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Journal Name

ARTICLE

Direct Synthesis of Carbamate from CO_2 Using a Task-Specific Ionic Liquid Catalyst

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A superbase-derived protic ionic liquid (IL, [DBUH][OAc]) catalyst was used to directly synthesize carbamate from an amine, CO_2, and a silicate ester. This IL catalyst was easily prepared using its precursors, DBU, and acetic acid. Using 10 mol% of the catalyst under a CO_2 pressure of 5 MPa in acetonitrile at 150°C, carbamate was isolated in up to 96% yield. Specifically, aliphatic and aromatic amines were activated even though aromatic amines exhibited low activities because of their low pK_a values. Other functional groups in amines were barely activated, affording exclusive chemoselectivity for amine activation. Isotope labeling experiments indicated that the proton in the counter cation is crucial in the catalytic cycle to produce water. In addition, a chemical shift corresponding to a mixture of aniline and [DBUH][OAc] was observed in the ^{1}H NMR spectrum, related to the formation of hydrogen bonds between aniline and basic acetate anion. The experimental results indicated that the designed IL catalysts require a protonated cation and a basic anion.

Introduction

All over the world, carbon is not only an essential element in everyday life, but also plays an important role in energy industries, because common energy resources, for instance, petroleum, coal, and natural gas, are derived from carbon. The development of modern industries leads to increased emissions of carbon dioxide (CO_2), which is a crucial component in the global carbon cycle.[1] CO_2 is the final product obtained from the oxidation of elemental carbon, hydrocarbons, and carbohydrates, as well as primarily increasing the earth's temperature. Global CO_2 emission is 36 billion tons in 2016.[2] Efforts have been focused on the development of methodologies for the recycling and conversion of CO_2 into valuable chemicals.[3] As a C1 building block, CO_2 is an inexpensive, non-flammable, and non-toxic gas, which can be added via the C–H, C–C, C–N, C–O, and C–S bonds to form alcohols, carboxylic acids, and their derivatives, e.g., urea, organic carbonates, and thiazoles.[4] Some of the methodologies have been industrialized. For instance, 150 million tons of urea was produced from CO_2 in 2000.[5] Nevertheless, in 2016, this number increased to 180 million tons,[6] and in this process, 132 million tons of CO_2 was consumed.

Meanwhile, carbamates (urethanes, RNHCOOR') are valuable chemicals in agricultural chemistry for producing pesticides,[7] medicinal chemistry for synthesizing hepatitis C virus (HCV) inhibitors and β-/γ-secretase inhibitors for treating Alzheimer's disease,[8] as well as in polyurethane (PU) industries.[9] Conventionally, PUs are synthesized in two steps: first, phosgene ($COCl_2$) and amine react to form isocyanate; second, polyaddition occurs between isocyanates and polyols, affording PUs. However, phosgene is highly toxic. In an attempt to replace $COCl_2$, researchers have investigated novel routes to produce PUs.[10] Carbamates are key precursors for synthesizing non-isocyanate polyurethane (NIPU). Scheme 1 shows the various C1 synthons for synthesizing carbamates. The carbon sources can be thought to be $COCl_2$ and its derivatives, organic carbonates, and CO_2.[11] Phosgene is toxic (Scheme 1A), which has been stated previously. Organic carbonate appears to be sustainable (Scheme 1B); however, its preparation increased the total number of steps in carbamate synthesis.[12] For example, dimethyl carbonate (DMC) is prepared from MeOH and CO_2, with a dehydrating reagent. The direct use of CO_2 as a C1 building block obviously minimizes the total steps in the carbamate synthesis. In 2016, over six million tons of carbamates were produced from CO_2, which is predicted to reach eleven million tons in 2030.[6] Various R' sources (Scheme 1C), e.g., organohalide (R'X),[13] alcohol (R'OH),[14] and metal alkoxide,[15] are used in the primary routes for directly synthesizing carbamates from CO_2. In the past two decades, considerable efforts have been developed in this regard; however, the disadvantages of these sources limit their use for synthesizing carbamates. For example, a majority of the organohalides are not natural products, possibly causing potential environmental issues. Moreover, alcohols appear to be a greener alternative as compared to organohalides; however, only aliphatic amines can be activated because aromatic amines are poor nucleophiles, with low pK_a values.[16]

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Electronic Supplementary Information (ESI) available: ^{1}H NMR, $^{13}C\{^1H\}$ NMR, and GC–MS spectra. See DOI: 10.1039/x0xx00000x

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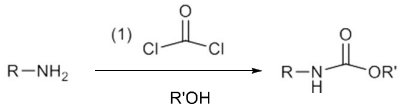
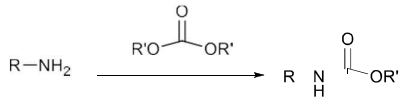
The use of metal alkoxide in industry is not preferred because of the stoichiometric $M(OR)_n$ coupling with amine and CO_2.

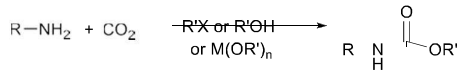
(A) Phosgene and its derivatives as a C1 synthon:



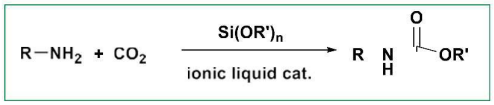
(B) Organic carbonate as a C1 synthon:



(C) CO_2 as a C1 synthon:



This work:



- **R = both alkyl and aryl**
- **Metal free; halogen free**
- **Sustainable carbon and alkoxide sources**
- **Easy catalyst preparation**
- **Isolated yield up to 96%**

Scheme 1 Evolution of C1 synthons for synthesizing carbamates

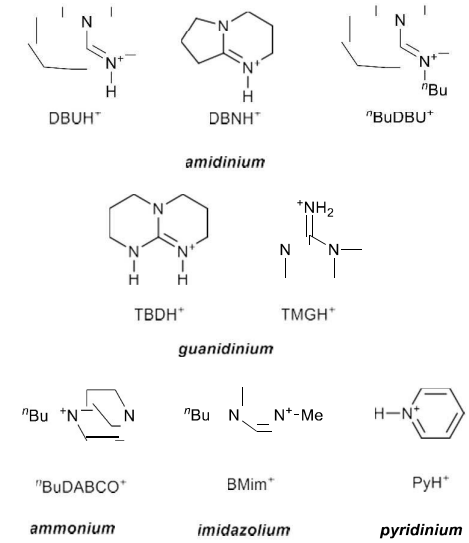
Ionic liquids (ILs) are molten salts, and majority of these ILs exhibit a high boiling temperature, excellent thermostability, solubility in various solvents, and negligible vapour pressures.[17] Task-specific ionic liquids (TSILs) are ILs with designed functional groups,[18] which are extensively used for CO_2 capture and utilization (CCU) and catalysts for various transformations to cyclic carbonates, ureas, and oxazolidinones.[18a, 19] Recently, our group has reported the synthesis of a carbamate from amine, CO_2, and silicate esters using zinc acetate as the catalyst;[20] however, an N-donor ligand, such as 1,10-phenanthroline (phen), is required to promote the reaction. Encouraged by the success of this synthesis, herein, we report a superbase-derived protic TSIL served as a catalyst for the synthesis of carbamates. This protocol is a metal- and halogen-free methodology to prepare carbamates from both aliphatic and aromatic amines. The organocatalyst is easily prepared using commercially available precursors, and both precursors are natural products. This catalytic system provided a green, sustainable route to synthesize carbamates, with a yield of up to 96%.

Results and Discussion

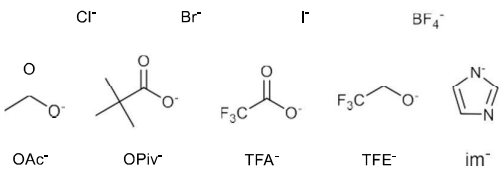
Catalyst screening and applications.

In order to search an optimum catalyst, a series of ILs were synthesized. Precursors to the counter cations, for instance, 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU), 1,5-diazabicyclo(4.3.0)non-5-ene (DBN), triazabicyclodecene (TBD), 1,1,3,3-tetramethylguanidine (TMG), 1,4-diazabicyclo[2.2.2]octane (DABCO), 1-butyl-3-methylimidazolium (BMim), and pyridine (Py), were selected, and acetic acid (AcOH), pivalic acid (PivOH), trifluoroacetic acid (CF_3CO_2H, TFA), trifluoroethanol (CF_3CH_2OH, TFE), and HCl as the precursors for the counter anions. Scheme 2 shows their structures. Notably, the precursors to the counter cations were basic, even superbases, e.g., DBU, TBD, and DBN, while the counter anion precursors were acids. The synthesis of ILs is straightforward, involving the careful mixing of a base and an acid in a Schlenk tube under N_2.[21] Even though heating was not required for neutralization, an oil bath at 60°C was sufficient to decrease the viscosity of the reaction mixture. ILs such as [^{n}BuDABCO][X] (X = Cl and Br) have been synthesized from DABCO and ^{n}BuCl or ^{n}BuBr in CH_2Cl_2.[22] [^{n}BuDBU][OAc] was synthesized from KOAc and [^{n}BuDBU][Br], the latter one generated from DBU and ^{n}BuBr in CH_2Cl_2.[21, 22c] [BMim][X] series compounds (X = Cl, Br, I, and BF_3) are commercially available. [PyH][Cl] was synthesized from pyridine and a 12 mol L^{-1} HCl aqueous solution.

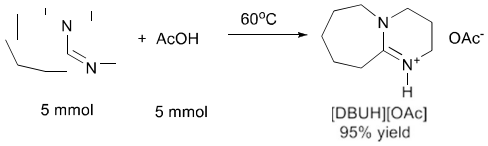
(A) Counter cations:



(B) Counter anions:



(C) Preparation of [DBUH][OAc]:



Scheme 2 Components and synthesis of ionic liquid

With various ILs in hand, their activities were examined (Scheme 3). Learning from our previous experience, aniline, the

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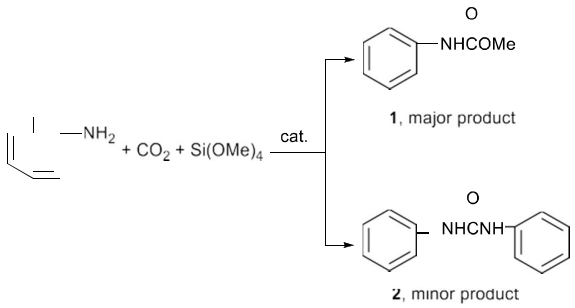
simplest aromatic amine, was selected as the substrate, and 2 equiv. of tetramethyl orthosilicate ($Si(OMe)_4$, TMOS) was selected as the silicate ester for synthesizing methyl phenyl carbamate (**1**) at 150°C for 24 h with MeCN (3 mL) as the solvent. Products were analyzed by high performance liquid chromatography (HPLC); in addition to the major product **1**, 1,3-diphenylurea (**2**), a by-product, was obtained via intertransformation. Table 1 summarizes the screening of the catalysts. First, DBU-based ILs were examined (entries 1–9). Using 10 mol% of [DBUH][OAc] (entry 1), **1** and **2** were obtained in 96% and 3%, respectively. However, with decreasing catalyst loading to 5 mol% (entry 2) and 1 mol% (entry 3), the yields of **1** decreased to 88% and 70%, respectively, indicating that catalyst loading affects the yield of **1** for a reaction time of 24 h. Hence, the catalyst loading is set to 10 mol% in further studies. Moreover, using other basic counter anions, e.g., $OPiv^-$, TFA^-, TFE^-, and im^- (entries 4–7), greater than 90% yields for **1** were observed. On the other hand, with Cl^- as the counter anion (entry 8), **1** was obtained in only 18% yield. These results implied that the basicity of counter anions strongly affects the reactivity of ILs, which was in agreement with previous studies.[21, 23] Nonetheless, basicity has been reported to affect the metal-base-catalyzed CO_2 transformation.[20, 24] Moreover, carboxylate- or carbonate-assisted metalation deprotonation was considered as key process for C–H activations.[25] O- or N-donor basic anions can abstract protons from aniline, forming hydrogen bonds, while the hydrogen bond is barely formed with Cl^-. *n*-Butyl-substituted IL [^{n}BuDBU][OAc] was also a poor catalyst (Table 1, entry 9), implying that the protonation of DBU is imperative for catalysis. Note that DBU itself was found as a promoter for carbamate synthesis in our study (entry 10) and in previous reports,[13c, 26] however, 10 to 100 equiv. DBU was used, [13c, 26] largely beyond catalyst scale. Furthermore, the difficulty of separation of DBU from product by Liu and coworkers[21] pushed us to choose DBU-derived IL as the preferred catalyst. From our results, counter anion and substitution group of counter cation of superbase-derived ILs are two keys for catalyst design. Furthermore, the addition of 1 equiv. DBU and 1 equiv. AcOH (entry 11), precursors of [DBUH][OAc], did not decrease the activity too much.



Scheme 3 Synthetic route

[DBNH][OAc], which is another amidinium-based catalyst, afforded **1** in moderate yield (67%, entry 12). In addition, guanidinium-based catalysts [TBDH][OAc] and [TMGH][OAc] effectively catalyzed the synthesis of carbamates (entries 13 and 14, respectively); however, their reactivities considerably depended on the basicity of the counter cation: using [TBDH][OAc] (pK_a = 26.0 for $TBDH^+$),[27] **1** was obtained in 92%, while **1** was obtained in only 25% using [TMGH][OAc] (pK_a = 23.3 for $TMGH^+$).[28]

Table 1 Screening of catalysts[a]

Entry	catalyst	yield of **1** (%)[b]	yield of **2** (%)[b]
1	[DBUH][OAc]	96	3
2[c]	[DBUH][OAc]	88	4
3[d]	[DBUH][OAc]	70	11
4	[DBUH][OPiv]	95	3
5	[DBUH][TFA]	96	3
6	[DBUH][TFE]	93	5
7	[DBUH][im]	92	4
8	[DBUH][Cl]	18	28
9	[^{n}BuDBU][OAc]	39	21
10	DBU	87	6
11[e]	DBU and AcOH	85	7
12	[DBNH][OAc]	67	3
13	[TBDH][OAc]	92	4
14	[TMGH][OAc]	25	14
15	[^{n}BuDABCO][OAc]	27	18
16	[^{n}BuDABCO][Cl]	5	15
17	[^{n}BuDABCO][Br]	<1	2
18	[BMim][Cl]	1	12
19	[BMim][Br]	<1	3
20	[BMim][I]	<1	3
21	[BMim][BF_4]	13	21
22	[PyH][Cl]	12	11
23[f]	[DBUH][OAc]	92	5
24[g]	[DBUH][OAc]	90	5
25[h]	[DBUH][OAc]	90	5
26[i]	[DBUH][OAc]	88	4
27[j]	[DBUH][OAc]	86	4

[a] Reaction conditions: 1 mmol aniline, 2 mmol TMOS, 10 mol% catalyst, 3 mL MeCN, 5 MPa CO_2, 24 h, 150°C. [b] Yields were determined by HPLC using toluene as the internal standard. [c] 5 mol% of the catalyst was used. [d] 1 mol% of the catalyst was used. [e] 1 mmol DBU and 1 mmol AcOH. [f] Catalyst was re- used once. [g] Catalyst was re-used twice. [h] Catalyst was re-used three times. [i] Catalyst was re-used four times. [j] Catalyst was re -used five times.

Ammonium-based catalysts [^{n}BuDABCO][X] and imidazolium -based catalysts [BMim][X] (X =Cl, Br, I, and BF_4), barely catalyzed the formation of carbamate, because of the low basicity and aprotic cations (entries 15–21). As compared to [^{n}BuDABCO][Cl] and [^{n}BuDABCO][Br], [^{n}BuDABCO][OAc] slightly promoted the reaction, probably related to the contribution from the acetate anion; however, the yield of **1** was not sufficiently high (27%, entry 15). The same observation was made with the use of a pyridine-based catalyst [PyH][Cl] (12% of **1**, entry 22). Based on the results in Table 1, the performance of amidinium- and guanidinium-based catalysts was better than that of the ammonium-, imidazolium-, and pyridinium-based catalysts. The performance of basic anions (e.g., carboxylate, im^-, and TFE^-) was better than that of halide and BF_4^-. Notably, the same result was observed for entries 1 and 5; however, [DBUH][OAc] was selected as the first choice rather than [DBUH][TFA] because of the cost-effectiveness and

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sustainability of the AcOH precursor as compared to the CF_3CO_2H precursor. The [DBUH][OAc] catalyst was reused at least five more times (entries 23 to 27), indicating that the catalyst exhibits thermal stability and negligible deactivation.

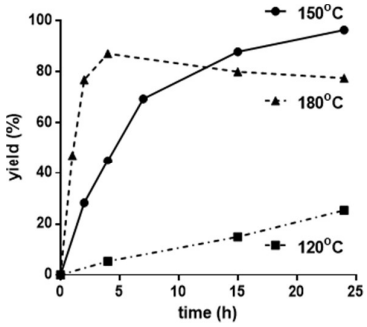

Figure 1 Temperature-dependent catalytic synthesis of **1**. Reaction conditions: 1 mmol aniline, 2 mmol TMOS, 0.1 mmol [DBUH][OAc], 3 mL MeCN, 5 MPa CO_2. The yield of **1** was determined by HPLC analysis. The yield of **2** was omitted for clarity.

The [DBUH][OAc]-catalyzed carbamate synthesis significantly depended on temperature, owing to the requirement of the Si–O bond cleavage in TMOS. The bond dissociation energy (BDE) of the Si–O bond is approximately 130 kcal mol^{-1}, greater than those of the N–H and C–O bonds.[29] Figure 1 shows the yield of **1** as a function of temperature. At 120°C, the yield of **1** slowly increased, and only 25% of **1** was obtained after 24 h. Moreover, in the initial step, the reaction at 150°C was eight times more rapid than that at 120°C, and the yield of **1** increased to 96% after 24 h. The initial reaction rate at 180°C was 2.7 times more rapid than that at 150°C. HPLC results indicated that the yield of **1** is 87% after 4 h, yet the yield decreases to 77% during 24 h, caused by the chemical interconversion between **1** and **2**: at a high temperature of 180°C, the reaction appeared to be more rapid, while the product thermodynamically shifted from **1** to **2**. Based on temperature-dependent experiments in Figure 1, a temperature of 150°C and a reaction time of 24 h are selected as the optimum conditions for the activation of various amines in further studies.

Table 2 Reactivities of various silicate esters[a]

silicate ester	**1** yield (%)[b]	hydrolysis product of silicate ester
$Si(OMe)_4$	96	$(MeO)_3SiOSi(OMe)_3$
$MeSi(OMe)_3$	88	$Me(MeO)_2SiOSi(OMe)_2Me$
$Me_2Si(OMe)_2$	37	$Me_2(MeO)$ $SiOSi(OMe)$ Me_2
Me_3SiOMe	8	$Me_3SiOSiMe_3$

[a] Reaction conditions: 1 mmol aniline, 0.1 mmol [DBUH][OAc], 3 mL MeCN, 5 MPa CO_2, 24 h, 150°C. Silicate esters: 2 mmol $Si(OMe)_4$, 2.67 mmol $MeSi(OMe)_3$, 4 mmol $Me_2Si(OMe)_2$, and 8 mmol Me_3SiOMe. [b] The yield of **1** was determined by ^1H NMR analysis.

Meanwhile, the applications of organosilicon compounds for the conversion of CO_2 to valuable products have attracted considerable attention. Hydrosilanes and polymethylhydrosiloxane (PMHS) can serve as reductants for the *N*-formylation and *N*-methylation of amines.[30] Silanediols have been used as a hydrogen-bonding donor catalyst to produce cyclic carbonate from epoxide.[31] Notably, PMHS is obtained from silicon industrial waste,[30b] and silanols are naturally abundant,[32] which can be used as sustainable reagents for the transformation of CO_2. In this study, silicate esters were selected as alkoxy donors for synthesizing carbamates, which were prepared from abundant SiO_2 or silicate minerals.[33] The amount of alkoxy groups strongly affects the reactivity of silicate esters in carbamate synthesis. $Me_nSi(OMe)_{4-n}$ (n = 0, 1, 2, and 3) was selected as the silicate esters, and the molarity of the methoxy group was maintained constant in every experiment. With the decrease in the number of methoxy groups, the yield of **1** decreased from 96% to 88%, 37%, and 8%, respectively (Table 2). This dramatic decrease is related to the hydrolysis rate of silicate esters.[34] With a high amount of alkoxy groups, the hydrolysis rate of the silicate ester was more rapid, thereby promoting reactivity. The hydrolysis products of $Me_nSi(OMe)_{4-n}$ (n = 0, 1, 2, and 3) were determined by ^{29}Si nuclear magnetic resonance (NMR), shown in Table 3 and Figure 2, and gas chromatography–mass spectrometry (GC–MS, see supporting information).

Table 3 ^{29}Si NMR analysis[a]

silicate ester	chemical shift of silicate ester (ppm)	chemical shift of hydrolysis product (ppm)
$Si(OMe)_4$	−78.29	−85.78
$MeSi(OMe)_3$	−39.08	−47.91
$Me_2Si(OMe)_2$	−0.76	−10.83
Me_3SiOMe	18.41	7.41

[a] ^{29}Si NMR (79.5 MHz) spectra were recorded in CD_3CN using J. Young NMR tubes under N_2.

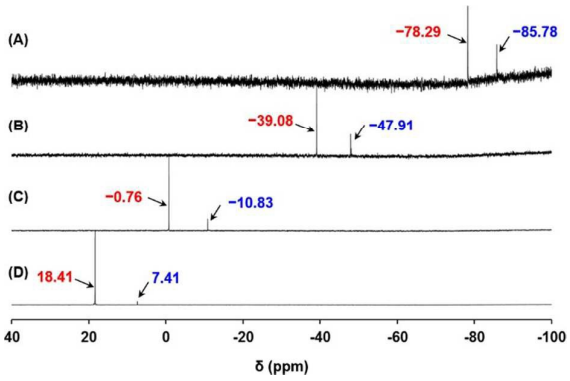

Figure 2 ^{29}Si NMR (79.5 MHz) analysis using various silicate esters: (A) $Si(OMe)_4$; (B) $MeSi(OMe)_3$; (C) $Me_2Si(OMe)_2$; and (D) Me_3SiOMe. Numerical values in red and blue denote the chemical shifts of the silicate esters and hydrolysis products, respectively.

CO_2 was considered as the carbonyl donor in the carbamate synthesis. As all experiments involving CO_2 were performed using autoclaves, safety issues are mentioned herein even though CO_2 is a non-toxic, inflammable gas. The CO_2 gas cylinder was located in an area with fresh air, and the autoclave with high-pressure CO_2 was tightly sealed and placed in a safe zone. Figure 3 shows the effect of CO_2 pressure on the yield of carbamates. Under a CO_2 pressure of 1 MPa, **1** was obtained in

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75% yield. Moreover, a similar yield was obtained despite the change in the CO_2 pressure from 3 MPa to 13 MPa, due to excellent gas solubility in IL. The negligible difference with respect to the CO_2 effect prompted the selection of a relative low-density CO_2 for carbamate synthesis. High-density supercritical CO_2 ($scCO_2$) was not required, further indicating that addition of CO_2 in carbamate synthesis is not the rate-determining step.

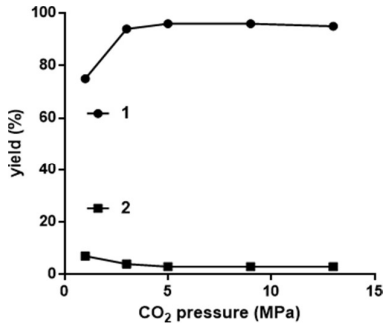
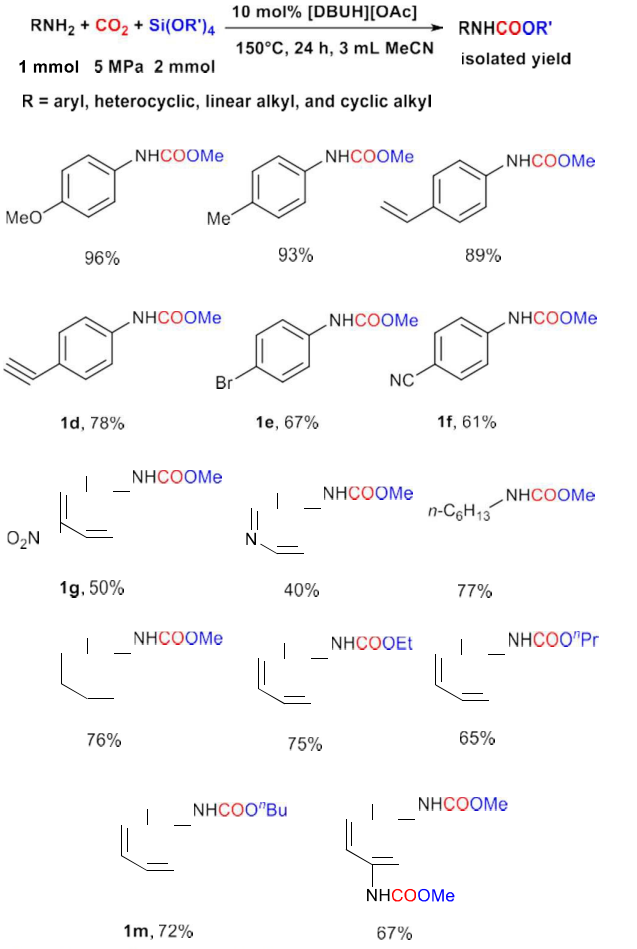


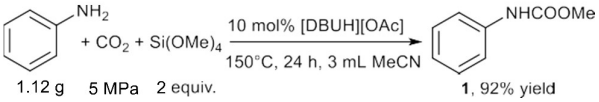
Figure 3 Effect of CO_2 pressure on the yield of carbamate. Reaction conditions: 1 mmol aniline, 2 mmol TMOS, 0.1 mmol [DBUH][OAc], 3 mL MeCN, 24 h, 150°C. Carbamate yield was determined by HPLC analysis.

With the optimized reaction conditions, the substrate scope was extended to various substituted amines, affording their corresponding carbamates directly using CO_2 (Scheme 4). Using substituted aniline, the isolated product yield varied from 50% to 96% during 24 h. Notably, electron-donating groups promoted carbamate formation (**1a**–**1d**), whereas electron-withdrawing groups hindered the reaction (**1e**–**1g**). Only the NH_2 group served as the activation site, while the other functional groups, e.g., –Br, $–NO_2$, –CN, C=C, and C≡C, were not affected, providing excellent chemoselectivity to NH_2 activation. In addition to aniline analogs, heterocyclic amines, aliphatic amines, and cycloalkylamine were activated to yield their corresponding carbamates (**1h**–**1j**). Notably, several studies have reported the activation of aliphatic amines rather than aromatic amines owing to the low reactivity of aromatic amines. Our research highlights the activation of *both aliphatic and aromatic amines* for synthesizing carbamates. Using various silicate esters, the yields of the corresponding carbamate ranged from 65% to 75% (**1k**–**1m**). Compound **1n** was the corresponding carbamate of toluene diisocyanate (2,4-TDI), which is an important starting material in the PU industry.

In addition, our synthetic protocol was expanded from the laboratory scale to the gram scale (Scheme 5). The reaction was carried out in a 20 mL autoclave using 1.12 g aniline (12 mmol) as the substrate. After 24 h, **1** was obtained in 92% yield. Although the yield was slightly less than that obtained on the laboratory scale, the protocol employed herein affording a high yield of **1** served as a potential route for industrial preparation.



Scheme 4 Carbamate synthesis using various substrates



Scheme 5 Gram-scale synthesis of **1**

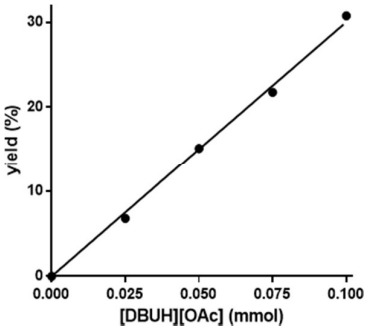


Figure 4 Determination of the rate order of [DBUH][OAc]. Reaction conditions: 1 mmol aniline, 2 mmol TMOS, 3 mL MeCN, 5 MPa CO_2, 4 h, 150°C. The amount of [DBUH][OAc] varied from 0.025 mmol to 0.1 mmol. The yield of **1** was determined by HPLC analysis. The yield of **2** was omitted for clarity.

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Mechanism study.

With the excellent activity of [DBUH][OAc], the mechanism for the catalytic synthesis of carbamate, especially the crucial requirements for designing the catalyst, was investigated. First, the rate order with respect to the catalyst was examined (Figure 4). Various amounts of [DBUH][OAc] as the catalyst were used to synthesize **1**, and the initial rates were obtained from the initial yield of **1** for a reaction time of 4 h. Using 2.5 mol%, 5.0 mol%, 7.5 mol%, and 10 mol% of the catalyst, **1** was obtained in yields of 6.8%, 15.1%, 21.8%, and 30.8%, respectively. The linear correlation indicated that the reaction is first order with respect to [DBUH][OAc].

The results from Scheme 4 suggested that the substitution group of aniline largely influenced the reactivity. Hammett plot was shown in Figure 5.[35] With methoxy, methyl, nitro, and cyano substituted aniline, a linear relationship and negative slope was obtained (ρ = −0.6095), indicating the binding between electrophilic $DBUH^+$ and nucleophilic amines.

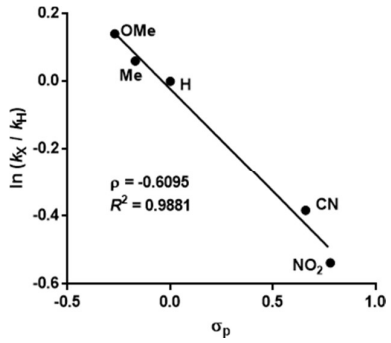

Figure 5 Hammett analysis of catalytic carbamate synthesis from *para*-substituted anilines. Reaction conditions: 1 mmol *para*-substituted aniline (p-X-C_6H_4-NH_2, X = OMe, Me, H, CN, and NO_2), 0.1 mmol [DBUH][OAc], 3 mL MeCN, 5 MPa CO_2, 150°C, 1 h. The linear correlation resulted in a slope of ρ = −0.6095 with a coefficient of determination of R^2=0.9881.

As indicated by the results shown in Table 1, two requirements are crucial for a highly reactive IL—a protic counter cation and a basic counter anion—respectively. [DBUH][OAc] satisfied both these requirements. To examine the role of the proton in the cation, an isotope labeled catalyst or substrate was used to trace the proton. Deuterium-labeled IL [DBUD][OAc] was synthesized from DBU and AcOD. The stoichiometric reaction between aniline, TMOS, and [DBUD][OAc] under CO_2 afforded product **1** (Figure 6A). From GC−MS analysis, both **1**-H (m/z = 151) and **1**-D (m/z = 152) were observed. Apparently, the deuterium atom in **1**-D originated from [DBUD][OAc], indicative of the dehydrogenation of the catalyst in the transition state. Analogously, the stoichiometric reaction between aniline-d_2 ($PhND_2$), TMOS, and [DBUH][OAc] under CO_2 furnished both **1**-D and **1**-H from GC−MS analysis (Figure 6B). This result is consistent with that shown in Figure 6A. Furthermore, ^{1}H NMR spectra of the mixtures revealed 33% and 52% proton (deuterium) exchange of the NH (ND) peaks, respectively (supporting information).

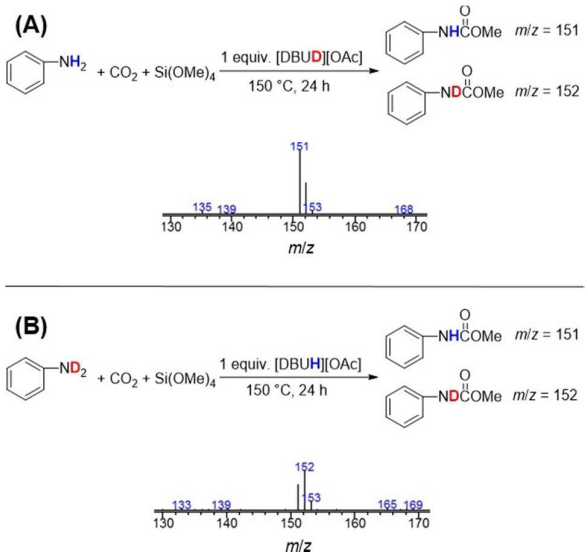

Figure 6 GC−MS analysis of **1** from isotope labeled materials. Reaction conditions: 1 mmol aniline, 2 mmol TMOS, 1 mmol [DBUH][OAc], 5 MPa CO_2, 24 h, 150°C. (A) Using [DBUD][OAc] instead of [DBUH][OAc]; (B) Using aniline-d_2 ($PhND_2$) instead of aniline.

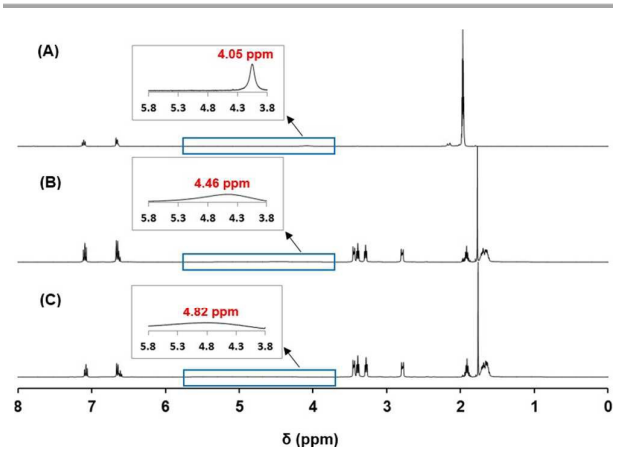

Figure 7 ^{1}H NMR (400 MHz, CD_3CN) analysis of (A) 1.0 M aniline; (B) 1.0 M aniline and 1.0 M [DBUH][OAc]; (C) 1.0 M aniline and 2.0 M [DBUH][OAc]. Inset: Magnified regions showing NH_2 shifts.

Using secondary amines, e.g., *N*-methylaniline, as the substrate, the corresponding carbamate was barely formed, leading us to consider the isocyanate pathway. Isocyanate has been reported as an intermediate in the synthesis of carbamates,[14f, 20] ureas,[36] benzimidazolones,[21, 37] and quinazoline-2,4(1*H*,3*H*)diones.[23c, 23h, 38] TMOS is considered to be a methoxy donor for **1**. The hydrolysis of TMOS yields MeOH, which directly reacts with isocyanate. Previously, our group, as well as other researchers, has reported good catalyst performance using basic anions.[20-21, 23 -24] The counter anion is considered to abstract protons from aniline. A hydrogen bond is formed with OAc^-. This interaction was barely observed between aniline and Cl^-. In addition, a high carbamate yield was

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observed with the use of counter anions such as $OPiv^-$, TFA^-, TFE^-, and im^-, with $DBUH^+$ (Table 1, entries 4–7). Either oxygen or nitrogen can serve as the hydrogen-bonding donor. The hydrogen bonding interaction was observed by ^1H NMR (Figure 7). The NH_2 group of aniline in CD_3CN exhibited a chemical shift of 4.05 ppm. With the addition of 1 equiv. of [DBUH][OAc], the peak shifted to 4.46 ppm, and looked broader. The addition of another equiv. of [DBUH][OAc] (a total of 2 equiv.) caused the peak to shift to 4.82 ppm. The chemical shift was in good agreement with the formation of hydrogen bonds between [DBUH][OAc] and aniline; hence, with increasing amounts of [DBUH][OAc], an increased chemical shift was observed. Such a large ^1H NMR chemical shift was also observed for a mixture of aniline and [DBNH][OAc] or [TBDH][OAc] in CD_3CN (supporting information). However, with 1.0 equiv. of [DBUH][Cl], the chemical shift of the NH_2 group in aniline shifted from 4.05 ppm to 4.28 ppm (Figure 8), which was less than that of [DBUH][OAc]. This result indicates a weaker interaction between aniline and [DBUH][Cl].

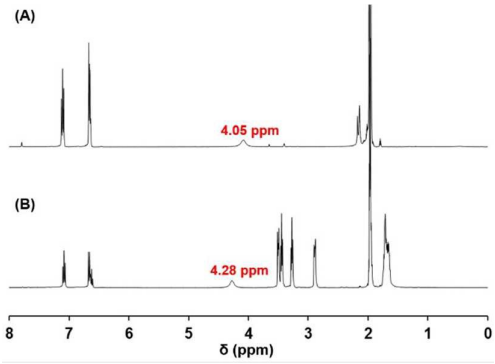
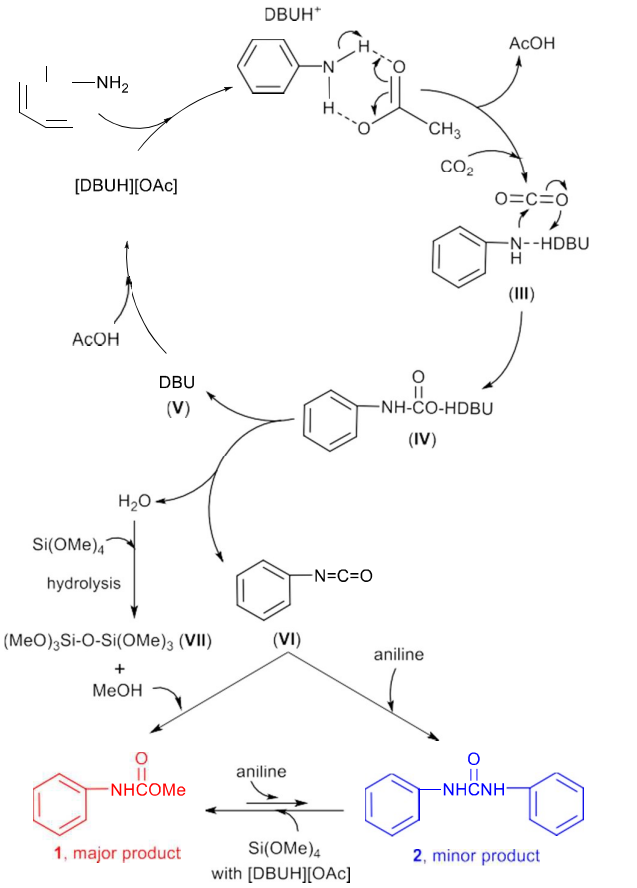


Figure 8 ^1H NMR (400 MHz, CD_3CN) analysis of (A) 1.0 M aniline; (B) 1.0 M aniline and 1.0 M [DBUH][Cl].

Scheme 6 shows the proposed mechanism based on the experimental results. First, the proton in aniline is activated by the [DBUH][OAc] catalyst (**I**), and the formation of hydrogen bonds between [DBUH][OAc] and aniline promotes the abstraction of proton in aniline (**II**), yielding AcOH and **III**. Second, CO_2 is inserted between PhNH and DBUH (from **III** to **IV**). Notably, the formation of carbamic acid (PhNHCOOH) directly from aniline and CO_2 is ruled out: the formation of carbamic acid from aliphatic amine and CO_2 is straightforward; however, this process appears to be difficult using aromatic amine owing to the low pK_a values of aromatic amines.[16] Next, phenyl isocyanate (**VI**) is formed, affording DBU (**V**) and H_2O. Isocyanate can be considered as an important intermediate as the major product **1** and minor product **2** are generated from isocyanate.

The hydrolysis of TMOS yields siloxane (**VII**) and MeOH; the latter is considered the direct OMe donor of **1**, while using MeOH in place of MeCN as the solvent did not yield **1**, indicating the interaction between the stronger nucleophile MeOH with $DBUH^+$, rather than formation of (**III**). In addition, **2** can be generated from isocyanate and aniline; however, with large amounts of TMOS, the yield of **2** is negligible because of the shift in the chemical equilibrium to **1**. In MeCN at 150°C, 87% yield of **1** could be generated from **2** and TMOS with the catalyst.



Scheme 6 A plausible mechanism

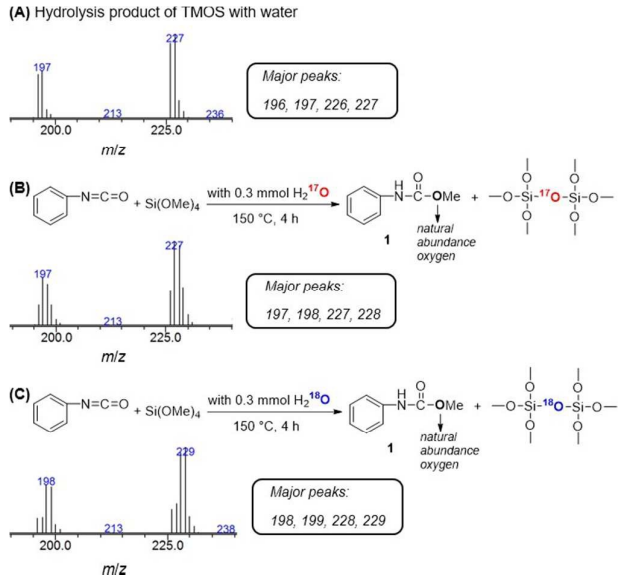


Figure 9 GC–MS analysis of the products from phenyl isocyanate and TMOS with the addition of ^{17}O or ^{18}O labeled water.

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The oxygen in water generated from (**IV**) to (**VI**) is finally the part of either **1** or hydrolysis product siloxane (**VII**). Adding ^{17}O or ^{18}O labeled water could track this oxygen (Figure 9). The reaction between phenyl isocyanate (**VI**) and TMOS yielded **1** and siloxane (**VII**) without any catalyst, which was reported previously.[20] The addition of $H_2{}^{17}O$ (Figure 9B) or $H_2{}^{18}O$ (Figure 9C) increased *m*/*z* values of (**VII**) determined by GC–MS. Moreover, we did not observe the increase of *m*/*z* values of **1**, suggesting that water was involved in the formation of siloxane (**VII**), rather than **1**. The methoxy group of **1** is from TMOS via Si–O cleavage.

Conclusions

Using a series of the prepared TSILs, [DBUH][OAc] was found to be the optimum catalyst to synthesize carbamate, with isolated yields of up to 96%, directly from an amine, CO_2, and a silicate ester. Notably, both aliphatic and aromatic amines can be activated by the developed protocol, broadening the potential applications in organic synthesis, drug discovery, and agricultural chemistry, as well as in the PU industry. The key step in the mechanism involves the activation of the N–H bond of aniline using the basic counter anion of the IL. In addition, protic cations are necessary as H_2O was formed in the catalytic cycle. [DBUH][OAc] meets these two requirements, and its straightforward preparation, thermostability, and reusability facilitated a greener route to synthesize carbamates. Currently, the design of other catalysts as well as studies on CO_2 transformation are underway in our laboratory.

Experimental Section

Materials

Unless stated otherwise, all chemicals were purchased from Sigma-Aldrich, Tokyo Chemical Industry (TCI), or Wako Chemicals in the best grade, stored under N_2, and used without further purification. Aniline-d_2 ($PhND_2$, 99% D) was purchased from C/D/N Isotopes. $H_2{}^{17}O$ (50% ^{17}O) was purchased from Nukem Isotopes. $H_2{}^{18}O$ (97% ^{18}O) was purchased from Sigma-Aldrich. CO_2 was purchased from Showa Tansan (99.99%). Caution: High-pressure CO_2 gas cylinders should be handled with care and located in an open area with fresh air, although no accident was encountered.

Instruments

Catalytic reactions were carried out in a 10 mL stainless steel autoclave equipped with a gas-pressure monitor (maximum pressure of 25 MPa). All the oxygen-free operation was conducted in either a glove box or a Schlenk line. Reaction mixtures were heated in a Sibata Chemi–300 Synthesizer. ^1H, $^{13}C\{^1H\}$, and ^{29}Si NMR spectra were recorded using a Bruker-400 NMR spectrometer at room temperature. Product mixtures were analyzed on a Shimadzu HPLC system with a Kinetex 5 µm C18 column and detected at 254 nm absorption. The sample was carried out in MeOH/H_2O (v:v = 7:3) as the mobile phase at 40°C with 0.5 mL min^{-1} flow rate. Carbamates were isolated on a single channel automated flash chromatography Yamazen AI–580 system using dichloromethane and *n*-hexane as the eluents. Molecular weights were determined using a Shimadzu GCMS–QP2010 Plus GC–MS system. High resolution mass spectroscopy (HR–MS) spectra were carried out in a Bruker MicroTOF II spectrometer.

General procedure for the synthesis of [DBUH][OAc]

[DBUH][OAc] was synthesized according to a previously reported procedure.[21, 39] DBU (0.76 g, 5.0 mmol) and AcOH (0.30 g, 5.0 mmol) were added to a 25 mL Schlenk tube. The reaction mixture was heated to 60°C, and after 18 h, unreacted materials were removed *in vacuo* to yield a colorless oil (1.01 g, 95%). ^1H NMR (400 MHz, D_2O): δ (ppm) 3.45 (d, 2H, *J* = 9.2 Hz), 3.39 (t, 2H, *J* = 5.8 Hz), 2.49 (d, 2H, *J* = 10.0 Hz), 1.88 (p, 2H, *J* = 6.0 Hz), 1.81 (s, 3H), 1.667–1.508 (m, 6H). ^{13}C NMR (100 MHz, D_2O): δ (ppm) 180.6, 165.9, 54.1, 48.2, 37.9, 32.8, 28.4, 25.8, 23.3, 22.8, 18.9. Other ILs were also synthesized according to previously reported procedures.[22, 23i, 40]

General procedure for the synthesis of 1

[DBUH][OAc] (21.2 mg, 0.1 mmol), MeCN (3 mL), aniline (93 mg, 1 mmol), and TMOS (304 mg, 2 mmol) were added in a 10 mL autoclave with a stir bar under N_2. The autoclave was tightly sealed and filled with CO_2 to 3 MPa. The autoclave was heated to 150°C, and the pressure was adjusted to 5 MPa. After 24 h, the autoclave was cooled to ambient temperature, and CO_2 was gently released. Next, toluene (85.3 mg, 0.1 mL) as the internal standard was added to the mixture. A small amount of the mixture was filtered for HPLC analysis. The isolated material was purified by automated flash chromatography with dichloromethane and *n*-hexane as eluents. All of the isolated products (**1a**–**1n**) were characterized by ^1H NMR, $^{13}C\{^1H\}$ NMR, and GC–MS (supporting information), consistent with either literature values or authentic materials.[13a, 20, 41]

The catalyst re-use experiments were carried out in a same way with our reported method.[20]

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Table of contents:

An easily synthesized ionic liquid was used as an organocatalyst to synthesize carbamates directly from amine, CO_2, and silicate esters.