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Pyridine-bridged bifunctional organocatalysts for the synthesis of cyclic carbonates from carbon dioxide

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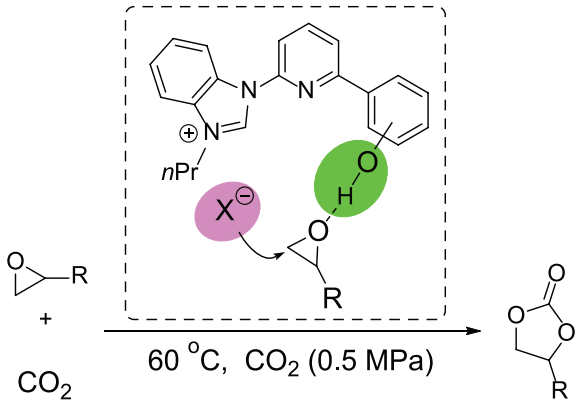
Abstract

Hydroxyl- and carboxyl-functionalized imidazolium halides are used as efficient bifunctional organocatalysts for the synthesis of cyclic carbonates from CO_2 and epoxides under mild reaction conditions. Control experiments suggest that the cycloaddition reaction is realized by the combination of the nucleophilic halide anions with hydroxyl and carboxyl groups as hydrogen bond donors. Moreover, the bifunctional organocatalysts can be easily recycled five times by simple filtration; however, a loss of activity was observed.

Keywords

carbon dioxide, cyclic carbonate, epoxide, hydrogen bond donor, organocatalysis

A family of pyridine-bridged bifunctional organocatalysts were synthesized that have proved to be an efficient and recyclable catalyst for the cycloaddition of CO_2 with epoxides in mild reaction conditions.



Introduction

Carbon dioxide (CO_2) holds great potential as an abundant, inexpensive, nonflammable, nontoxic, and renewable C1 building block.[1–9] The synthesis of cyclic carbonates from CO_2 and epoxides is a 100% atom economical process which has been extensively studied due to their high utility as industrial intermediates for fine chemicals,[10–12] green solvents,[13] monomers for polymer synthesis,[14–16] and electrolysis for lithium ion batteries.[17–19] A wide variety of catalytic systems for the coupling reaction of CO_2 with epoxides have been developed over the past decade to achieve these important types of compound.[20–32] Imidazolium-based compounds represent a class of organocatalysts for the synthesis of cyclic carbonates from CO_2 and epoxides,[33–39] because most of the imidazolium catalysts are synthesized via simple procedures using low-cost, readily available raw materials. We have recently reported a family of imidazolium salts for the cycloaddition reaction of epoxides with CO_2 at 90 °C under 1 MPa of CO_2.[40] However, our previously reported imidazolium-based catalytic system suffers from harsh reaction conditions.[40] Recent developments in the

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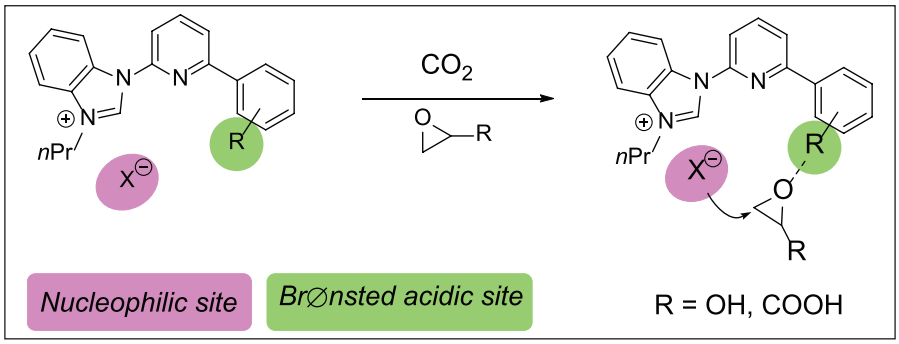
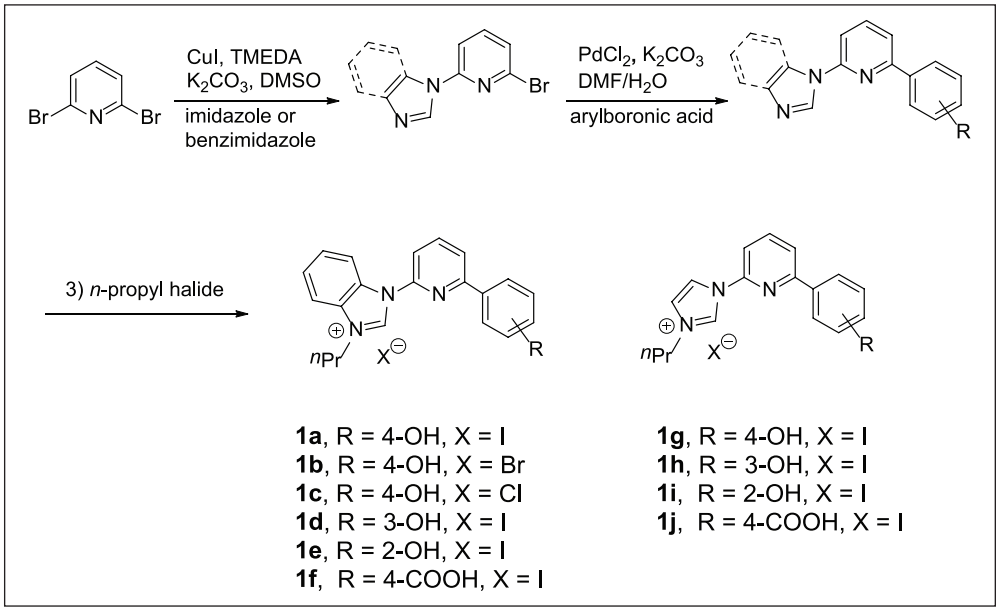


Figure 1. Design concept for the catalyst.



Scheme 1. The bifunctional organocatalysts used this work.

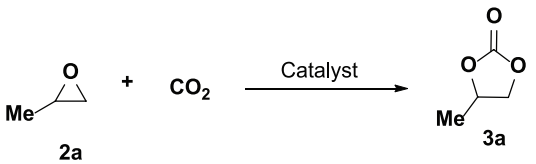
substrate activation strategy by introducing hydroxyl,[41–50] carboxyl,[51–57] and amino group[58–62] to imidazolium salts as hydrogen bond donors has demonstrated that the design of the catalysts plays an important role in tuning the catalytic activity. We have developed a method for the synthesis of unsymmetrical pyridine-bridged pincer-type ligand,[63] which has been applied in palladium-catalyzed the Suzuki cross-coupling reactions[64] and iron-catalyzed and organocatalyzed the cycloaddition of epoxides with CO_2.[40,57,65–67] Bowen et al. reported that CO_2 is capable of binding to the nitrogen atom of a quinoline to form the quinolone–CO_2 anionic complex.[68] Inspired by previously reported work, we became interested in designing bifunctional imidazolium salts by introducing a hydrogen bond donor, such as COOH or OH (Figure 1). In this work, we present efficient bifunctional organocatalysts composed of a nucleophilic site and a Brønsted acidic site for the synthesis of cyclic carbonates. It was demonstrated that the organocatalysts were highly effective for the cycloaddition of epoxides with CO_2 at 60 °C under 0.5 MPa of CO_2 pressure.

Results and discussion

The 10 bifunctional organocatalysts **1a–j** were synthesized according to procedures reported previously.[63] At the beginning of the reaction, 2,6-dibromopyridine reacts with benzimidazole or imidazole to generate a 2-monosubstituted product, which is further converted into the 2,6-disubstituted pyridine via Suzuki coupling. Finally, the resultant disubstituted product is reacted with the corresponding *n*-propyl halide to afford the organocatalysts (Scheme 1).

The ability of organocatalysts **1a–j** to catalyze the cycloaddition of propylene oxide (PO) with CO_2 to form propylene carbonate (PC) was evaluated (Table 1, entries 1–10). First, the influence of the halide counteranions with catalysts on the catalytic activity was investigated. The formation of products showed a dependence on the nature of the anions, and the activity order is $I^- > Br^- \approx Cl^-$ (Table 1, entries 1–3). This suggests that the halide leaving ability is crucial for excellent performance because iodides possess a stronger leaving ability. We selected an iodide ion (I^-) as the representative counteranion for investigating the effect of the position of the hydroxyl substituents on the aromatic ring on the catalytic activity (Table 1, entries 1, 4, and 5). The results indicated that the electronic nature and steric hindrance due to the hydroxyl group on the aromatic ring are important for the catalytic activity. The best catalytic efficiency was obtained when the hydroxyl group was located at the *para*-position of the aromatic ring (Table 1, entry 1). The hydroxyl group facilitates nucleophilic attack for ring opening of the epoxide

Table 1. Optimization of propylene carbonate synthesis[a].



Entry	Cat. (mol%)	T (°C)	Time (h)	Yield (%)[b]
1	**1a** (1.0)	90	3	90
2	**1b** (1.0)	90	3	67
3	**1c** (1.0)	90	3	63
4	**1d** (1.0)	90	3	78
5	**1e** (1.0)	90	3	39
6	**1f** (1.0)	90	3	81
7	**1g** (1.0)	90	3	84
8	**1h** (1.0)	90	3	77
9	**1i** (1.0)	90	3	36
10	**1j** (1.0)	90	3	78
11	**1a** (1.0)	60	3	23
12	**1a** (2.0)	60	7	75
13	**1a** (2.0)	60	24	96
14	**1a** (2.0)	rt	24	16

PO: propylene oxide; GC: gas chromatography.
[a]Conditions: PO (10.0 mmol), catalyst (indicated in Table 1), no solvent, CO_2 (0.5 MPa).
[b]Determined by GC analyses using biphenyl as an internal standard.

through hydrogen bonding with the epoxide. We assume that the carboxyl group would be advantageous since stronger acidity could be provided compared with the hydroxyl group. This led us to the assumption that the carboxyl-functionalized imidazolium halides would be more catalytically active than their hydroxyl-functionalized counterparts because the carboxyl group possesses stronger hydrogen bond interactions. However, the carboxyl-functionalized catalysts showed slightly lower activity than those of hydroxyl-functionalized imidazolium halides (Table 1, entries 1 vs 6). In order to understand the possible causes behind these unexpected results, we investigated the reaction process. The results indicated that the carboxyl-functionalized imidazolium iodide **1f** (0.0085 mmol mL^{-1}) displayed poor solubility in PO solution compared with the hydroxyl-functionalized iodide **1a** (0.021 mmol mL^{-1}). We assume that the solubility difference could be responsible for the results.

The type of imidazolium halide was also investigated, but there was no evident difference between benzimidazole salts and imidazolium salts, and a similar reactivities were observed (Table 1, entries 1 and 4–6 vs 7–10). An attempt to decrease the reaction temperature from 90 °C to 60 °C resulted in a low yield (Table 1, entries 1 vs 11), but excellent results were obtained when the loading of the catalyst **1a** was increased from 1.0 mol% to 2.0 mol% with prolonging the reaction time to 24 h (Table 1, entries 12 and 13). Further lowering of the reaction temperature to room temperature, however, gave a poor result (Table 1, entry 14).

With optimized reaction conditions in hand (Table 1, entry 13), the substrate scope of epoxides for the cycloaddition of CO_2 was investigated (Table 2). Epoxides bearing electron-donating substituents, such as PO (**2a**), 2-ethyloxirane (**2b**), 1,2-epoxyhexane (**2c**), and epoxyoctane (**2d**), were smoothly converted into the desired products in good to excellent yields. Epoxides bearing electron-withdrawing substituents also reacted smoothly with CO_2 to give the corresponding cyclic carbonates **3e** and **3f**. In addition, aliphatic and aromatic substrates were transformed with CO_2 into the desired products **3h–j** in yields of 84%–94%.

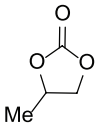
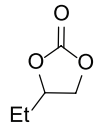
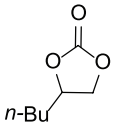
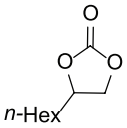
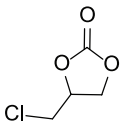
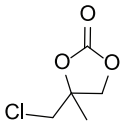
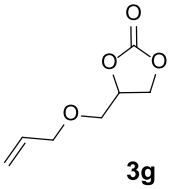
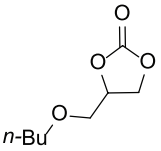
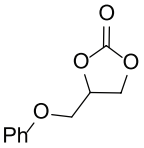
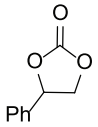
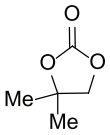
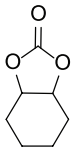
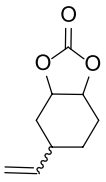
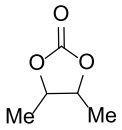
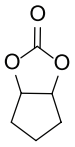
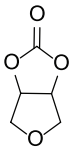
The challenging substrate 2,2-dimethyloxirane was also converted into the corresponding cyclic carbonates **3k** with 87% yield. Internal epoxides are challenging substrates because of their highly hindered nature and tendency to polymerize. An elevated reaction temperature was required to achieve the high conversion of internal epoxides, such as cyclohexene oxides **2l** and **2m** as well as bicyclic epoxide **2o**, into the desired products **3l**, **3m**, and **3o**. 2,3-Dimethyloxirane **2n** and bicyclic epoxide **2p** show lower reactivity even if a higher reaction temperature is employed.

Besides carboxyl and hydroxyl groups working as hydrogen donors, the proton at the C2 position of the imidazolium ring can also enhance the catalytic activity through the interaction with the epoxides.[69,70] In order to prove whether the hydrogen interaction occurs through the hydroxyl group or through the proton at the C2 position of the imidazolium ring, two control experiments were carried out with two designed catalysts (Scheme 2). To explore the function of the hydroxyl group on this reaction, a catalyst was synthesized by etherification of the phenolic hydroxyl group (**1k**, in Scheme 2, equation (1)). In the absence of hydroxyl protons, an evident reduction in the catalytic activity was observed (Scheme 2, equation (1)). In addition, the effect of the C2 proton in the imidazolium ring was investigated. When the C2 proton was protected by a methyl group (**1l**, in Scheme 2, equation (2)), the activity of the catalyst **1l** was slightly affected (91% yield in Scheme 2, equation (2)) in comparison with the catalyst **1a** (96% yield in Table 1, entry 13). The results indicate that the hydroxyl proton bearing aromatic ring activates epoxides more easily than the proton at the C2 position of the imidazolium ring.

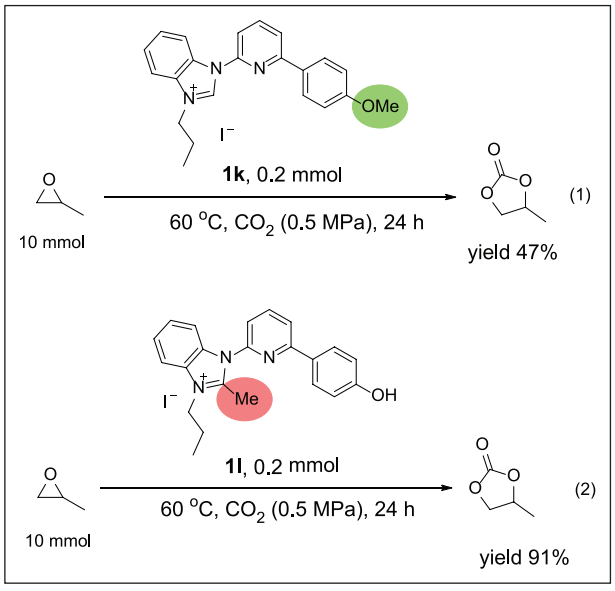
Based on the above investigations, a mechanism for the organocatalytic cycloaddition of epoxides with CO_2 using bifunctional imidazolium salts has been proposed (Figure 2). In the first step, the hydroxyl proton on the catalyst **1a** could coordinate to the epoxide through a hydrogen bond interaction, which results in polarization of the C–O bond. Subsequently, the epoxide ring is opened by nucleophilic attack by the iodide to form intermediate (**II**). Second, the negatively charged oxygen atom can nucleophilically attack the electrophilic carbon atom of CO_2, which leads to the formation of intermediate (**III**). The resulting open-ring intermediate (**III**) undergoes intramolecular nucleophilic attack, simultaneously releasing the catalytically active iodide and the cyclic carbonate product.

The recycling procedure for the catalysts is often through energy-intensive distillation of the cyclic carbonates. The separation of catalysts by precipitation is a sustainable strategy compared with distillation of the products. The recyclability of catalyst **1a** was investigated (Figures 3 and 4). During recycling experiments, the catalyst can be

Table 2. Scope of the substrates[a].

				
3a yield 91%	**3b** yield 95%	**3c** yield 93%	**3d** yield 96%	**3e** yield 95%
				
3f yield 97%	**3g** yield 92%	**3h** yield 94%	**3i** yield 92%	**3j** yield 84%
	**3k** yield 87%[b]		**3l** yield 87%[b] sel. 97% *cis/trans* = 99:1	
				3m yield 83%[b] sel. 91%[c] d.r. = 56:44[d] *cis/trans* = 97:3
	**3n** yield 13%[e] *cis/trans* = 16:84[e]		**3o** yield 77%[e]	
				3p yield 11%[e]

NMR: nuclear magnetic resonance.
[a]Conditions: epoxide (10 mmol), **1a** (0.2 mmol), no solvent, 60 °C, CO_2 (0.5 MPa), 24 h, isolated yield.
[b]90 °C.
[c]The selectivity refers to the ratio between cycloaddition product and polymerization product.
[d]The d.r. values were determined by ^1H and ^{13}C NMR spectroscopy.
[e]120 °C.



Scheme 2. Exploration of the hydrogen bond donor in the reaction.

precipitated from the product phase via the addition of ethyl acetate (Figure 3). The recycled catalyst is directly used without further purification, and another batch of starting materials is added and the catalyst reused for subsequent recycles. However, a loss of catalytic activity was observed during these recycling studies (Figure 4), which was mainly attributed to leaching of the catalyst.

Conclusion

In summary, a family of pyridine-bridged bifunctional organocatalysts has been prepared and the utility of these catalysts for the synthesis of cyclic carbonates from CO_2 and epoxides under mild reaction conditions was demonstrated. The one-component catalyst displayed a broad substrate scope and various functionalized terminal epoxides as well as internal epoxides could be converted into corresponding cyclic carbonates with good to excellent yields. Control experiments indicate that the cooperative role of the hydroxyl groups with the nucleophilic halide anions is crucial for the excellent performance.

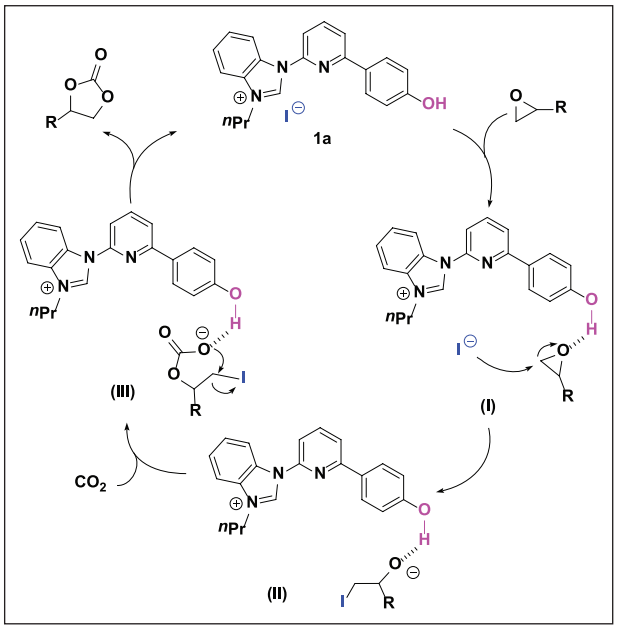


Figure 2. Proposed mechanism for bifunctional organocatalysis.

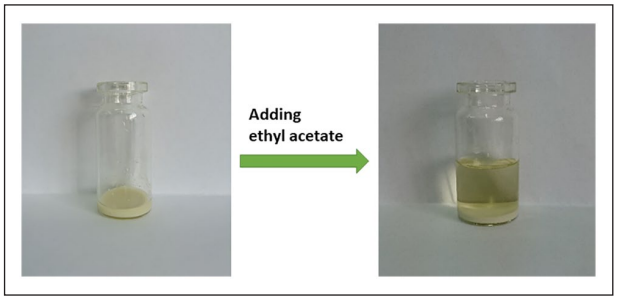


Figure 3. Recycling of the bifunctional organocatalyst.

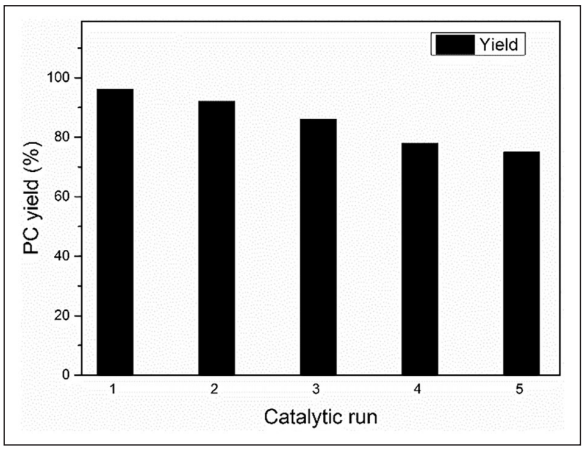


Figure 4. Recycling experiments. Reaction conditions: PO (10.0 mmol), no solvent, 60 °C, CO_2 (0.5 MPa), 24 h, yield was determined by GC analysis using biphenyl as an internal standard.

Experimental section

The bifunctional organocatalysts **1a–l***; general procedure.* The bifunctional catalysts were prepared according to procedures reported previously.[63] A mixture of 2,6-dibromopyridine (5 mmol), imidazole or benzimidazole (10 mmol), CuI (1 mmol), tetramethylethane-1,2-diamine (TMEDA, 2 mmol), and K_2CO_3 (15 mmol) in dimethyl sulfoxide (DMSO; 20 mL) was stirred for 30 min at room temperature and then heated to 90 °C for 24 h under a nitrogen atmosphere. Thereafter, the 2-bromo-6-substituted pyridine (5 mmol), arylboronic acid (7.5 mmol), $PdCl_2$ (0.2 mmol), and K_2CO_3 (10 mmol) in dimethylformamide (DMF)/H_2O (10 mL/10 mL) were allowed to react at 90 °C for 12 h under air. The resulting 2,6-disubstituted pyridine (5 mmol) and *n*-propyl halide (10 mL) were heated to 100 °C and reacted for 8 h under an air atmosphere. The solvent was concentrated under vacuum and the product organocatalyst **1a–l** was isolated by column chromatography on silica gel (dichloromethane (DCM)/methanol).

Data for 1-(6-(4-hydroxyphenyl)pyridin-2-yl)-3-propyl-1*H*-benzo[*d*]imidazol-3-ium iodide **1a** are as follows: Purification by column chromatography on silica gel (DCM/MeOH=30:1). Yellowish solid (1.09 g, 80%), m.p.=229.8 °C–230.7 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.55 (s, 1H), 9.99 (s, 1H), 8.51 (d, J=8.0 Hz, 1H), 8.27 (t, J=8.0 Hz, 2H), 8.15 (d, J=8.0, 1H), 8.10 (d, J=8.0 Hz, 2H), 7.90 (d, J=8.0 Hz, 1H), 7.85–7.78 (m, 2H), 6.95 (d, J=8.0 Hz, 2H), 4.60 (t, J=8.0 Hz, 2H), 2.06 (sext, J=7.2 Hz, 2H), 1.02 (t, J=8.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.55, 156.54, 146.95, 142.33, 141.27, 131.72, 129.52, 128.54, 127.85, 127.72, 127.10, 119.92, 115.87, 115.65, 114.16, 114.08, 48.70, 22.09, 10.80; high-resolution mass spectrometry (HRMS) (Matrix-Assisted Laser Desorption (MALDI): m/z [M−I]$^+$ calcd for $C_{21}H_{20}N_3O$: 330.1601; found: 330.1607.

Data for 1-(6-(4-hydroxyphenyl)pyridin-2-yl)-3-propyl-1*H*-benzo[*d*]imidazol-3-ium bromide **1b** are as follows: Purification by column chromatography on silica gel (DCM/MeOH=30:1): a yellowish solid (1.09 g, 89%), m.p.=246.5 °C–247.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.58 (s, 1H), 9.99 (s, 1H), 8.51 (d, J=8.0 Hz, 1H), 8.27 (t, J=8.0 Hz, 2H), 8.16–8.09 (m, 3H), 7.91 (d, J=8.0 Hz, 1H), 7.85–7.78 (m, 2H), 6.96 (d, J=8.0 Hz, 2H), 4.61 (t, J=7.2 Hz, 2H), 2.06 (sext, J=7.2 Hz, 2H), 1.02 (t, J=8.0 Hz, 3H), ppm; ^{13}C NMR (100 MHz, DMSO): δ 159.56, 156.53, 146.97, 142.36, 141.26, 131.72, 129.51, 128.52, 127.84, 127.71, 127.09, 119.90, 115.86, 115.66, 114.15, 114.07, 48.67, 22.09, 10.79, ppm; HRMS (MALDI): m/z [M−Br]$^+$ calcd for $C_{21}H_{20}N_3O$: 330.1601; found: 330.1609.

Data for 1-(6-(4-hydroxyphenyl)pyridin-2-yl)-3-propyl-1*H*-benzo[*d*]imidazol-3-ium chloride **1c** are as follows: Purification by column chromatography on silica gel (DCM/MeOH=50:1): a yellowish solid (864 mg, 77%), m.p.=226.5 °C–227.2 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.70 (s, 1H), 10.00 (s, 1H), 8.51–7.81 (m, 9H), 6.97 (s, 2H), 4.63 (s, 2H), 2.06 (s, 2H), 1.02 (s, 3H), ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.55, 156.47, 147.00, 142.33, 141.22, 131.70, 129.46, 128.49, 127.81, 127.69, 127.06, 119.84, 115.86, 115.69, 114.15, 114.03, 48.64, 22.10, 10.78, ppm; HRMS (MALDI): m/z [M−Cl]$^+$ calcd for $C_{21}H_{20}N_3O$: 330.1601; found: 330.1598.

Data for 1-(6-(3-hydroxyphenyl)pyridin-2-yl)-3-propyl-1*H*-benzo[*d*]imidazol-3-ium iodide **1d** are as follows: Purification by column chromatography on silica gel

(DCM/MeOH = 100:1): a yellowish solid (1.16 g, 84%), m.p. = 236.2 °C–237.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.57 (s, 1H), 9.75 (s, 1H), 8.54 (d, J = 8.0 Hz, 1H), 8.34 (t, J = 8.0 Hz, 1H), 8.27 (d, J = 8.0 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.85–7.79 (m, 2H), 7.63 (t, J = 8.0 Hz, 2H), 7.39 (t, J = 8.0 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 4.61 (t, J = 7.2 Hz, 2H), 2.06 (sext, J = 7.2 Hz, 2H), 1.02 (t, J = 7.2 Hz, 3H), ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 158.00, 156.30, 147.15, 142.38, 141.50, 138.25, 131.70, 130.18, 129.51, 127.83, 127.12, 121.10, 117.68, 117.17, 115.77, 115.43, 114.16, 113.55, 48.72, 22.06, 10.79, ppm; HRMS (MALDI): m/z $[M-I]^+$ calcd for $C_{21}H_{20}N_3O$: 330.1601; found: 330.1606.

Data for 1-(6-(2-hydroxyphenyl)pyridin-2-yl)-3-propyl-1*H*-benzo[*d*]imidazol-3-ium iodide **1e** are as follows: Purification by column chromatography on silica gel (DCM/MeOH = 30:1): a yellowish solid (1.206 g, 88%), m.p. = 254.5 °C–255.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.59 (s, 1H), 10.55 (s, 1H), 8.49–8.47 (m, 1H), 8.33 (d, J = 5.2 Hz, 2H), 8.28–8.26 (m, 1H), 8.01–7.96 (m, 2H), 7.81–7.76 (m, 2H), 7.35 (t, J = 6.0 Hz, 1H), 7.06–6.99 (m, 2H), 4.62 (t, J = 8.0 Hz, 2H), 2.06 (sext, J = 7.2 Hz, 2H), 1.02 (t, J = 7.2 Hz, 3H), ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 156.04, 155.80, 146.28, 142.27, 140.71, 131.64, 131.17, 129.94, 129.53, 127.72, 127.07, 124.53, 123.13, 119.60, 116.94, 115.52, 114.95, 114.14, 48.71, 22.03, 10.78, ppm; HRMS (MALDI): m/z $[M-I]^+$ calcd for $C_{21}H_{20}N_3O$: 330.1601; found: 330.1597.

Data for 1-(6-(4-carboxyphenyl)pyridin-2-yl)-3-propyl-1*H*-benzo[*d*]imidazol-3-ium iodide **1f** are as follows: Purification by column chromatography on silica gel (DCM/MeOH = 30:1): a yellowish solid (1.321 g, 91%), m.p. = 236.3 °C–236.7 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.18 (s, 1H), 10.61 (s, 1H), 8.54 (d, J = 8.0 Hz, 1H), 8.44–8.35 (m, 4H), 8.28 (d, J = 8.0 Hz, 1H), 8.15–8.09 (m, 3H), 7.86–7.79 (m, 2H), 4.62 (t, J = 8.0 Hz, 2H), 2.07 (sext, J = 7.2 Hz, 2H), 1.03 (t, J = 7.2 Hz, 3H), ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.91, 155.16, 147.29, 142.51, 141.85, 140.73, 132.00, 131.72, 130.03, 129.51, 127.96, 127.15, 121.87, 116.38, 115.69, 114.19, 48.75, 22.09, 10.80, ppm; HRMS (MALDI): m/z $[M-I]^+$ calcd for $C_{22}H_{20}N_3O_2$: 358.1550; found: 358.1544.

Data for 1-(6-(4-hydroxyphenyl)pyridin-2-yl)-3-propyl-1*H*-imidazol-3-ium iodide **1g** are as follows: Purification by column chromatography on silica gel (DCM/MeOH = 30:1): a yellowish solid (1.014 g, 83%), m.p. = 192.0 °C–192.8 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.20 (s, 1H), 9.96 (s, 1H), 8.65 (s, 1H), 8.20–8.14 (m, 3H), 8.08 (t, J = 8.0 Hz, 2H), 7.85 (d, J = 8.0 Hz, 1H), 6.92 (d, J = 8.0 Hz, 2H), 4.30 (t, J = 8.0 Hz, 2H), 1.94 (sext, J = 7.2 Hz, 2H), 0.94 (t, J = 7.2 Hz, 3H), ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.61, 155.98, 146.00, 141.26, 134.93, 128.66, 127.38, 123.55, 119.71, 119.32, 115.69, 110.85, 51.02, 22.78, 10.50, ppm; HRMS (MALDI): m/z $[M-I]^+$ calcd for $C_{17}H_{18}N_3O$: 280.1444; found: 280.1441.

Data for 1-(6-(3-hydroxyphenyl)pyridin-2-yl)-3-propyl-1*H*-imidazol-3-ium iodide **1h** are as follows: Purification by column chromatography on silica gel (DCM/MeOH = 100:1): a yellowish solid (1.007 g, 80%), m.p. = 190.4 °C–191.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.19 (s, 1H), 9.67 (s, 1H), 8.63 (s, 1H), 8.26 (t, J = 8.0 Hz, 1H), 8.12 (d, J = 8.0 Hz, 2H), 7.95 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.62 (s, 1H), 7.35 (t, J = 8.0 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H), 4.30 (t, J = 7.2 Hz, 2H),1.94 (sext, J = 7.2 Hz, 2H), 0.94 (t, J = 8.0 Hz, 3H), ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.92, 155.89, 146.11, 141.49, 137.94, 135.02, 129.96, 123.55, 121.02, 119.35, 117.80, 117.16, 113.75, 112.42, 51.00, 22.75, 10.47, ppm; HRMS (MALDI): m/z $[M-I]^+$ calcd for $C_{17}H_{18}N_3O$: 280.1444; found: 280.1445.

Data for 1-(6-(2-hydroxyphenyl)pyridin-2-yl)-3-propyl-1*H*-imidazol-3-ium iodide **1i** are as follows: Purification by column chromatography on silica gel (DCM/MeOH = 100:1): a yellowish solid (1.102 g, 90%), m.p. = 154.1 °C–154.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.40 (s, 1H), 10.14 (s, 1H), 8.61 (t, J = 2.0 Hz, 1H), 8.31 (d, J = 8.0 Hz, 1H), 8.22 (t, J = 8.0 Hz, 1H), 8.10–8.06 (m, 2H), 7.91 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.04–6.97 (m, 2H), 4.30 (t, J = 8.0 Hz, 2H), 1.93 (sext, J = 7.2 Hz, 2H), 0.93 (t, J = 7.2 Hz, 3H), ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 156.01, 155.16, 145.72, 140.59, 134.96, 131.17, 130.41, 124.86, 123.52, 123.11, 119.48, 119.42, 116.78, 111.78, 50.96, 22.74, 10.46, ppm; HRMS (MALDI): m/z $[M-I]^+$ calcd for $C_{17}H_{18}N_3O$: 280.1444; found: 280.1439.

Data for 1-(6-(4-carboxyphenyl)pyridin-2-yl)-3-propyl-1*H*-imidazol-3-ium iodide **1j** are as follows: Purification by column chromatography on silica gel (DCM/MeOH = 50:1): a yellowish solid (873 mg, 67%), m.p. = 213.7 °C–214.4 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.42 (s, 1H), 8.72 (s, 1H), 8.45 (s, 1H), 8.32–8.23 (m, 4H), 8.13 (s, 1H), 8.06 (d, J = 8.0 Hz, 3H), 4.32 (t, J = 7.2 Hz, 2H), 1.94 (sext, J = 7.2 Hz, 2H), 0.94 (t, J = 7.2 Hz, 3H), ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.10, 154.50, 146.26, 141.80, 140.13, 135.07, 132.40, 129.76, 127.14, 123.61, 121.58, 119.39, 113.21, 51.04, 22.78, 10.49, ppm; HRMS (MALDI): m/z $[M-I]^+$ calcd for $C_{18}H_{18}N_3O_2$: 308.1394; found: 308.1390.

Data for 1-(6-(4-methoxyphenyl)pyridin-2-yl)-3-propyl-1*H*-benzo[*d*]imidazol-3-ium iodide **1k** are as follows: Purification by column chromatography on silica gel (DCM/MeOH = 30:1): a yellowish solid (1.278 g, 90%), m.p. = 247.5 °C–248.2 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.59 (s, 1H), 8.51 (d, J = 8.0 Hz, 1H), 8.33–8.26 (m, 2H), 8.20 (d, J = 8.0 Hz, 3H), 7.95 (d, J = 8.0 Hz, 1H), 7.85–7.78 (m, 2H), 7.13 (d, J = 8.0 Hz, 2H), 4.62 (t, J = 7.2 Hz, 2H), 3.85 (s, 3H), 2.06 (sext, J = 7.2 Hz, 2H), 1.03 (t, J = 7.2 Hz, 3H), ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.94, 156.07, 147.00, 142.30, 141.36, 131.69, 129.45, 129.23, 128.41, 127.81, 127.09, 120.23, 115.63, 114.48, 114.16, 55.40, 48.70, 22.07, 10.78, ppm; HRMS (MALDI): m/z $[M-I]^+$ calcd for $C_{22}H_{22}N_3O$: 344.1757; found: 344.1762.

Data for 1-(6-(4-hydroxyphenyl)pyridin-2-yl)-2-methyl-3-propyl-1*H*-benzo[*d*]imidazol-3-ium iodide **1l** are as follows: Purification by column chromatography on silica gel (DCM/MeOH = 50:1): a yellowish solid (1.296 g, 92%), m.p. = 232.8 °C–233.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.18 (s, 1H), 8.30–8.20 (m, 3H), 8.01 (d, J = 8.0 Hz, 2H), 7.77–7.64 (m, 4H), 6.95 (d, J = 8.0 Hz, 2H), 4.60 (t, J = 7.2 Hz, 2H), 2.96 (s, 3H), 1.94 (sext, J = 7.2 Hz, 2H), 1.05 (t, J = 7.2 Hz, 3H), ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.73, 157.30, 151.88, 145.46, 141.28,

130.94, 130.70, 128.41, 127.53, 127.02, 126.61, 120.92, 118.85, 115.86, 113.46, 113.38, 46.83, 21.89, 11.86, 10.94, ppm; HRMS (MALDI): m/z $[M-I]^+$ calcd for $C_{22}H_{22}N_3O$: 344.1757; found: 344.1760.

Cyclic carbonates **3a–p***; general procedure.* PO (587 mg, 10.0 mmol) and catalyst **1a** (91.4 mg, 0.2 mmol) were successively put into a 25 mL stainless steel reactor that was equipped with a magnetic stir bar. The reactor was pressurized with CO_2 to 0.5 MPa and the contents reacted at 60 °C for 24 h. After the reaction was complete, the reactor was cooled to room temperature and excess CO_2 was carefully vented off. The reaction mixture was added to brine (50 mL) and extracted with dichloromethane (3 × 50 mL). The solvent was removed under reduced pressure and the product was isolated by column chromatography on silica gel (petroleum ether/ethyl acetate).

4-Methyl-1,3-dioxolan-2-one (**3a**): Purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) gave a colorless oil (918 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.79–4.73 (m, 1H), 4.48–4.43 (m, 1H), 3.94–3.89 (m, 1H), 1.36–1.34 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.16, 73.76, 70.68, 19.03.

4-Ethyl-1,3-dioxolan-2-one (**3b**): Purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) gave a yellow oil (1107 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.67–4.59 (m, 1H), 4.51–4.46 (m, 1H), 4.06–4.01 (m, 1H), 1.78–1.65 (m, 2H), 0.99–0.94 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.21, 78.11, 69.06, 26.79, 8.38.

4-Butyl-1,3-dioxolan-2-one (**3c**): Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) gave a colorless oil (1345 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.73–4.66 (m, 1H), 4.54–4.50 (m, 1H), 4.08–4.04 (m, 1H), 1.83–1.64 (m, 2H), 1.47–1.27 (m, 4H), 0.93–0.89 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.2, 77.2, 69.5, 33.6, 26.5, 22.3, 13.8.

4-Hexyl-1,3-dioxolan-2-one (**3d**): Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) gave a colorless oil (1652 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.73–4.66 (m, 1H), 4.52 (t, J = 8.0 Hz, 1H), 4.06 (dd, J = 8.4 Hz, J = 7.2 Hz, 1H), 1.82–1.74 (m, 1H), 1.71–1.63 (m, 1H), 1.49–1.28 (m, 8H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.15, 77.15, 69.43, 33.76, 31.46, 28.73, 24.26, 22.39, 13.91.

4-(Chloromethyl)-1,3-dioxolan-2-one (**3e**): Purification by flash chromatography (petroleum ether/EtOAc = 2:1) gave a yellow oil (1293 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.02–4.96 (m, 1H), 4.61(t, J = 8.0 Hz, 1H), 4.42 (dd, J = 8.8 Hz, J = 5.6 Hz, 1H), 3.83–3.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.54, 74.54, 66.99, 44.20.

4-(Chloromethyl)-4-methyl-1,3-dioxolan-2-one (**3f**): Purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) gave a yellow oil (1456 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.54 (d, J = 8.4 Hz, 1H), 4.11 (d, J = 8.4 Hz, 1H), 3.77 (d, J = 12.4 Hz, 1H), 3.53 (d, J = 12.4 Hz, 1H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.48, 84.04, 71.50, 65.80, 21.29.

4-((Allyloxy)methyl)-1,3-dioxolan-2-one (**3g**): Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) gave a colorless oil (1450 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.92–5.83 (m, 1H), 5.31–5.21 (m, 2H), 4.86–4.81 (m, 1H), 4.51 (t, J = 8.0 Hz, 1H), 4.41 (dd, J = 8.0 Hz, 6.0 Hz, 1H), 4.07–4.04 (m, 2H), 3.72–3.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.95, 133.67, 117.94, 75.04, 72.61, 68.85, 66.29.

4-(Phenoxymethyl)-1,3-dioxolan-2-one (**3h**): Purification by column chromatography on silica gel (petroleum ether/EtOAc = 2:1) gave a white solid (1825 mg, 94%), m.p. = 100.9 °C–101.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (t, J = 8.0 Hz, 2H), 7.04 (t, J = 8.0 Hz, 1H), 6.94 (d, J = 8.0 Hz, 2H), 5.08–5.02 (m, 1H), 4.64 (t, J = 8.4 Hz, 1H), 4.56 (dd, J = 8.8 Hz, J = 6.0 Hz, 1H), 4.26 (dd, J = 10.4 Hz, J = 4.4 Hz, 1H), 4.17 (dd, J = 10.8 Hz, J = 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.77, 154.71, 129.71, 121.99, 114.63, 74.18, 66.90, 66.25.

4-(Butoxymethyl)-1,3-dioxolan-2-one (**3i**): Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) gave a colorless oil (1637 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.84–4.78 (m, 1H), 4.50 (t, J = 8.0 Hz, 1H), 4.39 (dd, J = 8.0 Hz, 6.0 Hz, 1H), 3.70–3.59 (m, 2H), 3.51 (t, J = 6.4 Hz, 2H), 1.56 (quint, J = 6.4 Hz, 2H), 1.36 (sext, J = 8.0 Hz, 2H), 0.92 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.98, 75.10, 71.91, 69.64, 66.32, 31.52, 19.15, 13.83.

4-Phenyl-1,3-dioxolan-2-one (**3j**): Purification by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave a yellow solid (1386 mg, 84%), m.p. = 50.0 °C–51.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.43 (m, 3H), 7.38–7.36 (m, 2H), 5.69 (t, J = 8.0 Hz, 1H), 4.81 (t, J = 8.0 Hz, 1H), 4.34 (t, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.95, 135.87, 129.72, 129.23, 125.94, 78.05, 71.21.

4,4-Dimethyl-1,3-dioxolan-2-one (**3k**): Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) gave a colorless oil (1010 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.13 (s, 2H), 1.50 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.64, 81.81, 75.37, 25.95.

*Hexahydrobenzo[*d*][1,3]dioxol-2-one* (**3l**): Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) gave a colorless oil (1240 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.67–4.62 (m, 2H), 1.88–1.74 (m, 4H), 1.57–1.48 (m, 2H), 1.41–1.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.38, 75.78, 26.62, 19.03.

*5-Vinylhexahydrobenzo[*d*][1,3]dioxol-2-one* (**3m**): Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) give a colorless oil (1386 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.75–5.65 (m, 2H), 5.03–4.94 (m, 4H), 4.76–4.60 (m, 4H), 2.31–2.08 (m, 5H), 1.98 (s, 1H), 1.79–1.51 (m, 5H), 1.36–1.10 (m, 3H); ^{13}C NMR (100 MHz, mixture of diastereoisomers, $CDCl_3$): δ 155.13, 155.10, 141.03, 140.93, 114.14, 113.84, 75.97, 75.62, 75.57, 75.08, 36.21, 33.81, 33.47, 31.55, 26.60, 25.69, 25.58, 24.97.

(4R,5R)-4,5-dimethyl-1,3-dioxolan-2-one (**3n**): Purification by flash chromatography (petroleum ether/EtOAc = 2:1) gave a colorless oil (151 mg, 13%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.35–4.28 (m, 2H), 1.46–1.42 (m, 6H); ^{13}C NMR(100 MHz, $CDCl_3$) δ: 154.61, 80.01, 18.51.

*Tetrahydro-4H-cyclopenta[*d*][1,3]dioxol-2-one* (**3o**): Purification by column chromatography on silica gel

(petroleum ether/EtOAc = 5:1) gave a white solid (987.2 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.14–5.10 (m, 2H), 2.18–2.13 (m, 2H), 1.85–1.63 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.47, 81.85, 33.19, 21.57.

*Tetrahydrofuro[3,4-*d*][1,3]dioxol-2-one* (**3p**): Purification by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) gave a white solid (144.3 mg, 11%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.22–5.21 (m, 2H), 4.28–4.25 (m, 2H), 3.59–3.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.39, 80.04, 73.02.

Recycling experiments; typical procedure. PO (10.0 mmol) and catalyst **1a** (0.2 mmol) were successively put into a 25 mL stainless steel reactor equipped with a magnetic stir bar. The reactor was pressurized with CO_2 to 0.5 MPa and the contents reacted at 60 °C for 24 h. After the reaction was complete, the reactor was cooled to room temperature and excess CO_2 was carefully vented off. The catalyst could easily be precipitated from the cyclic carbonate upon addition of ethyl acetate (5 mL). After filtration, the recycled catalyst was directly used without further purification, and another batch of PO (10.0 mmol) was added and the experiment repeated for subsequent cycles under the same reaction conditions. The solvent was removed under reduced pressure and the products were isolated by column chromatography on silica gel.

Analytical methods. The NMR spectra were recorded on a Bruker Avance III HD 400 spectrometer using tetramethylsilane (TMS) as an internal standard (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). Mass spectroscopy data were collected on a Bruker ultrafleXtreme mass spectrometer.

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Supplemental material

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