catalysts

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*Review*

# Recent Advances in the Synthesis of Five-Membered Cyclic Carbonates and Carbamates from Allylic or Propargylic Substrates and $CO_2$

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**Abstract:** The organic carbamates and carbonates are highly desirable compounds that have found a wide range of applications in drug design, medicinal chemistry, material science, and the polymer industry. The development of new catalytic carbonate and carbamate forming reactions, which employ carbon dioxide as a cheap, green, abundant, and easily available reagent, would thus represent an ideal substitution for existing methods. In this review, the advancements in the catalytic conversion of allylic and propargylic alcohols and amines to corresponding five-membered cyclic carbonates and carbamates are summarized. Both the metal- and the organocatalyzed methods are reviewed, as well as the proposed mechanisms and key intermediates of the illustrated carbonate and carbamate forming reactions.

**Keywords:** carbamates; carbonates; carbon dioxide; mechanisms; metal-catalyzed; organocatalyzed

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## 1. Introduction

Very few molecules provoke as much controversy as carbon dioxide ($CO_2$). Since the beginning of the industrial age, the concentration of $CO_2$ in the Earth's atmosphere has increased by about 46% [1]. It is estimated that currently, 93% of anthropogenic $CO_2$ is generated by fossil fuel combustion [2], with the prediction that the atmospheric concentration of $CO_2$ will increase between 730 and 1020 ppm by the end of the century [3]. The connection between the increasing concentration of $CO_2$ and ocean acidity, as well as severe and obvious global climate changes, have initiated the trend towards the substantial reduction in fossil fuels and $CO_2$ emission [4], moving towards alternative energy sources and a "low-carbon economy".

The development of new strategies and techniques for carbon capture, utilization, and storage (CCUS) are currently subjects of intense research. However, it is important to note that energy technology deployment is slow [5], and not all CCUS processes are financially viable or amenable for scaling up [6]. In addition, with the advancement of $CO_2$ storage, scientists have developed novel and innovative approaches to direct the chemical

and pharmaceutical industries towards a carbon-sustainable chemical synthesis by using $CO_2$ gas as an abundant carbon source in terms of the concept of green chemistry. This movement remains challenging because of the exceptional thermodynamic stability of $CO_2$ and thus, the high energetic cost of its fixation. Indeed, the attempts to reduce $CO_2$ back to a synthetically useful compound might require comparable or more energy than obtained by its production by the combustion of fossil fuel, as $CO_2$ represents the final product of the carbon oxidation [7]. Likewise, the kinetic barrier of $CO_2$ reduction is high. Even though the methanation of $CO_2$ is an exergonic reaction, as $H_2$ gas is highly energetically rich, it does not proceed without a metal catalyst, and problems considering $H_2$ storage should also be addressed. The Sabatier reaction, discovered in 1902, uses an Ni catalyst and $H_2$ to reduce $CO_2$ to methane, and this reaction is currently experiencing a revival due to its potential use in long-haul space missions [8].

In the last two decades, several other reactions that use $CO_2$ as a C1-synthon have been developed, yielding highly valuable and interesting molecules [9]. Specifically, heterocyclic carbonates and carbamates have represented challenging synthetic targets for the employment as pharmaceuticals, polymers, and other functional materials or as valuable intermediates for further synthetic transformations. The reaction of epoxides and $CO_2$ is one of the most established and widely used methods to obtain five-membered cyclic carbonates, and a great array of catalytic systems, including transition metal porphyrin complexes [10], ionic liquids [11], and heterogeneous catalysts [12], have been developed. Some progress has also been made in the production of cyclic carbamates from aziridines [13].

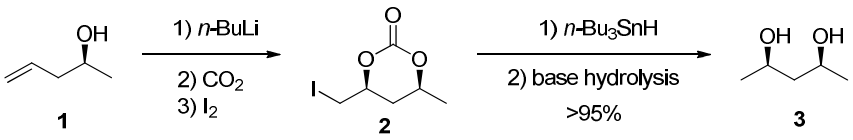
In this paper, we review the methods to obtain cyclic carbonates and carbamates from corresponding (homo)allylic and propargylic alcohols and amines by employing $CO_2$ as the source of the carbonyl functionality. The most relevant examples of cyclic carbonates and carbamates forming reactions by engaging the catalytic $CO_2$ fixation reactions will be discussed, as well as mechanistic considerations based on experimental and theoretical studies. Previous reviews in this field include Vessally's survey of the carboxylative cyclization of propargylic alcohols into $\alpha$-methylene cyclic carbonates [14], Das' review of the transition metal-free synthesis of carbamates [15], and Edjlali's survey of the three-component coupling reaction of propargyl alcohols, amines, and $CO_2$ [16].

## 2. Cyclic Carbonates

Cyclic carbonates are of great significance in the chemical industry, with a wide range of important applications. They are used as highly polar solvents [17], electrolytes in lithium batteries [18], precursors for polycarbonates forming the major class of commercial thermoplastics [19], and precursors for other organic compounds [20]. The simplest cyclic carbonate, ethylene carbonate, is synthesized industrially by the reaction of ethylene oxide with $CO_2$. Below, the most common methods for obtaining cyclic carbonates from allylic and propargylic alcohols are described.

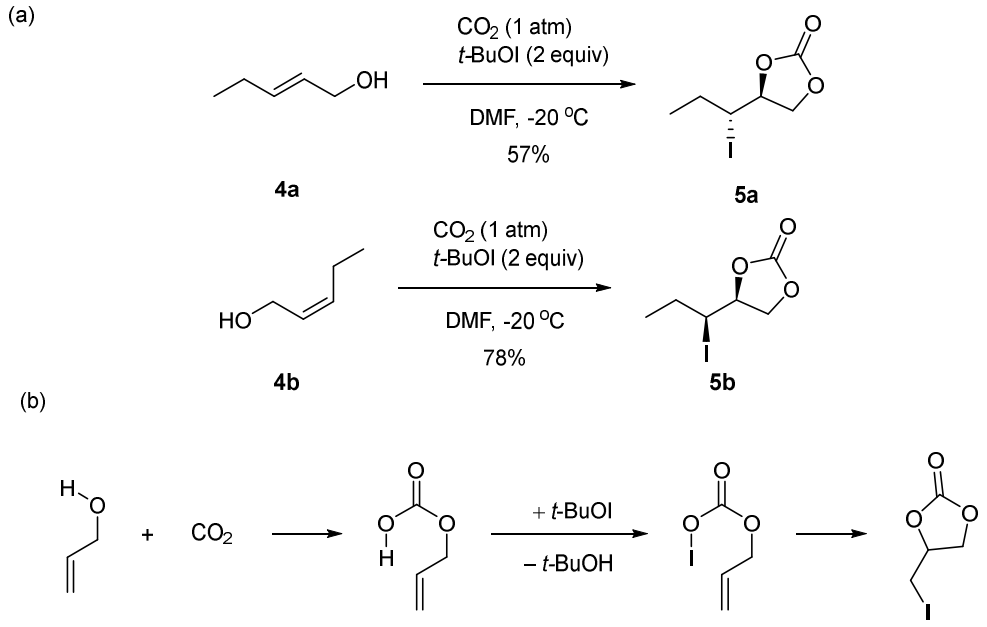
### *2.1. Five-Membered Cyclic Carbonates from Allylic Alcohols*

In 1981, Cardillo et al. demonstrated the first synthesis of 5-iodomethyl cyclic carbonates of type 2 by employing $CO_2$. The synthesis involved the engagement of a strong base (*n*-BuLi) in a $CO_2$-saturated THF solution of iodine [21]. This method showed a high degree of regioselectivity and stereoselectivity. For example, the allylic alcohols always led to the formation of 5-membered cyclic carbonates, while homoallylic alcohols yielded 6-membered rings. The high stereoselectivity of the carbonation of pent-4-en-2-ol (**1**) was proven by the almost exclusive formation of *syn*-diol 3 (>95%) produced by the treatment of the 5-iodomethyl cyclic carbonate **2** with $Bu_3SnH$ (to convert C–I into C–H) under basic conditions (Scheme 1). The mechanism of the reaction was proposed to include an iodonium ion as the key intermediate, which opens by nucleophilic attack of the in situ formed carbonate anion.



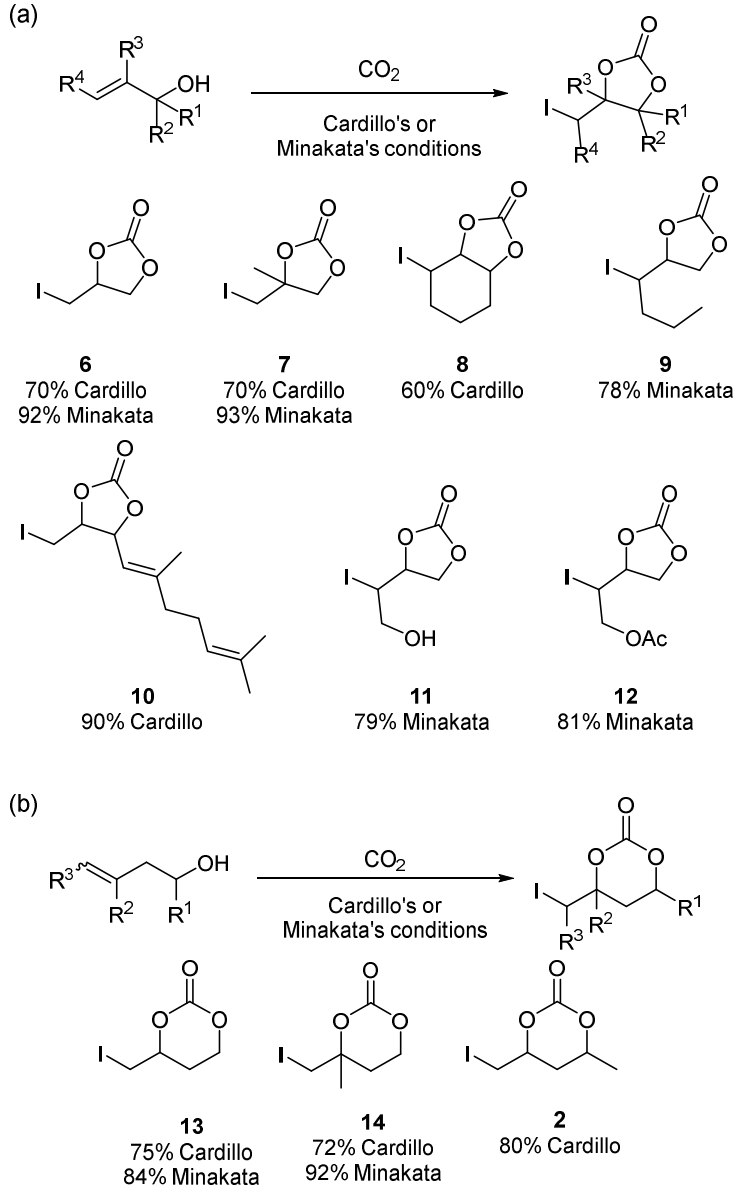

**Scheme 1.** Cardillo's synthesis of a 5-iodomethyl cyclic carbonate and its stereoselectivity [21].

In 2010, Minakata et al. reported an improved version of this reaction by using *t*-BuOI, a powerful iodinating agent, which was previously proven to be efficient for the cyclization of the unsaturated amines (Scheme 2a) [22]. In situ formed *t*-BuOI, by the reaction of *t*-BuOCl with NaI, gave higher yields than other iodine sources, such as *N*-iodosuccinimide and $I_2$. In addition, reaction conditions were simpler, as the reaction can be conducted under ambient pressure, avoiding the saturation of the solution with $CO_2$. This method was also more general and gave higher yields with allylic, homoallylic, and propargylic alcohols [19]. Interestingly, *E*-hex-2-en-1-ol (**4a**) gave the single *anti*-diastereomer of 4-(1-iodopropyl)-1,3-dioxolan-2-one (**5a**), whereas the *syn*-carbonate **5b** was exclusively obtained from **4b** (Scheme 2a). Although the products *anti*- and *syn*-**5** were formed in only 57% and 78% yields, respectively, the reaction was categorized as stereospecific. Further studies showed that the optimal reaction conditions are based on the use of *t*-BuOI (2 equiv) in THF at −20 °C. Under these conditions, the unsubstituted propargylic alcohol provided *E*-isomer in a 92% yield after 3 h. The mechanism is assumed to proceed through a hydrogen-iodine exchange at the carbonate oxygen junction, followed by cyclization (Scheme 2b).




**Scheme 2.** (**a**) The stereoselectivity of Minakata's synthesis of 5-iodomethyl cyclic carbonates; (**b**) the proposed mechanism of Minakata's synthesis of 5-iodomethyl cyclic carbonates. The nucleophilic attack of the alcohol group on $CO_2$ is followed by hydrogen–iodine exchange. The now electrophilic oxygen is attacked by the double bond, leading to cyclisation [22].

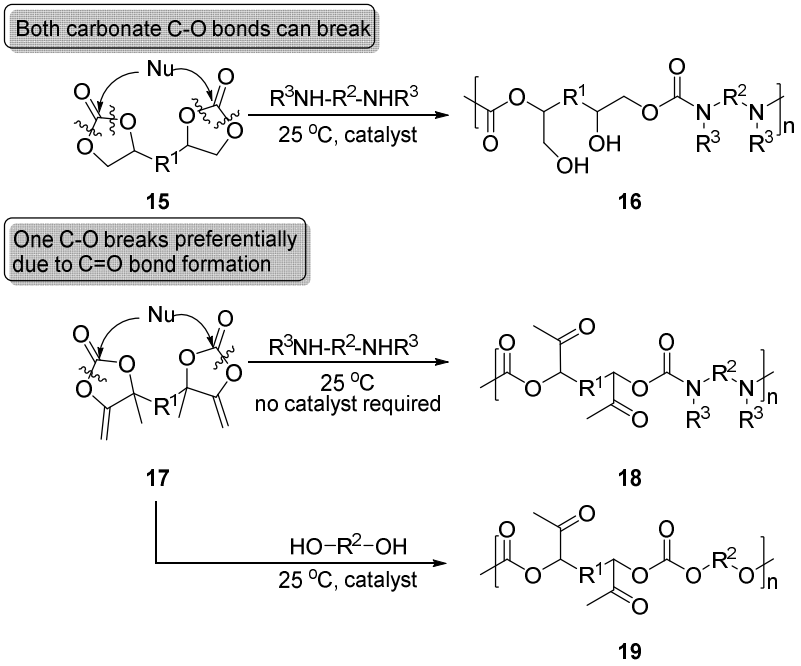
A comparison of Cardillo's and Minakata's methods for carboxylative cyclization of allylic a) and homoallylic b) alcohols is shown in Scheme 3. In all cases, Minakata's conditions led to the formation of pentacyclic and hexacyclic carbonates in higher yields.




**Scheme 3.** A comparison of Cardillo's and Minakata's carboxylative cyclization of allylic (**a**) and homoallylic alcohols (**b**). Conditions: Cardillo—(1 equiv $^{n}$BuLi in THF added to alcohol, then $CO_2$ bubbled and 2 equiv $I_2$ added, stirred for 14 h at rt) [21], and Minakata—(2 equiv *t*-BuOCl added to 1 equiv NaI and alcohol under $CO_2$ atmosphere, stirred for 3–72 h at −20 °C) [22].

### *2.2. α-Alkylidene Cyclic Carbonates from $CO_2$ and Propargylic Alcohols*

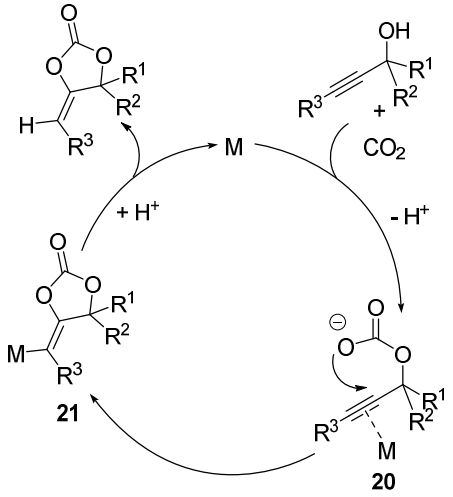
α-Alkylidene cyclic carbonates have recently attracted a lot of interest as reactants for the synthesis of pharmaceuticals and as monomers for polycarbonates and polyurethanes formation [23]. In addition to elevated reactivity with nucleophiles under mild reaction conditions and no need for a catalyst [24], the main advantage of the employment of α-alkylidene cyclic carbonates of type **17** over unsubstituted 5-membered analogues **15** includes the highly regioselectivity of the ring opening, as preferentially, only one C–O bond breaks (Scheme 4).




**Scheme 4.** Regioselective formation of polycarbonates starting with $\alpha$-alkylidene cyclic carbonates instead of regular cyclic carbonates [24].

### 2.2.1. Metal Catalysts

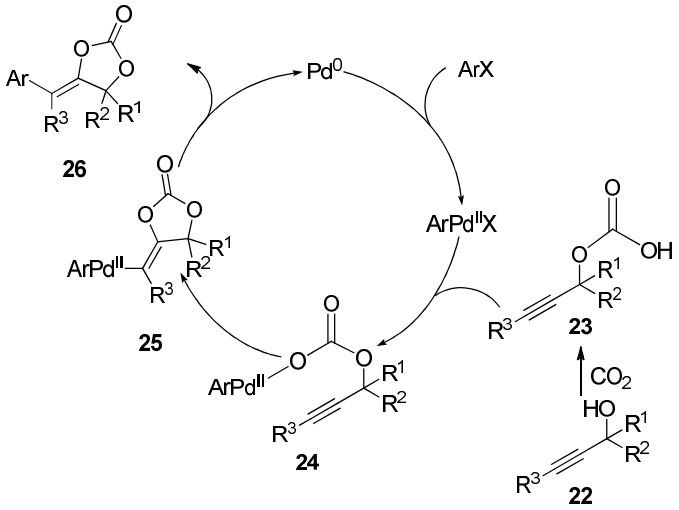
Scheme 5 shows the general catalytic cycle for the carboxylative cyclization of propargylic alcohols with organometallic catalysts, as suggested by Yamada [25]. The activation of the triple bond by the $\pi$-complexation to the metal and the formation of intermediate **20** facilitates the attack of the carbonate and formation of the cyclic vinyl complex **21**. Its protonolysis in the following step gives the methylidene carbonate. Various catalytic systems based on Pd, Ag, and Cu metals capable of the activation of the triple bond have been reported as efficient catalysts for this process.




**Scheme 5.** Metal-catalyzed carboxylative cyclization of propargylic alcohols. Metal ions coordinate to the triple bond, leading to an attack by the transiently formed carbonate anion. The resulting metal complex is protonated, which gives the final $\alpha$-alkylidene cyclic carbonate.

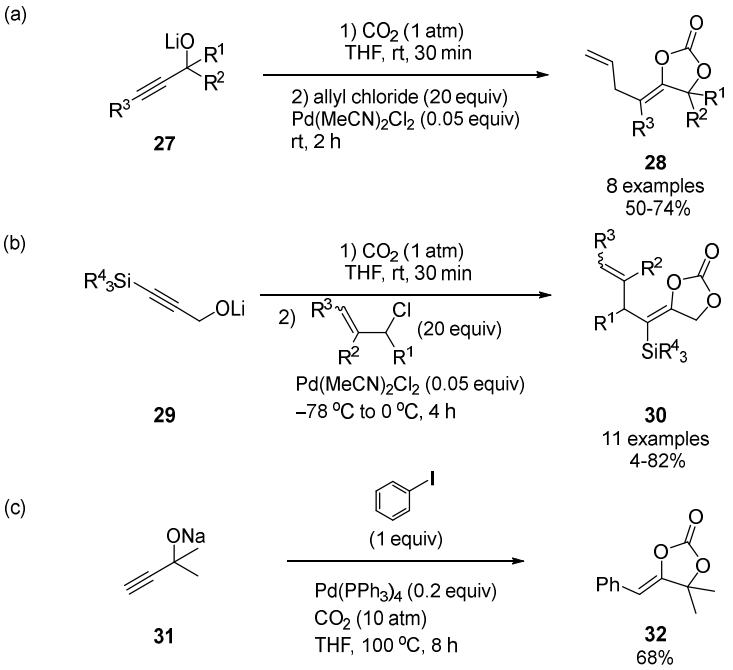
Palladium

Common homogeneous Pd-complexes have been identified as efficient catalysts for the carbonate formation employing propargylic alcohols and $CO_2$ under one-pot multi-component conditions. In these reactions Pd(0)-complexes first undergo oxidative addition with an aryl-halide to provide Pd(II)-aryl intermediates **24,** which then facilitate carbonate cyclization and form vinyl complexes of type **25**. In the reductive elimination step of Pd(II)-intermediate **25,** cyclic carbonate is formed **26,** as shown in Scheme 6.



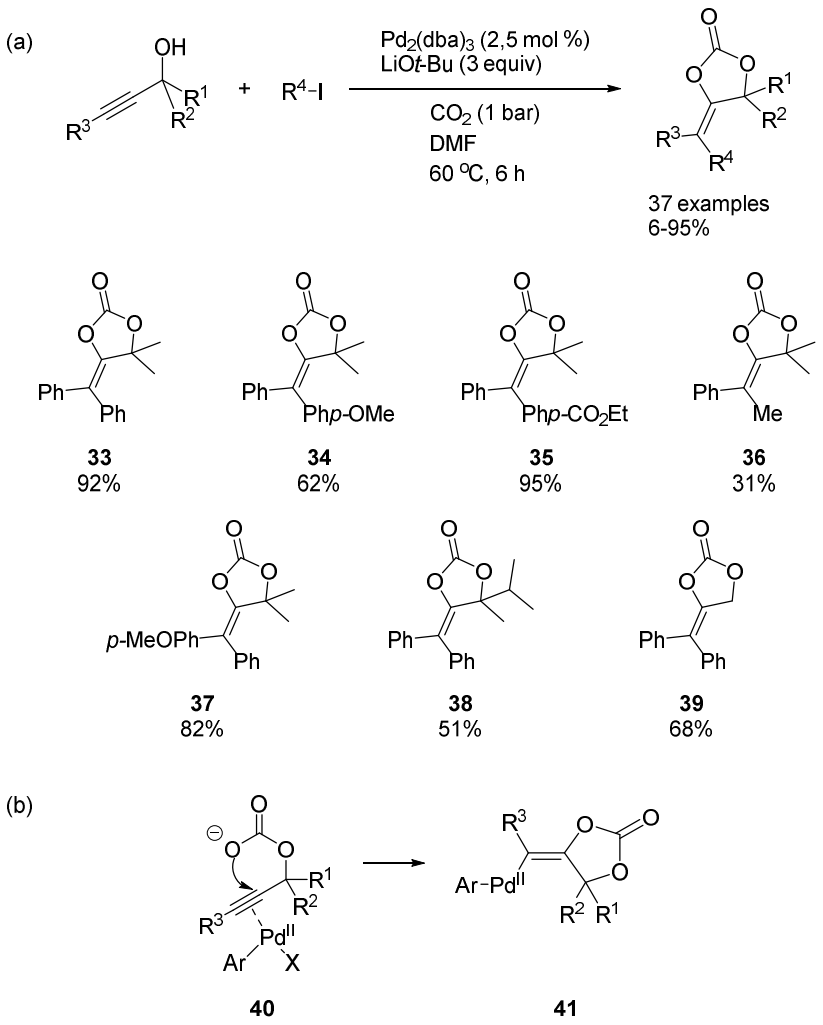

**Scheme 6.** The proposed mechanism of palladium-catalyzed carboxylative cyclisation of propargylic alcohols.

Early examples of this reaction include Iritani's carboxylative cyclization of propargylic alcohols of type **27** or **29**, followed by coupling with an allyl chloride, employing $PdCl_2(MeCN)_2$ as the catalyst (Scheme 7a,b) [26]. In this study, the Li-salts of the $R_3Si$-functionalized propargyl alcohol **29** were used as the starting materials. Another reaction reported by Inoue involves the carboxylation of sodium 1,1-dimethylpropargyl alkoxide **27** under $CO_2$ atmosphere (10 atm) and the subsequent coupling with an aryl halide [27]. When iodobenzene was used as the aryl halide, the yield of the corresponding cyclic carbonate **32** was 68% (Scheme 7c).




**Scheme 7.** (**a**) Iritani's carboxylative allylation of lithium alcoholates [26]; (**b**,**c**) Inoue's carboxylative cyclization and arylation of a terminal propargyl alcohol [27].

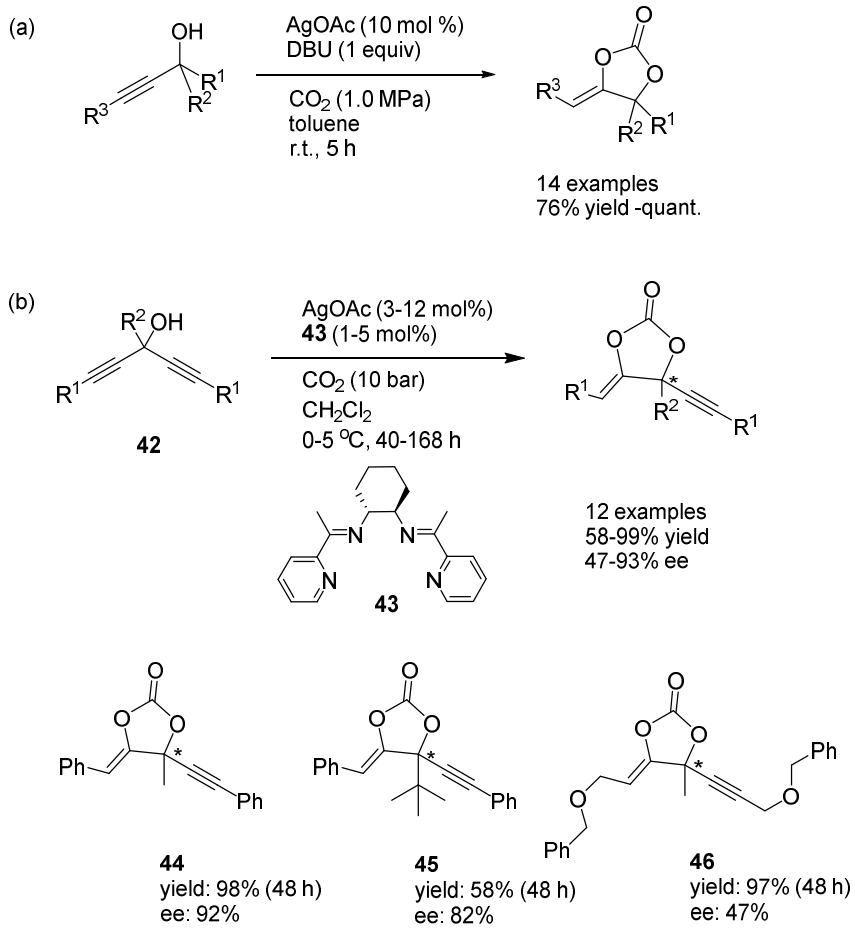
In 2017, Cheng's group advanced this approach by developing a three-component reaction of a propargylic alcohol, an aryl halide, and $CO_2$ at atmospheric pressure in the presence of a $Pd_2(dba)_3$ catalyst [28]. The reaction was successfully conducted with differently substituted propargylic alkoxides, as well as with both electron rich and electron poor aryl halides, giving yields of desired carbonates **33–39** ranging from 31% to 95%. A variety of sterically challenged tetra-substituted alkenes under relatively mild conditions were successfully formed (Scheme 8a). The carboxylation even proceeded with methyl iodide, albeit with a lower yield. The proposed mechanism implied an oxidative addition of aryl halides to the Pd(0)-complex (Scheme 8b). The following coordination of the triple bond of the in situ formed carbonate to the $ArPd^{II}X$ gave the intermediate **40**. An intramolecular *trans*-oxopalladation of **40**, followed by reductive elimination of thus formed **41** affords the products of the reaction **33–39** and regenerates the catalyst. The configuration of the double bond substituted by oxygen derived from $CO_2$ is *trans* to the aryl derived from the halide and is dictated by the last step.




**Scheme 8.** (**a**) The substrate scope of Cheng's three component Pd-catalyzed reaction of propargyl alcohols, aryl-iodides, and $CO_2$; (**b**) *trans*-oxopalladation step in the proposed reaction mechanism [28].

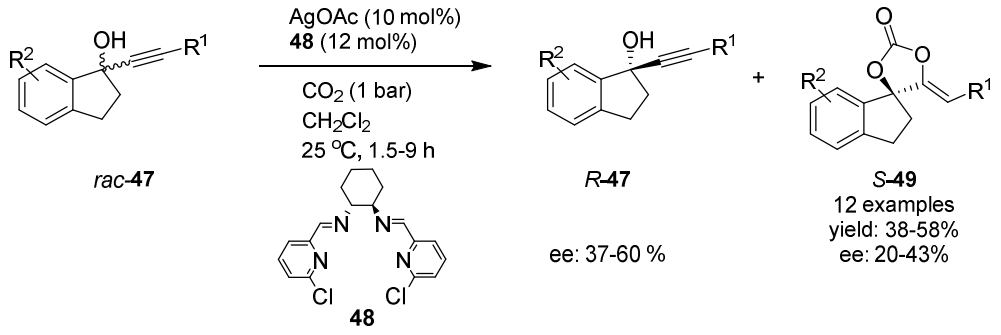
Silver

Silver(I)-salts and their complexes have been among the most effective catalysts for the fixation of $CO_2$ with propargylic alcohols. In 2007, Yamada reported a range of Ag(I)-catalysts for the formation of cyclic carbonates from a variety of terminal and internal propargylic alcohols [29] (Scheme 9a). Some of the desired carbonates were obtained in good yields even under the atmospheric pressure of $CO_2$. Interestingly, only *Z*-alkenes as final products were obtained. In a 2011, the same group reported that symmetric dipropargyl alcohols of type **42** underwent an enantioselective reaction, with up to 93% e.e. by employing an Ag complex containing a chiral salen ligand **43**. As expected, sterically bulky substrates had slow kinetics and needed up to 168 h for the full conversion (Scheme 9b) [30].



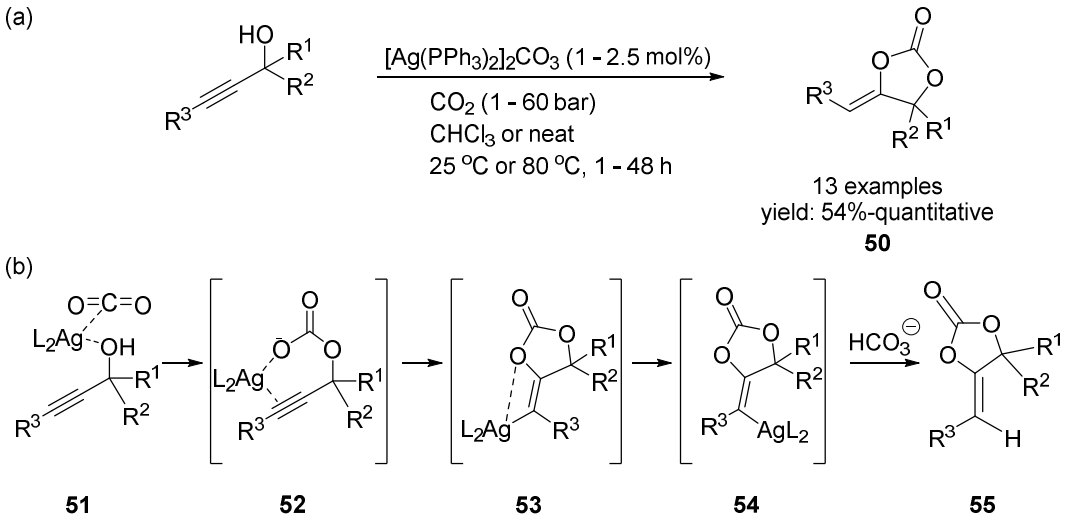

**Scheme 9.** (**a**) Yamada's Ag-catalyzed synthesis of carbonates from propargylic alcohols and $CO_2$ [29]; (**b**) enantioselective synthesis of $\alpha$-alkylidene carbonates from symmetrical bis-propargylic alcohols (* indicates the new chiral center) [30].

Zhou further explored the potential of the Ag-salen complex for the enantioselective conversion of the reaction of the 1-indanone-derived propargylic alcohols **47** (Scheme 10) [31]. Alcohols of type **47** were kinetically resolved into optical enriched isomers *R*-**47** and the corresponding chiral cyclic carbonates *S*-**49** under mild conditions (1 atm $CO_2$, r. t.). The observed racemization of enantiomerically enriched carbonates of type *S*-**49** during the reaction limited the e. e. to the range from 20 to 43% at around 50% conversion of each substrate. The kinetic resolution was also successful with acyclic propargylic alcohol, 1,4-diphenylbut-3-yn-2-ol. The reaction did not proceed with terminal alkynes or with terminal alkyl substituted alkynes.



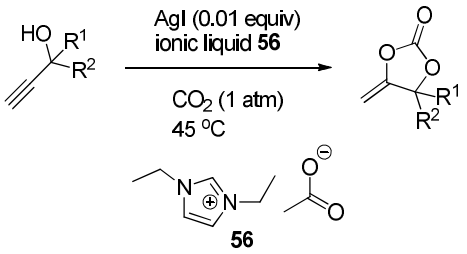

**Scheme 10.** The kinetic resolution of indane propargylic alcohols of type **47** by using AgOAc and salen ligand **48** [31].

In 2014, the same group reported on the carbonate formation of propargyl alcohols with $CO_2$ catalyzed by Ag(I)-complex, $[(PPh_3)_2Ag]_2CO_3$ (1 mol%) under ambient conditions ($CO_2$ 1 atm, 30 °C) (Scheme 11a) [32]. The 1,1-dimethylpropargyl alcohol was converted with 92% yield in 1 h to the corresponding carbonate of type **50**. The same reaction was performed on a 120 mmol scale at ambient conditions and gave a 92% yield of **50** after 15 h, indicating that the scale-up process is relatively simple. For sterically congested alcohol, such as 1-methyl-1-isopropyl propargyl alcohol, a lower yield of 54% was obtained at 80 °C and 60 bar. Based on DFT calculations and NMR studies, the silver complex, which can also be formed in situ from $Ag_2CO_3$ and $PPh_3$, bifunctionally activates both $CO_2$ and the triple bond and forms intermediate **51,** as depicted in Scheme 11b. Further joining of alcohol to $CO_2$ forms intermediate **52** that undergoes ~~oxasilveration~~ carboxylative cyclization and gives intermediate **53**. The hydrolysis affords final product **55** via Ag-complex **54**.



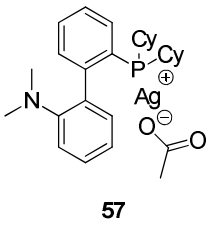

**Scheme 11.** (**a**) He's carboxylative cyclization of propargylic alcohols using a bifunctional silver catalyst; (**b**) the proposed mechanism of propargylic alcohol and $CO_2$ co-activation by this catalyst [32].

The combination of metal ions and ionic liquids can be a powerful catalyst for the cycloaddition of propargylic alcohols and $CO_2$. In 2017, Verpoort used a simple AgI/*N*-ethyl-*N*′-methylimidazolium acetate (**56**) system to achieve a highly efficient catalytic system under mild conditions and with high reusability (Scheme 12) [30]. The advantage of Verpoort's catalytic system is its very low catalyst loading (1 mol%). Several imidazolium ionic liquids were screened, and ionic liquid **56** gave the best results. A range of tertiary terminal propargyl alcohols were easily converted under atmospheric pressure. This included certain sterically congested alcohols, such as 1-phenyl-but-3-yn-2-ol. The mechanism of the reaction was thought to include $CO_2$ activation by the acetate anion.




**Scheme 12.** Verpoort's AgI/ionic liquid system for the incorporation of $CO_2$ into propargylic alcohols [33].

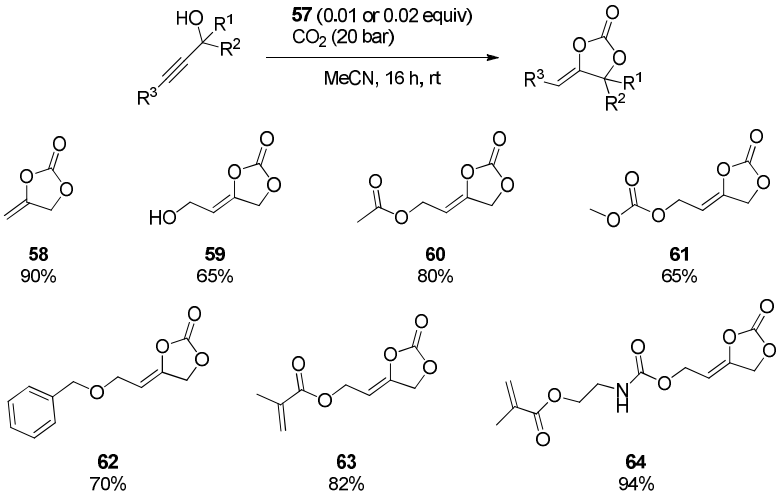
Recently, Schaub reported that a silver complex **57** could successfully catalyze the cycloaddition of propargylic alcohol and $CO_2$ [34], including the unsubstituted propargyl alcohol, which was previously difficult to achieve. This method used a complex of silver acetate and the DavePhos ligand as catalyst under relatively mild conditions ($CO_2$ 20 bar, r. t.) (Scheme 13).




**57**

**Scheme 13.** Schaub's DavePhos-silver acetate complex [34].

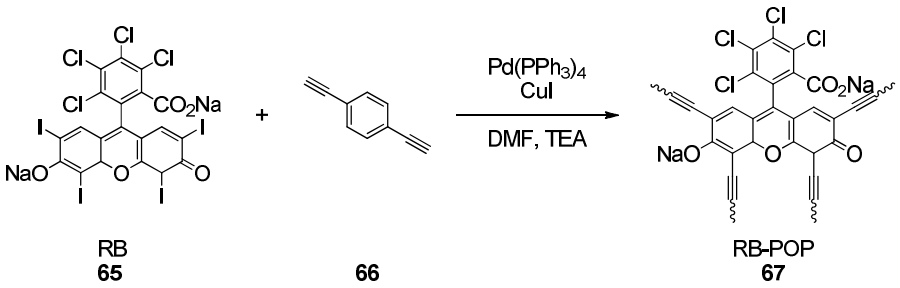
The obvious advantages of the developed method are the low loading of catalyst **57** (1 mol%) and the broader scope of the reaction, as the primary unsubstituted propargyl alcohols could be used as substates, although the $CO_2$ pressure needed for the reaction to ~~proceed~~ proceed is high. Nine primary propargylic alcohols were successfully converted to cyclic carbonates **58**–**64** with good to excellent yields, and the reaction conditions were compatible with different functional groups, including hydroxyl, ester, and amide moieties (Scheme 14). Secondary and tertiary alcohols were also used as substrates and were converted to corresponding carbonates in excellent yields. The catalyst is reusable, and mechanistic studies employing $^{31}$P-NMR and DFT calculations indicated that in situ formed propargyl carbonate replaces the acetate ligand at the silver center, which explains the ineffectiveness of silver(I)-nitrate and silver(I)-carbonate as catalysts.



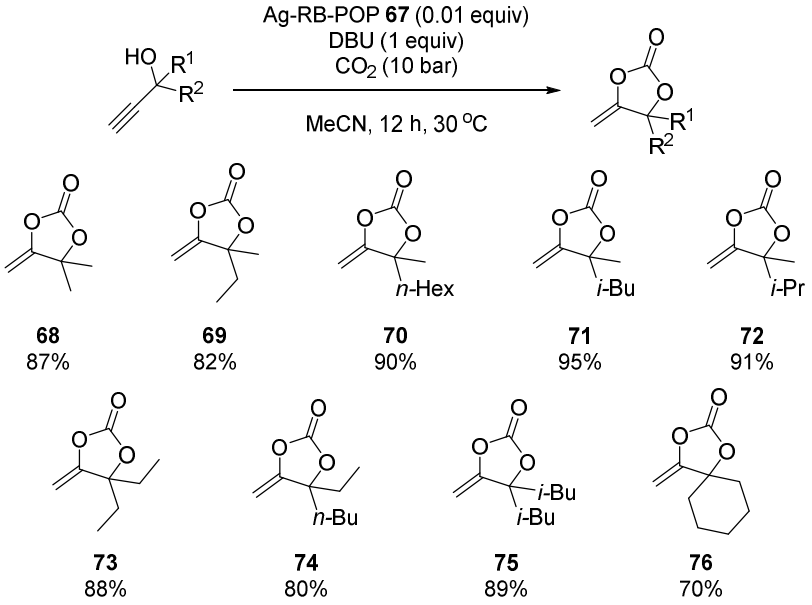

**Scheme 14.** Schaub's method of making cyclic carbonates from primary propargylic alcohols, with seven representative examples [34].

Using silver in a more sustainable way might include embedding silver complexes or nanoparticles into polymer surfaces. A recent development in this field includes a porous organic polymer (POP) functionalized with rose bengal (RB-POP **67**, Scheme 15) [35]. Porous organic polymers are a class of amorphous materials with high surface areas and micropores that can accommodate various catalytic systems [36]. In Zhao's paper, RB-POP had a high capacity to adsorb $CO_2$ (72 mg $g^{-1}$ at 1 bar at 273 K) and was treated with $AgBF_4$ to form the catalytically functional polymer. Under relatively mild reaction conditions (Ag 0.01 mol%, DBU 1 equiv, $CO_2$ 1 MPa, 30 °C), nine tertiary terminal propargylic alcohols were converted after 12 h to corresponding carbonates **68**–**76** in 70% to 95% yields

(Scheme 16). For the conversion of 2-methyl-3-butyn-2-ol to carbonate **68** under these conditions, a very high TOF (turnover frequency) was measured (5000 $h^{-1}$ after 0.5 h). Two internal propargylic alcohols were also converted to desired products, although with lower yields.



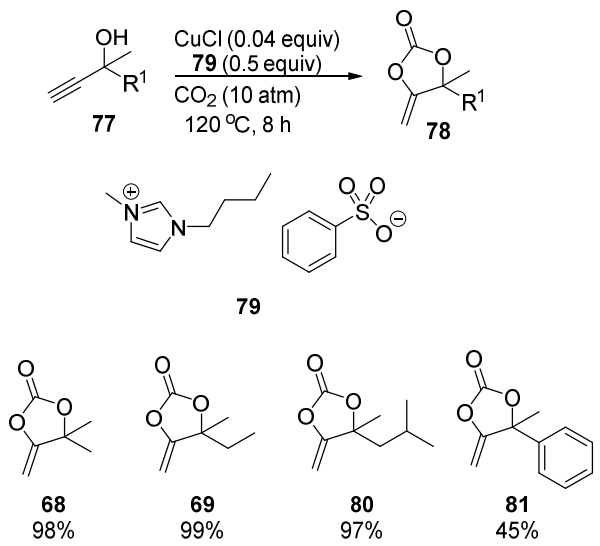

**Scheme 15.** The synthesis of rose bengal-based POP **67** [35].




**Scheme 16.** Zhao's method of carboxylative cyclization of terminal propargylic alcohols by using an Ag-rose bengal-based POP **67** system, with nine representative examples [36].

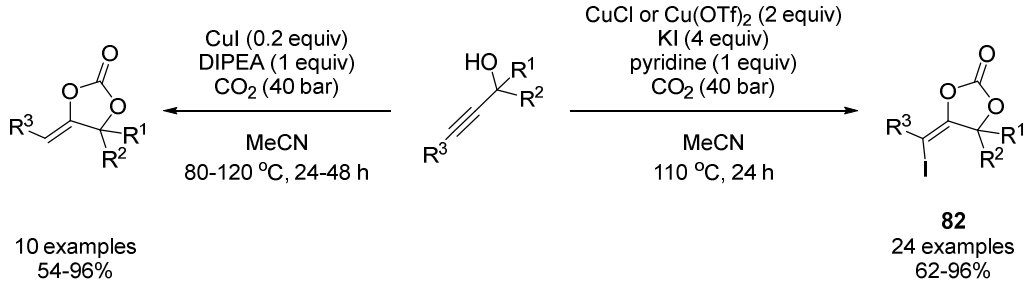
Copper

In 2004, Deng et al. reported the cyclic carbonate forming reaction of a range of $\alpha$-substituted propargylic alcohols using a catalytic system composed of CuCl and an ionic liquid 1-butyl-3-methylimidazolium phenylsulfonate ([BMIm][$PhSO_3$]) (**69**) [37]. Although the conditions were harsh, as $CO_2$ (10 atm) and heating to 120 °C were needed, four different tertiary terminal propargyl alcohols were converted to corresponding carbonates **68**–**81**, with from 45% to 99% yields (Scheme 17). Primary and secondary alcohols did not react.




**Scheme 17.** Deng's carboxylative cyclization of terminal propargylic alcohols, catalyzed by ionic liquid [BMIM][$PhSO_3$] **79** [37].

In 2016, Jiang showed that CuI can catalyze carboxylative cyclization of internal propargylic alcohols (Scheme 18) [38]. Jiang found that, along with $\alpha$-methylene cyclic carbonate, $\alpha$-iodomethylene cyclic carbonates of type **82** can be produced with the addition of an iodinating agent, such as KI, $I_2$ or NIS. Importantly, previously reported Cu-catalysts, such as Jiang's polymer-supported amine catalyst, had only been able to catalyze the reaction with terminal propargyl alcohols [39].

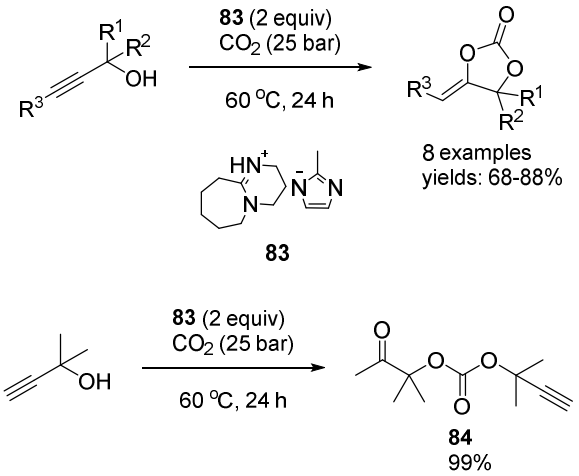



**Scheme 18.** Jiang's synthesis of $\alpha$-alkylene and $\alpha$-iodoalkylene cyclic carbonates **82** [38].

A metal-organic framework (MOF) of Cu(I)-salts based on polyoxovanadate (POV) has recently been shown to catalyze carboxylative cyclizations of propargylic alcohols [40]. POVOFs are very interesting potential class of catalysts as they are more stable than MOFs, which might be crucial for catalyst reusability. Liu's POVOF was synthesized from $Na_3VO_4$, $Cu(NO_3)_2 \times 3H_2O$, 1,4-bis(1*H*-imidazoly-1-yl)benzene) and $N_2H_4 \times H_2O$. The crystal structure shows that the VOF consists of $Cu_4V_4O_{12}$-clusters. The VOF had excellent catalytic activity, even at low catalyst loading (2.5 mol%), and relatively small pressure of $CO_2$ (0.4 MPa). The reactions were conducted in $CH_3CN$ with DBU as the base. Interestingly, when DIPEA or TEA were used instead of DBU, the reactivity was negligible. Six tertiary terminal propargylic alcohols were converted to corresponding carbonates in yields between 88% and 99% at r. t. in 10 h. Mechanistic studies indicated that the Cu(I) ion was the catalytic site, and that DBU activated the hydroxyl group through hydrogen bonding. The catalyst has high structural stability, which makes it greener and more sustainable than most metal-based catalysts reported thus far.

2.2.2. Ionic Liquids

In 2016, Wang et al. reported on an ionic liquid (IL) catalyst for the carboxylative cyclization of propargyl alcohols and $CO_2$ [41]. Different ionic liquids were tested, and the best results were obtained with ionic liquid [DBUH][MIm] **83** (2 equiv). By employing **83** as a catalyst, 1,1-dimethyl-3-phenyl-2-propyn-1-ol was converted to corresponding carbonate in an 89% yield (Scheme 19). Interestingly, while with 3-phenyl propargylic alcohols the latter system provided expected carbonates, the reaction of 1,1-dimethyl-2-propyn-1-ol led to formation of an acyclic carbonate **84** in a 99% yield. Similar products were also formed with phenyl-substituted alcohols at higher temperatures. Mechanistic studies conducted by using $^{1}$H-, $^{13}$C-NMR, and DFT calculations confirmed that both the cation and the anion of the IL are crucial for driving the reaction via cooperative H-donor/acceptor activation.



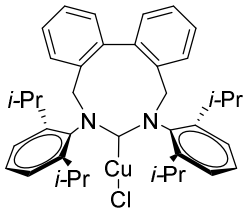

**Scheme 19.** The byproduct formed in Wang's ionic liquid catalyst [41].

2.2.3. Organocatalysts

Organocatalysts can be used as an alternative to toxic transition metal-based catalysts. Major classes of organocatalysts used for $CO_2$ fixation include *N*-heterocyclic carbenes and olefines, as well as guanidines, and will be further discussed.

*N*-Heterocyclic Carbenes

*N*-Heterocyclic carbenes (NHC) are excellent stabilizing ligands for many metal complexes. In 2020, Cervantes Reyes reported on a sterically hindered Cu(I)-NHC complex ($^{BP}$DPrCuCl) **85** that successfully catalyzed the carboxylative cyclization of primary propargylic alcohols (Scheme 20). The carboxylation of the latter substrates was previously obtained only by Schaub's silver-DavePhos catalyst [42]. For the quantitative conversion $^{BP}$DPrCuCl **85** (5 mol%), CsF, and AgOAc had to be added under the $CO_2$ atmosphere (2 MPa, r. t.). The $\alpha$-alkylidene cyclic carbonates were obtained from the unsubstituted propargylic alcohols in a 94% yield. Further, 16 terminally substituted primary propargylic alcohols and 13 secondary and tertiary propargylic alcohols were converted to corresponding carbonates with excellent yields, proving the versatility of this method. The developed procedure was also applied on a preparative scale by using terminally substituted primary propargylic alcohol, with excellent yields. The reusability of the catalyst was difficult to achieve due to its sensitivity to air and moisture. However, the successive substrate addition method gave the desired carbonate with TON of 103 in a 74% yield.

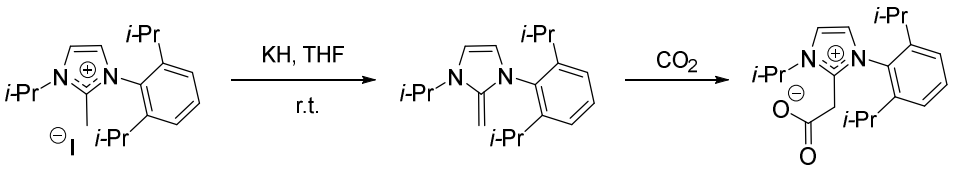



**85**

**Scheme 20.** Cervantes Reyes' Cu(I)-NHC catalyst **85** [42].

*N*-Heterocyclic Olefins

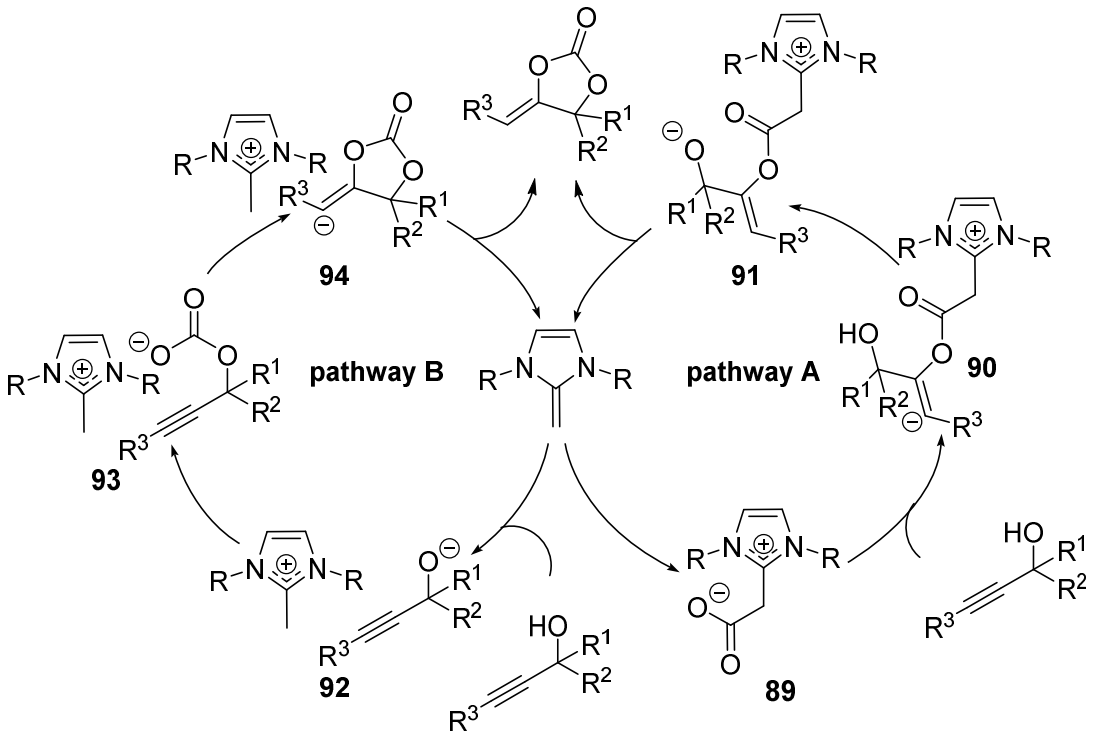
*N*-Heterocyclic olefins (NHO) are a class of nucleophilic molecules increasingly used as catalysts for olefin and heterocycle polymerization, as well as ligands for low-valence main group metals [43]. Lu's group prepared a series of NHO-$CO_2$ adducts by using the procedure depicted in Scheme 21 [44]. The sterically demanding adduct **88** was the most successful in catalyzing the cycloaddition of propargyl alcohol and $CO_2$. With NHO **87** used as a catalyst (5 mol%), a range of terminal and internal tertiary propargylic alcohols were converted into the corresponding cyclic carbonates. For example, at 60 °C and $CO_2$ pressure of 2 MPa, the 1,1-dimethyl propargyl alcohol was transformed into a corresponding carbonate in a >98% yield after 12 h. Twelve further internal tertiary propargylic alcohols gave over 50% yields.




**86** **87** **88**

**Scheme 21.** NHO-$CO_2$ adduct **88** formation, as proposed by Lu [44].

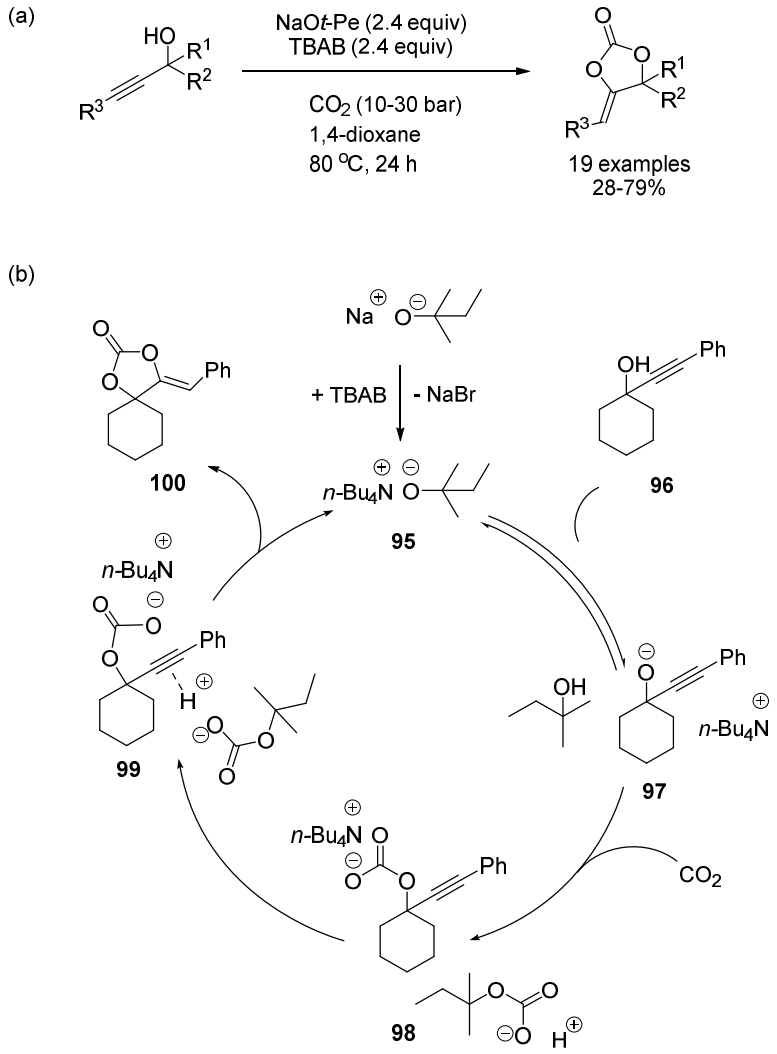
Two possible mechanistic pathways were proposed (Scheme 22). In pathway A, NHO reacts with $CO_2$ and forms intermediate **89**, which subsequently adds to the triple bond of the substate, giving zwitterionic structure **90**. The ring closure and fragmentation of intermediate **91**, obtained from **90** by $H^+$-shift, regenerates the catalyst. In pathway B, the deprotonation of propargyl alcohol by NHO forms the zwitterionic intermediate **92**. The carboxylation of the alkoxide ion of **92** with $CO_2$ produces intermediate **93**, which undergoes carbonate ring closure and gives structure **94**. The protonation of **94** forms the final carbonate molecule and closes the catalytic cycle. A theoretical study conducted in 2016 indicated that pathway A is the preferred mechanism for the *N*-heterocyclic olefin catalysts [45]. This suggests that further optimization should focus on the production of more thermodynamically stable HNO–$CO_2$ adducts.




**Scheme 22.** The two possible pathways for HNO-catalyzed $CO_2$ incorporation into propargylic alcohols, as proposed by Lu [45].

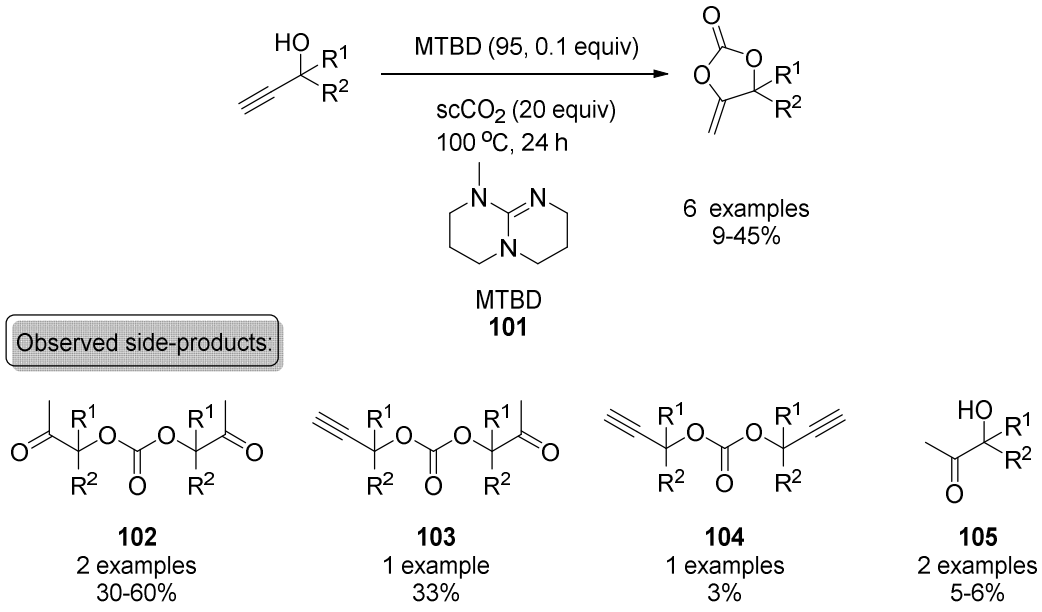
Other Organocatalysts

Many systems designed for the catalysis of the carboxylative cyclization of propargylic alcohol with $CO_2$ contain both Lewis acid and Lewis base species. In most of the reported systems, a transition metal ion plays the role of the Lewis acid. Due to toxicity, and often, the high cost of transition metal, more green catalytic systems should be developed. A recent study conducted by Ai, Zhang et al. demonstrated that a metal-free simple buffer solution could be used as a source of both basic and acidic species able to catalyze carboxylative cyclizations (Scheme 23a) [46]. The optimization studies established the mixture of NaO*t*-Pe/tetrabutylammonium bromide (TBAB) (2.4 equiv) as the most efficient catalytic system. In $CO_2$ atmosphere (2.0 MPa) and at 80 °C, twenty tertiary internal propargylic alcohols provided the desired carbonates in good yields (33% to 79%). Interestingly, terminal propargyl alcohols were not reactive. The conducted mechanistic studies suggested that the TBAO*t*-Pe **95** plays a crucial role in the activation of the triple bond (Scheme 23b). As proposed, the deprotonation of substrate **96** is achieved by employing TBAO*t*-Pe salt **95** that subsequently reacts with $CO_2$, giving carboxylated intermediate **98**. The activation of the triple bond of **99** by protonation facilitates its cyclization to provide the final product, carbonate **100**.



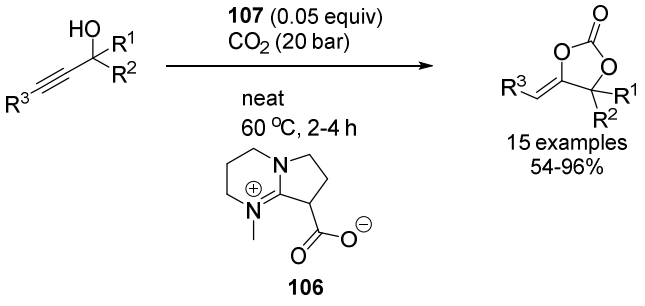

**Scheme 23.** (**a**) Ai's carboxylative cyclization of tertiary propargylic alcohols; (**b**) the catalytic mechanism proposed by Ai et al. [46].

Other metal-free systems for the carboxylative cyclizations of propargyl alcohols and $CO_2$ include organic bases. For example, Costa et al reported the reaction of propargylic alcohols with supercritical $CO_2$ catalyzed by organic guanidine 1,3,4,6,7,8-hexaydro-1-methyl-2*H*-pyrimido[1,2-*a*]pyrimidine (MTBD) (**101**) (Scheme 24) [47]. Although these reactions often gave very high conversion rates, $\alpha$-hydroxyl esters of type **102** to **104** and ketone **105** were identified as side-products and decreased the yields of the desired carbonates. The guanidines were also useful as catalysts for the conversion of the epoxides to cyclic carbonates. MTBD **101** was again established as the most efficient. Six tertiary terminal propargyl alcohols were transformed to corresponding carbonates in poor to good yields (9–45%), whereas the primary propargyl alcohols gave no desired products.




**Scheme 24.** Costa's carboxylative cyclization of terminal propargylic alcohols. The yields of cyclic carbonates were low to moderate, owing to the number of side-products (**102**–**105**) being formed [47].

In 2019, Zhou and Lu reported an organocatalyst based on a thermally stable *tetra*-hydropyrimidin-2-ylidene THPE-$CO_2$ adduct **106**, shown in Scheme 25 [48]. Fifteen terminal and internal tertiary propargylic alcohols were converted to the desired carbonates in good to excellent yields (54–96%). Compared to the previously reported NHC [42] and NHO [44] catalytic systems, the newly developed THPE catalyst showed increased reactivity. Mechanistic studies and in situ FTIR measurements with isotopically labeled $^{13}CO_2$ confirmed that the $CO_2$ in the final product does not originate from the the carboxylate in the catalyst. Accordingly, it was proposed that the catalyst acts as a Lewis base, initiating the $CO_2$ incorporation and cyclization process. The catalyst was also useful in the conversion of epoxides to cyclic carbonates.



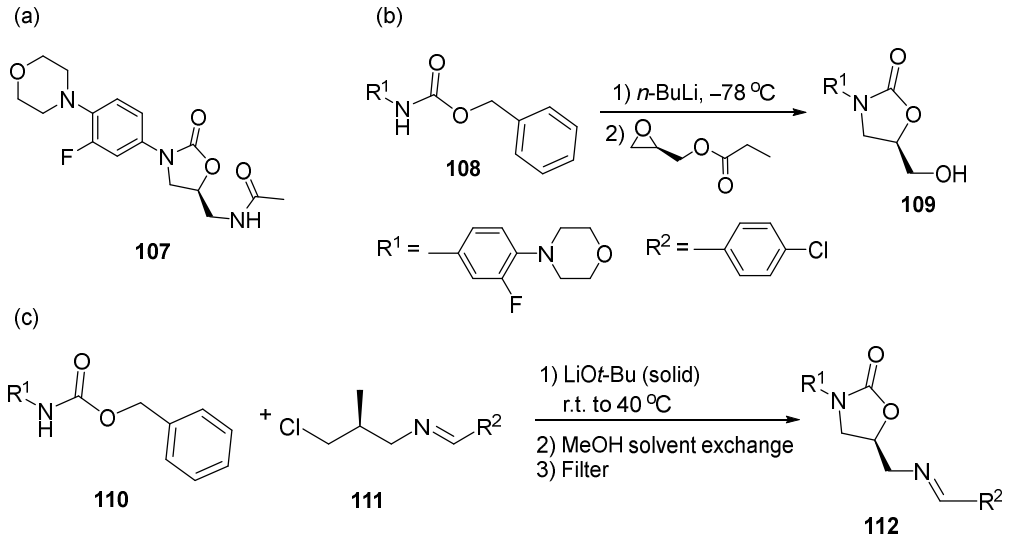

**Scheme 25.** Zhou's and Lu's THPE-$CO_2$ adduct **106** as a catalyst for $CO_2$ incorporation into propargylic alcohols [48].

## 3. Cyclic Carbamates

Because of its great chemical and proteolytic stability, as well as the ability to easily penetrate into cells, the carbamate motif is a very important peptide bond surrogate in the drug development process [49]. Vacondio et al. reviewed and examined medicinal applications of carbamates, concluding that cyclic carbamates are stable and prone to metabolic hydrolysis [50]. Thus, cyclic carbamates have become a subject of increased research for pharmaceuticals.

For example, a very important antibiotic used to treat infections by various Gram-positive bacteria is Linezolid **107**, a drug which contains the 5-membered cyclic carbamate

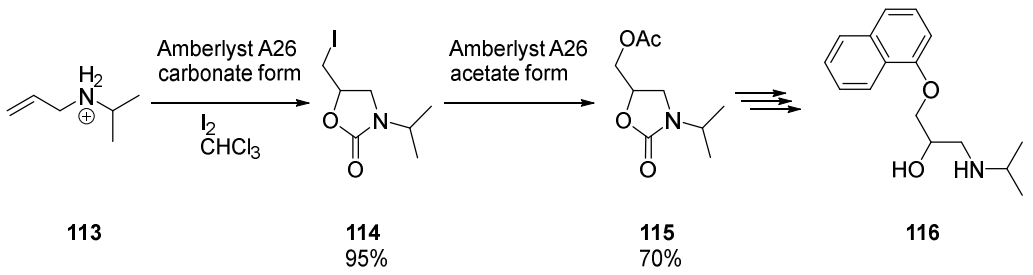
(2-oxazolidinone) motif (Scheme 26a). The first-generation synthesis of linezolid reported by Pfizer employed a glycidyl ester and a strong base (*n*-BuLi) at a low temperature to obtain the cyclic carbamate moiety (Scheme 26b) [51]. The "greener" second generation synthesis used imine derivative **111** under milder conditions (Scheme 26c). However, the latter method still employs a strong base and generates a lot of waste. Thus, the development of new reactions and reaction conditions with high atom economy, such as the carboxylative cyclizations of unsaturated amines and $CO_2$, is very desirable and could be directly applied in the green and highly valuable industrial synthesis of linezolid and its derivatives.




**Scheme 26.** (**a**) Linezolid **107**; (**b**) formation of the carbamate moiety in the first synthesis of linezolid [51] and (**c**) in the second-generation synthesis [52].

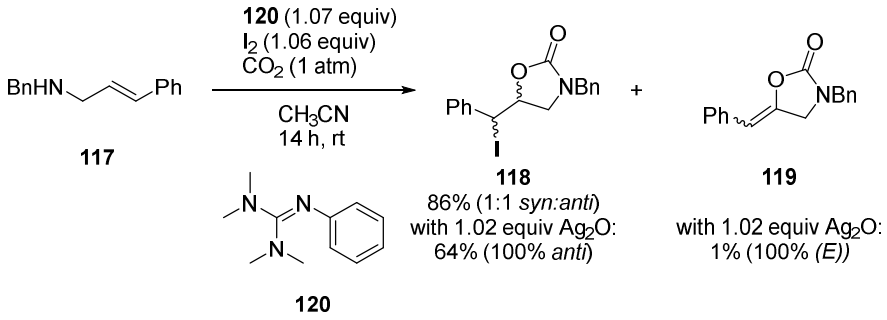
### *3.1. Five-Membered Cyclic Carbamates from $CO_2$ and Allylic or Homoallylic Amines*

In 1986, Cardillo et al. reported the first conversion of allyl amines into cyclic carbamates by using the Amberlyst® A 26 ion-exchange resin in its carbonate form [53]. The activated amberlyst (2 equiv) in $CHCl_3$ served to convert a series of $\alpha$-substituted allyl amines in the reaction with iodine to 5-(iodomethyl)oxazolidin-2-ones in very good yields. Although the trans product was more favored when the amine group was protected with the benzyl group, the reaction was not highly *Z*/*E* stereoselective. Using $LiAlH_4$ or *n*-$Bu_3SnH$ in boiling EtOH with AIBN successfully reduced the C–I bond, with slightly better yields for the second approach. The latter method was also successfully used for the synthesis of propranolol, a medicine for the treatment of various cardiovascular conditions (Scheme 27). In the Amberlyst® A 26 catalyzed formation of cyclic iodocarbamates, the allyl ammonium cation **113** was transformed to **114** with a 95% yield, which was further converted to a precursor of propranolol **116**, acetylcarbamate **115**, with a 70% yield.



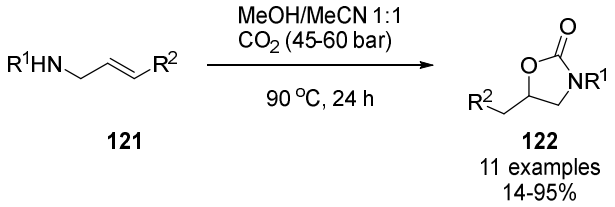

**Scheme 27.** Synthesis of (±)-propranolol **116** by Cardillo et al. [53].

Soon after, Toda and Kitagawa reported the first conversion of allyl amines into 5-(iodomethyl)oxazolidin-2-ones with iodine in a $CO_2$-saturated methanol solution [54]. The moderate yields were improved when the duration of the reaction was prolonged over a week by using $Cs_2CO_3$ as base. Further advancement was achieved by Muñoz et al. in 2006, who obtained desired carbamates in 51–97% yields [55]. The optimized conditions were based on the use of a hindered guanidine PhTMG as the base in a $CO_2$ saturated acetonitrile, with the subsequent addition of an iodine solution. Because of their lower nucleophilicity compared to aliphatic amines, anilines were not reactivated, even after a week [56]. Under the standard reaction conditions, the reaction of *N*-benzyl-*N*-*trans*-cinnamylamine **117** with iodine and $CO_2$ gave an equal mixture of *syn*- and *anti*-diastereomers of **118**, together with a small amount of elimination product **119** (Scheme 28). Based on this stereochemical observation, the mechanism via the iodonium ion was proposed. However, when $Ag_2O$ was added to the solution in order to remove iodide ions, only the formation of the more stable *anti*-diastereomer was observed.



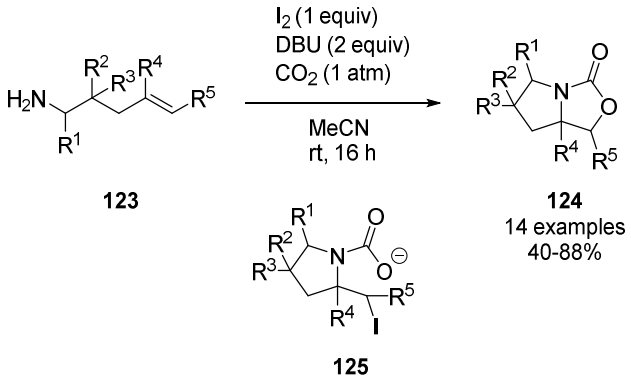

**Scheme 28.** Muñoz's synthesis of *N*-benzyl cyclic carbamates. The addition of $Ag_2O$ induced the formation of *anti*-diastereomer *anti*-**118** [56].

In 2014, Della Ca' et al. reported the first metal- and base-free carboxylative cyclization of allylic amines of type **121** (Scheme 29) [57]. The reaction required an electron-withdrawing substituent $R^2$ of substrate **121** and a high pressure, or the use of supercritical $CO_2$ in the absence of organic solvents, whereas reaction times were prolonged to 24 h.



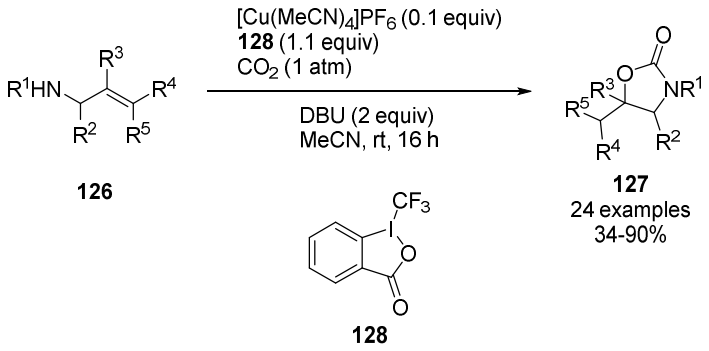

**Scheme 29.** Della Ca's synthesis of cyclic carbamates of type **122** [57].

Xi et al. managed to expand the carboxylative iodocyclization to produce bicyclic carbonates from 4-pentenamines **123** (Scheme 30) [58]. Fourteen bicyclic carbamates of type **124** were produced, with excellent regioselectivity. According to the proposed mechanism, the first ring was formed through an imide intermediate attack on the iodonium moiety, and the second, through a $S_N2$ carboxylate attack to iodonium intermediate **125**. Further carbamate cleavage provided a direct access to prolinol derivatives.




**Scheme 30.** Xi's synthesis of bicyclic carbamates **124** and the proposed tandem cyclization mechanism via intermediate **125** [58].

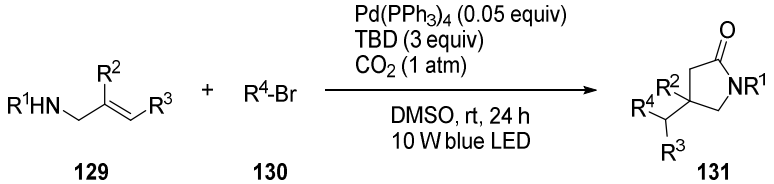
Metal-based catalysts for the conversion of allylic amines **126** into cyclic carbamates **127** have also been reported. In 2016, Yu reported a copper(I)/Togni's reagent **128** system that could produce $CF_3$-functionalized cyclic carbamates **127** (Scheme 31) [59]. Twenty-four secondary amines of type **126** were converted into corresponding 5-membered cyclic carbamates **127**, with good to excellent yields (34–90%). Furthermore, the method showed great functional group tolerance. The mechanistic studies suggested that the reaction proceeded via a radical $CF_3$ binding to the Cu-amine complex and the subsequent reductive elimination of Cu(I).




**Scheme 31.** Yu's carboxylation-cyclization/trifluoromethylation process [59].

The radical carboxylation-cyclization, followed by alkylation, can also be metal photocatalyzed. For example, Yu reported a Pd-catalyzed process (Table 1). As presented, an alkyl radical adds to the double bond and triggers the cyclization of the in situ formed carbamate anion [60]. The reaction can be conducted under ambient conditions and tolerates various aromatic substituents $R^1$ at substate **129**, as well as a range of aliphatic bromides **131**.

**Table 1.** Yu's carboxylative cyclization/alkylation process [60]. The yields of some representative examples are given in the table.



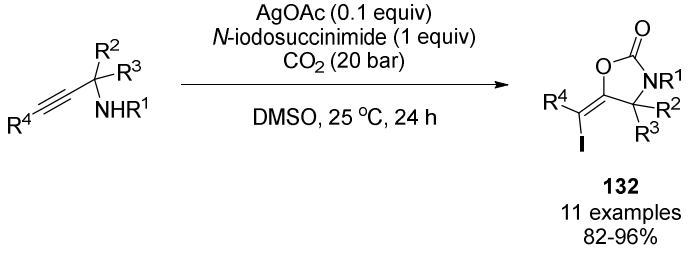

| $R^1$, $R^2$, $R^3$ | $R^4$ | Yield | Product |
|---|---|---|---|
| $R^1$ = Bn, $R^2$ = Ph, $R^3$ = H | 1-Adamantyl (1-Ad) | 86% | **131a** |
| $R^1$ = H, $R^2$ = Ph, $R^3$ = H | 1-Ad | 46% (48 h) | **131b** |

| | | | |
|---|---|---|---|
| $R^1$ = Bn, $R^2$ = *o*-Tol, $R^3$ = H | 1-Ad | 56% (48 h) | **131c** |
| $R^1$ = Bn, $R^2$ = *p*-$FC_6H_4$, $R^3$ = H | 1-Ad | 44% (48 h) | **131d** |
| $R^1$ = Bn, $R^2$ = Ph, $R^3$ = H | Cyclopropyl | 55% (48 h) | **131e** |
| $R^1$ = Bn, $R^2$ = Ph, $R^3$ = H | Isopropyl | 75% (48 h) | **131f** |
| $R^1$ = Bn, $R^2$ = Ph, $R^3$ = H | 4-Tetrahydropyranyl (4-THP) | 78% (60 h) | **131g** |
| $R^1$ = Bn, $R^2$ = Ph, $R^3$ = H | 3-Oxetanyl | 64% | **131h** |

### *3.2. Five-Membered Cyclic Carbamates from Propargyl Amines*

#### 3.2.1. Homogeneous Catalysts

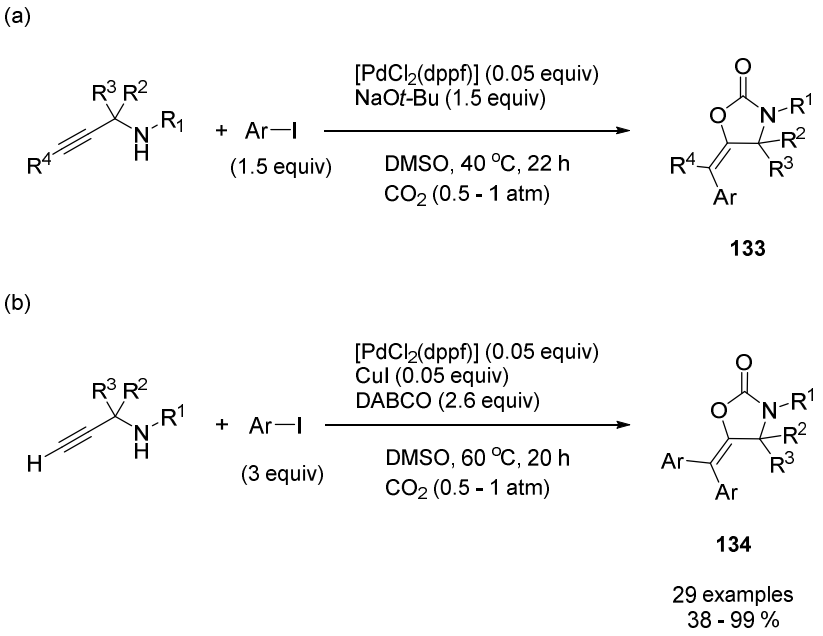
Similarly to propargyl alcohols, Ag-salts and complexes have been successfully used as catalysts for the cycloaddition of propargyl amines and $CO_2$. Yamada's early work on this topic showed that various internal and terminal, primary, and secondary propargyl amines can be converted under very mild conditions ($CO_2$ 1 atm, r. t.), even without the presence of a base, by using AgOAc as a catalyst [61]. Yamada's work was then extended to 5-(iodomethyl)oxazolidin-2-ones (**132**) (Scheme 32) [62]. The utilized conditions were mild, while the yields were excellent, and the reaction gave only *E*-stereoisomer.




**Scheme 32.** Yamada's AgOAc-catalyzed $CO_2$ incorporation/iodination procedure [62].

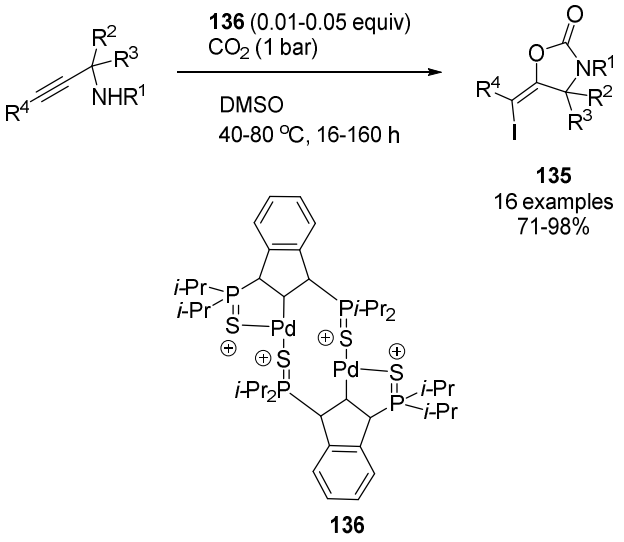
Another synthesis of 5-(iodomethyl)oxazolidin-2-ones was reported by Minakata et al. in 2012 by using *t*-BuOI, a powerful iodinating agent, as a substitute for $I_2$ [63]. The advantage of this reagent is its non-toxic character and no interference of the by-product *t*-BuOH in the reaction mechanism. The propargyl amines gave good yields (38–99%) under reaction conditions similar to Yamada's (Scheme 32), with the exception of the unreactive unsubstituted propargyl amine. The *E*/*Z*-ratios of the formed 5-(iodovinyl)oxazolidin-2-ones were not reported. Given that propargyl amines are much more nucleophilic towards $CO_2$, Yoshida developed a catalytic system able to produce cyclic carbamates from $CO_2$ contained in air (0.04% by volume) [64]. $AgNO_3$ (0.5 mol%) was employed as a catalyst, and the conditions were relatively mild (60 °C), whereas the utilization of DBU as a base was required. The mechanistic studies suggested that the DBU-$CO_2$ adduct was likely an intermediate in the reaction.

In 2016, Nevado et al. developed a Pd-catalyzed, one-pot, 3-component reaction which produced functionalized oxazolidinones **133** and **134** from propargyl amines, $CO_2$, and aryl iodides (Scheme 33) [65]. They reported that the reactions of the unsubstituted or $R^4$-substituted terminal propargyl amines and aryl iodides gave tetrasubstituted alkenes **133** and **134** in good to excellent yields.




**Scheme 33.** Nevado's one-pot Pd-catalyzed reactions for the synthesis of carbamates: (**a**) carboxylative cyclization/cross-coupling reactions; (**b**) Sonogashira-carboxylative cyclization/cross-coupling reactions [65].

Pd-indenediide catalyzed carboxylative cyclization of propargyl amides was reported by Bourissou [66]. As shown in Scheme 34, the unsaturated amines were converted into carbamates of type **135** in excellent yields under ambient $CO_2$ pressure by using the Pd-dimeric complex **136** as a catalyst. The less nucleophilic, more sterically hindered propargylic amines, such as anilines and secondary amines with tertiary alkyl groups, were converted under mild conditions to the desired products of type **135**. The DFT and NMR mechanistic studies suggested that the indenediide catalyst dimer **136** splits in the solution, giving a stabilized DMSO complex, which is also the resting state of the catalyst. The DMSO molecule easily dissociates and is replaced by the substrate. The authors also emphasized the importance of the $H^+$-transfer in the initial step of amine carboxylation.

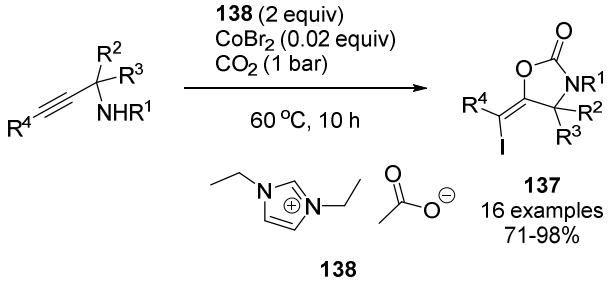



**Scheme 34.** Pd-Indenediide catalyzed carboxylative cyclization of propargyl amines [66].

Complexes based on zinc have also been proven useful as catalysts for the carboxylative cyclization of propargyl amines. He et al. reported that a simple in situ generated

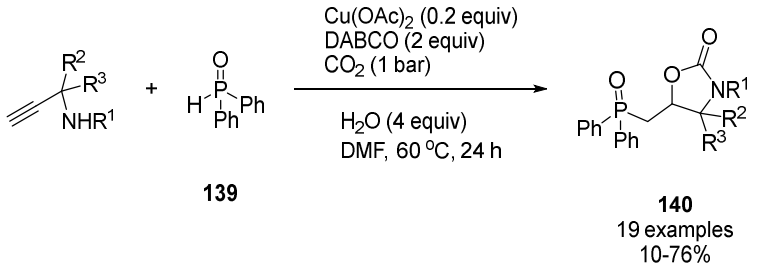
$ZnCl_2(TBD)_2$ complex is able to catalyze the incorporation of $CO_2$ into propargyl amines [67]. Nine different secondary propargyl amines were converted in the desired products in variable yields (8–96%) after 12 h. Notably, an $\alpha$-substituted propargyl amine gave a very low yield (8%), whereas the conversion of *N*-propargylaniline yielded 52% of the desired carbamate product. The mild reaction conditions, low loading of the catalyst (5 mol%) and pressure of $CO_2$ (1 atm) at 60 °C, and the lack of noble metals, as well as the easily available and inexpensive ligand, make this method attractive.

A recent work of He et al. demonstrates the conversion of various propargylic amines into 2-oxazolidin-2-ones **137** by using a $CoBr_2$/ionic liquid **138** as the catalytic system (Scheme 35) [68]. As shown, *N*-benzyl terminal propargyl amines were reacted with $CO_2$ and gave desired *Z*-products in good to excellent yields (51–99%) under mild conditions. While the internal propargyl amines gave a good yield, the *N*-propargylanilines and *N*-propargylamides did not react. The catalyst, $CoBr_2$ in only 2 mol% loading, could be re-used.




**Scheme 35.** He's Co/IL-catalyzed carboxylation/cyclization process [68].

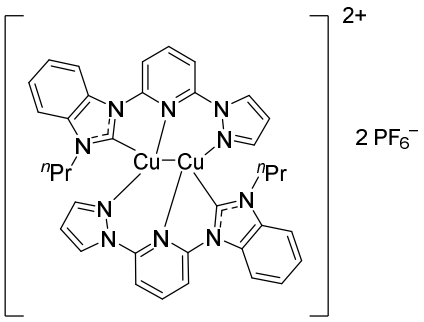
The same group recently published another useful multi-component reaction that produces cyclic carbamates with phosphonate groups of type **140** (Scheme 36) [69]. These useful compounds can be derivatized into a range of organic molecules, such as phosphines or unsaturated phosphonates. The reaction scope was examined, and a range of different terminal propargylic amines and phosphonates were tested. The reaction yields were low to moderate (10–76%). The reaction also proceeded easily on a preparative scale. Mechanistically, the reaction was thought to proceed through a copper-vinyl intermediate, which is attacked by a nucleophilic $POPh_2$ radical.




**Scheme 36.** He's Cu-catalyzed carbamation of various phosphonate-functionalized propargylic amines [69].

More recently, Dai reported on a hemilabile binuclear Cu(I)-catalyst for $CO_2$-incorporation into internal and terminal propargyl amines [70]. The success of this method is based on the trans effect of the NHC ligand in the catalyst **141** (Scheme 37), which causes easy dissociation of the nitrogen donor part of the ligand and enables efficient catalyst-amine bonding. Catalytic amounts of triazabicyclodecene (TBD) are also required for the reaction to proceed. With the developed catalytic system, internal and terminal propargylic amines, and even very challenging propargyl anilines, were easily converted to cor-

responding carbamates under very mild conditions (40 °C and 1 atm $CO_2$). The carbamation of unsubstituted *N*-propargyl aniline and the *p*-OMe substituted *N*-propargyl aniline proceeded in 93% and 87% yields, respectively.



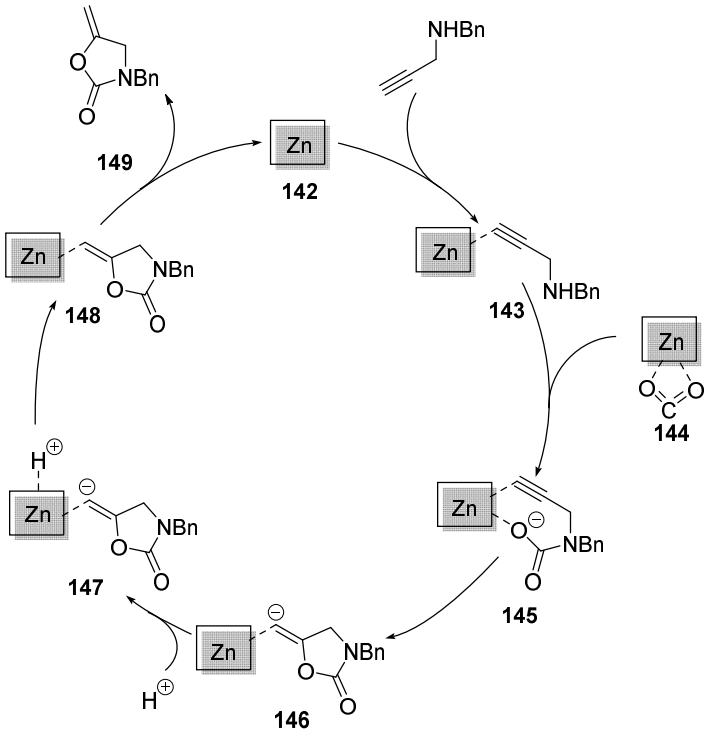

**141**

**Scheme 37.** Dai's binuclear copper catalyst [70].

Organic, metal-free catalysts have also been reported to catalyze the carbamation of propargyl amine derivatives. A particularly unexpected catalyst was discovered by Wang in 2017, who realized that triethanolamine (TEOA) can catalyze the conversion of seven different $\alpha$-mono- and disubstituted propargylic amines in good to excellent yields under 1 bar $CO_2$ and 90 °C [71]. *N*-Propargyl aniline was also converted, albeit under 1 MPa $CO_2$, giving the desired carbamate in a 71% yield after 10 h. DFT Calculations suggested that TEOA reacts with $CO_2$ and forms a zwitterionic structure that transfers $CO_2$ to the propargyl amine, followed by the protonation of the triple bond. Another recent catalyst for the carbamation of propargyl amines is the quaternary amine salt $Bu_4NF$ [72]. The simplicity and low loading of the catalyst (1 mol%) were promising; however, the reaction conditions were relatively harsh.

### 3.2.2. Heterogeneous Catalysts

Noble-metal-free nanocages [Zn116] have recently been synthesized by Zhao et al. [73]. The clusters were able to catalyze the incorporation of $CO_2$ into propargyl amines under relatively mild conditions (70 °C, 1 atm $CO_2$). Seven secondary amines were converted to corresponding carbamates in very good to excellent yields (80–99%). Only *N*-propargyl aniline gave a substantially lower yield (30%). The suggested mechanism implied the binding of the propargyl amine to Zn-nanocages to form an intermediate of type **143**, which subsequently reacts with activated $CO_2$, giving structure **145**. The cyclization of **145** and the protonation thus formed **148** affords the final carbamate **149** after the decomplexation (Scheme 38).




**Scheme 38.** The proposed mechanism for Zn166-catalyzed $CO_2$ incorporation into propargylic amines [73].

Recently, commercial mesoporous silica MCM-41 was found to be an effective catalyst for the propargyl amine-$CO_2$ cycloaddition [74]. Mechanistically, it is proposed that the silica hydroxyl group activates the triple bond through OH-π* interactions. Under quite harsh (3.0–5.0 MPa $CO_2$ and heating at 100–140 °C in toluene) reaction conditions, six secondary propargyl amines were converted to the desired carbamates in variable yields (10–93%). Unsubstituted propargyl amines were not reactive. However, a major advantage of mesoporous silica MCM-4 is its low-cost, easy recovery by filtration, and high reusability (over ten times without losing the reactivity).

## 4. Conclusions

The utilization of $CO_2$ to produce value-added compounds is currently one of the most researched topics in green chemistry. This paper summarized the progress in the synthesis of 5-membered cyclic carbonates and carbamates from the corresponding unsaturated alcohols and amines. These are valuable compounds in the chemical and pharmaceutical industry. Despite significant advancement in the methodologies of their production, there are still significant challenges associated with the $CO_2$ fixation process, such as the lack of environmentally friendly or metal-free catalysts, as well as catalyst reusability. Ongoing research in multiple directions aims to address these issues.

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