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Zinc(II) Catalyst In Situ Formed for Incorporation of CO_2 into 2-Oxazolidinones with Propargylic Amines at Atmospheric Pressure

Xi Liu,[a] Mei-Yan Wang,[a] Si-Yuan Wang,[a] Qi Wang,[a] Liang-Nian He*[a,b]

Abstract: Incorporation of CO_2 into heterocycle compounds *i.e.* 2-oxazolidinones under mild conditions, especially at atmospheric pressure still remains challenging. The mononuclear zinc(II) complex *viz.* $ZnCl_2(TBD)_2$ in this study was for the first time demonstrated as a robust catalyst for the carboxylative cyclization of propargylic amines with CO_2 to exclusively afford various 2-oxazolidinones in excellent yields. Notably, the zinc(II) catalytic species is readily generated in situ from zinc dichloride and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) without pre-preparation and further isolation. Such a CO_2 fixation protocol could proceed smoothly under atmospheric pressure at mild temperature in an atom economy and environmentally benign manner. ^{13}C NMR and control experiments were performed to explore possible interaction between zinc(II) and carbon-carbon triple bond of propargylic amine. The dual catalytic role of zinc catalyst on enhancing O-nucleophilicity of the carbamate anion intermediate and activating carbon-carbon triple bond is proposed based on mechanistic investigations.

Introduction

With the continuous growth of CO_2 concentration in the atmosphere, great efforts have been made to establish efficient strategies for the consumption and utilization of CO_2. In this context, chemical fixation of CO_2 into value-added chemicals represents a promising field in view of sustainable development and green synthesis. Though CO_2 as a highly attractive C_1 resource has been successfully incorporated into various organic compounds, efficient CO_2 transformation still remains great challenging especially at atmospheric pressure originating from the thermodynamic stability and kinetic inertness of CO_2.[1]

2-Oxazolidinones are a class of heterocyclic compounds which have broad applications as chemical intermediates, chiral auxiliaries as well as antibacterial pharmaceuticals in synthetic and medicinal chemistry.[2] Recently, upgrading CO_2 as a sustainable feedstock by constructing 2-oxazolidinone motif has received considerable interest,[3] among which the atom economy reaction through coupling easily accessible starting materials e.g. propargylic amines with renewable C_1 synthon CO_2 is particularly appealing. Besides, the 2-oxazolidinone framework bearing an exocyclic double bond can be further functionalized, for instance, through Sonogashira cross-coupling reaction with aryl halides, as demonstrated by Nevado *et al.* recently.[4] To date, several catalytic systems for the carboxylative cyclization of propargylic amines with CO_2 have been developed, including transition metal catalysts based on Ru,[5] Pd,[4,6] Ag,[7] Au,[8] Cu,[9] and organocatalysts such as superbases,[10] protic ionic liquids,[11] and N-heterocyclic carbene.[12] In addition, with stoichiometric amounts of *t*BuIO, 2-oxazolidinone bearing iodomethyl group can be obtained from allyl or propargyl amine and CO_2 under mild conditions.[13] Particularly, such carboxylative cyclization could also proceed under supercritical CO_2 conditions in the absence of any catalyst.[14] Despite of great achievements, examples of efficient processes based on readily available metal catalysts with utilization of CO_2 under atmospheric pressure are limited. Therefore, development of alternative methodologies with cheap low-toxic metal catalysts for the synthesis of 2-oxazolidinones using CO_2 under mild conditions is still highly desirable.

From the mechanistic perspective, the carboxylative cyclization is supposed to proceed through a carbamate intermediate and subsequent intramolecular nucleophilic addition of carbamate anion on carbon-carbon triple bond is considered to be the rate-determining step.[11] Thus, activation of carbon-carbon triple bond is the key to render the carboxylative cyclization to proceed smoothly under mild conditions. In this aspect, coinage metals *i.e.* Ag, Au, Cu have been employed originating from efficient activation of carbon-carbon triple bond due to the π-coordination with the alkyne, thus exhibiting superior properties. In particular, Yamada *et al.* have demonstrated that silver acetate is an efficient catalyst for incorporating CO_2 into 2-oxazolidinones by adopting various propargylic amines as substrates under ambient conditions.[7a] Interestingly, this dual-component catalytic system being composed of $AgNO_3$ and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) can fix CO_2 directly from air by propargylic amines to deliver corresponding 2-oxazolidinones.[7c] On the other hand, zinc appears to be ponderable since it has been well demonstrated to possess the capacity of activating carbon-carbon triple bond.[15] The coordinative flexibility combined with soft Lewis acidity makes zinc(II) significant in alkynes transformation. Carreira *et al.* have documented that zinc salts, typically $Zn(OTf)_2$ in conjunction with tertiary amine lead to the generation of the zinc acetylide species,[15a,d,e] being also

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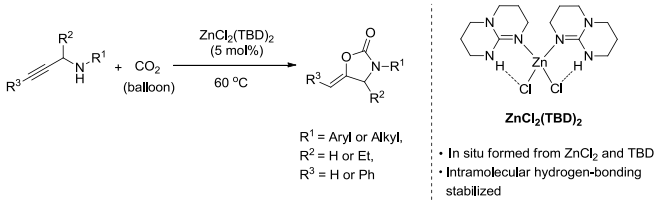
confirmed by in situ IR spectroscopy study.[16] Remarkably, the zinc-based catalysts are also receiving continuous attention in CO_2 transformations given its superiority of tunable Lewis acidity, high natural abundance and low environmental impact.[17] In this context, we envisioned that elaborately-designed zinc catalyst with potential activation of carbon-carbon triple bond could be an alternative to noble metal catalysts in promoting the coupling reaction of propargylic amines with CO_2.

As expected, the well-defined monodentate zinc(II) complex $ZnCl_2(TBD)_2$, being in situ generated from $ZnCl_2$ and TBD, was proven to be a robust catalyst for the carboxylative cyclization of propargylic amines with CO_2 to perform under mild conditions especially at atmospheric pressure, as shown in Scheme 1.

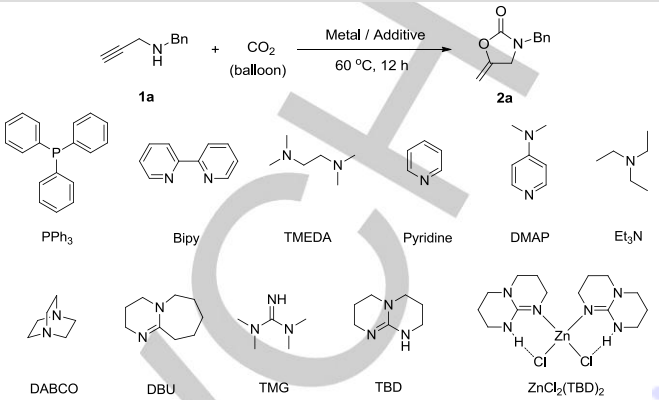


Scheme 1. In situ formed $ZnCl_2(TBD)_2$ as a robust catalyst for the carboxylative cyclization of propargylic amines with CO_2

Results and Discussion

The carboxylative cyclization of *N*-benzylprop-2-yn-1-amine (**1a**) with CO_2 was selected as the model reaction as summarized in Table 1. When no catalyst was employed, the starting material was recovered quantitatively (entry 1). $Zn(OAc)_2$ was initially tested in consideration of the potential hydrogen-bonding interaction between acetate anion and **1a**.[18] However, only 33% yield of 3-benzyl-5-methyleneoxazolidin-2-one (**2a**) was obtained, implying that single $Zn(OAc)_2$ was not effective enough under the applied reaction conditions (entry 2). Then a series of additives were investigated in conjunction with $Zn(OAc)_2$ to accelerate the cyclization reaction.[19] Monophosphine ligand e.g. PPh_3 was confirmed to be ineffective (entry 4 *vs.* 2). Unexpectedly, 2,2'-bipyridine (Bipy), tetramethylethylenediamine (TMEDA), pyridine and 4-dimethylaminopyridine (DMAP) had an adverse effect (entries 5–8 *vs*. 2), probably being attributed to their insignificant interaction towards carbon-carbon triple bond as a result of strong coordination of such nitrogen ligands with $Zn(OAc)_2$. Gratefully, 1,4-diazabicyclo[2.2.2]octane (DABCO) with steric hindrance gave a better result for enhancing the catalytic activity of $Zn(OAc)_2$ than trimethylamine (Et_3N) (entry 10 *vs.* 9). Those results inspired us to examine sterically hindered guanidine and amidine compounds (entries 11–13). As expected, **2a** was obtained in a quantitative yield by cooperating TBD with $Zn(OAc)_2$ even though TBD itself was almost inactive (entry 13 *vs.* 3). 1,1,3,3-Tetramethylguanidine (TMG) exhibited the similar catalytic behavior to that of TBD (entry 12 *vs.* 13). Noticeably, $ZnCl_2$ displayed a comparable activity to $Zn(OAc)_2$ but other zinc salts showed moderate activities (entries 14–18 *vs* 13).

Table 1. Catalyst screening for the carboxylative cyclization of propargylic amine **1a** with CO_2.[a]



Entry	Catalyst	Additive	Conversion [b]	Yield [b]
1	–	–	0	0
2	$Zn(OAc)_2$	–	53	33
3	TBD	–	13	3
4	$Zn(OAc)_2$	PPh_3	39	31
5	$Zn(OAc)_2$	Bipy	19	3
6	$Zn(OAc)_2$	TMEDA	2	2
7	$Zn(OAc)_2$	Pyridine	34	19
8	$Zn(OAc)_2$	DMAP	23	18
9	$Zn(OAc)_2$	Et_3N	48	43
10	$Zn(OAc)_2$	DABCO	91	82
11	$Zn(OAc)_2$	DBU	99	94
12	$Zn(OAc)_2$	TMG	99	97
13	$Zn(OAc)_2$	TBD	99, 93[c]	99, 92[c]
14	$ZnCl_2$	TBD	99, 99[c]	98, 99[c]
15	$Zn(OTf)_2$	TBD	57	53
16	$Zn(ClO_4)_2$	TBD	59	52
17	$Zn(BF_4)_2$	TBD	53	45
18	$Zn(NO_3)_2$	TBD	73	50
19[d]	$ZnCl_2(TBD)_2$	–	99, 99[e]	95, 96[e]

[a] Reaction conditions: **1a** (145.2 mg, 1 mmol), catalyst (0.1 mmol, 10 mol% relative to **1a**), additive (0.2 mmol, 20 mol% relative to **1a**), CO_2 balloon, 60 °C, 12 h, 0.5 mL CH_3CN; [b] Determined by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard. [c] Catalyst (0.05 mmol, 5 mol% relative to **1a**), TBD (13.9 mg, 0.1 mmol, 10 mol% relative to **1a**); [d] $ZnCl_2(TBD)_2$ (20.7 mg, 0.05 mmol, 5 mol% relative to **1a**) was prepared according to Ref.15a prior to use; [e] Under solvent-free conditions.

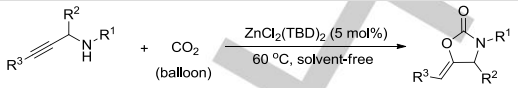
Halving the $Zn(OAc)_2$ caused a slightly reduction in **2a** yield, whereas $ZnCl_2$ still remained high catalytic efficiency (entry 14 *vs.* 13). Therefore, the combination of $ZnCl_2$ and TBD with best catalytic performance was selected for further investigation.

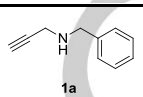
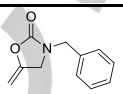
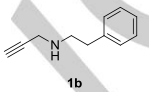
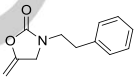
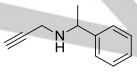
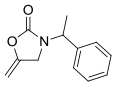
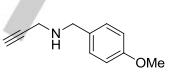
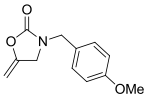
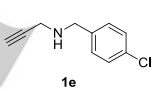
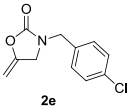
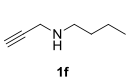
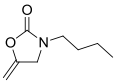
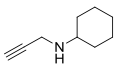
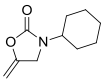
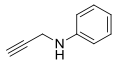
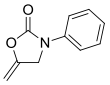
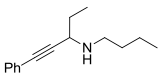
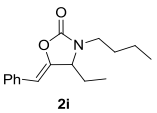
The mononuclear zinc(II) complex $ZnCl_2(TBD)_2$ can be readily generated from $ZnCl_2$ and TBD and stabilized by intramolecular N–H···Cl hydrogen bonding, X-ray crystal structure of which has been reported.[20] We speculated that the $ZnCl_2(TBD)_2$ that *in situ* generated could be an active species for this kind of cyclization reaction. To validate our hypothesis, $ZnCl_2(TBD)_2$ was prepared according to the published method (See Supproting Information for details).[20a] Indeed, the zinc(II) complex gave a comparable result in comparison with the two-component $ZnCl_2$/TBD system under otherwise identical conditions (entry 19 *vs.* 14), presumably suggesting that the $ZnCl_2(TBD)_2$ could be the active catalytic species. Notably, the reaction could also proceed under solvent-free conditions (entry 19).

Having established the $ZnCl_2(TBD)_2$-catalyzed carboxylative cyclization protocol, we then examined the reactivity of various propargylic amines to further explore the utility of this protocol. N-aryl substituted terminal propargylic amines were smoothly converted into the corresponding 2-oxazolidinones in excellent yields under optimized conditions (entries 1–5, Table 2). Notably, the catalytic system worked well with the substrates bearing electron-donating or electron-withdrawing group (**1d** and **1e**). Terminal propargylic amines with *n*-butyl and cyclohexyl substituent at N-position were also practicable, delivering the desired products in good yields (entries 6 and 7). Unfortunately, *N*-phenylprop-2-yn-1-amine (**1h**) displayed a moderate reactivity (entry 8). This is understandable because the weak N-nucleophilicity may hinder the nucleophilic attack at CO_2 to further generate the carbamate intermediate. The introduction of a phenyl group at terminal position caused a drastic decrease in the 2-oxazolidinone yield (entry 9), probably indicating that the internal propargylic amine is unreactive with atmospheric pressure of CO_2 in the present catalytic system.

Control experiments were carried out to gain insight into the reaction mechanism for identifying the possible intermediate as depicted in Scheme 2. Reaction of propargylic amine **1a** with equimolar TBD in DMSO under atmospheric pressure of CO_2 at room temperature resulted in the formation of $[TBDH]^+$ carbamate **3a** in a quantitative yield (Step 1). Similar processes have been well demonstrated by Jessop group and Weiss group.[21] They have developed binary system DBU/alkyl alcohol or DBU/alkyl amine as absorbents for CO_2 capture, generating the amidinium carbonate or amidinium carbamate, a kind of reversible ionic liquid. Remarkably, analogous structure of **3a** has been proposed by Costa *et al*. in the guanidine-promoted cyclization of propargylic amines with CO_2.[10b] This species is supposed to contain two intramolecular hydrogen bridges for carbamate anion stabilization. To verify the hypothesis, the structure of **3a** was identified by NMR analyses (See Supporting Information for details). Then **3a** was further converted into 2-oxazolidinone **2a** in the presence of catalytic amount of $ZnCl_2$ at elevated temperature in just 68% yield (Step 2). In addition, step 2 in the presence of CO_2 also gave the similar result (69% yield), suggesting the possible decomposition of **3a** can be ruled out. A reasonable interpretation may be that the hydrogen-bonding interaction between $[TBDH]^+$ and carbamate anion partially hinders subsequent nucleophilic addition of the carbamate anion on carbon-carbon triple bond as illustrated in Scheme 3 (mode A). Therefore, we proposed the bidentate

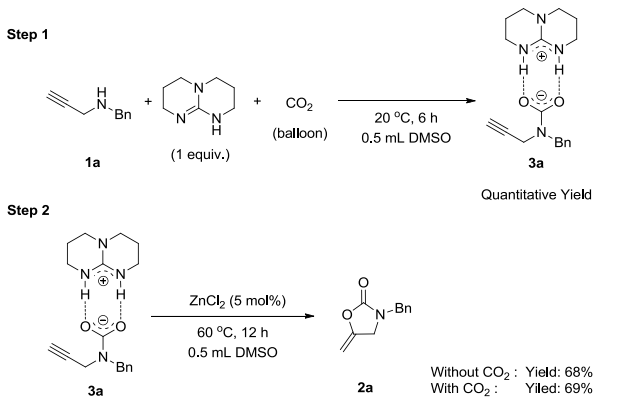
Table 2. $ZnCl_2(TBD)_2$-catalyzed cyclization of various propargylic amines with atmospheric pressure of CO_2.[a]



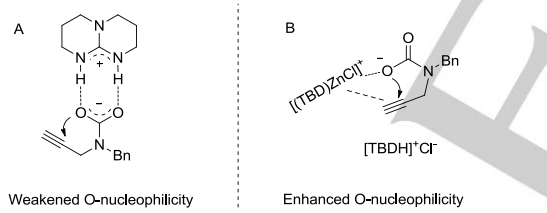
Entry	Substrate	Product	Yield [b]
1	 **1a**	 **2a**	96
2	 **1b**	 **2b**	94
3	 **1c**	 **2c**	93
4	 **1d**	 **2d**	95
5	 **1e**	 **2e**	93
6	 **1f**	 **2f**	91
7	 **1g**	 **2g**	90
8	 **1h**	 **2h**	52
9	 **1i**	 **2i**	8

[a] All the reactions were carried out with propargylic amine (1 mmol) and $ZnCl_2(TBD)_2$ (20.7 mg, 0.05 mmol, 5 mol% relative to the substrate **1**) under atmospheric pressure of CO_2 at 60 ^{0}C within 12 h. [b] Determined by ^{1}H-NMR with 1,3,5-trimethoxybenzene as internal standard.

ligation with alkyne and carbamate anion to zinc center as mode B. The presence of the bulky cation $[(TBD)ZnCl]^+$ may be favorable for stabilizing the carbamate anion; Whereas, the Lewis acid-carbamate interaction could be diminished due to steric hindrance of such bulky cation. As a result, the zinc(II) may play a critical role in facilitating the intramolecular nucleophilic addition towards carbon-carbon triple bond by enhancing the O-nucleophilicity of carbamate anion relative to **3a**.[22]



Scheme 2. Control experiments. Reaction conditions: Step 1: **1a** (145.2 mg, 1 mmol), TBD (139.2 mg, 1 mmol), CO_2 balloon, 20 °C, 6 h, 0.5 mL DMSO; Step 2: **3a** (330.4 mg, 1 mmol), $ZnCl_2$ (6.8 mg, 0.05 mmol), 60 °C, 12 h, 0.5 mL DMSO, in the presence or absence of CO_2 balloon.



Scheme 3. Two patterns of the ring-closure step promoted by TBD and the zinc complex, respectively

^{13}C NMR analyses were further applied to investigate the interaction between zinc(II) with propargylic amine **1a**. In the ^{13}C NMR spectrum of the mixture of half equivalent of $ZnCl_2$ with **1a**, the signals assigned to C1 and C2 of carbon-carbon triple bond shifted from δ = 73.78 to 74.38 ppm, and 82.82 to 82.21 ppm, respectively (Figure 1, (a) *vs* (b)). Increasing $ZnCl_2$ amount to one equivalent relative to **1a** resulted in further shift of signals corresponded to C1 and C2 ((b) *vs* (c)). However, the signals of C3 and C4 had no significant change upon the addition of $ZnCl_2$. The above observation probably indicates that alkyne has an interaction with $ZnCl_2$ rather than the amine coordinates with zinc center. Notably, the coordination of the carbon-carbon triple bond with zinc (II) has been described in the nucleophilic addition reaction of terminal alkynes to C=O and C=N bond,[15a,d,e] intramolecular hydroamination of alkynes,[23] redox cross-dehydrogenative coupling reaction of propargylic amines and terminal alkynes.[24] Similarly, Carreira *et al.* has reported ZnI_2/DMAP-catalyzed intramolecular cyclization of propargylic N-hydroxylamines. They also speculated that zinc (II) participates in the complexation and activation of carbon-carbon triple bond. The nature of amine and counterion effect might affect the equilibrium between free zinc (II) and the coordinated zinc(II).[25] Thus, it is reasonable to suppose that zinc(II) may serve as an activator of alkyne to make the carbon-carbon triple bond more vulnerable to the nucleophile such as carbamate anion.

A plausible mechanism for $ZnCl_2(TBD)_2$-promoted fixation of atmospheric pressure of CO_2 with propargylic amine **1a** is illustrated in Scheme 4. The reaction of $ZnCl_2$ and TBD initially furnishes $ZnCl_2(TBD)_2$, which then coordinates with the carbon-carbon triple bond of **1a** to afford the intermediate **I** with release of TBD. TBD is able to activate CO_2 by reversibly forming the zwitterionic adduct.[26] The TBD-CO_2 adduct further reacts with the zinc-coordinated propargylic amine **I** (the activated substrate to afford the carbamate **II** by inserting CO_2 into the N–H bond. Subsequently, intramolecular nucleophilic cyclization occurs to deliver the alkenylzinc(II) species **III**. Finally, the desired 2-oxazolidinone **2a** is obtained by proto-demetallation of the intermediate **III** with assistance of $[TBDH]^+$, concomitant with the regeneration of $ZnCl_2(TBD)_2$.

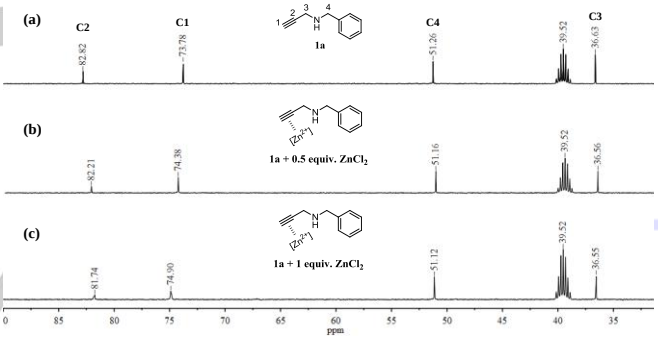
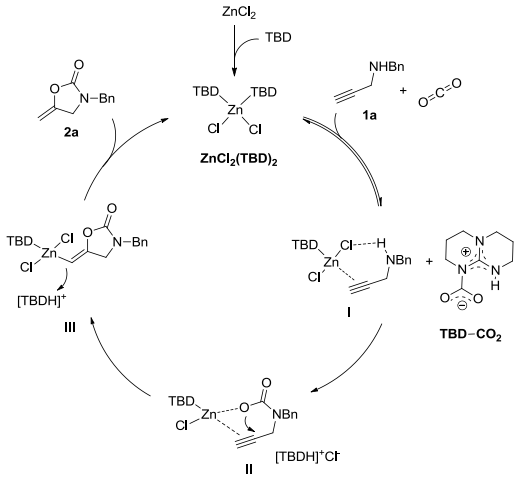


Figure 1. ^{13}C NMR study. (a) **1a** (29.0 mg, 0.2 mmol) in 0.5 mL d_6-DMSO. (b) $ZnCl_2$ (13.6 mg, 0.1 mmol) was added into **1a** (29.0 mg, 0.2 mmol) in 0.5 mL d_6-DMSO. (c) $ZnCl_2$ (27.2 mg, 0.2 mmol) was added into **1a** (29.0 mg, 0.2 mmol) in 0.5 mL $[D_6]$DMSO. All the NMR experiments were performed under ambient conditions.



Scheme 4. Mechanistic proposal for in situ formation of $ZnCl_2(TBD)_2$ complex and subsequent catalytic cycle.

Conclusions

In summary, an elaborate protocol has been demonstrated for efficient chemical fixation of atmospheric pressure of CO_2 to produce 2-oxazolidinones. The active zinc(II) complex *i.e.* $ZnCl_2(TBD)_2$, being in situ generated from $ZnCl_2$ and TBD, serves as a robust catalyst for the carboxylative cyclization of propargylic amines with CO_2 under mild conditions. Control experiments and ^{13}C NMR spectra have been applied to gain insight into the reaction mechanism. A hypothetic intermediate containing bulky zinc cation is proposed, the O-nucleophilicity of which is supposed to be enhanced. On the other hand, the interaction between zinc and carbon-carbon triple bond is shown in ^{13}C NMR spectra, indicating that zinc(II) may act as an activator of the alkyne. Such dual effects arising from zinc catalyst facilitate the intramolecular nucleophilic addition of carbamate anion towards carbon-carbon triple bond thus rendering the cyclization reaction to proceed smoothly under mild conditions. The application of non-noble, earth-abundant and nontoxic metal zinc features this method a sustainable procedure for the synthesis of 2-oxazolidinones with CO_2 as a C_1 building block.

Experimental Section

General procedure for the synthesis of 5-alkylideneoxazolidin-2-ones

Taking the carboxylative cyclization of N-benzylprop-2-yn-1-amine (**1a**) with CO_2 as an example: $ZnCl_2(TBD)_2$ (20.7 mg, 0.05 mmol) and **1a** (145.2 mg, 1 mmol) were added successively to a 10 mL Schlenk tube equipped with a magnetic stir bar. Then the flask was capped and attached to a CO_2 balloon with purity of 99.99 %. Subsequently, the reaction mixture was stirred at 60 ^oC for 12 h. Upon completion, the excessive CO_2 was carefully released, 1,3,5-trimethoxybenzene (42 mg, 0.25 mmol) was directly added into the reaction mixture as an internal standard to determine the yield of **2a** by ^1H NMR analysis. Alternatively, the reaction mixture was extracted with ethyl acetate (3 × 10 mL) and the organic phases were collected, which were further purified by column chromatography on silica gel (petroleum ether/ethyl acetate as an eluent) to afford the pure product **3a** as a white solid. Characterization of **3a**: ^1H NMR (400 MHz, $CDCl_3$): δ 7.39–7.27 (m, 5H), 4.75 (dd, J = 5.6, 2.7 Hz, 1H), 4.47 (s, 2H), 4.24 (dd, J = 5.2, 2.3 Hz, 1H), 4.02 (t, J = 2.4 Hz, 1H) ppm. ^{13}C NMR (101.6 MHz, $CDCl_3$): δ 155.78, 149.02, 135.05, 129.11, 128.39, 128.31, 86.95, 47.96, 47.33 ppm. IR (neat, KBr): 1783, 1680, 1427, 1282, 1237, 1083, 1060, 969, 877, 835, 754, 702 cm^{-1}. GC-MS (EI, 70 eV) *m/z* (%) = 189.15 (14), 105.15 (2), 92.10 (16), 91.10 (100), 89.10 (3), 77.10 (2), 65.10 (14).

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Keywords: Carbon dioxide chemistry • carboxylative cyclization • dual activation • synthetic methods • zinc catalysis

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Entry for the Table of Contents

FULL PAPER

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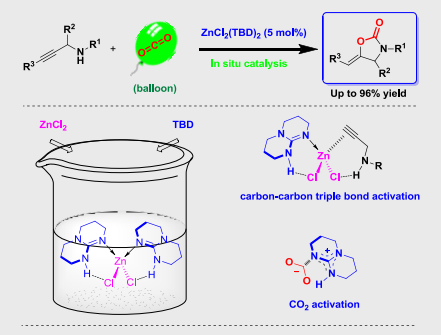

*Xi Liu, Mei-Yan Wang, Si-Yuan Wang, Qi Wang, Liang-Nian He**

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Zinc(II) Catalyst In Situ Formed for Incorporation of CO_2 into 2-Oxazolidinones with Propargylic Amines at Atmospheric Pressure