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ARTICLE

Bifunctional organocatalysts for conversion of CO_2, epoxides and aryl amines to 3-aryl-2-oxazolidinones

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A route to synthesize 3-aryl-2-oxazolidinones is developed, which is achieved through three component reaction between CO_2, aryl amines, and epoxides with a binary organocatalytic system composed of organocatalyts and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). The method allows wide scopes of epoxide and aryl amine substrates with various functional group in the mild reaction conditions. The control experiments indicate that a cyclic carbonate is formed via cycloaddition of epoxides with CO_2, which further reacts with the β-amino alcohol originated from epoxides and aryl amines, resulting in the formation of 3-aryl-2-oxazolidinones finally.

Introduction

The oxazolidinone heterocycles are important organic molecules in pharmaceutically active compounds and are widely used as Linezolid (antibacterial agents), and Toloxatone (antidepressant).[1]

The use of carbon dioxide as starting materials has emerged as an environmentally friendly method for synthesis of value-added chemicals.[2] The unique biological activities in the medicines containing oxazolidinone heterocycles has encouraged the development and application of many synthetic strategies (Figure 1),[3] such as using N-aziridines,[4] propargylamines,[5] allyl amines,[6] allenamines,[7] propargylic alcohols,[8] dibromoalkanes,[9] epoxy amines,[10] and multicomponent cycloaddition of alkyne.[11] Among the existing methods, the use of the three component reaction between CO_2, aryl amines, and epoxides has emerged as an alternative tool that affords access to the oxazolidinone heterocycles.

Since the first example of the direct conversion of CO_2, anilines, and epoxides to the 3-aryl-2-oxazolidinones with the binary ionic liquids catalytic systems,[12] various catalysts, such as DBU (1,8-diazabicyclo[5.4.0]undec-7-ene)/DBU-derived bromide ionic liquid,[13] K_3PO_4,[14] DBU/TBAI (tetrabutylammonium iodide),[15] Arthrospira-supported ionic liquid,[16] and Fe(II) complexes/DBU,[17] have been developed for the synthesis of the 3-aryl-2-oxazolidinones.

We have reported a new family of multifunctional organocatalysts that allows the cycloaddition between CO_2 and epoxides under ambient conditions.[18] Inspired by our previously reported work, we became interested in the catalytic activity in the three component reaction between CO_2, aryl amines, and epoxides. Here, we demonstrate that the organocatalysts were highly active for the three component reaction between CO_2, aryl amines, and epoxides under mild reaction condition (90°C), together with broad substrates scope.

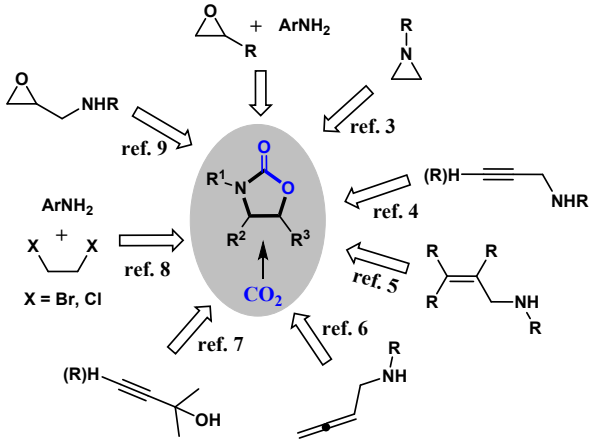

Figure 1 Synthetic method for the oxazolidinone heterocycles.

Results and discussion

Organocatalysts **1a-g** with different electronic properties were prepared as reported previously.[18] Organocatalysts **1a-g** were first tested as catalysts for the cycloaddition reaction of CO_2, anilines, and propylene oxide (PO) **2a** at 90 °C and 5 bar a CO_2 pressure (Table 1, entries 1-7). The combination of organocatalyst **1e** and DBU as cocatalyst was found to be the most efficient catalyst system. Control experiments indicated that neither organocatalyst **1e** nor DBU showed highly catalytic activity in the absence of the other catalyst component (Table

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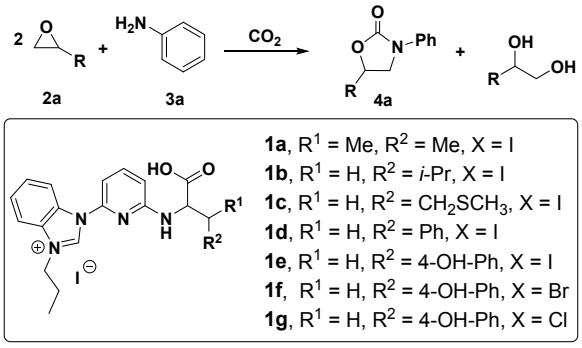
1, entries 8 and 9). A decrease in the product yield was observed by lowering the reaction temperature from 90 °C to 80 °C; even if the reaction time is prolonged, it is difficult to achieve excellent results under 90 °C (Table 1, entries 5 vs 10 and 11). The ratio of the catalyst **1e** to the substrates significantly influenced the reaction rate. A declination in the catalytic activity was observed by decreasing the amount of catalyst **1e** from 2.5 mol% to 1.25 mol% (Table 1, entries 5 vs 12).

Table 1 Optimization of reaction conditions[a]



Entry	R	Cat. (mmol)	Cocat.	T (°C)	P (bar)	T (h)	Yield (%)
1	Me	**1a** (0.05)	DBU	90	5	4	63
2	Me	**1b** (0.05)	DBU	90	5	4	52
3	Me	**1c** (0.05)	DBU	90	5	4	72
4	Me	**1d** (0.05)	DBU	90	5	4	86
5	Me	**1e** (0.05)	DBU	90	5	4	95
6	Me	**1f** (0.05)	DBU	90	5	4	59
7	Me	**1g** (0.05)	DBU	90	5	4	36
8	Me	**1e** (0.05)		90	5	4	0
9	Me		DBU	90	5	4	5
10	Me	**1e** (0.05)	DBU	80	5	4	80
11	Me	**1e** (0.05)	DBU	80	5	8	83
12	Me	**1e** (0.025)	DBU	90	5	4	43
13	Me	**1e** (0.05)	DBU	90	3	4	87
14[b]	Me	**1e** (0.05)	DBU	90	1	25	36
15[b]	Et	**1e** (0.05)	DBU	90	1	25	75
16[c]	Et	**1e** (0.1)	DBU	90	1	25	95

[a]Reaction condition: aniline (2 mmol), propylene oxide (2 mL), catalyst (as indicated in this table), DBU (0.4 mmol), CO_2 (the reaction carried out in a 25 mL stainless steel autoclave). [b]CO_2 balloon. [c]CO_2 balloon, **1e** (0.1 mmol), DBU (0.6 mmol).

When the CO_2 pressure was reduced from 5 bar to 3 bar, a slightly lower yield was observed (Table 1, entries 5 and 13). So we carried out the model reaction under atmospheric pressure of CO_2, but only 36% yield of product (Table 1, entry 14). We found that the low boiling point of propylene oxide is responsible for the poor result. So higher boiling point of butylene oxide is investigated under atmospheric pressure of CO_2, and a 75% yield of product was obtained (Table 1, entry 15). To our delight, the catalyst loading has an obviously promoted effect on reaction rate. When the catalyst loading of **1e** was increased from 2.5 to 5 mol % and cocatalyat of DBU from 20 to 30 mol%, the yield of **4m** reached 95% under atmospheric pressure of CO_2 (Table 1, entry 16).

The search for catalytic systems for the direct conversion of CO_2, anilines, and epoxides to the 3-aryl-2-oxazolidinones started with the discovery of Gao and co-workers in 2014 using the binary ionic liquids of 1-butyl-3-methyl-imidazolium bromide and 1-butyl-3-methyl-imidazolium acetate (Table 2, entry 1).[12] However, this catalytic system and this reported in 2016[13] operate under relatively harsh reaction conditions (> 140 °C, 25 bar CO_2), and a poor substrate of epoxides scope is reported (Table 2, entries 1 and 2). Recently, the search for efficient catalytic systems operating under milder reaction conditions, in particular low pressure of CO_2, has stimulated much interest, and significant progress has been achieved. Two important contributions have been significantly improved to atmospheric pressure of CO_2 using simple inorganic base of K_3PO_4 described by Chung co-workers[14] at 130°C under atmospheric pressure of CO_2 (Table 2, entry 3) and the binary system using TBAI in combination with one equivalent of DBU reported by Yao and co-workers at 115 °C under atmospheric pressure of CO_2 (Table 2, entry 4).[15] However, there are still issues to overcome: (i) K_3PO_4 catalytic system is difficult to control the regioselectivity in reaction, (ii) One equivalent of DBU is often needed in TBAI/DBU catalytic system. In this work, we have developed a binary organocatalytic system **1e** combined with DBU, which has shown to efficiently promote the direct conversion of CO_2, anilines, and epoxides to the 3-aryl-2-oxazolidinones at 90°C under atmospheric pressure of CO_2, together with good functional-group tolerance and broad substrate scope (Table 2, entry 5).

Table 2 Comparison of the efficiency, and scope between previously reported catalytic systems and bifunctional organocatalysts in this work

entry	author	Catalyst/amine	Cocatalyst/amine	T (°C)	P (bar)	Substrate scope	Regioselectivity
1	Gao[12]	BmimBr (10 mol%)	BminOAc (10 mol%)	140	25	ethylene oxide	excellent
2	Gao[13]	DBU (20 mol%)	HDBUBr (5 mol%)	130 160	25 25	ethylene oxide propylene oxide	excellent
3	Chung[14]	K_3PO_4 (20 mol%)	none	130	1	excellent	poor
4	Yao[15]	TBAI (5 mol%)	DBU (100 mol%)	115	1	excellent	excellent
5	This work	**1e** (5 mol%)	DBU (30 mol%)	90	1	excellent	excellent

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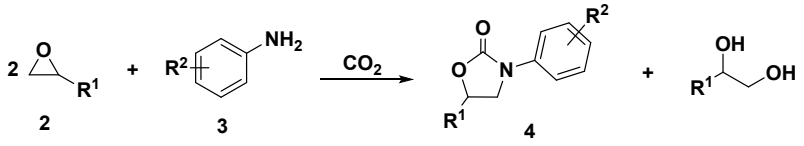
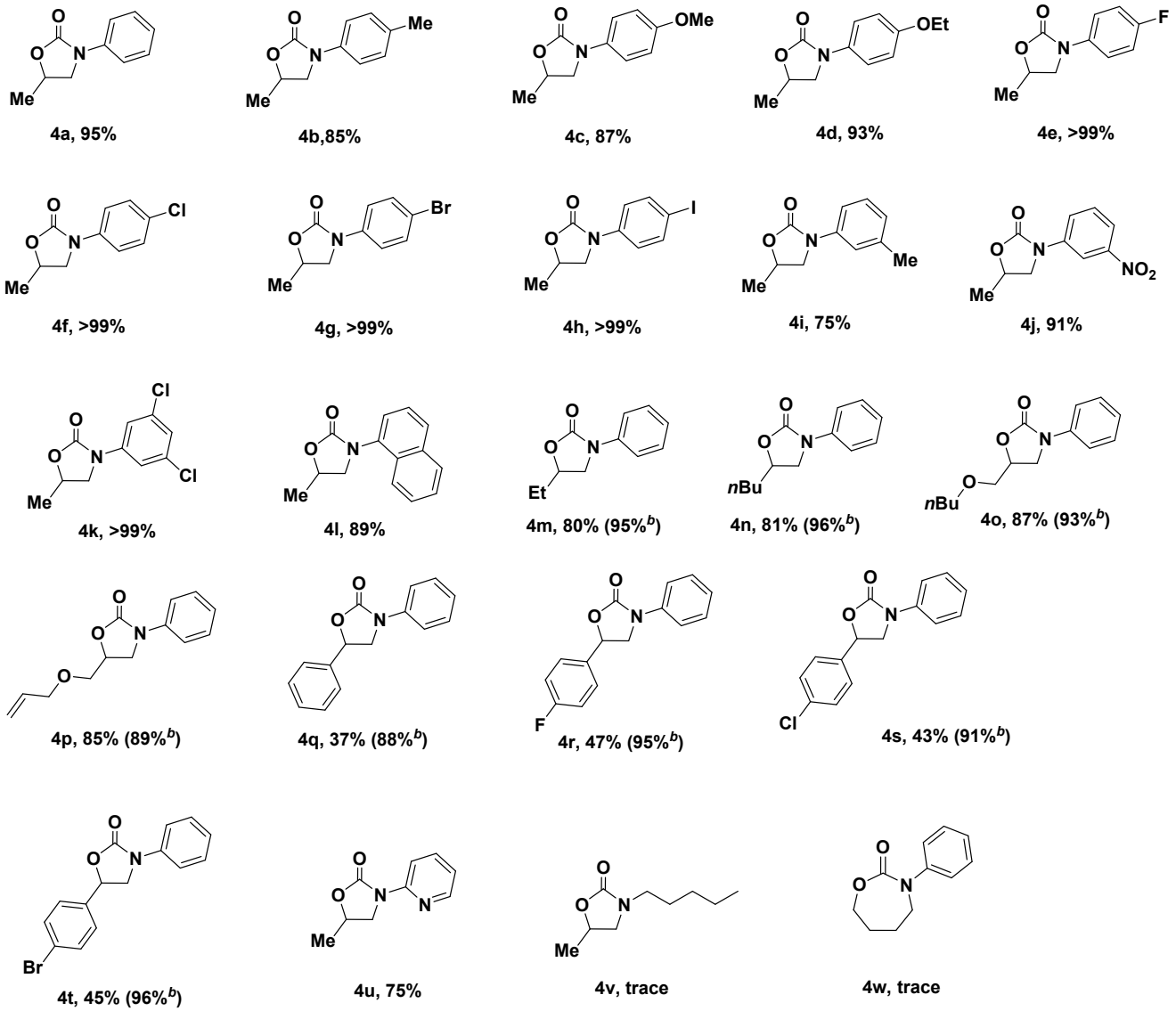
Table 3 Scope of substrates





[a] Reaction condition: aryl amine (2 mmol), terminal epoxides (2 mL), **1e** (0.05 mmol), DBU (0.4 mmol), 90 °C, CO_2 (5 bar), 4 h. [b]CO_2 balloon, **1e** (0.1 mmol), DBU (0.6 mmol).

Under 90 °C and 5 bar of CO_2, we selected PO as the model substrate for investigation of the scope of aryl amines as shown in Table 3. First, various aryl amines **3** were examined to explore the generality of the organocatalyst/DBU-catalyzed cycloaddition reaction. The *para*-substituted aryl amines with electron-withdrawing groups (Table 3, entries **4e-h**) showed higher reactivity than those with electron-donating groups (Table 3, entries **4b-d**). The reactivity of *meta*-substituted aryl amines were also tested, and the corresponding products were obtained in good to excellent yields. The *meta*-substituted aryl amines bearing electron-donating groups (Table 3, entry **4i**) presented lower reactivity than those bearing electron-withdrawing groups (Table 3, entries **4j** and **4k**). To expand the applicability of this method, naphthalen-1-amine **3l** was submitted to the optimized reaction conditions to provide the 89% yield (Table 3, **4l**).

Subsequently, the generality of cycloaddition of a series of terminal epoxides was investigated. First, the reaction of

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terminal epoxides with aliphatic groups, aniline, and CO_2 was performed, and good product yields were obtained (Table 3, entries **4m-p**). However, the reaction of terminal epoxides with aromatic substituents, aniline, and CO_2 is difficult to produce targeted products, excellent product yields were also achieved by increasing reaction temperature to 110 °C (Table 3, entries **4q-t**). The heterocyclic amine of 2-aminopyridine was also investigated in this catalytic system. 2-Aminopyridine smoothly reacted with PO and CO_2 to give 75% of yield (Table 3, **4u**). The alkylamine of *n*-pentylamine was also explored. However, no desired product was obtained (Table 3, entry **4v**). GC-MS analysis showed that the reaction of *n*-pentylamine with PO is difficult to occur, which is responsible for the poor results. These results indicated this catalytic system is limited to aromatic amines.

Because the limitation of the low boiling point of propylene oxide, the scope of aryl amines was not evaluated. The substrate scope of epoxides was investigated as shown in Table 3. Under atmospheric pressure of CO_2 and 90 °C, various epoxides smoothly reacted with aniline to the desired products in excellent yield (please see data in parentheses in Table 3 correspond to the isolated yield of products).

In order to clarify the function between organocatalysts and DBU in every catalytic process, we conducted control experiments by using the two component substrates in different catalytic process (Figure 2). A quantitative yield of cyclic carbonate was achieved in the cycloaddition between PO and CO_2 only using **1e** as catalyst, however, only a 10% yield was obtained using DBU in the absence of **1e**, which suggested that the DBU was not an essentially active species in the reaction of PO with CO_2 (Figure 2, eq 1). The reaction of PO with aniline showed that neither organocatalyst **1e** nor DBU played an important role in the transformation, and the combination of **1e** as catalyst and DBU as cocatalyst was demonstrated to be a highly efficient catalyst system (Figure 2, eq 2). The reaction between above resulting cyclic carbonate and *β*-amino alcohol proceeded smoothly catalyzed by DBU in the absence of **1e**. This observation evidently demonstrated that DBU was only catalytic species in this reaction (Figure 2, eq 3).

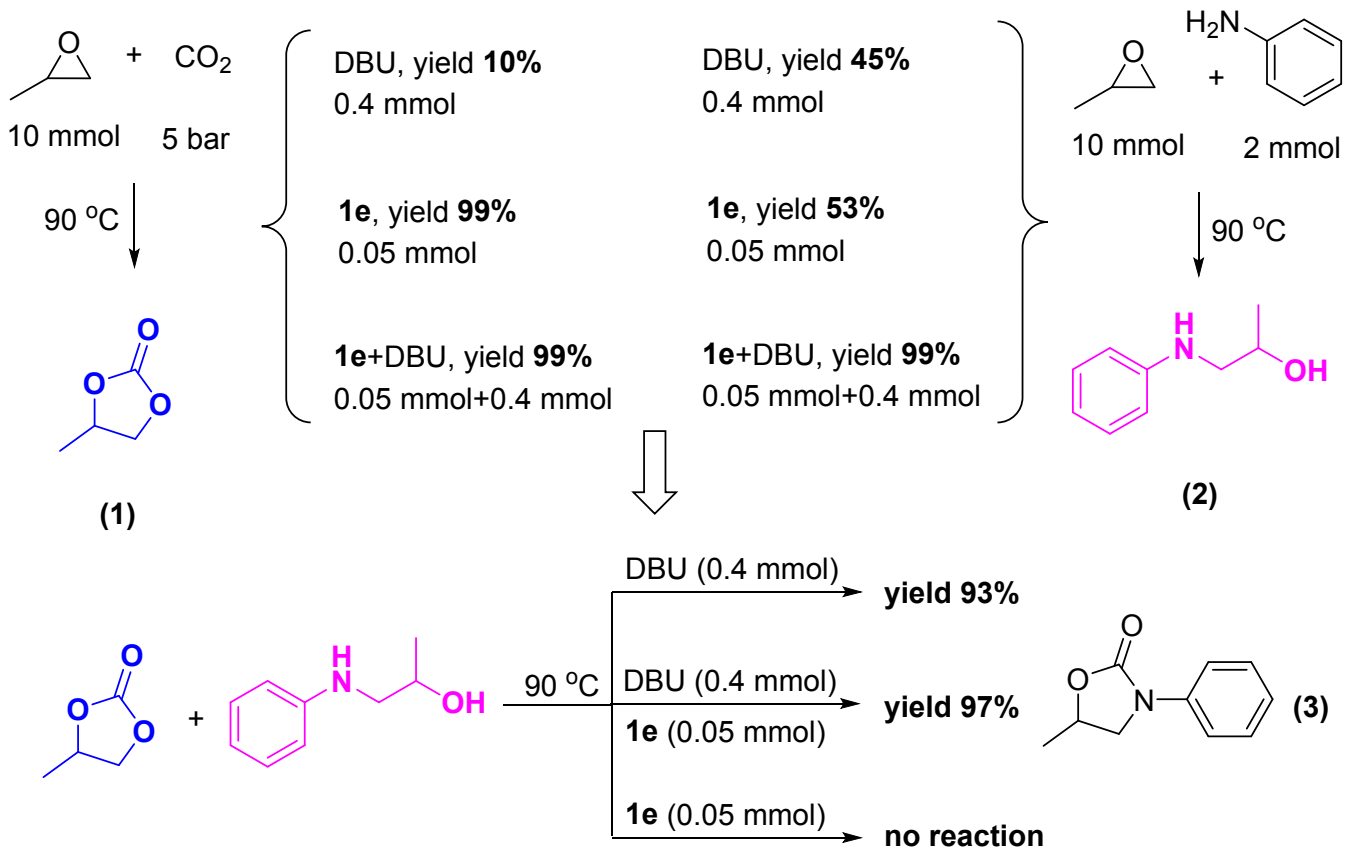

Figure 2 Control experiments for the reaction pathway.

According to the reports of the literature, the formation of the intermediate β-amino alcohol underwent two possible reaction pathways. To determine how the β-amino alcohol was generated under our catalytic condition, two control experiments were performed to investigate the real reaction pathway. The β-amino alcohol could be formed through the reaction between epoxides and aniline as shown in Figure 2, eq 2. The cyclic carbonate reacted also with aniline to afford the β-amino alcohol as shown in Figure 3. Figure 2, eq 2 indicates that PO reacted with aniline to generate the β-amino alcohol, however, the pathway based on the reaction of cyclic carbonate with aniline can be rule out as shown in Figure 3.

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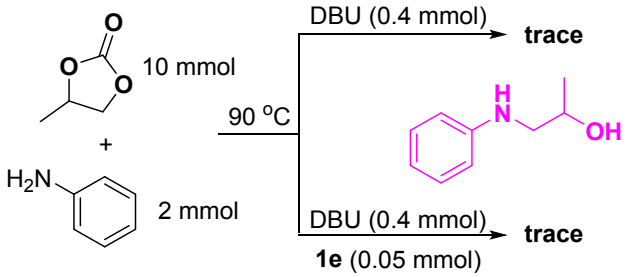
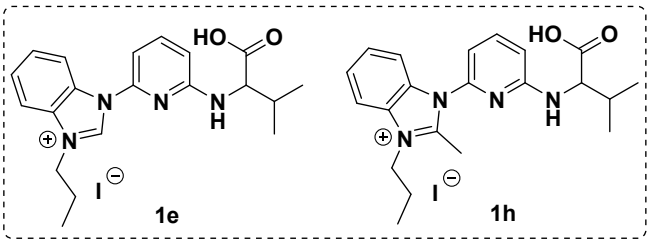


Figure 3 Investigation of possible reaction pathway.

In order to prove the function of the proton in the C2 position of the imidazolium ring with the catalyst **1e** in cycle 2 and cycle 3 in Figure 5, a catalyst **1h** (Figure 4) was designed by introducing a methyl group to the C2 position of the catalyst **1e**. The catalyst **1e** can be transferred to NHC (N-heterocyclic carbene) by the release of a molecule HI in the presence of DBU, but the catalyst **1h** cannot produce the NHC under the same reaction condition. To explore the function of NHC in cycle 1, PO and CO_2 were selected as model substrates to investigate the whether or not the NHC is involved in this reaction using the catalysts **1e** and **1h**, respectively (Figure 4, eq 4). The proton in the C2 position of the imidazolium ring was needed for a high yield of cyclic carbonate, because the absence of proton resulted in an obvious decrease in the yield of cyclic carbonate from 99% to 79% (Figure 4, eq 4), which might be explained by NHC is difficult to produce because the absence of the proton in the C2 position of the imidazolium ring with the catalyst **1e**. In cycle 2, both the NHC and iodine anion can be used as nucleophilic reagents. In order to prove the nucleophilic attack to epoxide occurs whether in the NHC or iodine anion, PO and aniline were selected as model substrates to investigate the whether or not the NHC is involved in this reaction using the catalysts **1e** and **1h**, respectively (Figure 4, eq 5). The results showed that the iodine anion preferentially nucleophilic attack to epoxide in the reaction of PO with aniline.

Since the NHC is not involved in the nucleophilic attack of epoxide, nucleophilic activation may be done by the iodine anion. If the halide anions play an important role of the nucleophilic attack of epoxide, the halide anions have different catalytic performance in the reaction of epoxide with aniline. Therefore, the effect of halide anion bearing catalysts in the reaction of PO with aniline was investigated in Figure 5. As shown in Figure 5, the activity order of anion is $I^- > Br^- > Cl^-$. It well-known that Cl^- has the highest nucleophilicity, whereas I^- has the strongest leaving ability. The results showed that the leaving ability of halide anion is responsible for the reaction of epoxide with aniline.

Supported by these control experiments, we propose the mechanism of **1e**/DBU-catalyzed the three component reaction of CO_2, aniline, and epoxides in Figure 6. In the case of previously reported multifunctional organocatalyzed the cycloaddition of CO_2 with epoxides, it has been revealed that the intramolecular synergistic activation mechanism was realized, in which the *in situ* generated the carbene could activate CO_2, simultaneously the carboxyl group bearing amino acids plays a role of a proton transfer agent.[18] Cycle 1 in this work is consistent with the previous work (Figure 6).



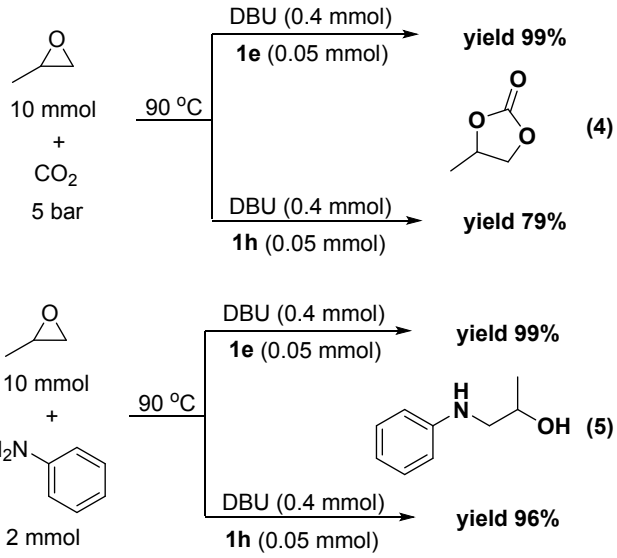


Figure 4 Investigation of function of NHC (N-heterocyclic carbene) in cycle 1 and cycle 2.

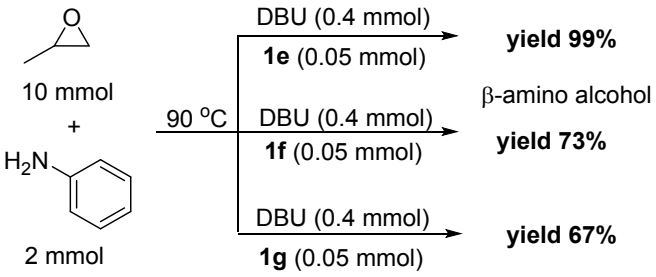


Figure 5 Effect of halide anion in the reaction of PO with aniline.

The observation from control experiments (Figure 2, eq 2) disclosed the synergistic activation between catalyst **1e** and DBU in cycle 2. First, the carboxyl group of catalyst **1e** activates the C-O bond of epoxide through hydrogen bonding. In turn, nucleophilic attack of the iodide anion to the sterically less hindered carbon atom of the epoxide resulted in epoxide ring opening. The aniline is activated by DBU through hydrogen bonding, which resulted in the polarization of the N-H bond. Next, the negatively charged nitrogen atom of the aniline nucleophilically attacks the carbon atom of the ring opening intermediate **I** to form the β-amino alcohol.

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In cycle 3, hydroxyl groups bearing the β-amino alcohol could be activated through DBU, then nucleophilically attacks the carbonyl group of the cyclic carbonate resulting from cycle 1, which further occurs a subsequent intermolecular proton transfer process to afford intermediate **II**. Second, amino group with intermediate **II** could intramolecular coordinate to oxygen of ester group through hydrogen bonding, which resulted in the polarization of the C-O bond. Subsequently, a nucleophilically attack from nitrogen atom to carbon atom of carbonyl group with the intermediate **III**, thereby forming the targeted product and the diol byproduct.

In summary, the multifunctional organocatalysts in combination with DBU displayed high catalytic activity for the synthesis of 3-aryl-2-oxazolidinones through the three component reaction between CO_2, aryl amines, and epoxides. The binary organocatalytic system was found to be robust for a series of terminal epoxides and applicable to various aryl amines under relatively mild condition. In addition, the catalytic behavior of organocatalysts/DBU has been identified by control experiments. In cycle 1, only organocatalysts were necessary for the cycloaddition reaction of epoxides with CO_2. In cycle 2, the reaction of epoxides with aryl amines was realized by the synergistic activation between organocatalysts and DBU. In the final cycle, DBU without organocatalysts could activate the reaction between the β-amino alcohol and the cyclic carbonate.

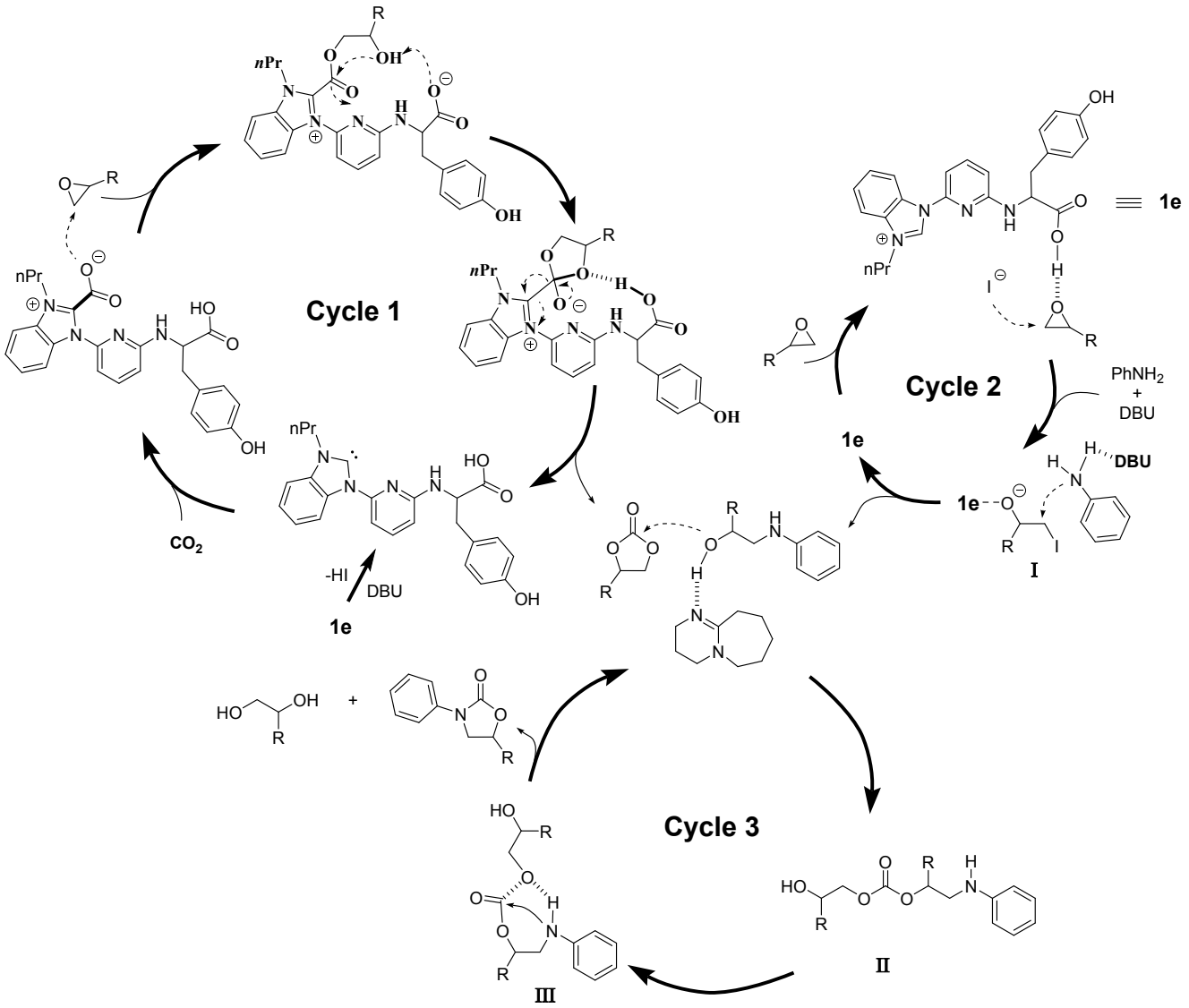

Figure 6 Proposed reaction mechanism.

Experimental

General procedure for synthesis of 3-aryl-2-oxazolidinones.

Epoxides (2.0 mL), aryl amines (2.0 mmol), organocatalyst (0.05 mmol), and DBU (0.4 mmol) were introduced into a 25 mL stainless steel autoclave that was equipped with a magnetic stirrer. The reactor was pressurized with CO_2 to 5 bar and then heated at 90 °C for the required time. The reactor was cooled to room temperature after the reaction. The reaction mixtures

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were added to brine (15 mL) and extracted three times with dichloromethane (3 × 15 mL). The solvent was removed under reduced pressure, and the products were isolated by flash chromatography.

Characterization data for 3-aryl-2-oxazolidinones.

5-methyl-3-phenyloxazolidin-2-one (**4a**).[3g] Purification by flash chromatography (petroleum ether/EtOAc = 5:1) gave a white solid (337 mg, 95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.6 Hz, 2H), 7.36 (t, J = 8.8 Hz, 2H), 7.12 (t, J = 7.6 Hz, 1H), 4.81-4.72 (m, 1H), 4.10 (t, J = 8.6 Hz, 1H), 3.60 (dd, J = 8.0, 7.2 Hz, 1H), 1.51 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.98, 138.50, 129.12, 124.02, 118.27, 69.63, 51.97, 20.80; IR (KBr): 1754 cm^{-1} (C=O); Elemental analysis: calcd for $C_{10}H_{11}NO_2$: C 67.78, H 6.26, N 7.90; found C 67.97, H 6.38, N 8.01.

5-methyl-3-(*p*-tolyl)oxazolidin-2-one (**4b**).[3g] Purification by flash chromatography (petroleum ether/EtOAc = 2:1) gave a white solid (326 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.8 Hz, 2 H), 7.16 (d, J = 8.4 Hz 2H), 4.78-4.70 (m, 1H), 4.08 (t, J =7.6 Hz, 1H), 3.58 (dd, J = 8.8, 7.2 Hz, 1H), 2.30 (s, 3H) 1.50 (d, J =6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.35, 136.28, 133.92, 129.90, 118.64, 69.88, 52.39, 21.07; IR (KBr): 1745 cm^{-1} (C=O); Elemental analysis: calcd for $C_{11}H_{13}NO_2$: C 69.09, H 6.85, N 7.32; found C 69.75, H 6.32, N 7.52.

3-(4-methoxyphenyl)-5-methyloxazolidin-2-one (**4c**).[3g] Purification by flash chromatography (petroleum ether/EtOAc = 2:1) gave a white oil (316 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.8 Hz, 2) 6.87 (d, J = 9.2 Hz, 2H), 4.75-4.70 (m, 1H), 4.04 (t, J = 8.4 Hz, 1H), 3.77 (s, 3H), 3.55 (dd, J = 12.4, 7.2 Hz, 1H), 1.49 (d, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.24, 155.19, 131.62, 120.15, 114.23, 69.53, 55.50, 52.36, 20.68; IR (CH_2Cl_2): 1741 cm^{-1} (C=O); Elemental analysis: calcd for $C_{11}H_{13}NO_3$: C 63.76, H 6.32, N 6.76; found C 64.31, H 6.79, N 6.83.

3-(4-ethoxyphenyl)-5-methyloxazolidin-2-one (**4d**).[19] Purification by flash chromatography (petroleum ether/EtOAc = 5:1) gave a white solid (412 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.38 (m, 2H), 6.90-6.86 (m, 2H), 4.79-4.71 (m, 1H), 4.08-3.98 (m, 3H), 3.57 (dd, J = 7.2, 8.8 Hz, 1H), 1.50 (d, J = 7.2 Hz, 3H), 1.40 (t, J = 3.0 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 155.78, 155.35, 131.64, 120.30, 115.02, 69.65, 63.88, 52.55, 20.86, 14.98; IR (KBr): 1741 cm^{-1} (C=O); Elemental analysis: calcd for $C_{12}H_{15}NO_3$: C 65.14, H 6.83, N 6.33; found C 65.83, H 7.05, N 6.67.

3-(4-fluorophenyl)-5-methyloxazolidin-2-one (**4e**).[3g] Purification by flash chromatography (petroleum ether/EtOAc = 3:1) gave a white solid (388 mg, 99%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.44 (m, 2H), 7.07-7.01 (m, 2H), 4.80-4.72 (m, 1H), 4.07 (t, J = 8.4, 1H), 3.58 (dd, J = 8.8, 3.2 Hz, 1H), 1.50 (d, J =6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.49, 158.07, 155.09, 134.65, 120.10, 120.02, 115.90, 115.68, 69.69, 52.23, 20.76. ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.75; IR (KBr): 1741 cm^{-1} (C=O); Elemental analysis: calcd for $C_{10}H_{10}FNO_2$: C 61.53, H 5.16, N 7.18; found C 61.65, H 4.96, N 7.36.

3-(4-chlorophenyl)-5-methyloxazolidin-2-one (**4f**).[3g] Purification by flash chromatography (petroleum ether/EtOAc = 5:1) gave a white solid (419 mg, 99%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 9.2 Hz,2H), 7.32 (d, J = 8.8 Hz, 2H), 4.82-4.72 (m, 1H), 4.08 (t, J =8.4 Hz, 1H), 3.58 (dd, J = 6.8, 8.4 Hz, 1H), 1.52 (d, J = 6.8 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 154.81, 137.12, 129.22, 129.13, 119.40, 69.70, 51.90, 20.79; IR (KBr): 1741 cm^{-1} (C=O); Elemental analysis: calcd for $C_{10}H_{10}ClNO_2$: C 56.75, H 4.76, N 6.62; found C 55.76, H 4.49, N 6.69.

3-(4-bromophenyl)-5-methyloxazolidin-2-one (**4g**).[3g] Purification by flash chromatography (petroleum ether/EtOAc = 3:1) gave a white solid (508 mg, 99%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.40 (m, 4 H), 4.82-4.74 (m, 1H), 4.07 (d, J = 4.4 Hz, 1 H), 3.58 (dd, J = 8.4, 6.8 Hz, 1 H), 1.53 (d, J =6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.72, 137.60, 132.02, 119.69, 116.76, 69.70, 51.79, 20.76; IR (KBr): 1737 cm^{-1} (C=O); Elemental analysis: calcd for $C_{10}H_{10}BrNO_2$: C 46.90, H 3.94, N 5.47; found C 46.21, H 3.75, N 5.61.

3-(4-iodophenyl)-5-methyloxazolidin-2-one (**4h**).[9b] Purification by flash chromatography (petroleum ether/EtOAc = 5:1) gave a white solid (602 mg, 99%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.4 Hz, 2H) 7.30 (d, J = 8.8 Hz, 2H), 4.80-4.75 (m, 1H), 4.08 (t, J = 8.6 Hz, 1H), 3.57 (d, J = 8.0 Hz, 1H), 1.52 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.66, 138.31, 137.96, 119.99, 87.34, 69.70, 51.68, 20.78; IR (KBr): 1745 cm^{-1} (C=O); Elemental analysis: calcd for $C_{10}H_{10}INO_2$: C 39.63, H 3.33, N 4.62; found C 40.12, H 3.46, N 4.75.

5-methyl-3-(*m*-tolyl)oxazolidin-2-one (**4i**).[20] Purification by flash chromatography (petroleum ether/EtOAc = 5:1) gave a yellow oil (288 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.31-7.23 (m, 2H), 6.96 (d, J = 7.6 Hz, 1H), 4.81-4.73 (m, 1H), 4.10 (t, J = 8.4 Hz, 1H), 3.63-3.59 (m, 1H), 2.37 (s, 3H), 1.53 (d, J = 6.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$-*d*) δ 155.02, 139.11, 138.47, 128.96, 124.93, 119.10, 115.44, 69.61, 52.15, 21.75, 20.83; IR (CH_2Cl_2): 1750 cm^{-1} (C=O); Elemental analysis: calcd for $C_{11}H_{13}NO_2$: C 69.09, H 6.85, N 7.32; found C 69.58, H 6.62, N 7.59.

5-methyl-3-(3-nitrophenyl)oxazolidin-2-one (**4j**).[20] Purification by flash chromatography (petroleum ether/EtOAc = 2:1) gave a yellow solid (405 mg, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) 8.20 (t, J = 2.2 Hz,1H) δ 8.13-8.10 (m, 1H), 7.98-7.95 (m, 1H), 7.55 (t, J = 8.4 Hz, 1H), 4.90-4.82 (m, 1H), 4.20 (t, J = 8.4 Hz,1H), 3.70 (dd, J = 8.4, 6.8Hz, 1H), 1.58 (d, J = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.60, 148.73, 139.71, 130.10, 123.97, 118.51, 112.33, 70.04, 51.77, 20.80; IR (KBr): 1754 cm^{-1} (C=O); Elemental analysis: calcd for $C_{10}H_{10}N_2O_4$: C 54.05, H 4.54, N 12.61; found C 54.39, H 4.73, N 12.95.

3-(3,5-dichlorophenyl)-5-methyloxazolidin-2-one (**4k**). Purification by flash chromatography (petroleum ether/EtOAc = 5:1) gave a white solid (488 mg, 99%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 2.0 Hz, 2H), 7.11 (t, J = 1.8Hz, 1H), 4.85-4.77 (m, 1H), 4.10 (t, J = 8.4 Hz 1H), 3.61 (dd, J = 7.2, 1.6 Hz, 1H), 1.55 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.34, 140.33, 135.56, 123.87, 116.34, 69.89, 51.73, 20.79; IR (KBr): 1758 cm^{-1} (C=O); Elemental analysis: calcd for $C_{10}H_9Cl_2NO_2$: C 48.81, H 3.69, N 5.69; found C 49.17, H 3.57, N 5.82; HRMS (ESI) calcd for $C_{10}H_9Cl_2NO_2$ $[M+Na]^+$ 267.9908, found 267.9898.

5-methyl-3-(naphthalen-1-yl)oxazolidin-2-one (**4l**).[3a] Purification by flash chromatography (petroleum ether/EtOAc = 2:1) gave a white solid (406 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.82 (m, 3H), 7.58-7.44 (m, 4H), 4.95-4.90 (m, 1H), 4.11 (t, J = 4.0 Hz, 1H), 3.62 (dd, J = 6.0, 8.8 Hz, 1H), 1.60 (d, J = 8.8 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 157.10, 134.56, 134.02, 129.91, 128.60, 128.58, 126.90, 126.47, 125.59, 124.50, 122.35, 70.84, 55.81, 20.65; IR (KBr): 1741 cm^{-1} (C=O); Elemental analysis: calcd for $C_{14}H_{13}NO_2$: C 73.99, H 5.77, N 6.16; found C 74.86, H 5.93, N 6.34.

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5-ethyl-3-phenyloxazolidin-2-one (**4m**).[3d] Purification by flash chromatography (petroleum ether/EtOAc = 2:1) gave a colorless oil (310 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 7.2 Hz, 2H), 7.10 (t, J = 8.0 Hz, 1H), 4.59-4.52 (m, 1H), 4.04 (t, J = 8.8 Hz, 1H), 3.62 (t, J = 8.0 Hz, 1H), 1.90-1.72 (m, 2H), 1.05 (t, J = 7.6 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 154.93, 138.38, 128.96, 123.82, 118.10, 74.13, 49.99, 27.95, 8.72; IR (CH_2Cl_2): 1754 cm^{-1} (C=O); Elemental analysis: calcd for $C_{11}H_{13}NO_2$: C 69.09, H 6.85, N 7.32; found C 69.72, H 7.06, N 7.68.

5-butyl-3-phenyloxazolidin-2-one (**4n**).[3d] Purification by flash chromatography (petroleum ether/EtOAc = 2:1) gave a white solid (356 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 6.8 Hz, 2H), 7.38 (t, J = 8.0 Hz, 2H), 7.12 (t, J = 7.2 Hz, 1H), 4.66-4.59 (m, 1H), 4.07 (t, J = 8.8 Hz, 1H), 3.65 (d, J = 7.2 Hz, 1H), 1.89-1.81 (m, 1H), 1.77-1.68 (m, 1H), 1.55-1.49 (m, 1H), 1.43-1.38 (m, 3H), 0.94 (t, J = 8.0 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 155.13, 138.61, 129.21, 124.09, 118.34, 73.27, 50.69, 34.92, 26.83, 22.57, 14.10; IR (KBr): 1745 cm^{-1} (C=O); Elemental analysis: calcd for $C_{13}H_{17}NO_2$: C 71.21, H 7.81, N 6.39; found C 71.76, H 8.15, N 6.61.

5-(butoxymethyl)-3-phenyloxazolidin-2-one (**4o**).[20] Purification by flash chromatography (petroleum ether/EtOAc = 2:1) gave a colorless oil (435 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J =8.4 Hz, 2H), 7.32 (t, J = 8.8 Hz, 2H), 7.08 (t, J = 6.4 Hz, 1H), 4.71-4.65 (m, 1H), 3.99 (t, J = 8.8 Hz, 1H), 3.87 (t, J = 8.8 Hz, 1H), 3.62 (d, J = 3.2Hz, 2H), 3.48 (t, J = 6.4Hz, 2H), 1.55-1.48 (m, 2H), 1.34-1.29 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 154.65, 138.31, 128.94, 123.83, 118.12, 71.74, 71.41, 70.75, 47.12, 31.55, 19.13, 13.81; IR (CH_2Cl_2): 1741 cm^{-1} (C=O); Elemental analysis: calcd for $C_{14}H_{19}NO_3$: C 67.45, H 7.68, N 5.62; found C 68.25, H 7.83, N 5.77.

5-((allyloxy)methyl)-3-phenyloxazolidin-2-one (**4p**).[3g] Purification by flash chromatography (petroleum ether/EtOAc = 2:1) gave a colorless oil (397 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J =8.8 Hz, 2H), 7.36 (t, J =8.0 Hz, 2H), 7.12 (t, J =7.2 Hz, 1H), 5.93-5.82 (m, 1H), 5.30-5.18 (m, 2H), 4.78-4.72 (m, 1H), 4.07-4.03 (m, 3H), 3.94 (dd, J =6.0, 8.8 Hz, 1H), 3.69 (d, J =7.2 Hz, 2H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 154.70, 138.37, 134.03, 129.13, 124.08, 118.28, 117.87, 72.75, 71.36, 70.14, 47.34; IR (CH_2Cl_2): 1750 cm^{-1} (C=O); Elemental analysis: calcd for $C_{13}H_{15}NO_3$: C 66.94, H 6.48, N 6.00; found C 67.39, H 6.76, N 6.28.

3,5-diphenyloxazolidin-2-one (**4q**).[14] Purification by flash chromatography (petroleum ether/EtOAc = 2:1) gave a white solid (326 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.8 Hz, 2H), 7.44-7.36 (m, 7H), 7.15 (t, J = 7.6 Hz, 1H), 5.65-5.60 (m, 1H), 4.40-4.35 (m, 1H), 3.98-3.93 (m, 1H); ^{13}C NMR(100 MHz, $CDCl_3$) δ 154.81, 138.26, 138.23, 129.23, 129.16, 125.80, 124.30, 118.42, 74.15, 52.82; IR (KBr): 1750 cm^{-1} (C=O); Elemental analysis: calcd for $C_{15}H_{13}NO_2$: C 75.30, H 5.48, N 5.85; found C 74.88, H 5.23, N 6.01.

5-(4-fluorophenyl)-3-phenyloxazolidin-2-one (**4r**).[14] Purification by flash chromatography (petroleum ether/EtOAc = 5:1) gave a white solid (506 mg, 98%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.4 Hz, 2H), 7.44-7.37 (m, 4H), 7.18-7.10 (m, 3H), 5.62 (t, J =8.0 Hz, 1H), 4.38 (t, J = 8.4 Hz, 1H), 3.96-3.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.44, 161.97, 154.64, 138.17, 134.05, 134.01, 129.29, 127.89, 127.81, 124.44, 118.46, 116.35, 116.13, 76.63, 52.86; IR (KBr): 1745 cm^{-1} (C=O); Elemental analysis: calcd for $C_{15}H_{12}FNO_2$: C 70.03, H 4.70, N 5.44; found C 70.62, H 4.83, N 5.56.

5-(4-chlorophenyl)-3-phenyloxazolidin-2-one (**4s**).[14] Purification by flash chromatography (petroleum ether/EtOAc = 5:1) gave a white solid (510 mg, 93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.8 Hz, 2H), 7.43-7.36 (m, 6H), 7.18-7.14 (m, 1H), 5.62 (t, J = 8.0 Hz, 1H), 4.39 (t, J = 8.4 Hz, 1H), 3.95-3.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.59, 138.11, 136.75, 135.23, 129.44, 129.30, 127.23, 124.49, 118.47, 73.48, 52.75; IR (KBr): 1762 cm^{-1} (C=O); Elemental analysis: calcd for $C_{15}H_{12}ClNO_2$: C 65.82, H 4.42, N 5.12; found C 66.28, H 4.59, N 5.33.

5-(4-bromophenyl)-3-phenyloxazolidin-2-one (**4t**).[14] Purification by flash chromatography (petroleum ether/EtOAc = 5:1) gave a white solid (500 mg, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.53 (m, 4H), 7.39 (t, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.16 (t, J = 8.0 Hz, 1H), 5.61 (t, J = 8.0 Hz, 1H), 4.39 (t, J = 8.8 Hz, 1H), 3.92 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.45, 137.96, 137.16, 132.25, 129.17, 127.36, 124.37, 123.19, 118.35, 73.37, 52.56; Elemental analysis: calcd for $C_{15}H_{12}BrNO_2$: C 56.63, H 3.80, N 4.40; found C 56.54, H 3.81, N 4.56.

5-methyl-3-(pyridin-2-yl)oxazolidin-2-one (**4u**).[3a] Purification by flash chromatography (petroleum ether/EtOAc = 5:1) gave a white solid (273 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31-8.29 (m, 1H), 8.21 (d, J = 8.0 Hz, 1H), 7.71-7.66 (m, 1H), 7.03-7.00 (m, 1H), 4.84-4.76 (m, 1H), 4.35 (t, J = 8.6 Hz, 1H), 3.82 (dd, J = 10.4, 7.6 Hz, 1H), 1.52 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.59, 150.97, 147.44, 137.68, 118.91, 112.92, 70.32, 50.68, 20.65; Elemental analysis: calcd for $C_9H_{10}N_2O_2$: C 60.66, H 5.66, N 15.72; found C 60.87, H 5.72, N 15.98.

Conflicts of interest

The authors declare no competing financial interest.

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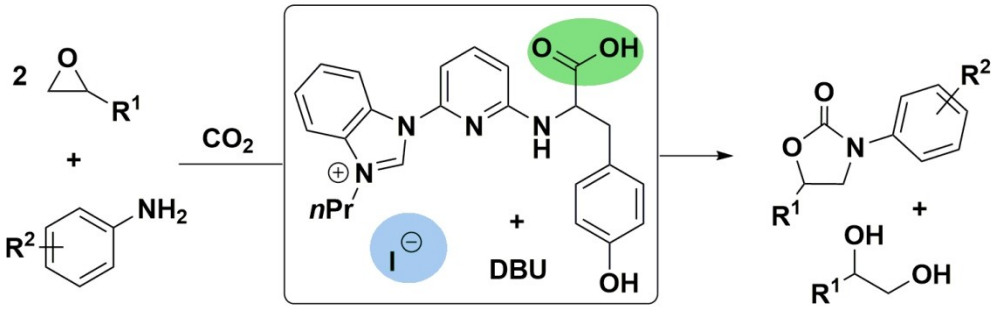

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