

Article

Cu(I)/Ionic Liquids Promote the Conversion of Carbon Dioxide into Oxazolidinones at Room Temperature

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Abstract: Recently, the efficient chemical fixation of carbon dioxide (CO₂) into high value chemicals without using noble metal catalysts has become extremely appealing from the viewpoint of sustainable chemistry. In this work, a one-pot three component reaction of propargylic alcohols, amines and CO₂ that can proceed in an atom economy and environmentally benign manner by combination of CuI and tetrabutylphosphonium imidazol ([P₄₄₄₄][Im]) as a catalyst was described. Catalysis studies indicate that this catalytic system is an effective catalyst for the conversion of CO₂ into oxazolidinones at room temperature and ambient pressure without any solvent. The results provide a useful way to design novel noble metal-free catalyst systems for the transformation of CO₂ into other valuable compounds.

Keywords: carbon dioxide; ionic liquids; catalysis; oxazolidinones

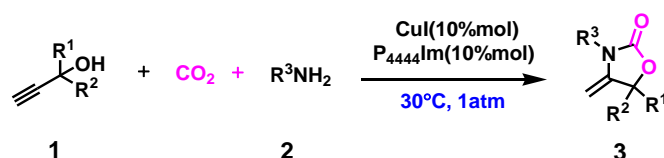
1. Introduction

With the global consumption of fossil fuels, the increasing concentration of CO₂ in the atmosphere could have a significant impact on the global climate [1,2]. Therefore, the development of efficient strategies to reduce CO₂ emissions has become an imperative task for scientific researchers [3–5]. The chemical fixation and transformation of CO₂ into valuable chemicals is an ideal pathway for reducing CO₂ emissions and fully utilize this cheap C₁ source [6–10]. Thus, considerable efforts have been devoted to the exploration of efficient strategy for chemical utilization of CO₂ to produce high-value chemical commodities [11–16].

Oxazolidinones are a class of nitrogen-containing heterocyclic compounds which have been used as organic intermediates, chiral additives, antibacterial drugs and muscle relaxants, etc. [17–20]. The synthesis of oxazolidinones between propargyl alcohol, CO₂ and an amine is an important and atom-economic reaction for chemical utilization of CO₂ [12,21]. However, the biggest obstacle is the lack of an effective catalyst to facilitate its activation and conversion, since CO₂ is a highly oxidized and thermodynamically stable molecule [22]. In recent years, various metal catalysts [23–28] and metal-free catalysts [29,30] have been verified to be efficient for the reaction. Nevertheless, most of the catalytic systems usually required high temperatures, high pressures, toxic organic solvents and noble

metals. Therefore, a cheap, green and highly active catalyst is urgently needed in order to make the reaction go smoothly at room temperature and atmospheric pressure.

Our previous work has revealed that metal salts combined with ionic liquid (IL) represent a new hybrid catalyst that can be regarded as one of the most promising and efficient catalysts for chemical transformations of CO₂ because of their remarkable synergistic catalysis mechanism [31]. For example, a Cu(I) salt/protic IL catalytic system can efficiently catalyze the cycloaddition of CO₂ with propargylic alcohols to produce α -alkylidene cyclic carbonates under mild conditions. Inspired by these works, we now report that Cu(I) salt and the IL tetrabutylphosphonium imidazol([P₄₄₄₄][Im]) act as a catalyst for the three component reaction of terminal propargyl alcohols, CO₂ and amines (Scheme 1). The results show that the CuI/[P₄₄₄₄][Im] catalyst system exhibits excellent catalytic performance for the reaction with a wide range of substrates under atmospheric pressure and room temperature conditions. In addition, the ionic liquid could be recovered and reused at least five times without an obvious loss of catalytic activity and selectivity.



Scheme 1. Cycloaddition reaction of propargyl alcohol and amines with CO₂.

2. Result and Discussion

Owing to the unique catalytic performance of ILs in CO₂ conversion [32–34], several quaternary phosphonium-based ILs and various copper (I) salts were selected to catalyze the reaction. Figure 1 shows the structures of the ILs.

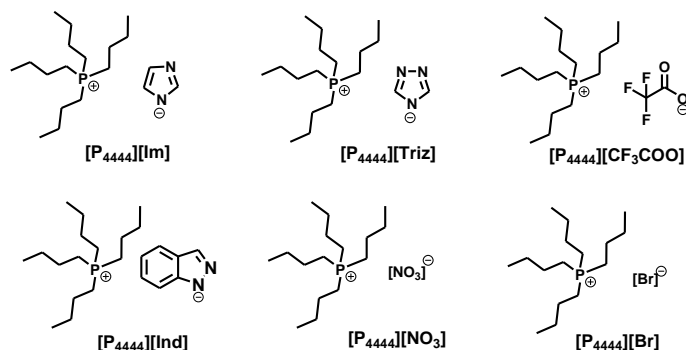


Figure 1. The structure and abbreviations of CO₂-reactive ILs employed in this work.

The synthesis of 1,3-oxazolidin-2-one **3a** was carried out to systematically investigate the effect of various parameters on the reaction. The reaction was performed at 30 °C, 1 atm CO₂, and 24 h, and the results are shown in Table 1. As expected, the reaction did not occur in the absence of any catalysts. The individual IL [P₄₄₄₄][Im] and CuI as a catalyst were ineffective for the reaction, giving a low yield of product (Table 1, entries 2–3). To our delight, the yield of the product reached rose to 91% in the presence of CuI and [P₄₄₄₄][Im] (Table 1, entry 4). Encouraged by the result, we investigated the effect of the type of anion on the yield of **3a** in the reaction. The yield of **3a** was found to be 70%, 41%, 35%, 30%, and 28%, respectively, when CuI/[P₄₄₄₄][Triz], CuI/[P₄₄₄₄][Ind], CuI/[P₄₄₄₄][CF₃COO], CuI/[P₄₄₄₄][NO₃] and [P₄₄₄₄][Br] were used as catalysts (Table 1, entries 5–9). The significant differences in their catalytic activity may be ascribed to the different nucleophilicity of these ILs as a result of their different basicity (Table S1). A larger IL pK_a resulted in an improved absorption capacity of CO₂ in the reaction system, which led to stronger reactivity between CO₂ with propargylic alcohol, amine and the catalyst, to afford a higher product yield [35]. The result indicated that the ionic liquid anions play an

important role in this conversion. Next, a variety of copper (I) salts with [P₄₄₄₄][Im] were used for this reaction. The activity of these copper salts followed the order: CuI > CuBr > CuCl (Table 1, entries 4, 10–11). Owing to the fact that among the halogenated metal salts the iodide anion had a stronger dissociation capacity, the metal cation and iodide anion could efficiently activate the substrates and promote the reaction in high yields [36]. The result suggested that the dissociation capacity of the anions acted a significant role in determining the catalytic activity of the halogenated copper salts. In addition, Cu₂O and CuCN could also catalyze the reaction, affording moderate yields (65% and 32%, respectively) (Table 1, entries 12,13). Thus, CuI/[P₄₄₄₄][Im] was the best catalyst to further investigate this reaction.

Table 1. Reaction of 2-methyl-3-butyn-2-ol (**1a**), *n*-butylamine (**2a**) and CO₂ in various catalyst systems ^a.

Reaction scheme: **1a** + CO₂ + **2a** $\xrightarrow[30^\circ\text{C, 1atm}]{\text{CuI(10\%mol), P}_{4444}\text{Im(10\%mol)}}$ **3a**

Entry	Catalyst	IL	Yield/% ^b
1	– ^c	– ^d	0
2	– ^c	[P ₄₄₄₄][Im]	5
3	CuI	– ^d	34
4	CuI	[P ₄₄₄₄][Im]	91
5	CuI	[P ₄₄₄₄][Triz]	70
6	CuI	[P ₄₄₄₄][Ind]	41
7	CuI	[P ₄₄₄₄][CF ₃ COO]	35
8	CuI	[P ₄₄₄₄]NO ₃	30
9	CuI	[P ₄₄₄₄]Br	28
10	CuBr	[P ₄₄₄₄][Im]	71
11	CuCl	[P ₄₄₄₄][Im]	42
12	Cu ₂ O	[P ₄₄₄₄][Im]	65
13	CuCN	[P ₄₄₄₄][Im]	32
Entry	Catalyst	IL	Yield/% ^b

^a Reaction condition: **1a**, 1.0 mmol, **2a**, 1.0 mmol, catalyst, 0.1 mmol, CO₂ (0.1 MPa, 99.999%), 24 h, 30 °C; ^b Isolated yield; ^c Without copper salt; ^d Without IL.

Subsequently, the influence of catalyst amount on the yield of product was studied at 30 °C and 1 atm CO₂ with a reaction time of 24 h. As seen in Figure S1, the yield of **3a** was strongly dependent on the catalyst amount, and a maximum yield of 90% was obtained in the presence of 10 mol% CuI. It was shown that the yield of **3a** will slowly decrease with further increase of the catalyst loading. Similar results were also obtained for the effect of IL amount in this reaction (Figure S2). Also, the dependence of reaction time on the yield of **3a** was studied and the results are shown in Figure 2. The reaction was carried out at 30 °C, 1 atm CO₂ using CuI (10 mol%) and [P₄₄₄₄][Im] (10 mol%) as catalyst. It is shown that a yield of 92% could be obtained after 24h, and the yield of **3a** does not improve with further prolonged reaction time. Moreover, the effect of CO₂ pressure on the reaction was studied. As shown in Table S2, the yield of **3a** increased significantly with increasing pressure. More CO₂ could be dissolved in the liquid phase with further increasing pressure, which led to more contact between CO₂ with the substrates and the catalyst, and thus a higher yield of product was obtained. From the above findings, the optimal reaction conditions for the reaction were: CuI/[P₄₄₄₄][Im] as the catalyst, 30 °C, 24 h, and 1 atm CO₂.

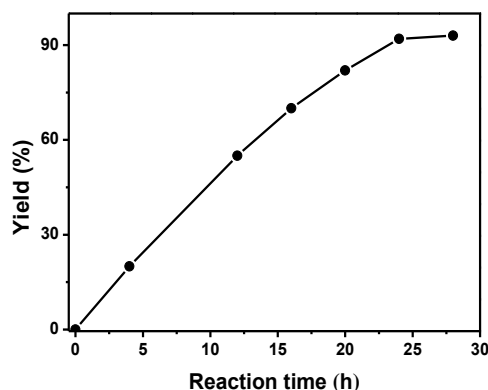


Figure 2. Effect of reaction time on the product yield over CuI and [P4444][Im]; Reaction conditions: **1a**, 1.0 mmol, **2a**, 1.0 mmol, CuI, 0. mmol, [P4444][Im], 0.1 mmol, CO₂ (1 atm), 30 °C. The yield was isolated yield.

The reactions of CO₂ with different kinds of propargylic alcohols and amines were evaluated under the optimized reaction conditions, and the results are listed in Table 2. It was shown that the coupling reaction of different alkyl substituted propargylic alcohols with CO₂ and amines proceeded smoothly, producing the corresponding oxazolidinones in good yields under mild conditions. It was noted that a moderate yield of product was obtained for the propargylic alcohol with a cyclohexyl group (**3i**), indicating the steric hindrance of the substituent seemed to hamper the reaction. Furthermore, we also investigate the effect of amines with various substituents in this transformation. It was clearly shown that most of alkyl-substituted amines were efficient substrates to produce the corresponding oxazolidinones. However, when the R³ group of amines was a phenyl group, no product was obtained (compound **3k**), even after a prolonged reaction time of 36 h. This phenomenon can be attributed to both the weak N-nucleophilicity and steric hindrance of the substrates, which further hamper the reaction [37]. From the above analysis, the catalyst system reported here is more favorable for alkyl amines than aromatic amines.

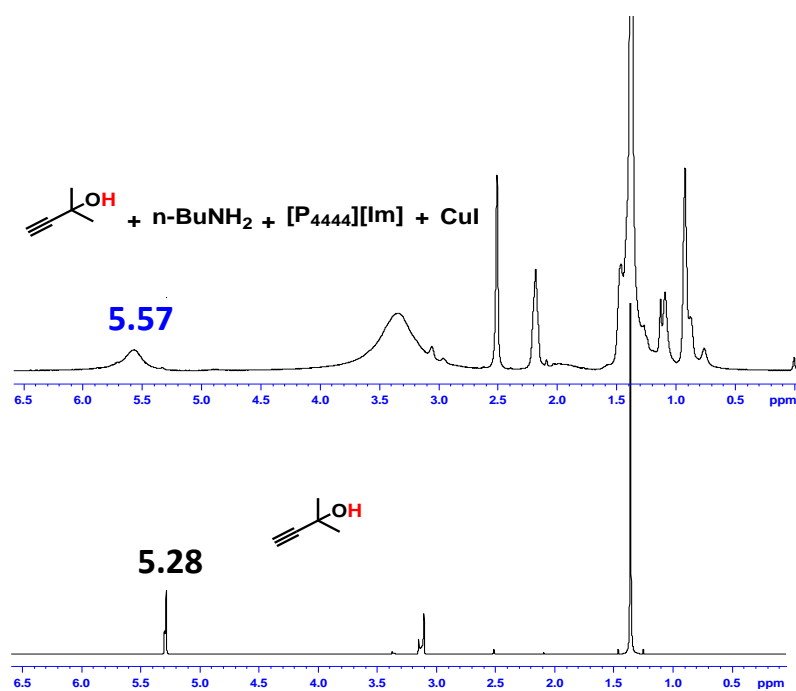
To gain insight into the reaction mechanism, the catalytic role of [P4444][Im]/CuI with CO₂ and the substrates were elucidated by ¹H-NMR and ¹³C-NMR spectroscopy. In the ¹H-NMR spectrum of the mixture of [P4444][Im]/CuI with **1a** and *n*-BuNH₂ (Figure 3), the OH signal became broad and shifted from 5.28 to 5.57, which indicated the formation of a hydrogen bond between [P4444][Im] and **1a** [35]. In addition, the ¹³C-NMR signal assigned to the C1, C2, and C3 sites could be attributed to the interaction between CuI with the C≡C bond, leading to the activation of propargylic alcohol (Figure 4). These analysis suggested that the -OH and C≡C bond on the substrate **1a** were synergistically activated by [P4444][Im] and CuI. Moreover, several additional control experiments were performed and the results are shown in Scheme 2. It was shown that the CuI/[P4444][Im] catalyst could efficiently catalyze the reaction of **1a** with CO₂ to form cyclic carbonate **4a** with a yield of 70%. In addition, **4a** reacted with *n*-butylamine to afford **3a** smoothly without any catalyst. Therefore, the reaction of propargylic alcohols, amines and CO₂ can be assumed to go through the cyclic carbonate pathway [37].

Based on the above results, a plausible mechanism for the reaction catalyzed by CuI/[P4444][Im] as depicted in Scheme 3 is proposed. Firstly, the hydroxyl group of the propargyl alcohol is activated by IL [P4444][Im], then it reacts with CO₂ to generate a zwitterionic carbamate species **1**. Meanwhile, the C≡C triple bond of the propargyl alcohol was activated by CuI, and then the intermediate **2** was obtained. Then the intermediate cyclic carbonate **3** was formed by an intramolecular ring-closing reaction with the release of the catalyst. Finally, the cyclic carbonate undergoes a nucleophilic attack by a primary amine to generate the product oxazolidinone **5**.

Table 2. Three-component reactions of propargylic alcohols (1), amines (2) and CO₂ under optimized conditions ^a.

$\text{R}^1 \text{C}(\text{OH})(\text{R}^2)\text{C}\equiv\text{C} + \text{CO}_2 + \text{R}^3\text{NH}_2 \xrightarrow[30^\circ\text{C, 1atm}]{\text{CuI(10\%mol), P}_{4444}\text{Im(10\%mol)}} \text{R}^3\text{N}(\text{R}^2)\text{C}(\text{R}^1)\text{C}(\text{R}^1)=\text{C}(\text{R}^2)\text{O}$			
1	2	3	
3a (87%) ^b	3b (81%) ^b	3c (82%) ^b	3d (85%) ^b
3e (81%) ^b	3f (70%) ^b	3g (75%) ^b	3h (73%) ^b
3i (71%) ^b	3j (54%) ^b	3k (0) ^c	

^a Reaction conditions: 1, 1.0 mmol, 2, 1.0 mmol, CuI, 0.1 mmol, [P₄₄₄₄][Im], 0.1 mmol, CO₂ (1 atm), within 24 h, 30 °C. ^b Isolated yield. ^c The reaction time is prolonged to 36 h.

**Figure 3.** ¹H-NMR spectra of propargylic alcohol, *n*-BuNH₂ with and without CuI/[P₄₄₄₄][Im] catalyst.

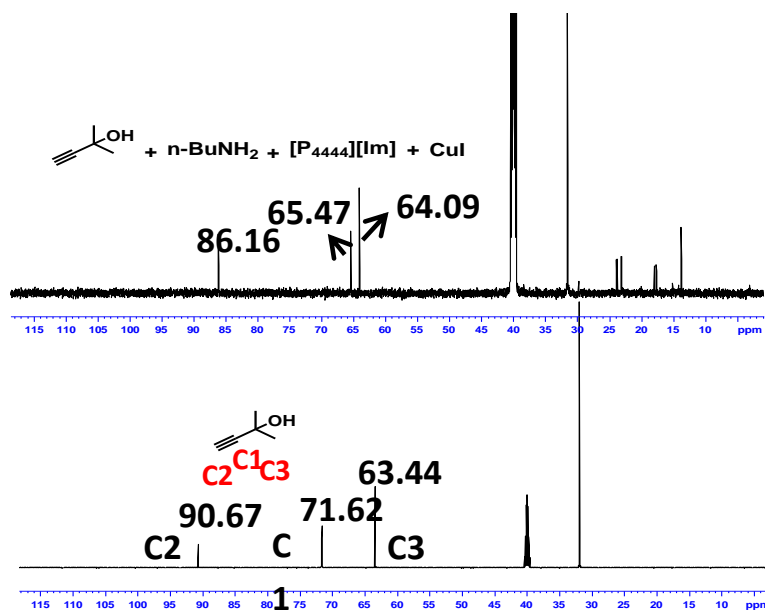
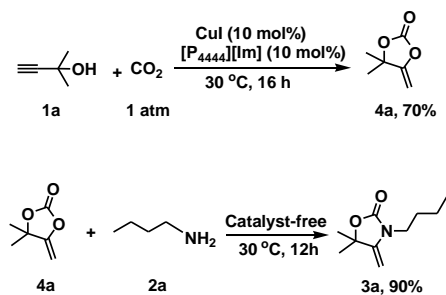
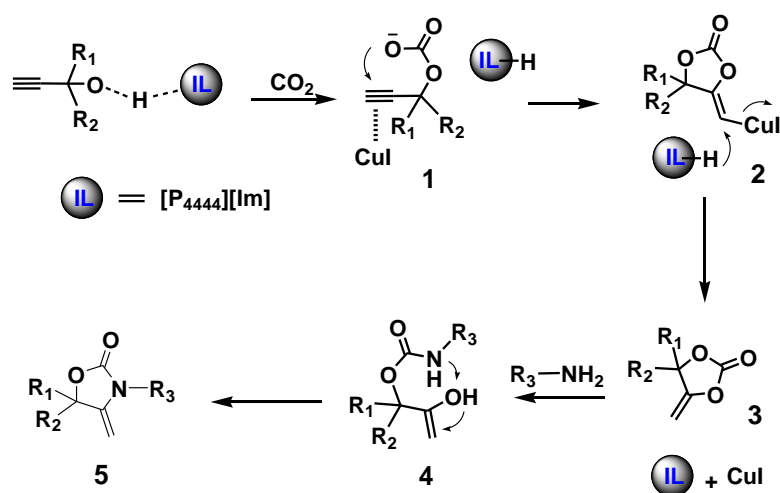


Figure 4. ^{13}C -NMR spectra of propargylic alcohol, $n\text{-BuNH}_2$ with and without $\text{CuI}/[\text{P}_{4444}][\text{Im}]$ catalyst.



Scheme 2. Control experiments.



Scheme 3. The proposed mechanism for the reaction of propargyl alcohol, CO_2 and an amine catalyzed by $[\text{CuI}]/[\text{P}_{4444}][\text{Im}]$.

3. Experimental Section

3.1. Chemicals

Propargylic alcohols, amines, CuI , Cu_2O , CuCl , CuBr , CuCN were obtained from J&K Scientific Company Limited (Beijing, China). The ILs $[\text{P}_{4444}][\text{CF}_3\text{COO}]$, $[\text{P}_{4444}][\text{NO}_3]$ and $[\text{P}_{4444}][\text{Br}]$ were

purchased from Lanzhou Greenchem ILs (Lanzhou, Gansu, China). Other ILs such as [P₄₄₄₄][Triz], [P₄₄₄₄][Ind] and [P₄₄₄₄][Im] were synthesized by the ion exchange method [38].

3.2. General Procedures for the Synthesis of Oxazolidinones

Typically, propargylic alcohol **1a** (1.0 mmol), *n*-butylamine (**2a**, 1.0 mmol) and CuI (0.1 mmol)/[P₄₄₄₄][Im] (0.1 mmol) were mixed in a 10 mL Schlenk flask. Then the reaction mixture was stirred at 30 °C for 24 h in the pressure of 0.1 MPa CO₂. After the reaction was completed, water (5 mL) was added into this mixture, and the organic phase was purified through column chromatography. The ionic liquid was collected and reused without further treatment by removing any water under vacuum.

3.3. Characterization of the Products

The products were confirmed by using ¹H-NMR analysis on Avance NEO 400 spectrometer (Bruker, Beijing, China) and Avance III HD 600 spectrometer (Bruker, Beijing, China). All of the products matched well with the previously reported experimental results [26].

3-butyl-5,5-dimethyl-4-methyleneoxazolidin-2-one (3a), orange oil; ¹H-NMR (CDCl₃, 400 MHz does not match above) δ: 4.07 (d, *J* = 4.0 Hz, 1 H), 3.98 (d, *J* = 4.0 Hz, 1 H), 3.44 (t, *J* = 8.0 Hz, 2 H), 1.61–1.52 (m, 2 H), 1.49 (s, 6 H), 1.37–1.29 (m, 2 H), 0.95 (t, *J* = 7.2 Hz, 3 H) ppm.

3-butyl-5-isobutyl-5-methyl-4-methyleneoxazolidin-2-one (3b), orange solid; ¹H-NMR (CDCl₃, 600 MHz) δ: 4.09 (s, 1 H), 3.93 (s, 1 H), 3.51–3.38 (m, 2 H), 1.80–1.43 (m, 8 H), 1.40–1.31 (m, 2 H), 1.02–0.89 (m, 9 H) ppm.

3-cyclohexyl-5,5-dimethyl-4-methyleneoxazolidin-2-one (3c), orange solid; ¹H-NMR (CDCl₃, 600 MHz) δ: 4.19 (d, *J* = 3.0 Hz, 1 H), 3.97 (d, *J* = 3.0 Hz, 1 H), 3.55 (t, *J* = 12.0 Hz, 1 H), 1.86–1.66 (m, 13 H), 1.25–1.14 (m, 4 H) ppm.

3-isobutyl-5,5-dimethyl-4-methyleneoxazolidin-2-one (3d), colorless oil; ¹H-NMR (CDCl₃, 600 MHz) δ: 4.27 (s, 1 H), 3.11–3.04 (m, 1 H), 2.96–2.89 (m, 1 H), 1.99–1.92 (m, 1 H), 1.51 (s, 3 H), 1.43 (s, 2 H), 1.34 (d, *J* = 12 Hz, 2 H), 0.92–0.87 (m, 6 H) ppm.

3-hexyl-5,5-dimethyl-4-methyleneoxazolidin-2-one (3e), colorless oil; ¹H-NMR (CDCl₃, 600 MHz) δ: 4.07 (d, *J* = 2.4 Hz, 1 H), 3.97 (d, *J* = 3 Hz, 1 H), 3.43 (t, *J* = 7.8 Hz, 2 H), 1.63–1.58 (m, 2 H), 1.49 (s, 1 H), 1.32–1.30 (m, 6H), 0.89–0.88 (m, 3H) ppm.

5-ethyl-3-isobutyl-5-methyl-4-methyleneoxazolidin-2-one (3f), colorless oil; ¹H-NMR (CDCl₃, 600 MHz) δ: 4.10 (d, *J* = 3 Hz, 1 H), 3.92 (d, *J* = 3 Hz, 1 H), 3.30–3.19 (m, 2 H), 1.85–1.80 (m, 1 H), 1.48–1.45 (d, *J* = 7.2 Hz, 5 H), 1.02 (t, *J* = 7.8 Hz, 2 H), 0.93–0.90 (m, 6 H), 0.89 (s, 1 H) ppm.

3,5-diisobutyl-5-methyl-4-methyleneoxazolidin-2-one (3g), orange solid; ¹H-NMR (CDCl₃, 600 MHz) δ: 4.09 (s, 1 H), 3.93 (s, 1 H), 3.28–3.23 (m, 2 H), 2.14–2.04 (m, 1 H), 1.51 (s, 1 H), 1.04–0.98 (m, 2 H), 0.97–0.91 (m, 12 H) ppm.

3-cyclohexyl-5-isobutyl-5-methyl-4-methyleneoxazolidin-2-one (3h), orange solid; ¹H-NMR (CDCl₃, 600 MHz) δ: 4.24 (s, 1 H), 3.93 (s, 1 H), 3.64–3.53 (m, 1 H), 2.15–1.45 (m, 12 H), 1.34–1.15 (m, 4 H), 0.94–0.91 (m, 6 H) ppm.

3-cyclohexyl-5-ethyl-5-methyl-4-methyleneoxazolidin-2-one (3i), orange solid; ¹H-NMR (CDCl₃, 600 MHz) δ: 4.25 (d, *J* = 3.0 Hz, 1 H), 3.93 (d, *J* = 3.0 Hz, 1 H), 3.62–3.55 (m, 1 H), 1.66–1.47 (m, 11 H), 1.35–1.18 (m, 4 H), 0.88 (t, *J* = 7.8 Hz, 3 H) ppm.

3-Butyl-4-methylene-1-oxa-3-azaspiro[4.5]decan-2-one (3j), orange oil; ¹H-NMR (CDCl₃, 600 MHz) δ: 4.07 (d, *J* = 3.0 Hz, 1 H), 3.95 (d, *J* = 2.4 Hz, 1 H), 3.43 (t, *J* = 7.8 Hz, 2 H), 1.76–1.65 (m, 5 H), 1.61–1.50 (m, 7 H), 1.40–1.31 (m, 2 H), 0.94 (t, *J* = 7.2 Hz, 3 H) ppm.

4. Conclusions

In conclusion, we have developed an excellent and cost-competitive catalytic process catalyzed by the CuI/[P₄₄₄₄][Im] system for the transformation of CO₂ to form oxazolidinones. The reaction can proceed efficiently under room temperature and atmospheric pressure conditions to give high yields of product. A wide range of propargylic alcohols and amines has been employed, which confirmed the versatility of the catalyst system for the synthesis of oxazolidinones. Preliminary mechanistic studies suggest that the reaction of propargylic alcohols, amines and CO₂ could involve the cyclic carbonate pathway. This work reveals the great potential of ionic liquids combined with metal salts as an efficient type of catalysts for CO₂ conversion under mild conditions.

Supplementary Materials: The following are available online.

Author Contributions: Organic synthesis and compound characterization, J.Q. and Y.Z. (Yue Zhao); NMR spectroscopy, Y.Z. (Yue Zhao); writing—original draft preparation, J.Q.; writing-review and editing, Y.Z. (Yuling Zhao), J.W., Z.L., H.W.; project administration, Z.L. and H.W.; formal analysis, T.J.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

[P ₄₄₄₄][Im]	Tetrabutylphosphonium imidazole
[P ₄₄₄₄][CF ₃ COO]	Tetrabutylphosphonium 2,2,2-trifluoroacetic acid
[P ₄₄₄₄][Triz]	Tetrabutylphosphonium 1,2,4-triazole
[P ₄₄₄₄][Ind]	Tetrabutylphosphonium indazole
[P ₄₄₄₄][Br]	Tetrabutylphosphonium bromide
[P ₄₄₄₄][NO ₃]	Tetrabutylphosphonium nitrate

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Sample Availability: Samples of the compounds of **3a–3j** are available from the authors.



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