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One-Pot Conversion of Carbon Dioxide, Ethylene Oxide, and Amines to 3-Aryl-2-oxazolidinones Catalyzed with Binary Ionic Liquids

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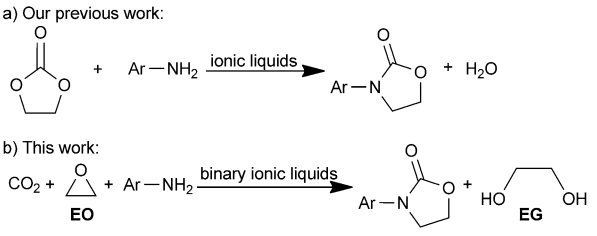
An effective one-pot method for the conversion of carbon dioxide, ethylene oxide, and amines to 3-aryl-2-oxazolidinones has been developed. This one-pot method consists of two parallel reactions and a subsequent cascade reaction between the two products of the corresponding parallel reactions. Notably, the binary ionic liquids of 1-butyl-3-methyl-imidazolium bromide and 1-butyl-3-methyl-imidazolium acetate demonstrate a synergistic catalytic effect on this new strategy. 1-Butyl-3-methyl-imidazolium bromide is essential in two parallel reactions owing to the good nucleophilicity and leaving ability of bromide, and 1-butyl-3-methyl-imidazolium acetate plays a dominant role in the subsequent cascade reaction owing to the strong basicity of acetate. In addition, the binary ionic liquids can be used thrice without significant loss of catalytic activity.

Introduction

Carbon dioxide originating from the combustion of fossil fuel is regarded as the main greenhouse gas.[1] With the growth of world population, it is apparent that atmospheric CO_2 concentration will continue to increase monotonically for the foreseeable future owing to the energy demand. The projected global CO_2 emissions are 36 billion metric tons by 2020 and 45 billion metric tons by 2040.[2] However, CO_2 is an abundant, economical, and nontoxic biorenewable carbon resource.[3] Thus, in the last decade, a growing number of studies have been conducted on the fixation of CO_2 to valuable chemicals.[4] To overcome the thermodynamic stability of CO_2 molecules, the fixation processes typically require harsh reaction conditions (high temperature and high pressure) or high-energy substances such as small-ring compounds, hydrogen, unsaturated compounds, and metal organic compounds.[5]

As a small-ring compound, ethylene oxide (EO; the annual worldwide production of which is approximately 19 million metric tons) is used mainly to produce ethylene glycol (EG) through hydrolysis in the conventional chemical industry.[6] This hydrolysis process, however, does not take full advantage of the inherent high energy of EO.[7] Therefore, it would be practically useful to maintain downstream EG unchanged as well as to utilize the high-energy molecule of EO to fix CO_2. Although several studies on the transformation of CO_2 to value-added chemicals have been performed with epoxides as coupling agents, the products are limited to carbonates, such as glycerol carbonate,[8] dimethyl carbonate,[5a,9] and diethyl carbonate.[10]

3-Aryl-2-oxazolidinones are important heterocyclic compounds that have attracted much attention owing to their bioactivity. They can serve as reversible monoamine oxidase inhibitors, HIV-1 protease inhibitors, and antimicrobial agents.[11] The conventional conversions to oxazolidinones are through the reaction of phosgene and 2-alkamine[12] and the reaction of epoxide and isocyanate,[13] which are considered nongreen as toxic starting materials are used. The alternative synthetic conversions through the reaction of CO_2 and aziridines are also reported.[14] In another study, we developed a strategy for the ionic liquid-catalyzed formation of 3-aryl-2-oxazolidinones from cyclic carbonates and aromatic amines (Scheme 1 a).[15] Herein, we report a new approach for the straightforward conversion of CO_2 to 3-aryl-2-oxazolidinones via the high-energy molecule of EO catalyzed with binary ionic liquids (Scheme 1 b). The binary ionic liquids of 1-butyl-3-methyl-imidazolium bromide



Scheme 1. a) Synthesis of 3-aryl-2-oxazolidinones from cyclic carbonate and aromatic amines and b) the present approach for the straightforward conversion of CO_2 to 3-aryl-2-oxazolidinones.

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(BmimBr) and 1-butyl-3-methyl-imidazolium acetate (BmimOAc) demonstrate a synergistic catalytic effect on the one-pot conversion.

Results and Discussion

Reaction of CO_2, EO, and aniline catalyzed with ionic liquids under various conditions

The reaction of CO_2, EO, and aniline was performed under various conditions to optimize reaction parameters. The effects of a single ionic liquid, binary ionic liquids, the ratio of binary ionic liquids, the amount of ionic liquids, reaction time, temperature, and CO_2 pressure were investigated, and the results are summarized in Table 1.

Table 1. Optimization of reaction conditions for the conversion of CO_2 to 3-phenyl-2-oxazolidinone.[a]

Entry	Ionic liquid	Mol[b] [%]	t [h]	T [°C]	P [MPa]	Yield (Conversion)[c] [%]
1[d]	$BmimBF_4$	20	9	140	2.5	2 (>99)
2[d]	BmimBr	20	9	140	2.5	24 (>99)
3[d]	BmimCl	20	9	140	2.5	45 (>99)
4	BmimOAc	20	9	140	2.5	70 (>99)
5[d]	$BmimBF_4$ + BmimOAc	10 + 10	9	140	2.5	33 (>99)
6	BmimCl + BmimOAc	10 + 10	9	140	2.5	74 (>99)
7	BmimBr + BmimOAc	10 + 10	9	140	2.5	94 (>99)
8	BmimBr + BmimOAc	15 + 5	9	140	2.5	84 (>99)
9	BmimBr + BmimOAc	5 + 15	9	140	2.5	81 (>99)
10	BmimBr + BmimOAc	10 + 10	12	140	2.5	94 (>99)
11	BmimBr + BmimOAc	15 + 15	12	140	2.5	94 (>99)
12	BmimBr + BmimOAc	5 + 5	12	140	2.5	70 (>99)
13	BmimBr + BmimOAc	10 + 10	6	140	2.5	83 (>99)
14	BmimBr + BmimOAc	10 + 10	9	130	2.5	72 (>99)
15	BmimBr + BmimOAc	10 + 10	9	140	2	81 (>99)

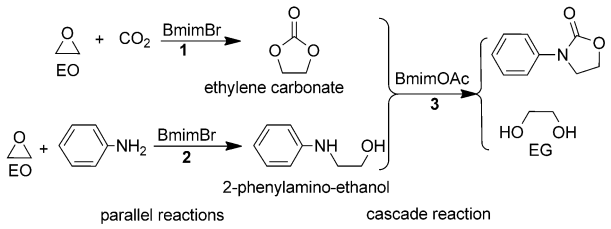
[a] Reaction conditions: aniline (2 mmol), EO (2 mL); [b] Based on aniline; [c] GC yield of 3-phenyl-2-oxazolidinone and conversion of aniline; [d] A mixture of 2-(phenylamino)ethanol and its oligomers was detected.

Under different reaction conditions, the conversion of aniline was extremely high (>99%); however, the yield of 3-phenyl-2-oxazolidinone changed considerably. Upon using 20 mol% of 1-butyl-3-methyl-imidazolium tetrafluoroborate ($BmimBF_4$), BmimBr, 1-butyl-3-methyl-imidazolium chloride (BmimCl), or BmimOAc alone, we obtained 3-phenyl-2-oxazolidinone in 2, 24, 45, and 70% yields, respectively (Table 1, entries 1–4). Then, binary ionic liquids were investigated. The mixture of $BmimBF_4$ and BmimOAc and the mixture of BmimCl and BmimOAc afforded the product in 33 and 74% yields, respectively (entries 5 and 6). Notably, the mixture of 10 mol% of BmimBr and 10 mol% of BmimOAc afforded the product in approximately 94% yield, which revealed a synergistic catalytic effect of binary ionic liquids (entry 7). By varying ratios of BmimBr and BmimOAc, no improvement in the yields was achieved (entries 8 and 9). In addition, increasing the reaction time or catalyst amount did not improve the yield (entries 10 and 11). Decreasing the catalyst amount, reaction time, temperature, or CO_2 pressure led to lower yields (entries 12–15). Furthermore, an equal amount of 3-phenyl-2-oxazolidinone and EG was generated under optimal reaction conditions (entry 7) as determined from ^{1}H NMR analysis of the reaction mixture (Figure S1).

Reaction mechanism studies

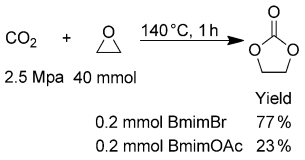
During the reaction under optimal conditions (entry 7), a small amount of 2-(phenylamino)ethanol was detected in 1 h and EG was obtained as a byproduct after the completion of the reaction. 2-(Phenylamino)ethanol was probably the intermediate in this one-pot conversion of CO_2 to 3-phenyl-2-oxazolidinone. Hence, a reaction mechanism was proposed (Scheme 2): EO as a high-energy molecule is used to fix CO_2 to ethylene carbonate [reaction (1)]. At the same time, EO reacts with aniline to form the intermediate 2-(phenylamino)ethanol [reaction (2)]. Then, 2-(phenylamino)ethanol reacts with ethylene carbonate to yield 3-phenyl-2-oxazolidinone and EG [reaction (3)]. Notably, two reactions [reactions (1) and (2)] proceed in parallel, followed by a cascade reaction [reaction (3)] between the two products of the corresponding parallel reactions. Notably, the binary ionic liquids of BmimBr and BmimOAc synergistically catalyze this one-pot conversion: BmimBr is essential in the parallel reactions involving EO [reactions (1) and (2)] because bromide promotes ring opening of epoxides owing to its good nucleophilicity and leaving ability,[5c,9f,16] and BmimOAc plays a dominant role in the subsequent cascade reaction of 2-(phenylamino)ethanol and ethylene carbonate [reaction (3)], in which the strong basicity of acetate results in increase of nucleophilicity of 2-(phenylamino)ethanol.

To validate the proposed reaction mechanism, the following experiments and calculations were performed. First, in the presence of BmimBr or BmimOAc



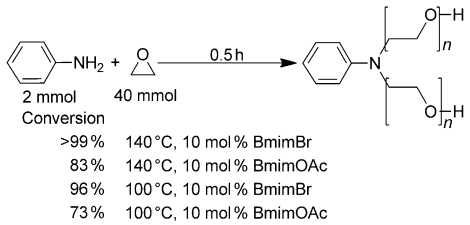
Scheme 2. The proposed reaction mechanism.

alone, the reaction of EO and CO_2 [Scheme 2, reaction (1)] afforded ethylene carbonate in 77 and 23% yields, respectively (Scheme 3). This finding indicated that BmimBr was more effective than BmimOAc in the cycloaddition of CO_2 and EO [Scheme 2, reaction (1)]. Second, the enthalpy changes calculated by using DFT indicated that 2-(phenylamino)ethanol was



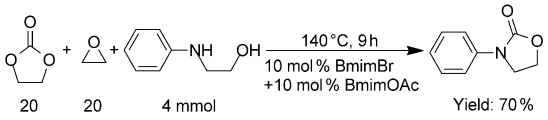
Scheme 3. Reaction of CO_2 and EO.

favorably formed through the reaction of aniline and EO [$\Delta H_1 = -27.7$ kcal mol^{-1}; Scheme 2, reaction (2)] rather than through the reaction of aniline and ethylene carbonate ($\Delta H_2 = -17.3$ kcal mol^{-1}) (Scheme S1). However, the use of BmimBr in the reaction of aniline and EO [Scheme 2, reaction (2)] gave only a mixture of oligomers. These oligomers could be due to the further reaction of 2-(phenylamino)ethanol with EO.[17] In contrast, the use of BmimOAc gave the lower conversions of aniline (>99% vs. 83% at 140 °C; 96% vs. 73% at 100 °C), which indicated that BmimBr was more effective than BmimOAc for the ring-opening reaction of EO [Scheme 2, reaction (2); Scheme 4]. Adding ethylene carbonate and EO to

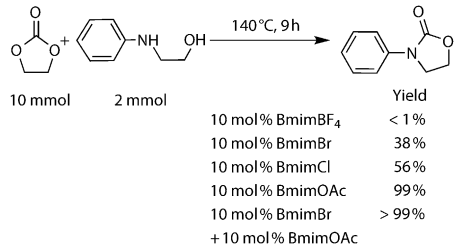


Scheme 4. Reaction of aniline and EO.

2-(phenylamino)ethanol (5:5:1) simultaneously afforded 3-phenyl-2-oxazolidinone (major product, in 70% yield) instead of the above-mentioned oligomers (Scheme 5). These results revealed that the 2-(phenylamino)ethanol intermediate could react with ethylene carbonate more efficiently and favorably than EO. Third, with use of different ionic liquids in the reaction of ethylene carbonate and 2-(phenylamino)ethanol to produce 3-phenyl-2-oxazolidinone [Scheme 2, reaction (3)], the catalytic activity followed the order BmimOAc > BmimCl > BmimBr > $BmimBF_4$, which was consistent with the order of the basicity of anions of ionic liquids (Scheme 6).[15] This finding indicated that BmimOAc played the dominant role in this reaction owing to the strong basicity of acetate. Finally, as a supplement, the reaction of ethylene carbonate, EO, and aniline

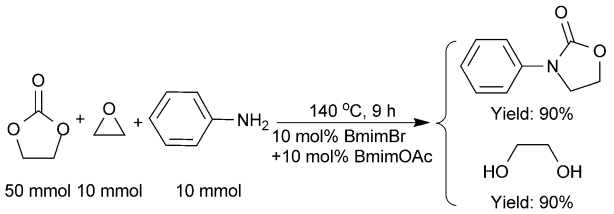


Scheme 5. Reaction of ethylene carbonate, EO, and 2-(phenylamino)ethanol.



Scheme 6. Reaction of ethylene carbonate and 2-(phenylamino)ethanol.

(5:1:1) affording an equal amount of 3-phenyl-2-oxazolidinone and EG (90% yields) also testified the proposed reaction mechanism (Scheme 7).



Scheme 7. Reaction of ethylene carbonate, EO, and aniline.

Reusability of binary ionic liquids

To investigate their reusability, the binary ionic liquids of BmimBr and BmimOAc were recycled after the reaction of CO_2, EO, and aniline.

The binary ionic liquids could be recovered easily through simple extraction with water from chloroform and desiccation under vacuum. As shown in Figure 1, the yields of the first three cycles were constant whereas the yield of the fourth cycle decreased. After the fourth cycle, the ionic liquids were decomposed partially as determined from ^{1}H NMR analysis (Figure S2); this decomposition was probably due to the volatilization of acetic acid during the desiccation of ionic liquids under vacuum at 130 °C.[18] Another reason for the decrease in

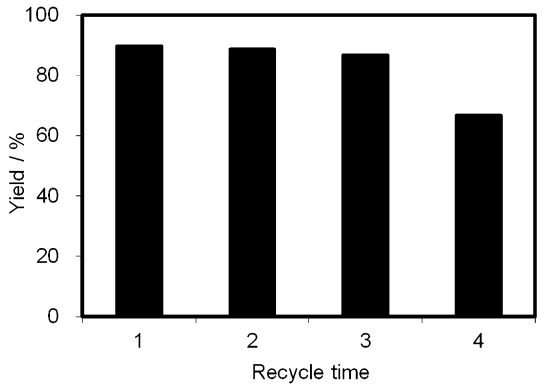


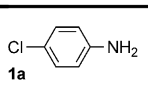
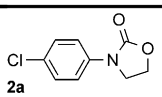
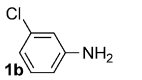
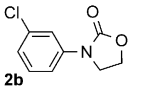
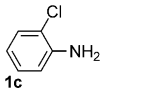
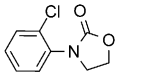
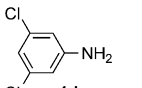
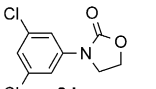
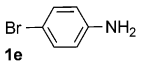
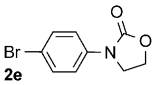
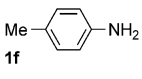
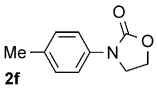
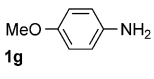
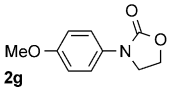
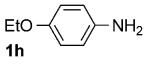
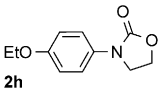
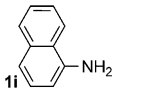
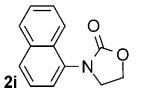
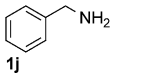
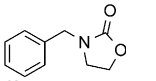
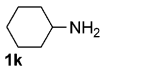
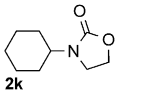
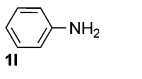
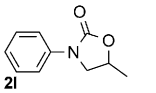
Figure 1. Reusability of binary ionic liquids. Reaction conditions: aniline (4 mmol), EO (4 mL), BmimBr (0.4 mmol), BmimOAc (0.4 mmol), 9 h, 140 °C, 2.5 MPa CO_2 pressure.

the yield could be that EG was not removed completely under the above recycling conditions. The residue EG could hinder the reaction of 2-(phenylamino)ethanol and ethylene carbonate [Scheme 2, reaction (3)]. Instead, 2-(phenylamino)ethanol was converted to its oligomers. A control experiment was performed to demonstrate the prohibiting effect of EG: After adding 1 equiv. of EG, the model reaction of CO_2, EO, and aniline under optimal reaction conditions afforded 3-phenyl-2-oxazolidinone in only 48% yield. In addition, with the desiccation of ionic liquids under vacuum at 70 °C (water can be removed; however, EG was removed with difficulty under these conditions), the yields of the second and third cycles decreased considerably to 74 and 28%, respectively.

Reaction of CO_2, EO, and other amines catalyzed with binary ionic liquids of BmimBr and BmimOAc

To investigate the generalities of this method, the reactions of CO_2, EO, and other amines catalyzed with binary ionic liquids of BmimBr and BmimOAc were performed (Table 2). *p*-Chloroaniline (**1a**) and *m*-chloroaniline (**1b**) gave the corresponding 3-aryl-2-oxazolidinones **2a** and **2b** in >99% yields (entries 1 and 2). In contrast, *o*-chloroaniline (**1c**) afforded the product **2c** in a slightly lower yield (96%) owing to the steric effect (entry 3). Aromatic amines with electron-withdrawing substituents (such as halides) **1a**–**e** gave the desired products **2a**–**e** in quantitative yields (entries 1–5). However, aromatic amines with electron-donating substituents (such as alkyl or alkoxy species) **1f**–**h** provided target products **2f**–**h** in 63–77% yields and *N*,*N*-(dihydroxyethyl)amines in 11–17% yields (entries 6–8). The formation of byproducts could be attributed to the increased electronegativity of amidos. In addition, naphthalen-1-ylamine (**1i**) could be converted to **2i** in an excellent yield (entry 9). Aliphatic amines that possess stronger electronegativity, such as benzylamine (**1j**) and cyclohexylamine (**1k**), were tolerated, which afforded 3-substituted-2-oxazolidinones **2j** and **2k** in 31 and 29% yields, respectively (entries 10 and 11). The reaction of CO_2, propylene oxide, and aniline afforded 5-methyl-3-phenyl-oxazolidin-2-one (**2l**) in 31% yield (entry 12).

Table 2. Conversion of CO_2 to various 3-substituted-2-oxazolidinones catalyzed with binary ionic liquids.[a]

Entry	Amine	Product	Yield[b] [%]
1	 **1a**	 **2a**	>99
2	 **1b**	 **2b**	>99
3	 **1c**	 **2c**	96
4	 **1d**	 **2d**	>99
5	 **1e**	 **2e**	>99
6	 **1f**	 **2f**	77
7	 **1g**	 **2g**	63
8	 **1h**	 **2h**	75
9	 **1i**	 **2i**	>99
10	 **1j**	 **2j**	31
11	 **1k**	 **2k**	29
12[c]	 **1l**	 **2l**	31

[a] Reaction conditions: amine (2 mmol), EO (2 mL), BmimBr (0.2 mmol), BmimOAc (0.2 mmol), 9 h, 140 °C, 2.5 MPa CO_2 pressure; [b] GC yield; [c] Propylene oxide (40 mmol).

Conclusions

We have developed an effective strategy for the direct conversion of CO_2 to a series of 3-aryl-2-oxazolidinones via the high-energy molecule of ethylene oxide catalyzed with binary ionic liquids. This one-pot method consists of two parallel reactions and a subsequent cascade reaction between the two products of the corresponding parallel reactions. The binary ionic liquids of 1-butyl-3-methyl-imidazolium bromide (BmimBr) and 1-butyl-3-methyl-imidazolium acetate (BmimOAc) demonstrate a synergistic catalytic effect on this process. BmimBr promotes two parallel reactions owing to the good nucleophilicity and leaving ability of bromide, and BmimOAc accelerates the subsequent cascade reaction owing to the strong basicity of acetate. Furthermore, the binary ionic liquids of BmimBr and BmimOAc can be recycled by using the simple extraction method and used thrice without significant loss of catalytic activity.

Experimental Section

General

CO_2 with a purity of 99.995% was commercially available. All ionic liquids were supplied by the Centre for Green Chemistry and Catalysis, LICP, CAS. 2-(Phenylamino)ethanol was supplied by TCI. Ethylene carbonate was supplied by Sigma–Aldrich. The other compounds were supplied by Sinopharm. All chemicals were used without further purification.

GC analysis was performed by using a Shimadzu GC-14B equipped with a capillary column DM-1701 (30 m × 0.32 mm × 0.25 μm) equipped with a flame ionization detector. The NMR spectra were recorded by using a Bruker Ascend 400 and Bruker DRX500 MHz NMR spectrometers with tetramethylsilane as the internal standard.

Typical method for the reaction of CO_2, EO, and aniline catalyzed with binary ionic liquids of BmimBr and BmimOAc

In a typical experiment, BmimBr (0.044 g, 0.2 mmol), BmimOAc (0.040 g, 0.2 mmol), aniline (0.186 g, 2.0 mmol), and EO (2 mL, 40 mmol) were added to a stainless steel autoclave reactor with an inner volume of 25 mL. The reactor was pressurized with approximately 1 MPa of CO_2 pressure at ambient temperature. Then, the reactor was heated to 140 °C and the CO_2 pressure was adjusted to 2.5 MPa for 9 h. After the completion of the reaction, the autoclave was cooled to RT, followed by slow venting of the remaining CO_2. The reaction mixture (0.07 g) was taken out for NMR analysis. Next, chloroform (7 mL) was added to the reaction mixture. The organic phase was washed with water (3×7 mL) to remove ionic liquids and EG and then analyzed by using GC with *n*-dodecane as the internal standard. The pure 3-phenyl-2-oxazolidinone was obtained by using chromatography on silica gel and structurally characterized by using NMR spectroscopy.

To investigate the reusability of binary ionic liquids, chloroform (14 mL) was added to the reaction mixture after slow venting of the remaining CO_2. The organic phase was extracted with water (5×14 mL) and then analyzed by using GC with *n*-dodecane as the internal standard. The ionic liquids were recovered after the aqueous phase was evaporated under vacuum at 130 °C for 10 h to remove water and EG. The same method was repeated for the next cycle.

Characterization data

3-Phenyl-2-oxazolidinone: ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.54 (d, J = 8.0 Hz, 2H), 7.38 (t, J = 8.0 Hz, 2H), 7.15 (t, J = 8.0 Hz, 1H), 4.47–4.52 (m, 2H), 4.09 ppm (t, J = 7.5 Hz, 2H).

3-(4-Chloro-phenyl)-oxazolidin-2-one (**2a**): ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.49 (d, J = 8.8 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 4.49 (t, J = 8.0 Hz, 2H), 4.03 ppm (t, J = 8.0 Hz, 2H).

3-(3-Chloro-phenyl)-oxazolidin-2-one (**2b**): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.61 (s, 1H), 7.46–7.49 (m, 1H), 7.32 (t, J = 8.3 Hz, 1H), 7.13–7.15 (m, 1H), 4.50–4.54 (m, 2H), 4.05–4.09 ppm (m, 2H).

3-(2-Chloro-phenyl)-oxazolidin-2-one (**2c**): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.47–7.49 (m, 1H), 7.42–7.44 (m, 1H), 7.30–7.35 (m, 2H), 4.52–4.57 (m, 2H), 4.03 ppm (t, J = 8.0 Hz, 2H).

3-(3,5-Dichloro-phenyl)-oxazolidin-2-one (**2d**): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.52 (s, 2H), 7.15 (s, 1H), 4.53 (t, J = 8.0 Hz, 2H), 4.05 ppm (t, J = 8.0 Hz, 2H).

3-(4-Bromo-phenyl)-oxazolidin-2-one (**2e**): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.45–7.51 (m, 4H), 4.49–4.52 (m, 2H), 4.05 ppm (t, J = 8.0 Hz, 2H).

3-*p*-Tolyl-oxazolidin-2-one (**2f**): ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.42 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 4.48 (t, J = 8.0 Hz, 2H), 4.04 (t, J = 8.0 Hz, 2H), 2.33 ppm (s, 3H).

3-(4-Methoxy-phenyl)-oxazolidin-2-one (**2g**): ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.43 (d, J = 9.2 Hz, 2H), 6.91 (d, J = 9.2 Hz, 2H), 4.46 (t, J = 8.0 Hz, 2H), 4.02 (t, J = 8.0 Hz, 2H), 3.79 ppm (s, 3H).

3-(4-Ethoxy-phenyl)-oxazolidin-2-one (**2h**): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.42–7.44 (m, 2H), 6.90–6.92 (m, 2H), 4.45–4.48 (m, 2H), 4.00–4.04 (m, 4H), 1.41 ppm (t, J = 7.0 Hz, 3H).

3-Naphthalen-1-yl-oxazolidin-2-one (**2i**): ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.85–7.87 (m, 3H), 7.47–7.59 (m, 4H), 4.64 (t, J = 8.0 Hz, 2H), 4.09 ppm (t, J = 8.0 Hz, 2H).

3-Benzyl-oxazolidin-2-one (**2j**): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.29–7.40 (m, 5H), 4.46 (s, 2H), 4.33 (t, J = 8.0 Hz, 2H), 3.45 ppm (t, J = 8.0 Hz, 2H).

3-Cyclohexyl-oxazolidin-2-one (**2k**): ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 4.31 (t, J = 8.0 Hz, 2H), 3.66–3.70 (m, 1H), 3.53 (t, J = 8.0 Hz, 2H), 1.65–1.85 (m, 4H), 1.68 (d, J = 13.5 Hz, 1H), 1.34–1.39 (m, 4H), 1.08–1.13 ppm (m, 1H).

5-Methyl-3-phenyl-oxazolidin-2-one (**2l**): ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.53 (d, J = 7.2 Hz, 2H), 7.37 (t, J = 7.2 Hz, 2H), 7.13 (t, J = 7.2 Hz, 1H), 4.75–4.83 (m, 1H), 4.11 (m, 1H), 3.62 (m, 1H), 1.53 ppm (d, J = 6.4 Hz, 3H).

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Keywords: 3-aryl-2-oxazolidinones · carbon dioxide fixation · ethylene oxide · ionic liquids · one-pot reaction

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