Preprint Title	Synthesis of *N*-Substituted Oxazolidin-2-ones via Organocatalytic Aziridine-CO_2 Cycloaddition
Authors	Caterina Damiano, Emma Gallo, M. Mar Díaz-Requejo and Pedro J. Pérez
Publication Date	16 Sept. 2026
Article Type	Full Research Paper
Supporting Information File 1	Supporting Information.pdf; 1.9 MB
ORCID® iDs	Caterina Damiano - https://orcid.org/0000-0001-5903-238X; Pedro J. Pérez - https://orcid.org/0000-0002-6899-4641

Synthesis of *N*-Substituted Oxazolidin-2-ones via Organocatalytic Aziridine-CO_2 Cycloaddition

Caterina Damiano,*[1] Emma Gallo,[1] M. Mar Díaz-Requejo,[2] and Pedro J. Pérez[2]

Address: [1]Department of Chemistry, University of Milan, Via C. Golgi 19, 20133, Milan, Italy and [2]Laboratorio de Catálisis Homogénea, Unidad Asociada al CSIC, CIQSO-Centro de Investigación en Química Sostenible and Departamento de Química, Universidad de Huelva, 21007 Huelva, Spain.

Email: Caterina Damiano - caterina.damiano@unimi.it

* Corresponding author

‡ Equal contributors

Abstract

Given the growing interest in utilizing CO_2 under mild and environmentally friendly conditions, this study investigates the potential of a simple and inexpensive imidazolium salt to promote the CO_2 cycloaddition of *N*-alkyl aziridines to generate *N*-alkyl oxazolidin-2-ones. Optimization of the reaction parameters revealed that 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (**1**) effectively catalyzes the synthesis of *N*-alkyl oxazolidin-2-ones in acetonitrile under mild experimental conditions (40 °C and 0.1 MPa CO_2). The bifunctional nature of **1** enabled the synthesis of various oxazolidin-2-ones in the absence of any co-catalyst, achieving yields up to 90% and regioisomeric ratios up to 96:4. A tandem procedure has also been investigated, where *N*-tosyl aziridine is first formed via copper catalysis, and then converted into the corresponding oxazolidin-2-ones in the same reactor, with tetrabutylammonium chloride (TBACl) as co-catalyst. This tandem approach, while still at an early stage, has the potential to avoid the isolation and purification of the aziridine intermediate in future optimized versions.

Keywords

oxazolidin-2-ones, carbon dioxide, imidazolium salts, tandem procedure, copper

Introduction

Carbon dioxide (CO_2) has become one of the most significant environmental threats in recent years. Despite its chemical inertness, the accumulation of CO_2 in the atmosphere is a major driver of global warming and ocean acidification, with far-reaching consequences for ecosystems and human societies. In response to these

concerns, high scientific interest has been directed toward the development of strategies for CO_2 capture and utilization (CCU) [1–3]. Rather than viewing carbon dioxide solely as a waste product, research has turned toward utilizing CO_2 as a readily available, inexpensive, and safe carbon feedstock for the synthesis of value-added chemicals.

Over the past two decades, numerous homogenous and heterogenous catalytic systems, especially those based on transition metals, have been developed to incorporate CO_2 as a C1 building block in a variety of chemical transformations [4–9]. Notable examples include the synthesis of cyclic carbonates, which are used as solvents and electrolytes in lithium-ion batteries, polycarbonates (important materials in the plastics industry) and urea derivatives, which have a large applications including in agriculture and pharmaceutical industry. However, the widespread industrial application of CO_2-based processes still faces significant limitations. Most current methods require harsh reaction conditions, such as high pressures and temperatures, and the use of costly or toxic metal complexes, which compromise the overall sustainability and energy efficiency of the process. In some cases, the environmental footprint of the activation step can outweigh the benefits of CO_2 utilization itself.

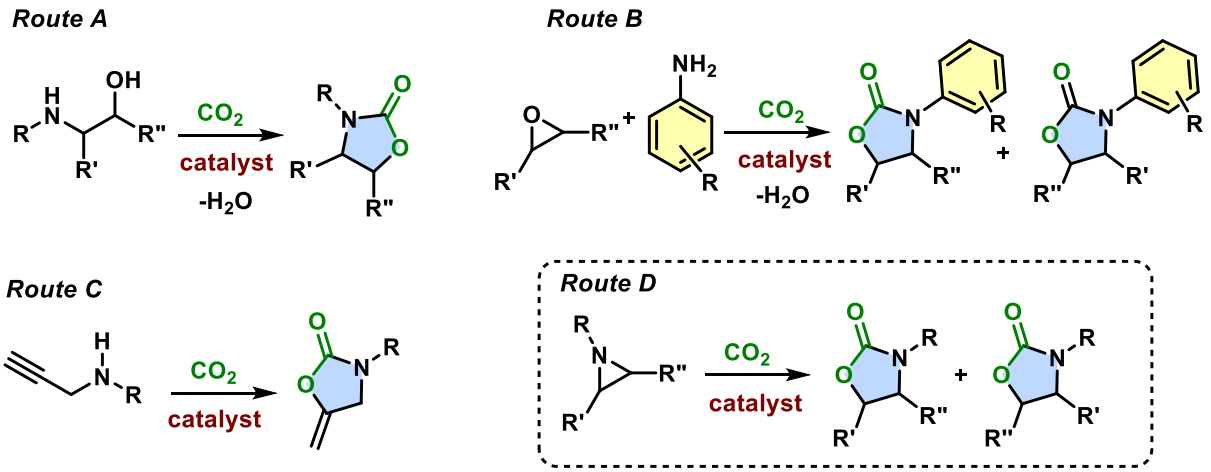
For this reason, current research is increasingly focused on the development of more sustainable and energy-efficient CO_2 valorization strategies. These include the use of earth-abundant metal catalysts [10,11], organocatalysis [12–14], electrochemical [15] and photochemical approaches [16], and even enzymatic systems inspired by biological CO_2 fixation [17]. The goal is to enable the conversion of CO_2 under mild reaction conditions, ideally at ambient temperature and pressure, while maximizing the net consumption of carbon dioxide and minimizing the use of non-renewable resources.

Significant progress has been made in the synthesis of cyclic carbonates using both metal-based catalysts [18,19] and organocatalysts [20,21], with the latter generally representing a more cost-effective option. Among these systems, imidazolium salts have yielded particularly promising results [22–26]. This success is largely attributed to their ability to form ionic liquids [27,28] and activate three-membered rings, such as epoxides, thereby facilitating the insertion of carbon dioxide and enabling the formation of the desired carbonate. Several studies have demonstrated the effectiveness of imidazolium-based ionic liquids in catalyzing the synthesis of cyclic carbonates under mild reaction conditions, including atmospheric CO_2 pressure [29–34]. However, despite their efficiency in promoting CO_2 valorization under such conditions, their application in the synthesis of oxazolidin-2-ones, a nitrogen-containing heterocycle structurally analogous to cyclic carbonates, has been less investigated [35,36].

Oxazolidin-2-ones are valuable compounds widely used in organic synthesis, as synthetic intermediates or chiral auxiliars, and largely employed as pharmaceuticals thanks to their proved antimicrobial and antidepressant activities (e.g., Linezolid [37], Tedizolid [38], Toloxatone [39]). These heterocycles can be synthesized from CO_2 *via* several pathways (Scheme 1) [40,41], among which two routes are particularly attractive due to their excellent sustainability and 100% of atom economy. While the imidazolium salt-catalyzed synthesis of oxazolidinones from propargyl amines (route C, Scheme 1) has been well studied [36], the corresponding CO_2 cycloaddition to aziridines (route D, Scheme 1) employing imidazolium salt catalysts remains under investigated. Notably, a single example has been reported in which an imidazolium-based ionic liquid supported on a polymeric resin catalyzed the CO_2 cycloaddition to aziridines at room temperature, albeit under a CO_2 pressure of 5.0 MPa [35].

Considering these results and the effectiveness of both binary [42–44] and bifunctional catalytic systems [45,46], where the coexistence of electrophilic and nucleophilic

species enables the conversion of aziridines into oxazolidin-2-ones, even at very low CO_2 pressures, as demonstrated by the activity of cinchonine-based salts [46], we have explored the catalytic potential of a simple and easily accessible imidazolium salt for promoting CO_2 cycloaddition to aziridines. Herein we describe the use of IPrHCl (1,3-bis(2,6-diisopropylphenyl)imidazolium chloride, **1**) as effective catalyst for the carboxylation of *N*-alkyl aziridines, as well as that of IPrCuCl [47–49] for the olefin aziridination-carbon dioxide cycloaddition tandem reaction.

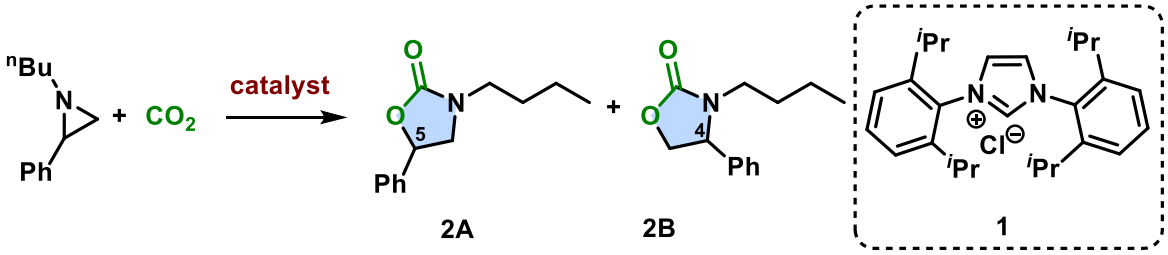


Scheme 1. Synthetic routes for the synthesis of oxazolidin-2-ones from CO_2.

Results and Discussion

Use of IPrHCl as catalyst for aziridine carboxylation

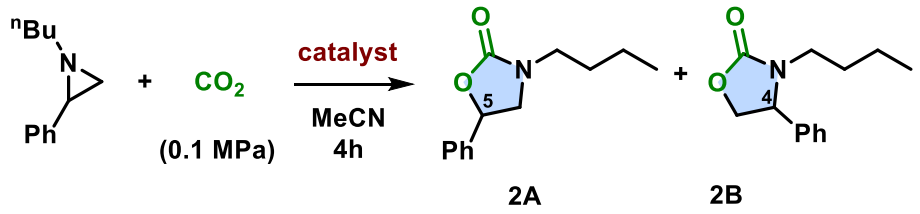
We first investigated the capability of imidazolium salts for the CO_2 cycloaddition to aziridines using 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (**1**) (Scheme 2) as the model organocatalyst [50]. Compound **1** was tested in the model reaction between CO_2 and *N*-butyl phenyl aziridine to yield the target oxazolidin-2-one **2**, which can be formed in two possible regioisomers: the 5-substituted (**A**) and 4-substituted (**B**) products (**2A** and **2B**, Scheme 2).



Scheme 2. Synthesis of oxazolidin-2-ones **2A** and **2B** and structure of imidazolium salt **1**.

Preliminary tests were conducted under atmospheric CO_2 pressure using acetonitrile (MeCN) as the reaction solvent, in which both CO_2 and compound **1** exhibit high solubility. The catalytic activity of compound **1** was initially compared to that of tetrabutylammonium chloride (TBACl), a common catalyst used either alone [51] or as co-catalyst in CO_2 cycloaddition to aziridines [42,43]. As summarized in Table 1, the experiments were performed at two catalytic loadings (2.5 mol% and 5 mol%) and two temperatures (25°C and 40°C). The results revealed a very low ability of both compounds to form the desired product within 4 h of reaction under ambient conditions (0.1 MPa CO_2 and 25°C, entries 1–2, Table 1). However, raising the reaction temperature to 40°C resulted in a higher formation of oxazolidin-2-one **2**, highlighting the positive influence of a slight temperature increase (entries 1–2, Table 1). A further improvement in yield was observed when compound **1** was used in 5 mol% of loading, affording the desired product **2** in 34% yield after 4 h at 40°C (entry 4, Table 1). The use of TBACl led to compound **2** in comparable yield of 24% (entry 3, Table 1). However, the use of **1** slightly favored the synthesis of the desired regioisomer **2A** (dr values of 95:5 *vs* 90:10, see Table 1).

Table 1: Synthesis of oxazolidin-2-ones **2A** and **2B** catalyzed by TBACl or **1** under atmospheric CO_2 pressure.



2A 2B

Entry	Catalyst	Loading (mol%)	Temperature (°C)	Yield (%)[b]	**2A/2B** ratio[b]
1	TBACl	2.5	25 (40)	5 (9)[c]	90:10 (90:10)[c]
2	**1**	2.5	25 (40)	11(23)[c]	95:5 (95:5)[c]
3	TBACl	5	40	24	90:10
4	**1**	5	40	34	95:5

[a]Reactions were stirred at the desired temperature for 4 hours in 0.5 mL of solvent under 0.1 MPa of CO_2 (plastic ballon). [b]Determined by ^{1}H-NMR spectroscopy by using 2,4-dinitrotoluene as the internal standard. [c]Reactions run at 40°C.

In light of these promising results, the reaction conditions were optimized by varying the solvent, catalytic loading, and reaction time (Figure 1), while maintaining mild pressure and temperature conditions. The effect of the solvent was first examined by replacing MeCN with alcohols and ethers, including green solvents such as cyrene, methyl ethyl ketone (MEK), and 2-MeTHF (Figure 1A). As shown in figure 1A, no product formation was observed under solvent-free conditions or in any of the tested green solvents. A slight increase in yield was noted with longer-chain alcohols, and a noticeable amount of product **2** was obtained when tetrahydrofuran (THF) was used as the solvent. However, the highest yield was reached in MeCN, probably due to the higher solubility of compound **1** in this solvent with respect to that observed in all the others. Acetonitrile was then selected as the reaction solvent. At this point the reaction conditions were optimized in terms of reaction time and catalyst loading. The yield was

enhanced from 34% to 60% by extending the reaction time to 24 h (Figure 1B). Additional 24 h did not led to significant improvement in yield. Finally, the catalytic loading was optimized and the highest yield of 85% and the **2A**/**2B** ratio of 95:5, were achieved by employing 10 mol% of **1** (Figure 1C). The concomitant use of 10 mol% of catalyst loading and 48 h of reaction time induced the complete conversion into the desired product (>98%).

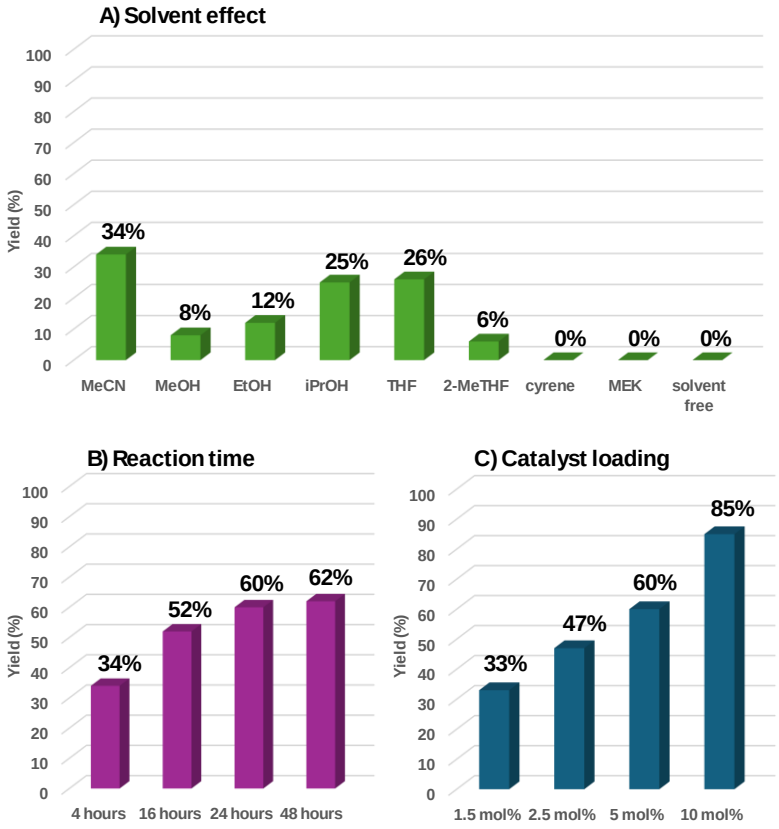
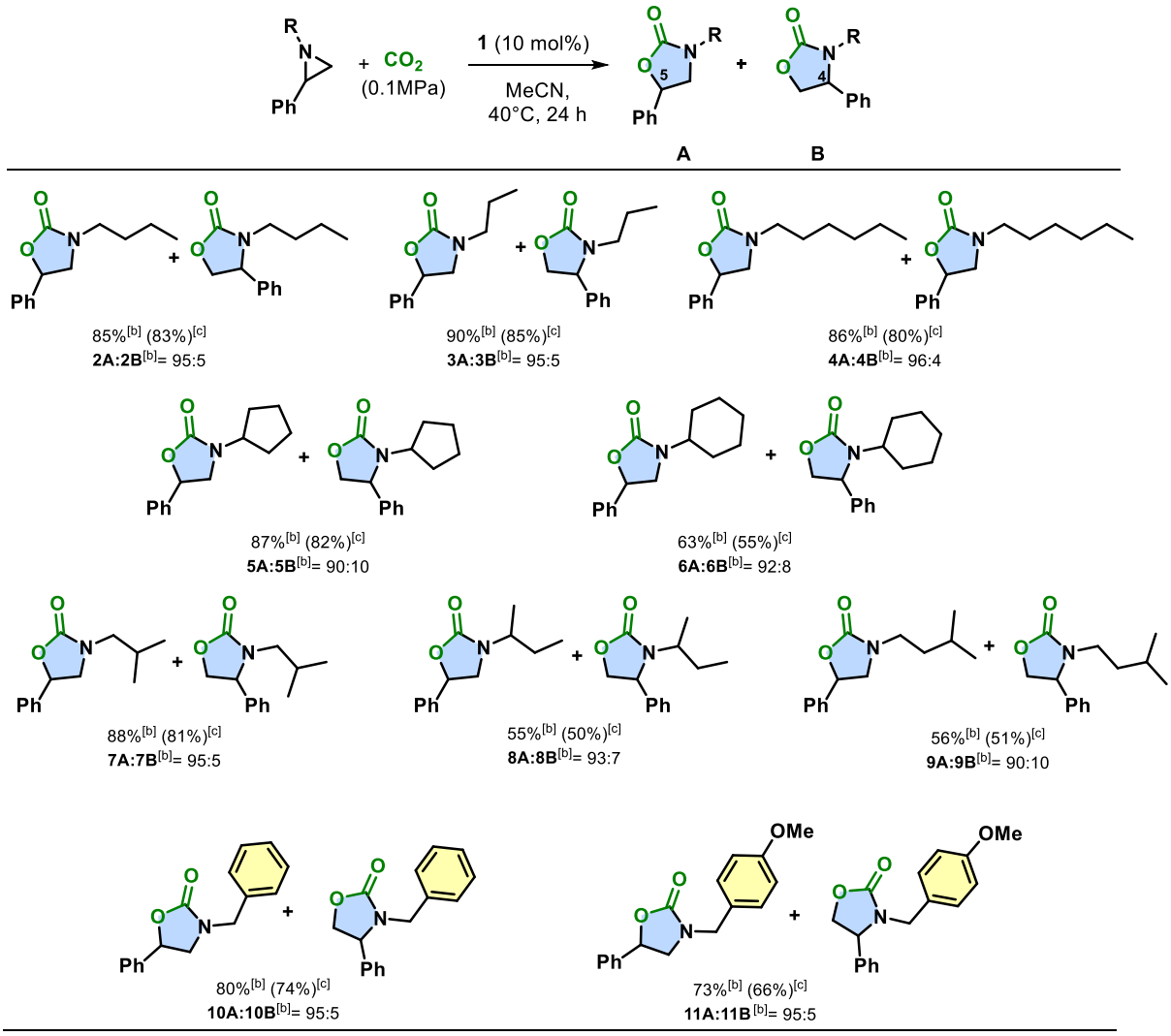


Figure 1. Optimization of the reaction condition for the **1**-catalyzed synthesis of oxazolidin-2-one **2**.

The scope of this catalytic system is shown in Scheme 3. Overall, the desired products **2**–**11** were obtained in moderate to very good yields (55-90%) and regioselectivities up to 96:4 under the optimized reaction conditions (see Supporting Information). Lower yields were achieved in the case of sterically hindered substituents onto the nitrogen atom of the aziridine ring, according to previous reported studies for analogous

substrates (Scheme 3) [42,45]. In view of the successful results obtained under very mild experimental conditions, the activity of the imidazolium salt **1** was further investigated by employing more challenging *N*-aryl and *N*-tosyl aziridine substrates. Unfortunately, a complete inactivity of catalyst **1** was observed towards these substrates suggesting that less reactive aziridines need stronger reaction conditions and the presence of more active catalysts and co-catalysts.



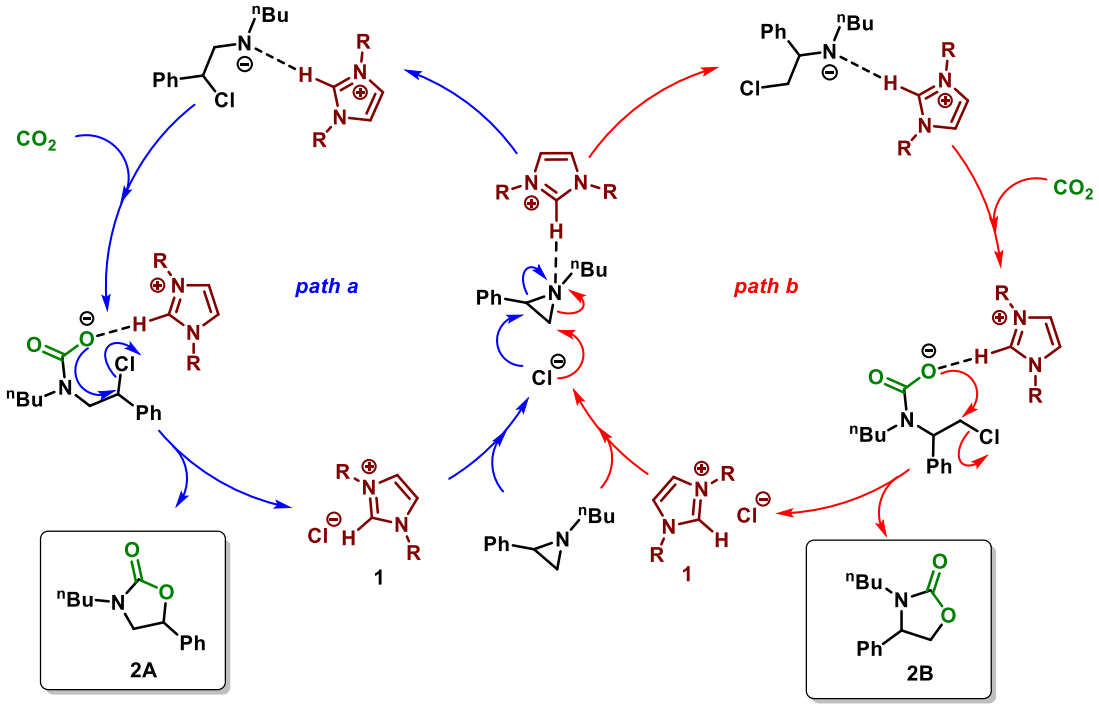
[a]Reactions were stirred at 40°C for 24 h in 0.5 mL of solvent under 0.1 MPa of CO_2 (plastic ballon).
[b]Determined by ^{1}H NMR spectroscopy by using 2,4-dinitrotoluene as the internal standard. [c]Isolated yields.

Scheme 3. Synthesis of oxazolidin-2-ones (**2** – **11**) catalyzed by imidazolium salt **1** under 0.1 MPa of CO_2.

However, the promising results obtained using *N*-alkyl aziridines as substrates prompted us to conduct exploratory studies aimed at elucidating the role of the imidazolium salt in CO_2 activation. To this end, preliminary experiments to investigate the interaction between **1** and CO_2 were performed. It is well established that imidazolium salts are precursors to free *N*-heterocyclic carbenes (NHCs), which can form stable zwitterionic NHC-CO_2 adducts capable of activating carbon dioxide [52]. On this basis, compound **1** was treated with CO_2 under the catalytic reaction conditions, and the reaction was monitored by IR spectroscopy to detect the characteristic absorption of the NHC-CO_2 adduct at 1692 cm^{-1} [53]. No evidence of adduct formation was observed. This result is consistent with the lack of sufficiently basic conditions required to deprotonate the imidazolium salt and generate the free NHC [53]. In light of these findings, and in agreement with previous literature on CO_2 cycloaddition to three-membered rings catalyzed by imidazolium salts [22], a plausible mechanism can be proposed in which the NHC-CO_2 adduct is not involved. Instead, compound **1** likely acts both as a hydrogen-bond donor and as a halide source (Scheme 4). The relatively acidic proton at the C2 position of the imidazolium cation may facilitate the aziridine ring-opening through hydrogen-bonding interactions, thereby promoting nucleophilic attack by chloride. Depending on the site of nucleophilic attack, two regioisomers can be formed, with regioisomer **A** (path a, Scheme 4) generally obtained as the major product after the CO_2 incorporation [52].

It is noteworthy that this mechanism, which is fully consistent with the catalytic data reported in Scheme 3, does not appear to operate when aziridines bearing alkyl chains at the C2 position are employed. Indeed, the **1**-catalyzed CO_2 cycloaddition to enantiopure *(S)*-1-benzyl-2-octylaziridine, selected as a model substrate to evaluate both the reactivity of C2-alkyl-substituted aziridines and the reaction stereochemistry, afforded the unexpected regioisomer **B** as the major product [54]. Under the optimized

reaction conditions (10 mol% of **1**, 0.1 MPa CO_2, 40 °C, 24 h), *(S)*-1-benzyl-2-octylaziridine was converted into the corresponding 3-benzyl-4-octyloxazolidin-2-one in 54% yield with a **A**/**B** ratio of 19:81. Due to the chiral nature of the substrate, optical rotation measurements ($[\alpha]^d$) indicated retention of configuration in the product ((*S*)-1-benzyl-2-octylaziridine $[\alpha]^d$ = - 4,22° *vs* (*S*)-3-benzyl-4-octyloxazolidin-2-one $[\alpha]^d$ = - 4,44°), in accordance with previously reported data regarding the CO_2 cycloaddition to aziridines [55]. This outcome can be attributed to the distinct reactivity of aziridines bearing an alkyl substituent at the C2 position, in which nucleophilic attack may preferentially occur at the less substituted carbon [56-57], in contrast to the more common mechanism observed for C2-aryl-substituted aziridines, where the nucleophile typically attacks the more hindered carbon of the three-membered ring. These findings will therefore be the subject of more in-depth future investigations aimed at elucidating better the reaction mechanism when C2-aryl-substituted aziridines are employed as staring reagents.



Scheme 4. Proposed reaction mechanism for the CO_2 cycloaddition to aziridines promoted by imidazolium salt **1**.

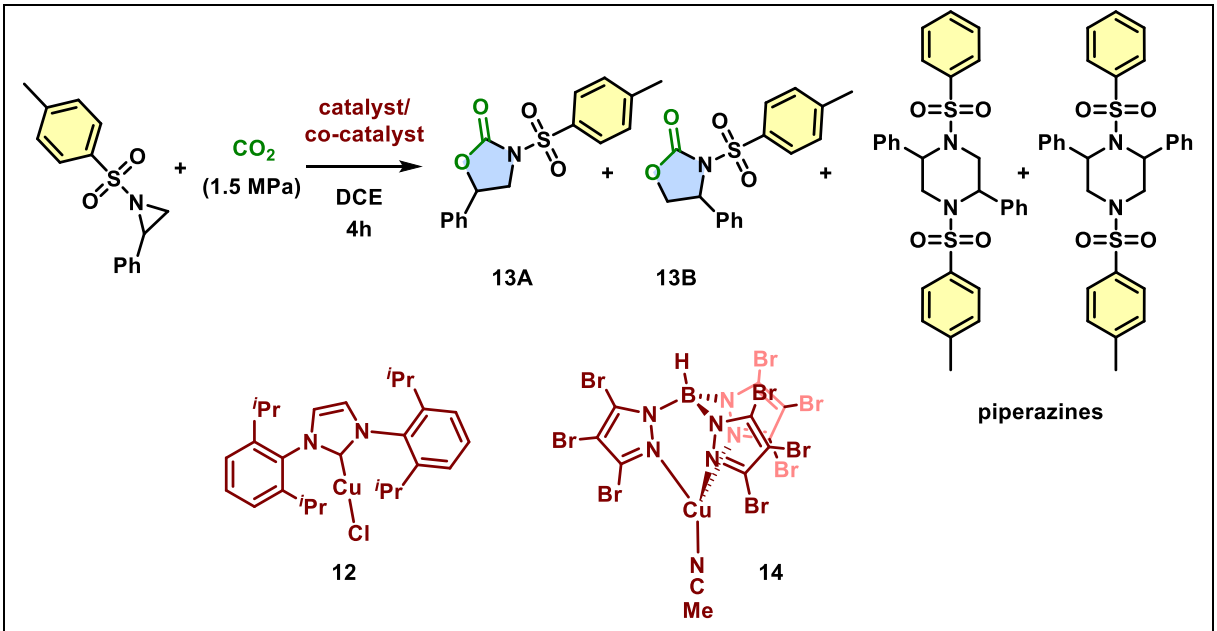
Use of a copper catalyst for the cycloaddition reaction

The successful synthesis of *N*-alkyl oxazolidin-2-ones under mild reaction conditions encouraged us to explore the possibility to develop a tandem protocol for the synthesis of oxazolidin-2-ones in which first the aziridine is formed and then reacted with CO_2. Considering that a metal complex is needed to promote the synthesis of aziridines from styrene derivatives and nitrene precursors, we decided to investigate whether copper-based catalysts, known for their high activity in aziridine formation from styrenes and imidoiodinanes [47–49,58], could promote in two consecutive steps the synthesis of aziridine and CO_2 cycloaddition. With this idea in mind, we tested (NHC)CuCl complex **12** (Table 2), for the two consecutive reactions, given its potential for the olefin aziridination step [58] and the availability of a chloride ligand which could potentially act as the nucleophile in the cycloaddition step.

First we screened the catalytic activity of **12** in the formation of oxazolidine-2-one **13** using a pre-synthetized aziridine. Complex **12** itself was unactive (16 h, 85 ºC, 1.5 MPa CO_2, DCE as solvent) suggesting that the chloride ligand was not available as nucleophile species in the CO_2 cycloaddition (Table 2, entry 2). Consequently, the activity of **12** was tested in combination with TBAX (X = Cl^-, I^-) co-catalyst which catalyzes per se this transformation (Table 2, entry 1). The combination **12**/TBACl system leads to the desired product **13** in moderate yields and in high selectivities, with values similar to those promoted by the TBAX as the sole catalyst. It is of note that under these reaction conditions, piperazine side-products were formed, in contrast to the exclusive formation of 5-member rings when using IPrHCl (**1**) as catalyst. We have also tested Tp^{Br3}Cu(NCMe) (**14**) as catalyst, given its well-known capability to transfer nitrenes to olefins [47–49]. In combination with ammonium salts under the same reaction conditions applied with the **12**/TBACl binary system (Table 2, entry 5), it did

not show any activity towards the cycloaddition reaction. This compound reacts with the ammonium chloride or iodide salt thus inhibiting the process. Finally, simple CuX salts were tested in the CO_2 cycloaddition to *N*-tosyl aziridines, also showing no activity (Table 2, entry 6).

Table 1: Synthesis of oxazolidin-2-ones **2A** and **2B** catalyzed by TBACl or **1** under atmospheric CO_2 pressure.



Entry	Cat/co-cat	Loading (mol%)	Conversion (%)[b]	Selectivity (%)[b] **13A+13B**	Yield (%)[b] **13A+13B**	**13A/13B** ratio[b]
1	TBACl (TBAI)	10 (10)	85 (80)	35 (40)	30 (32)	82:18 (82:18)
2	**12**	10	-	-	-	-
3	**12**/TBACl (**12**/TBAI)	5/10 (5/10)	79 (93)	63 (56)	50 (52)	80:20 (77:23)
4	**12**/TBACl (**12**/TBAI)	10/10 (10/10)	92 (92)	62 (53)	57 (49)	81:19 (78:22)
5	**14**/TBACl (**14**/TBAI)	10/10 (10/10)	- -	- -	- -	- -

6	CuCl (CuI)	10 10	- -	- -	- -	- -

[a]Reactions were stirred in DCE for 16 hours at 1.5 MPa of CO_2 and 85 °C. [b]Determined by ^{1}H-NMR spectroscopy by using 2,4-dinitrotoluene as the internal standard.

The above results showed that the binary **12**/TBACl system could potentially be employed for the tandem goal, albeit the drawback of piperazine formation should be surpassed. Piperazines are formed upon coupling of two aziridine rings, and therefore an optimization of the reaction conditions to minimize the formation of piperazine side-products was performed (Figure 2). Collected data underlined that by using 10 mol% of **12** (combined with 10 mol% of TBACl) and decreasing the aziridine concentration to 0.25 M (Figure 2A), an improvement of the reaction yield can be achieved and the desired oxazolidin-2-ones **13A** + **13B** were formed in 58% yield and 67% of reaction selectivity. Further enhancement was achieved by increasing the CO_2 pressure to 2.0 MPa, which resulted in a 66% yield and 73% selectivity for compounds **13A** + **13B** (Figure 2B). No product formation was observed when THF was used as the solvent, and replacing DCE with MeCN led to lower yield and selectivity, confirming that DCE is the optimal solvent for this reaction. Data comparison in Figure 2D indicated that the reaction temperature is a key parameter for improving catalytic efficiency: performing the reaction at 65 °C, oxazolidin-2-ones **13A** + **13B** were exclusively obtained, with no piperazine being detected. As shown in Figures 2E and 2F, the desired products **13A** + **13B** were obtained in high yield (88%) and reaction selectivity by extending the reaction time to 24 hours, under 2.0 MPa CO_2 pressure and in the presence of 20 mol% catalyst and co-catalyst.

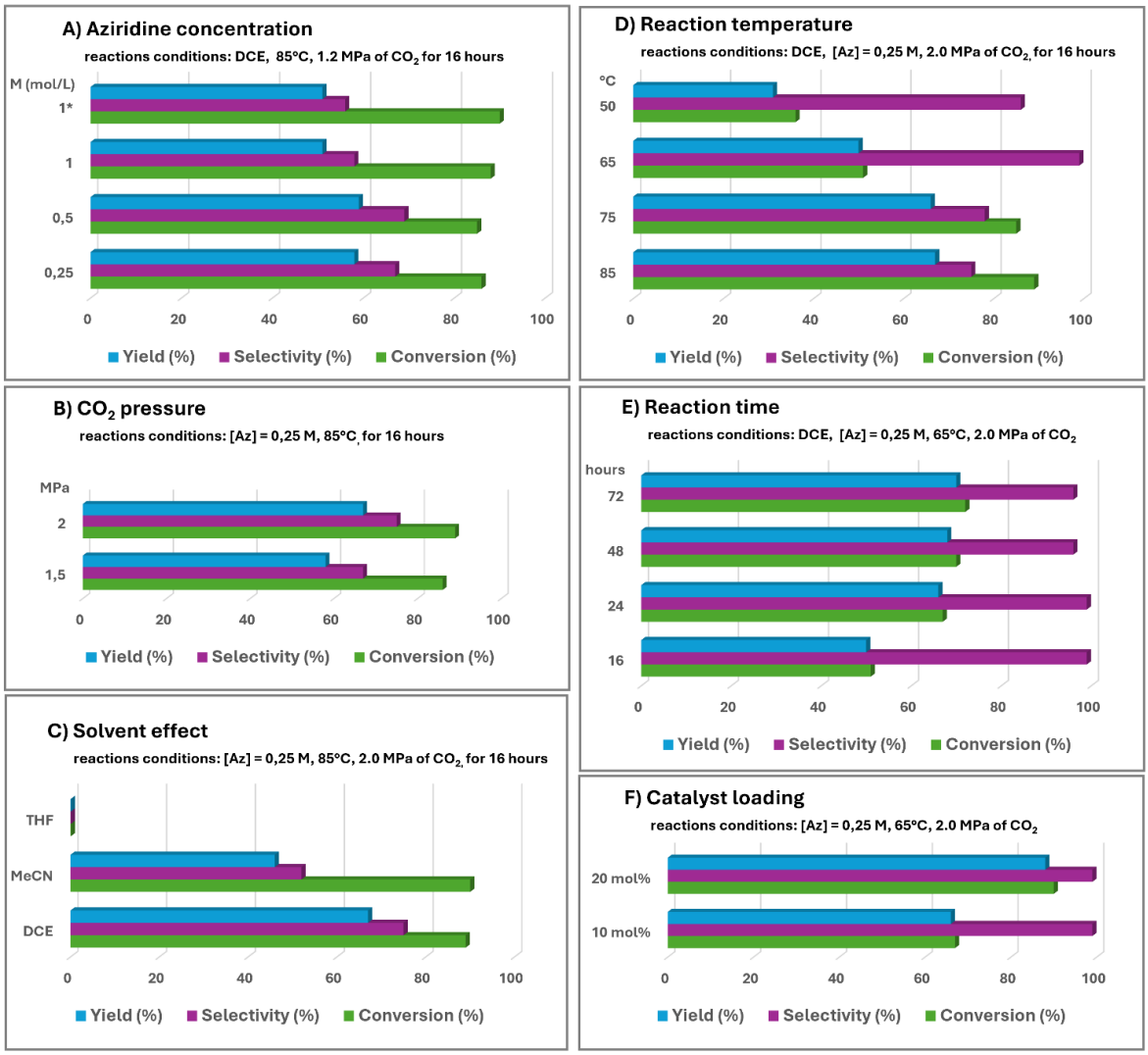
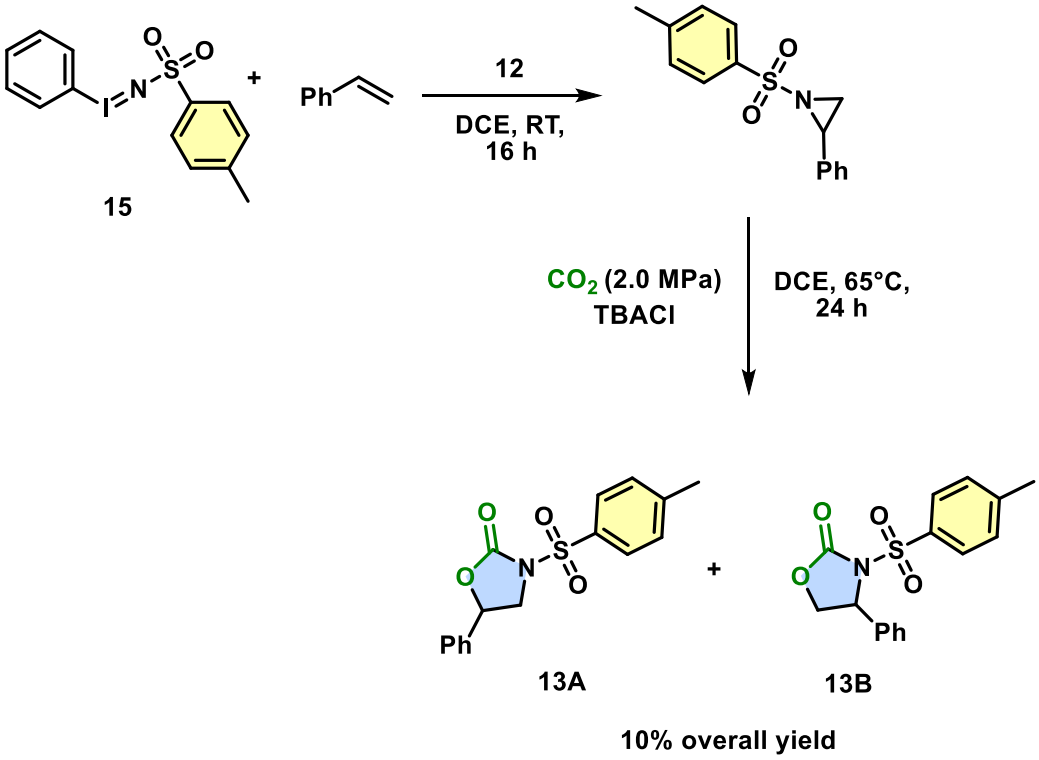


Figure 2. Optimization of the reaction condition for the **12-**catalyzed synthesis of oxazolidin-2-one **13A** + **13B**. Selectivities are related to the formation of oxazolidin-2-ones **13A** + **13B**.

In view of results achieved up to now, a preliminary experiment has been conducted to evaluate the feasibility of synthesizing oxazolidin-2-ones **13A** + **13B** without purifying the intermediate aziridine in a tandem procedure. The double activity of **12** in promoting both the synthesis of aziridines and the CO_2 cycloaddition opened the door to first synthesize aziridine which can be then transformed *in situ* into the corresponding *N*-tosyl oxazolidin-2-ones. Phenyl *N*-tosyl aziridine was formed in 80% yield (NMR

analysis of the crude) after 16 h in DCE at room temperature by employing catalyst **12**, imidoiodinane **15**, and styrene in a 1:20:200 ratio, respectively (Scheme 5). Then, the reaction mixture was filtered and 10 mol% of TBACl was added to the mixture, which was then transferred to a high pressure reactor and charged with 2.0 MPa of CO_2. After stirring for 24 h at 65 °C, analysis of the reaction crude revealed the presence of the desired oxazolidinones **13A** + **13B** in 10% yield. Although the desired products were obtained in low yield, these preliminary findings provide an important proof of concept, demonstrating that **12** can promote both reaction steps without the need for isolation and purification of the aziridine intermediate prior to CO_2 cycloaddition. As such, these results represent a promising starting point for the development of a tandem process. Ongoing and future studies will be directed toward optimizing the reaction conditions to enhance efficiency and productivity, with the goal of establishing a practical and effective tandem protocol.



Scheme 5. Synthesis of oxazolidin-2-one **13** by tandem process.

Conclusion

This study highlighted the effectiveness of the simple and inexpensive 1,3-*bis*(2,6-diisopropylphenyl)imidazolium chloride (**1**) as a valuable organocatalyst for the synthesis of *N*-alkyl oxazolidin-2-ones from CO_2 and aziridines under mild and sustainable reaction conditions. The optimized protocol, employing low CO_2 pressure (0.1 MPa) and moderate temperature (40 °C) in acetonitrile, allowed the synthesis of the desired products in very high yields (up to 90%) and excellent regioselectivities (up to 95:5), confirming the crucial role of the bifunctional nature of the catalyst in facilitating the cycloaddition process. A copper derivative of **1,** assisted by TBACl as co-catalyst also promoted this transformation, allowing the consecutive one-pot reactions of styrene aziridination and CO_2 cycloaddition, albeit at a minor extent.

Experimental

General methods. All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen atmosphere. Unless otherwise specified, MeCN and DCE were distilled over calcium hydride and kept under nitrogen. *N*-alkyl aziridines [6], *N*-tosyl aziridine [58], (*S*)-1-benzyl-2-octylaziridine [46], 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (**1**) [50], (NHC)CuCl (**12**) [58] and $TpBr^3Cu(NCMe)$ (**14**) [59 were synthesized by following already reported procedures. All the other starting materials were commercial products and used as received. NMR spectra were recorded at room temperature either on a Bruker Avance 300-DRX, operating at 300 MHz for ^1H and at 75 MHz for ^{13}C or on a Bruker Avance 400-DRX spectrometers, operating at 400 MHz for ^1H and at 101 MHz for ^{13}C. Chemical shifts (ppm) are reported relative to TMS. ^1H NMR signals of the compounds described in the following were attributed by 2D NMR techniques. Assignments of the resonances

in ^{13}C NMR were made by using the APT pulse sequence, HSQC and HMBC techniques. Infrared spectra were recorded on a Varian Scimitar FTS 1000 spectrophotometer. UV-Visible spectra were recorded on an Agilent 8453E instrument. Mass spectra were recorded in the analytical laboratories of Milan University.

General catalytic procedure for the cycloaddition of CO_2 to aziridines at atmospheric pressure. In a 10.0 mL test tube equipped with a screw cap with a silicon/PTFE septum, 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (**1**) (8×10^{-5} mol) was dissolved in MeCN (0.5 mL) and then the desired aziridine (8×10^{-4} mol) was added. At this point, CO_2 was bubbled into the mixture for 15 minutes, and then a plastic balloon filled with CO_2 was connected to the top of the flask to maintain a carbon dioxide atmosphere. The reaction was stirred at 40 °C for 24 hours, then the CO_2 balloon was removed, the solvent evaporated to dryness and the crude analyzed by ^1H NMR spectroscopy by using 2,4-dinitrotoluene as the internal standard.

General catalytic procedure for the cycloaddition of CO_2 to *N*-tosyl aziridine. In a 3.5 mL glass liner equipped with a screw cap and glass wool, the desired amount of catalyst, TBAX salt and *N*-tosyl aziridine were dissolved in DCE (0.5 mL). The vessel was transferred into a stainless-steel autoclave and the required CO_2 pressure was charged at room temperature. The autoclave was placed in a preheated oil bath at the desired temperature, stirred for the required time and then quenched in an ice bath and slowly vented (see Table 2, Figure 2 and Supporting Information for experimental details). The solvent was evaporated to dryness and the crude analyzed by ^1H NMR spectroscopy by using 2,4-dinitrotoluene as the internal standard.

Synthesis of *N*-tosyl oxazolidin-2-one by tandem procedure. In a Schlenk flask, (NHC)CuCl (**12**) (2.0 x 10^{-4} mmol), styrene (1.0 x 10^{-2} mmol) and imidoiodinane **15** (1.0 x 10^{-3} mmol) were stirred in DCE (3.2 mL) for 16 hours at room temperature. At the end of the reaction the mixture was filtered to remove solid residues and 0.5 mL of the obtained solution were taken, dried *in vacuo* and analyzed by ^{1}H NMR using 2,4-dinitrotoluene as the internal standard in order to determine the aziridine yield (80%).Then, 0.5 mL of the aziridine-containing mixture were transferred in a 3.5 mL glass liner equipped with a screw cap and glass wool. TBACl (2.5 x 10^{-5} mmol) was added and the vessel was transferred into a stainless-steel autoclave. 2.0 MPa of CO_2 were charged at room temperature, and the autoclave was placed in a preheated oil bath at 65°C and stirred for 24 hours. At the end of the reaction the autoclave was cooled to room temperature and slowly vented. The solvent was evaporated to dryness and the crude analyzed by ^{1}H NMR spectroscopy by using 2,4-dinitrotoluene as the internal standard.

Supporting Information

Supporting Information File 1:

File Name: supporting Information

File Format: pdf

Acknowledgements

CD and EG thank Università degli Studi di Milano for the PSR 2023 grant. We also thank Ministerio de Ciencia e Innovación for grant PID2020-113797RB-C21.

References

1. Rafiee, A; Rajab Khalilpour, K; Milani, D.; Panahi, M. *J. Environ. Chem. Eng.*, **2018**, *6*, 5771 – 5794.
2. Kim, C.; Yoo, C. J.; Oh, H. S.; Min, B. K.; Lee, U., *J. CO_2 Util.* **2022**, *65*, 102239.
3. Zhang, Z.; Pan, S. Y.; Li, H.; Cai, J.; Olabi, A. G.; Anthony, E. J.; Manovic, V. *Renew. Sustain. Energy Rev*., **2020**, *125*, 109799.
4. Intrieri, D.; Damiano, C.; Sonzini, P.; Gallo, E. *J. Porphyr. Phthalocyanines* **2019**, *23*, 305 – 328.
5. C. Damiano, C. P. Sonzini, P.; Intrieri, D.; Gallo, E. *J. Porphyr. Phthalocyanines* **2020**, *24*, 809 – 816.
6. Carminati, D.; Gallo, E.; Damiano, C. Caselli, A.; Intrieri, D. *Eur. J. Inorg. Chem.* **2018**, *2018*, 5258 – 5262.
7. Lopes, E. J. C.; Ribeiro, A. P. C.; Martins, L. M. D. R. S. *Catalysts*, **2020**, 10, 479.
8. Yabushita, M.; Fujii, R.; Nakagawa, Y.; Tomishige, K. *ChemCatChem* **2024**, e202301342.
9. Tomishige, K.; Gu, Y.; Chang, T.; Tamura, M.; Nakagawa, Y. *Materials Today Sustainability* **2020**, *9*, 100035.
10. Rotundo, L.; Gobetto, R.; Nervi, C. *Green Sustain. Chem.* **2021**, *31*, 100509.
11. Damiano, C.; Fata, A.; Cavalleri, M.; Manca, G.; Gallo, E. *Catal. Sci. Technol.* **2024**, *14*, 3996–4006.
12. Fiorani, G.; Guo, W.; Kleij, A. W. *Green Chemistry* **2015**, *17*, 1375–1389.
13. Cherubini-Celli, A.; Mateos, J.; Bonchio, M.; Dell'Amico, L.; Companyó, X. *ChemSusChem* **2018**, *11*, 3056–3070.
14. Schilling, W.; Das, S. *ChemSusChem* **2020**,*13*, 6246–6258.

15. Wiranarongkorn, K.; Eamsiri, K.; Chen, Y. S.; Arpornwichanop, A. *J. CO2 Util.* **2023**, 71, 102477.
16. Schuurmans, J. H. A.; Masson, T. M.; Zondag, S. D. A.; Pilon, S.; Bragato, N.; Claros, M.; den Hartog, T.; Sastre, F.; van den Ham, J.; Buskens, P.; Fiorani, G.; Noël, T. *Chem. Sci.* **2024**, *15*, 19842–19850.
17. Appel, A. M.; Bercaw, J. E.; Bocarsly, A. B.; Dobbek, H.; Dubois, D. L.; Dupuis, M.; Ferry, J. G.; Fujita, E.; Hille, R.; Kenis, P. J. A.; Kerfeld, C. A.; Morris, R. H.; Peden, C. H. F.; Portis, A. R.; Ragsdale, S. W.; Rauchfuss, T. B.; Reek, J. N. H.; Seefeldt, L. C.; Thauer, R. K.; Waldrop, G. L. *Chem. Rev*. **2013**, *113*, 6621–6658.
18. Yan, T.; Liu, H.; Zeng, Z. X.; Pan, W. G. *J. CO2 Util.* **2023**, *68*, 102355.
19. Tyagi, P.; Singh, D.; Malik, N.; Kumar, S.; Singh Malik, R. *Materials Today*, **2023**, *65*, 133–165.
20. Guo, L.; Lamb, K. J.; North, M. *Green Chem*. **2021**, *23*, 77–118.
21. Eftaiha, A. F.; Qaroush, A. K.; Hasan, A. K.; Helal, W.; Al-Qaisi, F. M. *React. Chem. Eng.* **2022**, *7*, 1807–1817.
22. Bobbink, F. D.; Vasilyev, D.; Hulla, M.; Chamam, S.; Menoud, F.; Laurenczy, G.; Katsyuba, S.; Dyson, P. J. *ACS Catal.* **2018**, *8*, 2589–2594.
23. Qaroush, A. K.; Eftaiha, A. F.; Al-Qaisi, F. M.; Assaf, K. I.; Hammad, S. B.; Al-Anati, M. H.; Radwan, E. S.; Awwadi, F. F. *Catal. Sci. Technol.* **2023**, *13,* 3245–3257.
24. Zhang, Y.; Chan, J. Y. G. *Energy Environ. Sci.* **2010**,*3*, 408-417.
25. Qiu, J.; Zhao, Y.; Li, Z.; Wang, H.; Shi, Y.; Wang, J. *ChemSusChem* **2019**, *12*, 2421–2427.
26. Chen, K.; Chen, Y.; Zhang, Z.; Luo, R. *Ind. Eng. Chem. Res.* **2025**, *64*, 53–60.
27. Miró, R.; Lara-Rimbau, F. X.; Vicente, I.; Gual, A. *ACS Sustain. Chem. Eng.* **2023**, *11*, 17600–17606.
28. Wang, L.; Li, L.; Xu, Y.; Li, Y.; Wang, Y.; Chu, T. *J. Mol. Liq.* **2023**, *379*, 121646.

29. Wang, Y.; Sun, J. *J. Mol. Struct.* **2026**, *1362*, 145732.
30. Liu, Y.; Cao, Z.; Zhou, Z.; Zhou, A. *J. CO2 Util.* **2021**, *53*, 101717.
31. Wang, T.; Zheng, D.; An, B.; Liu, Y.; Ren, T.; Ågren, H.; Wang, L.; Zhang, J.; Ahlquist, M. S. G. *Green Energy Environ.* **2022**, *7*, 1327–1339.
32. Liu, J.; Yang, G.; Liu, Y.; Wu, D.; Hu, X.; Zhang, Z. *Green Chem.* **2019**, *21*, 3834–3838.
33. Seong, Y.; Lee, S.; Cho, S.; Kim, Y. *Catalysts* **2024**, *14*, 90.
34. Qian, Z.; Shang, X.; Wang, W.; Zhang, D.; Sun, S. *Catal. Letters* **2024**, *154*, 1201–1208.
35. Watile, R. A.; Bagal, D. B.; Deshmukh, K. M.; Dhake, K. P.; Bhanage, B. M. *J. Mol. Catal. A Chem.* **2011**, *351*, 196–203.
36. Hu, J.; Ma, J.; Zhu, Q.; Zhang, Z.; Wu, C.; Han, B. *Angew. Chem.* **2015**, *127*, 5489–5493.
37. Bialvaei, A. Z.; Rahbar, M.; Yousefi, M.; Asgharzadeh, M.; Kafil, H. S. *J. Antimicrob. Chemother.* **2017**, *72*, 354–364.
38. McBride, D.; Krekel, T.; Hsueh, K.; Durkin, M. J. *Expert Opin. Drug Metab. Toxicol.* **2017**, *13*, 331–337.
39. Moureau, F.; Wouters, J.; Vercauteren, D.; Collin, S.; Evrard, G.; Durant, F.; Ducrey, F.; Koenig, J.; Jarreau, F. *Eur. J. Med. Chem.* **1992**, *27*, 939–948.
40. Yang, X.; Xu, L.; Zhu, Y.; Zhang, S.; Jia, G.; Du, J. *J. CO2 Util.* **2023**, *74*, 102531.
41. Zhang, Q.; Jin, X. *Chem. Eur. J.* **2025**, *31*, e202500933.
42. Damiano, C.; Sonzini, P.; Manca, G.; Gallo, E. *Eur. J. Org. Chem.* **2021**, *2021*, 2807–2814.
43. Sonzini, P.; Damiano, C.; Intrieri, D.; Manca, G.; Gallo, E. *Adv. Synth. Catal.* **2020**, *362*, 2961–2969.

44. Sonzini, P.; Berthet, N.; Damiano, C.; Dufaud, V.; Gallo, E. *J. Catal.* **2022**, *414*, 143–154.
45. Cavalleri, M.; Damiano, C.; Manca, G.; Gallo, E. *Chem. Eur. J.* **2023**, *29*, e202202729.
46. Invernizzi, L.; Damiano, C.; Gallo, E. *Chem. Eur. J.* **2025**, *31*, e202500473.
47. Pérez, P. J.; Brookhart, M.; Templeton, J. L. Organometallics, **1993**, *12*, 261–262.
48. Maestre, L.; Sameera, W. M. C.; Díaz-Requejo, M. M.; Maseras, F.; Pérez, P. J. *J. Am. Chem. Soc.* **2013**, *135*, 1338–1348.
49. Pérez-Ruíz, J.; Rosales Martínez, A.; Díaz-Requejo, M. M.; Pérez, P. J. *Angew. Chem. Int. Ed.* **2025**, *23*, e202419188.
50. Bantreil, X.; Nolan, S. P. *Nat. Protoc.* **2011**, *6*, 69–77.
51. Bresciani, G.; Bortoluzzi, M.; Pampaloni, G.; Marchetti, F. *Org. Biomol. Chem.* **2021**, *19*, 4152–4161.
52. Song, Q.-W.; Zhou, Z.-H.; He, L.-N. *Green Chem.* **2017**, *19*, 3707–3728.
53. Zhou, H.; Zhang, W.-Z.; Liu, C.-H.; Qu, J.-P.; Lu, X.-B. *J. Org. Chem.* **2008**, *73*, 8039–8044.
54. Sengoden, M.; North, M.; Whitwood, A. C. *ChemSusChem* **2019**, *12*, 3296–3303.
55. Du, Y.; Wu, Y.; Liu, A.-H.; He, L.-N. *J. Org. Chem.* **2008**, *73*, 4709–4712.
56. Truong, C. C.; Mishara, D. K. *Environ. Chem. Lett.* **2021**, *19*, 911–940.
57. Damiano, C.; Cavalleri, M.; Invernizzi, L.; Gallo, E. *Eur. J. Org. Chem.* **2024,** *27,* e202400616.
58. Pérez-Ruíz, J.; Pérez, P. J.; Díaz-Requejo, M. M. *Organometallics* **2022**, *41*, 3349–3355.
59. Díaz-Requejo, M. M.; Belderraín, T. R.; Nicasio, M. C.; Trofimenko, S.; Pérez, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 12078–12079.