /%[b]	Selectivity /%[b]
1		79.5	94.3
2		80.7	93.6
3		80.2	92.9
4		78.6	94.1
5		79.4	93.7
6		75.2	93.2
7		74.3	92.6
8		73.9	93.0

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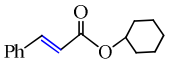
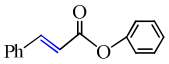
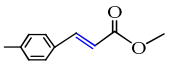
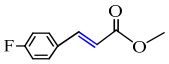
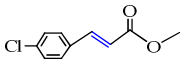
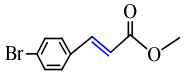
9		70.1	93.2
10		68.8	89.9
11		84.2	95.0
12		79.5	94.0
13		80.3	93.8
14		81.2	92.9

[a]Reaction condition: benzaldehyde (0.2 mmol, 0.1 M in CH_2Cl_2), the molar ratio of methyl acetate to BSA and benzaldehyde was 2:2:1, [Bmim]F: 20 mol. %, [Bmim]Cl/$AlCl_3$ (the molar fraction of $AlCl_3$ was 0.67): 20 mol. %, reaction temperature: 20℃, reaction time: 4 h.[b]determined by GC-MS, GC part for quantification and MS part for structure confirmation.

Conclusions

A series of ILs-F were firstly prepared and applied in combination with ILs-L for one-pot catalytic synthesis of *α, β*-unsaturated esters from esters and aldehydes.In this catalytic system, BSA as a probase could be converted into strong base onium amide with the catalysis of ILs-F, meanwhile esters could be deprotonated by such strong base and transformed into enolates. The onium amide could be also recycled through the trimethylsilyl etherification of enolates with BSA. While ILs-L play important role in condensation between enol silyl ether and aldehyde. The cations of ILs-F,Lewis acidic concentration and strength of ILs-Las well assolventhave effect on this reaction. The kinetic parameters and equilibrium constants of each reaction step were calculated through mechanism-based kinetic analysis and simulation. The results also revealed the condensation process was the rate-controlled step, all the equilibrium reactions were exothermal and insensitive to reaction temperature. This ILs catalyzed probase method was also universal for synthesis of other *α, β*-unsaturated esters besidesmethyl cinnamate.The yield and selectivity could reach up 84.2 % and 95.0 % respectively.

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