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Efficient Acid–Base Bifunctional Catalysts for the Fixation of CO_2 with Epoxides under Metal- and Solvent-Free Conditions

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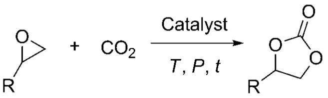
A series of acid–base bifunctional catalysts (ABBCs) that contain one or two Brønsted acidic sites in the cationic part and a Lewis-basic site in the anionic part are used as efficient catalysts for the synthesis of cyclic carbonates by cycloaddition of CO_2 to epoxides, without the use of additional co-catalyst or co-solvent. The effects of the catalyst structures and various reaction parameters on the catalytic performance are investigated in detail. Almost complete conversion can be achieved in 1 h for propylene oxide using $[\{(CH_2)_3COOH\}_2im]Br$ under mild reaction conditions (398 K and 2 MPa). Furthermore, the catalyst can be recycled over five times without substantial loss of catalytic activity. This protocol is found to be applicable to a variety of terminal epoxides, producing the corresponding cyclic carbonates in good yields and high selectivities. A synergistic effect of the acidic and the basic sites as well as suitable hydrogen-bonding strength of ABBCs are considered crucial for the reaction to proceed smoothly. The activities of the ABBCs increase remarkably with increasing carboxylic-acid chain length of the cation. This metal- and solvent-free process thus represents an environmentally friendly process for BTC-catalyzed conversion of CO_2 into value-added chemicals.

Introduction

Many efforts towards the fixation of CO_2 have been reported during the past two decades. An important incentive is the problem of global warming, caused mainly by CO_2. Another reason for these efforts is the use of CO_2 as a C_1 feedstock in organic synthesis.[1] Atom-efficient cycloaddition of CO_2 to epoxides (Scheme 1) is one of the most successful examples of CO_2 fixation, producing cyclic carbonates that find use as, amongst others, excellent aprotic polar solvents, intermediates for the pharmaceutical and fine chemical industries, and precursors for polycarbonate materials.[1–2] Therefore, it is not surprising that these kinds of reactions have been studied extensively.



Scheme 1. Synthesis of cyclic carbonates from CO_2 and epoxides.

Numerous catalysts for the synthesis of cyclic carbonates have been developed successfully. Among these, there have been many reports on imidazolium, ammonium, phosphonium and pyridinium salts, many of which may be classified as ionic liquids, as efficient catalysts for CO_2 fixation through the synthesis of cyclic carbonates from epoxides.[3–8] The combination of these salts with Lewis acidic co-catalysts has resulted in many diverse and flexible "platforms," establishing highly effective catalytic systems.[3–8] Although the advances are significant, unsatisfactory activities, harsh reaction conditions, the water and/or air sensitivity of the metal-containing catalysts, and/or the need for organic solvents (e.g., DMF, toluene, CH_2Cl_2) are still disadvantages that need to be overcome. Therefore, research towards a metal- and solvent-free catalyst system that combines stability with activity under relatively mild reaction conditions is essential from the viewpoints of large-scale manufacturing and environmental concerns.

Recently, research interest in task-specific ionic liquids has increased strongly because these "tailor-made" materials can be designed for specific applications in diverse areas, ranging from synthetic and catalytic chemistry to biotechnology, electrochemistry, and materials science by introducing certain functional groups into the cation or/and anion of traditional ionic liquids.[9–15] Among these, imidazolium salts that contain carboxylic acidic groups have attracted much attention because they offer the new possibility of developing environmentally friendly acidic catalysts. This is due to a combination of the advantages of liquid acids and solid acids, that is, uniform acid sites, stability in water and air, ease of separation, and reusability.[10–15] They have been applied to numerous fundamental organic transformations, such as Friedel–Crafts alkylation,[10f]

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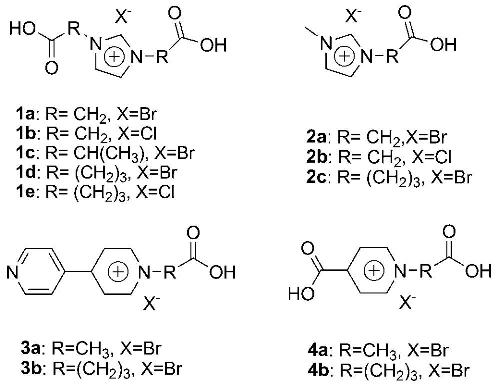
condensation,[11c] Beckmann rearrangement,[11e] esterification,[12b,14b] and toluene carbonylation.[14a]

Han and co-workers made an attempt to use carboxylic acid groups in functionalized ammonium salts (HBetX, X = Cl, Br, I) for the synthesis of cyclic carbonates from CO$_2$ and epoxide.[16a] The co-existence of a hydrogen-bond donor (–CO$_2$H), ammonium cation, and halide anion led to a synergy effect, promoting the reaction.[16a] However, the activity of the catalysts was still unsatisfactory, and further effects of the carboxylic acid group structure on the activities of these betaine-based salts were not investigated. In 2005, a series of imidazolium chlorides with one or two carboxylic acidic substituent, and their zwitterions, were synthesized and characterized by Fei et al.[15] Subsequently, these types of carboxylic-acid-functionalized imidazolium salts were applied to several reactions, such as the aerobic oxidation of alcohols,[17a] oxidative desulfurization of fuels,[17b] and palladium-catalyzed selective oxidation of styrene.[17c] However, to the best of our knowledge these Brønsted acid–Lewis base bifunctional imidazolium-type compounds were not applied to the synthesis of cyclic carbonates.

Herein, we report the first use of four kinds of acid–base bifunctional catalysts (Scheme 2) as catalysts for the reaction of epoxides with CO$_2$. More importantly, the effect of the catalyst structure on catalytic performance was investigated in detail. The catalysts were proved to be efficient for the chemical fixation of CO$_2$, being environmentally friendly substitutes for Lewis-acid/Lewis-base binary catalytic systems.



Scheme 2. Acid–base bifunctional catalysts used in this study.

Results and Discussion

Effect of catalysts

The reaction of propylene oxide (PO, **5b**) with CO$_2$ to produce propylene carbonate (PC, **6b**) was chosen as the model reaction to test the catalytic activities of various acid–base bifunctional catalysts (ABBCs), and the results are summarized in Table 1.

Compared to the other catalysts, [{(CH$_2$)$_3$CO$_2$H}$_2$im]Br **1d** exhibits the best activity and selectivity (Table 1<xtabr1). As a traditional ionic liquid, 1-ethyl-3-methylimidazolium bromide ([emim]Br) by itself is not efficient for the synthesis of cyclic carbonate (entry 2). However, its activity is greatly improved in the presence of equal amount of CH$_3$CO$_2$H (entry 3). A better result (91% PO conversion) is obtained in the presence of more CH$_3$CO$_2$H (entry 4). When CH$_3$CH$_2$OH is introduced into the catalytic system as a promoter, instead of CH$_3$CO$_2$H, the obtained 2CH$_3$CH$_2$OH/[emim]Br catalytic system resulted in a lower PO conversion (84%) (entry 5). The carboxylic acid group thus appears to be more beneficial to activating the epoxide ring than the hydroxyl group.

Table 1. Synthesis of PC (**5b**) catalyzed by different ABBCs.[a]

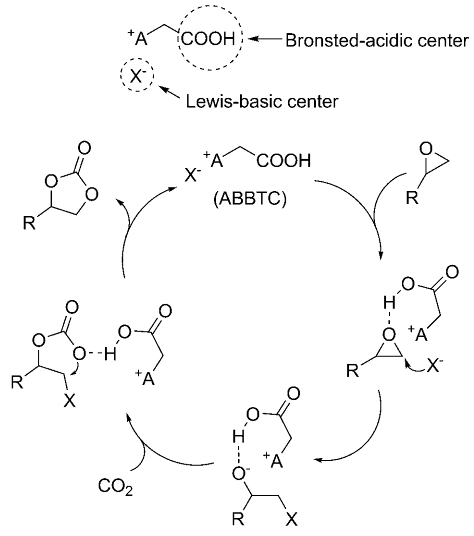
Entry	Catalysts	Conversion [%]	Yield [%][b]
1	[(CH$_2$CH$_2$OH)mim]Br	82	81
2	[emim]Br	60	59
3[c]	CH$_3$CO$_2$H/[emim]Br	80	78
4	2CH$_3$CO$_2$H/[emim]Br	91	88
5[d]	2CH$_3$CH$_2$OH/[emim]Br	84	83
6	[(CH$_2$CO$_2$H)$_2$im]Br (**1a**)	78	77
7	[(CH$_2$CO$_2$H)$_2$im]Cl (**1b**)	12	11
8	[{CH(CH$_3$)CO$_2$H}$_2$im]Br (**1c**)	89	88
9	[{(CH$_2$)$_3$CO$_2$H}$_2$im]Br (**1d**)	99	98
10	[{(CH$_2$)$_3$CO$_2$H}$_2$im]Cl (**1e**)	30	29
11	[(CH$_2$CO$_2$H)mim]Br (**2a**)	66	65
12	[(CH$_2$CO$_2$H)mim]Cl (**2b**)	10	9
13	[{(CH$_2$)$_3$CO$_2$H}mim]Br (**2c**)	92	91
14	[(CH$_2$CO$_2$H)bpy]Br (**3a**)	60	59
15	[{(CH$_2$)$_3$CO$_2$H}bpy]Br (**3b**)	84	83
16	[(CH$_2$CO$_2$H)inic]Br (**4a**)	53	52
17	[{(CH$_2$)$_3$CO$_2$H}inic]Br (**4b**)	73	70

[a] Reaction conditions: PO (0.2 mol), catalyst (1 mol%), $T = 398$ K, $P = 2.0$ MPa, $t = 1$ h. [b] GC yield. [c] [emim]Br (2 mmol), CH$_3$CO$_2$H (2 mmol). [d] [emim]Br (2 mmol), CH$_3$CH$_2$OH (4 mmol).

The structure of the cation of ABBCs has a strong effect on catalytic activity towards the synthesis of PC. With Br$^-$ as an anion, the effect of different types of cations on the reaction has been studied under the same reaction conditions. For imidazolium, the activity orders are [{(CH$_2$)$_3$CO$_2$H}$_2$im]$^+$ > [{CH(CH$_3$)CO$_2$H}$_2$im]$^+$ > [(CH$_2$CO$_2$H)$_2$im]$^+$ (Table 1, entries 6, 8, and 9), and [{(CH$_2$)$_3$CO$_2$H}mim]$^+$ > [(CH$_2$CO$_2$H)mim]$^+$ (entries 11 and 13). For bipyridinium- and isonicotinic-based ABBCs, the activity of cations varies in the order [{(CH$_2$)$_3$CO$_2$H}bpy]$^+$ > [(CH$_2$CO$_2$H)bpy]$^+$ and [{(CH$_2$)$_3$CO$_2$H}inic]$^+$ > [(CH$_2$CO$_2$H)inic]$^+$ (entries 14–17). As reported, hydrogen bonding has a positive effect on the ring-opening of epoxide to promote the synthesis of cyclic carbonate.[17–18] However, hydrogen bonding may also weaken the nucleophilicity of the anions by, to some extent limiting, their flexibility. Because in ABBCs the acidity of carboxylic acids with a short alkyl chain is stronger than the acidity of those with a longer chain,[15] we propose that the increase in the acidity of ABBCs might weaken the nucleophilicity of anions and thus strengthen the ring-opening capability of cations, causing a decrease in the yield of PC. Although dicarboxylic acidity is slightly higher than carboxylic acidity,[15] dicarboxylic ABBCs **1a** and **1d** show higher activities than carboxylic ABBCs **2a** and **2c**, respectively (Table 1, entries 6, 9,11, and 13). This can be partially explained by the fact that the additional –CO$_2$H group in the cation of ABBCs strengthen the ring-opening capability of the cation. Compared to imidazolium-based ABBCs, isonicotinic- and bipyridinium-based ABBCs show lower activities in the synthesis of PC (entries 14–17).

The effect of the counter anions on the catalytic performance was also evaluated. The activity order of anion is $Br^- > Cl^-$, which is consistent with the order of the nucleophilicity of these anions (Table 1, entries 6, 7, 9–12). Perhaps due to the strong hydrogen-bonding between $-CO_2H$ groups and Cl^-, **1 b**, **1 e**, and **2 b** show very low activities for the synthesis of PC (entries 7, 10, and 12). Thus, a moderate hydrogen-bonding effect to efficiently realize nucleophilicity is very important for the ABBCs anion. Hence, we selected $[\{(CH_2)_3CO_2H\}_2im]Br$ **1 d** as a model catalyst for further investigations.

A possible mechanism for the ABBC-catalyzed coupling of epoxides with CO_2, according to previous reports,[16] is shown in Scheme 3. This mechanism is different from that of the corresponding two-component metal–salt-complex catalyzed reaction. The enhancement of catalytic performance is presumably attributable to a synergistic effect of the two functional groups to the epoxide ring, that is, abduction polarization of the oxygen atom by hydrogen-bonding of the Brønsted-acidic center and nucleophilic activation of the carbon atom by the Lewis-basic center (halide anion). Therefore, the epoxy ring was opened easily. This efficient process suggests that a two-component metal salt–ionic liquid catalytic system could be substituted for a single hydrogen-bonding donor (e.g., $-CO_2H$ or phenolic hydroxyl group) functional ionic liquid catalyst. Because it is well-accepted that synergistic catalysis of Lewis acid and Lewis base is necessary for obtaining high yields of cyclic carbonates, this work provides a concept for the development of novel efficient acid–base type catalysts for the synthesis of cyclic carbonates.



Scheme 3. A tentative mechanism for cycloaddition of epoxide to CO_2.

Effect of other reaction parameters

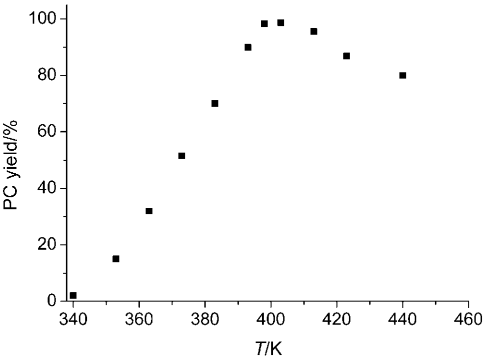


Figure 1. Effect of temperature on PC yield with catalyst **1 d**. Conditions: PO (0.2 mol), **1 d** (1 mol %), $P = 2.0$ MPa, $t = 1$ h.

Figure 1 shows the effect of reaction temperature on the PC yield. The catalytic activity of **1 d** is sensitive to reaction temperature. The PC yield increases sharply with increasing temperature from 340 to 403 K. However, further increase in temperature causes a decrease of the yield. It is plausible that the decrease of PC yield is a result of side reactions under higher temperature, such as PC polymerization, PO isomerization, and a reaction between PO and water.[4c, 18] Therefore, from a practical standpoint the optimal reaction temperature is 398 K.

The effect of CO_2 pressure on the PC yield in the presence of catalyst **1 d** was also studied. As shown in Figure 2, the pressure has a great effect on the yield of PC upon varying the CO_2 pressure in the range 0.5–2.0 MPa, whereas the yield changes only slightly in the range 2.0–3.5 MPa. This can be explained by a pressure effect on the concentrations of CO_2 and epoxide in the two phases.[4c, 18] Since PO is in its liquid form under the adopted reaction conditions, and when the reaction was carried out in a low-pressure region of 0.5–2.0 MPa, higher CO_2 pressure enhanced PC yield due to the higher CO_2 concentration in the liquid phase of the reaction system. A significant drawback of using CO_2 as a reagent in organic synthesis are the potential dangers associated with high-pressure operations. The experimental results above demonstrate that the reaction can be operated smoothly at low pressure in the presence of catalyst **1 d**.

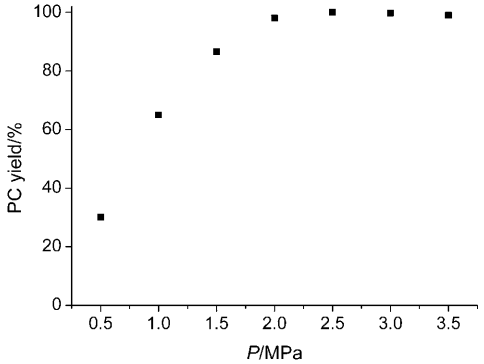


Figure 2. Effect of CO_2 pressure on PC yields. Conditions: PO (0.2 mol), **1 d** (1 mol %), $T = 398$ K, $t = 1$ h.

Figure 3 shows the dependence of the PC yield on the amount of catalyst. An increase of the molar ratio of **1 d** to PO,

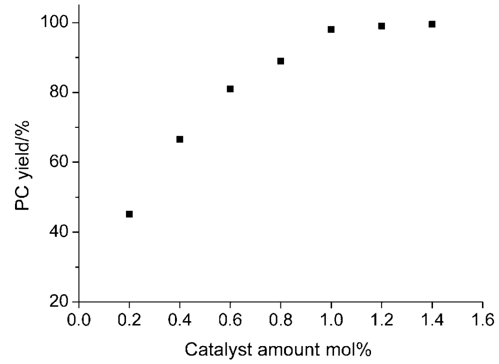


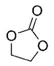
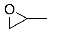
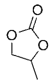
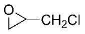
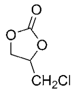
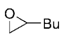
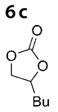
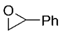
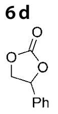
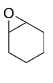
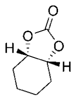
Figure 3. Effect of catalyst (**1 d**) amount on the reaction. Conditions: PO (0.2 mol), $T = 398$ K, $P = 2.0$ MPa, 1 h.

from 0.1 to 1.4 mol%, results in a sharp increase of the PC yield, from 30 to 99%. At a low catalyst loading (1 mol%), a 98% PC yield with >99% selectivity can be obtained, indicating the high activity of catalyst. Because further increases of the amount of catalyst increase the PC yield by only a small margin, 1 mol% was chosen.

Catalytic activity towards other terminal epoxides

To survey the substrate scope, the cycloaddition of other epoxides with CO_2 was performed with the same amount of catalyst **1 d**. The results are summarized in Table 2. As shown, catalyst **1 d** exhibits a high activity and selectivity towards a variety of terminal epoxides (**5 a**–**f**) in mild conditions. Aliphatic **5 a**, **5 b**, **5 d**, and aromatic **1 e** epoxides are preferred substrates for the reaction (entries 1, 2, 4 and 5). These reactions could be completed in about 1 h. Notably, epoxide **5 f**, due to its higher hindrance originating from the two rings, needs a long reaction time to reach a satisfying conversion (entry 6). The cyclic carbonate **6 f** obtained is exclusively the *cis*-isomer, as confirmed by ^{1}H NMR and ^{13}C NMR.[7] From the results, it can be seen that -CO_2H group has not obviously negative effect on the selectivity of products, the selectivity values are still kept at 99% except **5 c** (Table 2, entry 3).

Table 2. Synthesis of other cyclic carbonates catalyzed by **1 d**.[a]

Entry	Substrate	Product	*T* [K]	*t* [h]	Selectivity [%]	Yield[b] [%]
1	 **5 a**	 **6 a**	373	0.7	98	99
2	 **5 b**	 **6 b**	373	1	99	99
3	 **5 c**	 **6 c**	373	0.4	93	91
4	 **5 d**	 **6 d**	398	1	99	97
5	 **5 e**	 **6 e**	398	1	99	95
6	 **5 f**	 **6 f**	398	15	99	85

[a] Reaction conditions: epoxide (0.2 mol), **1 d** (1 mol%), $P = 2.0$ MPa. [b] GC yield.

Catalyst recycling

Catalyst **1 d** showed an excellent activity under mild conditions towards the synthesis of PC. Thereafter, a series of runs with recycled catalyst were used to investigate the reusability of the catalyst under the optimized conditions. In each cycle, the catalyst was separated from the volatile organic products and starting materials by distillation, and reused for subsequent reactions. As shown in Figure 4, the yields and selectivities of the product obtained from the second to fifth runs were similar to those obtained with the fresh catalyst. After five re-uses, a 97% PO conversion with 99% PC selectivity could also be obtained using this optimal catalyst, indicating its stable activity.

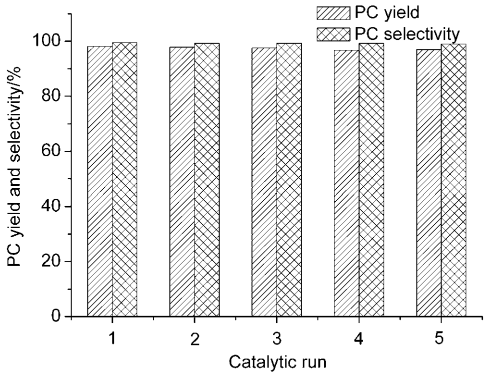


Figure 4. Recycling of the catalyst in the cycloaddition of CO_2 (reaction conditions similar to those of Table 1, entry 9).

Conclusions

For the first time, a type of acid–base bifunctional catalysts such as $[\{(CH_2)_3CO_2H\}_2im]Br$ proved to be highly efficient for the cycloaddition of CO_2 to epoxides under metal- and solvent-free conditions. The catalysts used in this study are stable, easily synthesized, and environmentally benign catalysts that can effectively activate epoxides through a synergistic effect of a carboxylic acid center in the cation part of the salts and a Lewis basic center in the anion part of the salts. The catalyst can be reused at least five times without significant loss of its catalytic activity. The results of this work are an example of the applications of acid–base bifunctional catalysts as environmentally benign alternatives to acids in organic synthesis and catalysis.

Experimental Section

TGA was performed by using a TGA-50 (Shimadzu) in a nitrogen atmosphere between 298 and 873 K at a heating rate of 10 $K\,min^{-1}$. DSC was carried out by using a TGA-50 (Shimadzu) in a nitrogen atmosphere between 298 and 873 K at a heating rate of 10 $K\,min^{-1}$. Elemental analysis was carried out by using a Vario EL (Elementar Analysensysteme GmbH). ^1H NMR was detected at room temperature on a Bruker 400 MHz NMR spectrometer using [D_6]DMSO as solvent. ^{13}C NMR was detected at room temperature on Bruker 400 MHz NMR spectrometer using $CDCl_3$ as solvent.

The ABBCs were prepared according to procedures reported earlier.[15] A typical synthesis route to [$(CH_2CO_2H)_2$im]Br (**1a**) is as follows: a mixture of trimethylsilylimidazole (0.010 mol) and $BrCH_2CO_2CH_3$ (0.020 mol) was refluxed in toluene (20 mL) at 298 K for 24 h under an inert atmosphere of dry nitrogen. The reaction mixture was washed with diethyl ether (3×30 mL) and dried under vacuum for 24 h to give product **1**. Thereafter, a mixture of **1** (0.010 mol) and 16.7% HCl (10 mL) was refluxed for 2 h. The solvent was removed under reduced pressure and the remaining solid was washed with acetone and diethyl ether to give the product **1a** as a white powder. It should be noted that the addition of methyl bromoacetate to *N*-methylimidazole or trimethylsilylimidazole to afford **1a** and **2a** could be completed at room temperature (298 K). In comparison with *N*-methylimidazole, trimethylsilyl-imidazole, and *iso*-nicotine, reactions of bipyrid did not afford the desired $-CO_2H$ group *bis*-substituted bipyridinium-based ABBCs using the same method. Therefore, compounds **3a** and **3b** were also tested for the synthesis of cyclic carbonates.

[$(CH_2CO_2H)_2$im]Br (**1a**): yield: 97%; a white solid; mp: 194–195 °C, T_{dec} 240 °C; ^1H NMR (400 MHz, [D_6]DMSO): $\delta=5.21$ (s, 4H), 7.76 (s, 2H), 9.13 ppm (s, 1H); Anal. calcd for $C_7H_9N_2O_4Br$: C 31.72, H 3.42; N 10.57, found: C 32.02, H 3.56, N 10.74.

[$(CH_2CO_2H)_2$im]Cl (**1b**): yield: 95%; a white solid; mp: 259–260 °C, T_{dec} 260 °C; ^1H NMR (400 MHz, [D_6]DMSO): $\delta=5.26$ (s, 4H), 7.79 (s, 2H), 9.24 ppm (s, 1H); Anal. calcd for $C_7H_9N_2O_4Cl$: C 38.10, H 4.10, N 12.70, found: C 38.25, H 4.12, N 12.85.

[$\{CH(CH_3)CO_2H\}_2$im]Br (**1c**): yield: 95%; a white solid; mp: 178–179 °C, T_{dec} 250 °C; ^1H NMR (400 MHz, [D_6]DMSO): $\delta=1.78$ (d $J=7.6$ Hz, 6H), 5.45 (t, $J=22.0$ Hz, 2H), 7.93 (s, 2H), 9.41 ppm (s, 1H); Anal. calcd for $C_9H_{13}N_2O_4Br$: C 36.86, H 4.44, N 9.56, found: C 37.01, H 4.54, N 9.81.

[$\{(CH_2)_3CO_2H\}_2$im]Br (**1d**): yield: 94%; a white solid; mp: 110–111 °C, T_{dec} 300 °C; ^1H NMR (400 MHz, [D_6]DMSO): $\delta=2.02$–2.05 (m, 4H), 2.47 (t, $J=8$ Hz, 4H), 4.17 (t, $J=11.2$ Hz, 4H), 7.78 (s, 2H), 9.20 ppm (s, 1H); Anal. calcd for $C_{11}H_{17}N_2O_4Br$: C 41.14, H 5.34, N 8.72, found: C 40.89, H 5.33, N 8.88.

[$\{(CH_2)_3CO_2H\}_2$im]Cl (**1e**): yield: 96%; a white solid; mp: 172–173 °C, T_{dec} 250 °C; ^1H NMR (400 MHz, [D_6]DMSO): $\delta=2.08$–2.13 (m, 4H), 2.48 (t, $J=9.6$ Hz, 4H), 4.18 (t, $J=14.4$ Hz, 4H), 7.80 (s, 2H), 9.23 ppm (s, 1H); Anal. calcd for $C_{11}H_{17}N_2O_4Cl$: C 47.75, H 6.19, N 10.12, found: C 47.78, H 6.20, N 10.08.

[(CH_2CO_2H)mim]Br (**2a**): yield: 97%; a white solid; mp: 181–182 °C, T_{dec} 280 °C; ^1H NMR (400 MHz, [D_6]DMSO): $\delta=3.93$ (s, 3H), 5.21 (s, 2H), 7.77 (s, 1H), 7.78 (s, 1H), 9.22 ppm (s, 1H); Anal. calcd for $C_6H_9N_2O_2Br$: C 32.73, H 4.09, N 12.73, found: C 32.74, H 4.10, N 12.74.

[(CH_2CO_2H)mim]Cl (**2b**): yield: 98.3%; a white solid; mp: 203–204 °C, T_{dec} 250 °C; ^1H NMR (400 MHz, [D_6]DMSO): $\delta=3.94$ (s, 3H), 5.23 (s, 2H), 7.78 (s, 1H), 7.80 (s, 1H), 9.31 ppm (s, 1H); Anal. calcd for $C_6H_9N_2O_2Cl$: C 40.81, H 5.14, N 15.86, found: C 40.78, H 5.20, N 15.86.

[$\{(CH_2)_3CO_2H\}$mim]Br (**2c**): yield: 97%; a yellow liquid; T_{dec} 270 °C; ^1H NMR (400 MHz, [D_6]DMSO): $\delta=2.06$ (m, 2H), 2.31 (t, $J=10.1$ Hz, 2H), 3.94 (s, 3H), 4.27 (t, $J=9.6$ Hz, 2H,), 7.82 (s, 1H), 7.88 (s, 1H), 9.37 ppm (s, 1H); Anal. calcd for $C_8H_{13}N_2O_2Br$: C 38.71, H 5.24, N 11.29, found: C 38.74, H 5.26, N 11.34.

[(CH_2CO_2H)bpy]Br (**3a**): yield: 85%; a white solid; mp: 199–200 °C, T_{dec} 220 °C; ^1H NMR (400 MHz, [D_6]DMSO): $\delta=5.70$ (s, 2H), 8.25 (s, 2H), 8.75 (s, 2H), 9.00 (s, 2H), 9.26 ppm (s, 2H); Anal. calcd for $C_{12}H_{11}N_2O_2Br$: C 49.15, H 3.76, N 9.56, found: C 48.90, H 3.86, N 9.36.

[$\{(CH_2)_3CO_2H\}$bpy]Br (**3b**): yield: 80%; a yellow solid; mp: 199–200 °C, T_{dec} 230 °C; ^1H NMR (400 MHz, [D_6]DMSO): $\delta=2.09$–2.25 (m, 2H), 2.40 (t, $J=14.6$ Hz, 2H), 4.74 (t, $J=16.9$ Hz, 2H), 8.32 (s, 2H), 8.72 (s, 2H), 9.03 (s, 2H), 9.34 ppm (s, 2H); Anal. calcd for $C_{14}H_{15}N_2O_2Br$: C 52.01, H 4.64, N 8.67, found: C 50.23, H 4.58, N 8.41.

[(CH_2CO_2H)inic]Br (**4a**): yield: 97%; a white solid; mp: 190–191 °C, T_{dec} 195 °C; ^1H NMR (400 MHz, [D_6]DMSO): $\delta=5.67$ (s, 2H), 8.46 (s, 2H), 9.20 ppm (s, 2H); Anal. calcd for $C_8H_8NO_4Br$: C 36.64, H 3.05, N 5.35, found: C 37.21, H 3.11, N 5.47.

[$\{(CH_2)_3CO_2H\}$inic]Br (**4b**): yield: 93%; a white solid; mp: 159–160 °C, T_{dec} 200 °C; ^1H NMR (400 MHz, [D_6]DMSO): $\delta=2.04$–2.09 (m, 2H), 2.32 (t, $J=12.6$ Hz, 2H), 4.15 (t, $J=14.2$ Hz, 2H), 7.90 (s, 2H), 9.33 ppm (s, 2H); Anal. calcd for $C_{10}H_{12}NO_4Br$: C 41.38, H 4.14, N 4.83, found: C 41.41, H 4.13, N 4.92.

All the coupling reactions were conducted in a 100 mL stainless-steel reactor equipped with a magnetic stirrer and automatic temperature control system. Typically, in the reactor, an appropriate volume of CO_2 (ca. 1.0 MPa) was added to a mixture of PO (14.0 mL, ca. 0.2 mol), and catalyst (ca. 2.0 mmol) at room temperature. The temperature was then raised to 398 K while more CO_2 was added from a reservoir tank to maintain a constant pressure (2.0 MPa). After the reaction had proceeded for 1.0 h, the reactor was cooled to 273 K in an ice–water bath, and the remaining CO_2 was removed slowly. After the volatile organic products and starting materials were removed from the catalyst by distillation, the products were analyzed by using an Agilent 6890/5973B GC-MS equipped with a FID detector and a DB-wax column, using acetophenone as the internal standard. The product was purified by distillation or silica gel column chromatography if necessary.

Spectral characteristics of the products (cyclic carbonates **6a**–**f**) in Table 2 are as follows:

1, 3-dioxolan-2-one (**6a**): ^1H NMR (400 MHz, $CDCl_3$): $\delta=4.2$ ppm (t, $J=10$ Hz, 4H); ^{13}C NMR (400 MHz, $CDCl_3$): $\delta=63.3$, 155 ppm (C=O).

4-methyl-1, 3-dioxolan-2-one (**6b**): ^1H NMR (400 MHz, $CDCl_3$): $\delta=1.49$ (d, $J=6.0$ Hz, 3H), 4.05 (t, $J=8.8$ Hz, 1H), 4.60 (t, $J=8.0$ Hz, 1H), 4.86–4.94 ppm (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): $\delta=18.95$, 70.46, 73.51, 154.95 ppm (C=O).

4-chloromethyl-1,3-dioxolan-2-one (**6c**): ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 1.490$ (d, $J = 6.0$ Hz, 3H), 4.05 (t, $J = 8.4$ Hz, 1H), 4.60 (t, $J = 8.0$ Hz, 1H), 4.86–4.94 ppm (m, 1H); ^{13}C NMR (400 MHz, CDCl$_3$): $\delta =$ 18.95, 70.46, 73.51, 154.95 ppm (C=O).

4-butyl-1,3-dioxolan-2-one (**6d**): ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 0.96$ (t, $J = 7.2$ Hz, 3H); 1.33–1.38 (m, 2H), 1.29–1.31 (m, 2H), 1.53 (m, 2H), 4.16 (d, $J = 8.0$ Hz, 2H), 4.19 ppm (t, $J = 6.2$ Hz, 1H); ^{13}C NMR (400 MHz, CDCl$_3$): $\delta = 14.00$, 23.12, 26.19, 36.23, 68.04, 75.61, 155.07 ppm (C=O).

4-phenyl-1, 3-dioxolan-2-one (**6e**): ^{1}H NMR (400 MHz, CDCl$_3$): $\delta =$ 4.34 (t, $J = 8.4$ Hz, 1H), 4.80 (t, $J = 8.4$ Hz, 1H), 5.68 (t, 1H, $J = 8.0$ Hz), 7.35–7.44 ppm (m, 5H); ^{13}C NMR (400 MHz, CDCl$_3$): $\delta =$ 71.10, 77.92, 125.81, 129.12, 129.63, 135.70, 154.81 ppm (C=O).

4, 5-tetramethylene-1, 3-dioxolan-2-one (**6f**): ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 1.80$–1.86 (m, 2H), 1.97–2.05 (m, 2H), 2.28 (d, $J = 4.8$ Hz, 4H), 5.06–5.11 ppm (m, 2H); ^{13}C NMR (400 MHz, CDCl$_3$): $\delta = 19.00$, 26.61, 75.65, 155.27 ppm (C=O).

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