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An Experimental and Theoretical Study on the Unexpected Catalytic Activity of Triethanolamine for the Carboxylative Cyclization of Propargylic Amines with CO_2

Yuling Zhao, [a] Jikuan Qiu, [a] Zhiyong Li, [a] Huiyong Wang, [a] Maohong Fan [b] and Jianji Wang*[a]

Abstract: The chemical conversion of CO_2 under atmospheric pressure and metal-free conditions remains a great challenge. In this work, a series of alkylolamines, low-cost and biodegradable bases, were used to catalyze the carboxylative cyclization of propargylic amines with CO_2. It was found that among these alkylolamines, triethanolamine (TEOA) was shown to be a highly efficient organocatalyst for this important transformation at atmospheric pressure, and a series of desired products were synthesized in good to excellent yields. After the reactions, TEOA could be easily recoveried and reused without obvious reduction in the efficiency. Density functional theory studies reveal that TEOA may activate CO_2 to form a ring-shaped carbonate intermediate which plays an important role in the catalysis of the reaction. This finding provides an effective and environmentally friendly alternative route for the production of 2-oxazolidinones.

Introduction

With increasing awareness of growing carbon dioxide (CO_2) levels in the atmosphere, great efforts have been made to develop new strategies and technologies towards the reduction of carbon emissions[1-3]. In fact, CO_2 is usually considered as a ubiquitous, non-toxic, and renewable carbon resource, and can replace commonly used toxic C1 building blocks[4]. Thus, fixation and conversion of CO_2 hold great promise for the recycling of CO_2 into value-added products. At present, many useful organic chemicals which are currently derived from fossil fuel-based resources have been produced by using CO_2 as a feed stock, such as alcohols[5], cyclic carbonates[6,7], formamide[8] and carboxylic acid derivatives[9,10]. However, only a small proportion of the total abundance of CO_2 is currently being consumed in industry because to establish ecological and economical CO_2 conversion processes is still a great challenge. Thus the development of efficient green process to solve energy and environment problems has gained more and more attentions these days.

2-Oxazolidinones are important heterocyclic compounds used as building blocks for different synthetic purposes[11, 12]. Synthesis of 2-oxazolidinones from cycloaddition of propargylic amines with CO_2 has attracted extensive attention in recent years. Many investigations have been conducted for this reaction in the presence of metal catalysts, such as Cu[13-15], Pa[16, 17], Ag[18-23], Ru[24] and Au[25-27]. It is demonstrated that those transition metals are good activator for the C≡C triple bond, thus catalyzing the chemical transformation of substrates with CO_2. Although CO_2 can be efficiently transformed using these catalytic systems, the metal catalysts used in the reactions are both expensive and toxic. Metal-free catalytic process can reduce the cost and avoid the pollution caused by metals, and is thus regarded as greener process.

In the past decades, a number of metal-free catalysts, such as superbase[28,29], N-heterocyclic carbene[30] and ionic liquids[13, 31] had been reported to catalyze the carboxylative cyclization of propargylic amines with CO_2. The most exciting implication is that these catalysts also shown high activity in comparison with the transition-metal catalysts under comparable reaction conditions. Nevertheless, these reaction systems still have disadvantages such as the use of high pressure and tedious process for the preparation of catalysts. Therefore, development of new organocatalytic systems that can operate under the conditions of low pressure, room temperature and low cost is an urgent task.

As a class of low-cost and biodegradable base, alkanolamines have been used in a wide variety of industrially important processes such as natural gas stripping, adhesives, acid neutralization, paint stripping, surfactants and derivatives in drug formulations[32-34]. It is known that as early as 1931, alkanolamines had been utilized to capture carbon dioxide from natural gas[35]. This gives us an inspiration: maybe alkanolamines can strongly activate CO_2 in CO_2 conversion process. At present, it is widely recognized that only superbase and its derivatives can serve as single catalyst or can coordinate with metal catalysts to catalyze the transformation of CO_2 and propargylic amines[28, 29, 31]. Is it possible for us to move sideways and develop a new type of mild base catalyst for efficient synthesis of 2-oxazolidinones?

Herein, we used a series of alkylolamines to catalyze this important transformation reaction (Scheme 1). It was found that several alkylolamines could be used as catalyst for the reactions under solvent-free and atmospheric pressure conditions. Unexpectedly, triethanolamine (TEOA) was shown to be a highly efficient catalyst at ambient pressure, and a series of desired products were synthesized in good to excellent yields. Moreover, the catalyst could be easily recovered from the reaction system

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and then reused without obvious activity loss. A possible reaction mechanism was proposed through a detailed density functional theory (DFT) study.

Scheme 1. Carboxylative cyclization of propargylic amines with CO_2 catalyzed by TEOA.

Results and Discussion

Screening of the catalyst

Since alcohol amines are cheap, commercially available and recyclable compounds and their basicity can be tuned conveniently by changing their chemical structure, a series of such compounds (Figure 1) were used as homogeneous catalysts in this work. First, the catalytic activity of these typical bases for the reaction between N-butyl-1-phenylhex-1-yn-3-amine (1a) and atmospheric CO_2 was investigated at 90℃ for 10 h, and the results were listed in Table 1. It can be seen that in the absence of a base, the reaction did not occur (Table 1, entry 1). Then different types of alkylolamines were tried for the reaction. To our delight, high yield and good selectivity were obtained for the desired product through tuning the basicity of the alkylolamines. It was shown that the basicity decreased in the sequence: MEA>DEA>MDEA>TIPA>TEOA, which is consistent with the order of the catalytic activity of these bases for the reaction (entries 2-6). Surprisingly, among these screened bases, the polyhydric substituted alcohol amines were found to be excellent catalysts and 97% yield (entry 6) was obtained for the desired product by using TEOA. This observation can possibly be rationalized by assuming that stable carbamates were more prone to be formed from the reactions of primary and secondary amines with CO_2, which decreased the base-catalytic ability. As a result of the steric hindrance imposed by the substituent, TEOA exhibited better catalytic activity for the reaction than TIPA. Additionally, traditional inorganic bases NaOH and Cs_2CO_3 were also used to catalyze this reaction (Table 1, entries 7 and 8). However, the yield was quite low and it is very difficult to recover these bases after the reaction.

Based on the above results, TEOA was selected as the catalyst for the reaction under atmospheric pressure of CO_2 to study the effects of reaction temperature, reaction time and catalyst dosage on the yields (see ESI, Figures S1-S3). It was shown that under the optimized conditions (90°C, 10h and 0.1 mmol of TEOA), the yield of the desired product could reach 97%. The recyclability of the catalyst TEOA was also investigated, and the results were shown in Figure S4. In a typical experiment, the catalyst was reused four times in the reaction between 1a and CO_2, and the catalytic activity of the catalyst remained unchanged. This indicates that the used catalyst was recyclable for catalyzing the reaction of CO_2 with propargylic amine.

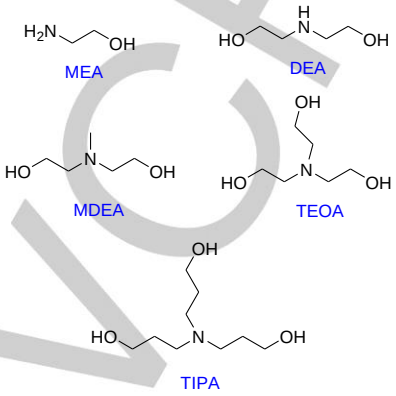
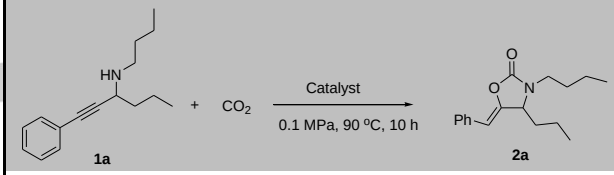


Figure 1. The structures of the substituted MEA alkylolamine derivatives

Table 1. Carboxylic cyclization of propargylic amines with CO_2[a]



Entry	Catalyst	pKa	Yield(%)[b]
1[c]	---	---	0
2	MEA	9.45	42
3	DEA	8.88	49
4	MDEA	8.56	54
5	TIPA	7.82	87
6	TEOA	7.74	97
7	NaOH	15.74	<1
8	Cs_2CO_3	---	<1

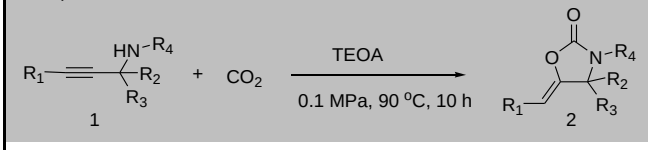
[a]Reaction conditions: 1a (1.0 mmol), catalyst (0.1 mmol), CO_2 (0.1 MPa), 90°C, 10 h. [b]The yield was determined by ^{1}H NMR spectroscopy using anisole as an internal standard. [c]Without catalyst

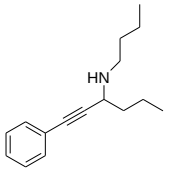
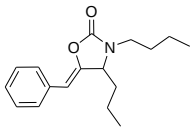
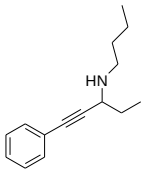
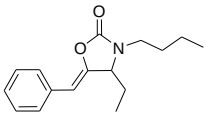
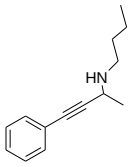
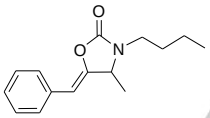
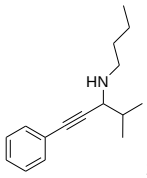
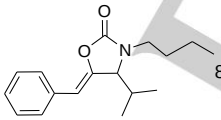
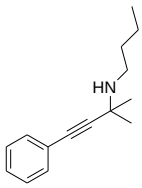
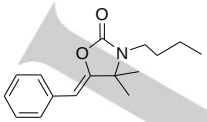
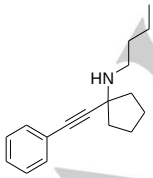
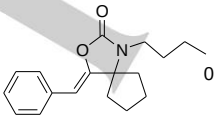
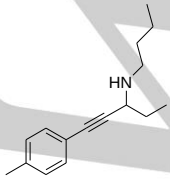
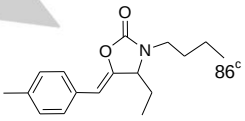
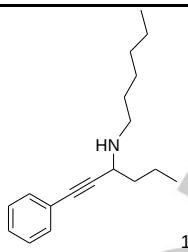
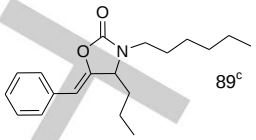
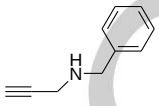
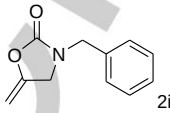
Versatility of the catalyst

With the optimized conditions established, we further investigated the reaction scope using a variety of propargylic amines as the substrates, and the results were given in Table 2. It can be seen that both terminal and internal propargylic amines performed smoothly to give the corresponding 2-oxazolidinones in moderate to excellent yields (entries 1-5, 7-9). However, the reaction activity depended strongly on the substitute groups of propargylic amines. When the R_2 and R_3 groups were combined into a cyclopentane group, no product was obtained (entry 6), probably due to the steric hindrance (1f). In addition, propargylic amines with different R_1 and R_4 groups were also studied (1g-1i), and good yields were obtained for the corresponding 2-

oxazolidinones (2g-2i). These results confirmed the versatility of the new catalyst for the production of 2-oxazolidinones.

Table 2 Scope of the propargylic amine substrates for the reaction under the optimized conditions[a]

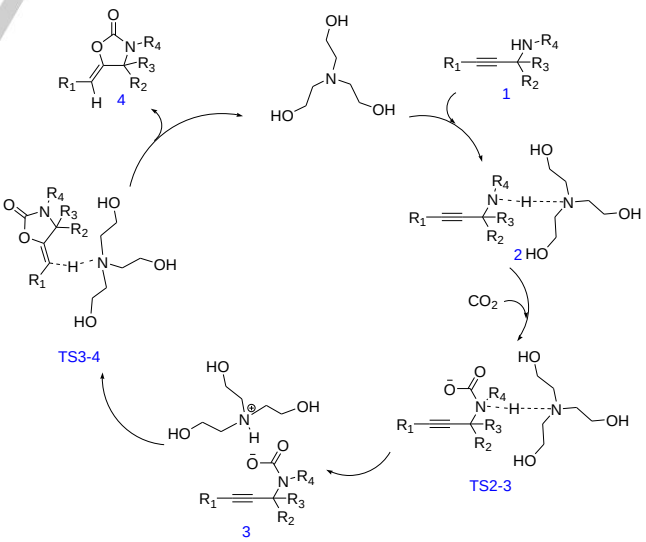


Entry	Substrate	Product	Yield(%)[b]
1	 1a	 2a	97
2	 1b	 2b	99
3	 1c	 2c	99
4	 1d	 2d	80
5	 1e	 2e	74[c]
6	 1f	 2f	0
7	 1g	 2g	86[c]
8	 1h	 2h	89[c]
9	 1i	 2i	71[c]

[a]Reaction conditions: 1 (1.0 mmol), TEOA (0.1 mmol), CO_2 (99.999%, 0.1 MPa), 10 h, 90°C. [b]The yield was determined by ^{1}H NMR spectroscopy using anisole as an internal standard. [c]1 MPa.

Possible reaction mechanism

To investigate the reaction mechanism catalyzed by TEOA in detail, DFT calculations were performed. In the DFT calculations, the simplest propargylic amine substrate 1c (see Table 2) was used as the representative substrate molecule to reduce the computing complexity. Before the computation begins, we were interested in thought about the mechanistic pathway of the reaction. Since the reaction of propargylic amine substrates and CO_2 did not occur in the absence of TEOA catalyst, it is possible that both propargylic amines and CO_2 may be activated by TEOA. For propargylic amines, their amino group is prone to be activated by TEOA base, and CO_2 can also be activated by TEOA to form zwitterionic ammonium carbonate adduct[36-38]. Therefore, the mechanisms for amino-activated and CO_2-activated reaction pathways were investigated by DFT calculations, respectively.



Scheme 2. The amino-activated mechanism for the carboxylative cyclization reactions of propargylic amines with CO_2 catalyzed by TEOA.

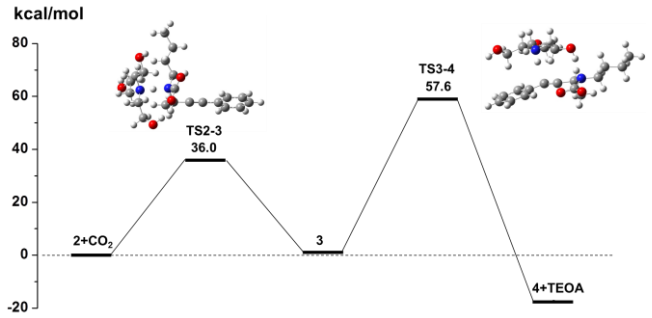
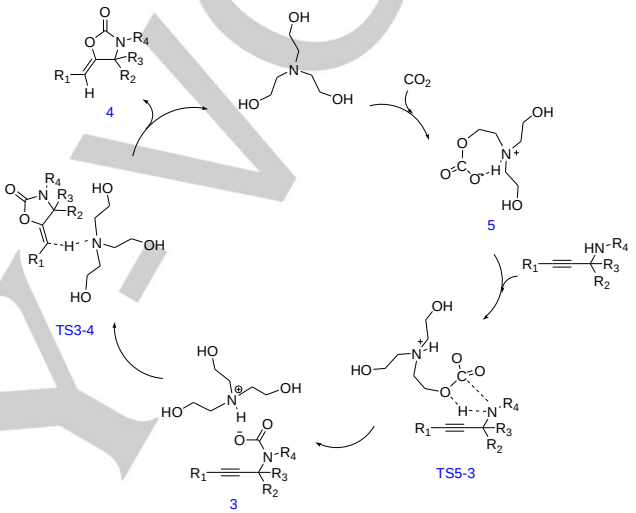


Figure 2. Free energy profiles of the amino-activated pathway for the carboxylative cyclization of propargylic amines with CO_2 catalyzed by TEOA.

The amino-activated mechanism and its free energy profiles were illustrated in Scheme 2 and Figure 2, respectively. The details for the optimized geometries of the transition states were shown in supporting information. As a result of the amino group being activated by TEOA, the electrophilic attack of CO_2 on N atom of the amino group was more favorable. In this case, a lower free energy barrier of 36.0 kcal/mol was observed (via transition state TS2–3). After this step, the zwitterionic carbamate species was formed (Scheme 2, structure 3). In the following intramolecular cyclization step, the attack of the O atom and the proton transfer to the C≡C bond took place simultaneously. The proton was transferred from the positively charged N atom of TEOA to the C≡C bond with an energy barrier of 57.6 kcal/mol (via transition state TS3–4).Then the target Z-isomer product and TEOA were regenerated. In this step, TEOA promoted the attack of O atom on the C atom of the C≡C bond and made the proton transfer easier. It was also found from Figure 2 that the intramolecular cyclization step was the rate-determining step, and the overall energy barrier was 57.6 kcal/mol for the amino-activated mechanism.

Next, the CO_2-activated mechanism and free energy profiles were illustrated in Scheme 3 and Figure 3, respectively. It can be seen that at the beginning, TEOA could capture CO_2 and then made CO_2 active. Unlike primary and secondary amines, tertiary amines did not form ammonium carbamates. The ring-shaped zwitterionic ammonium carbonate intermediate (Scheme 3, structure 5) was only formed when CO_2 was absorbed by TEOA, and the three dimensional structures were shown in Figure 4. Clearly, CO_2 molecule was inserted in hydroxyl group of TEOA to form carbonate intermediate, while the hydroxyl hydrogen had a hydrogen bond interaction with N atom to make its charge more positive. As the ammonium carbonate intermediate was very unstable and the C atom of carbonate was more positively charged, the attack of N atom of propargylic amine on C atom of carbonate would be more favorable. In the subsequent attack of N atom of propargylic amine on C atom of carbonate, the H atom connected to N atom of propargylic amine transferred to the hydroxyl oxygen atom of TEOA synchronously. This corresponds to the transition state of TS5–3, and the energy barrier of this step was 27.3 kcal/mol. After this step, CO_2 was moved from carbonate intermediate to propargylic amine, and then the Z-isomer product and TEOA were regenerated in the followed intramolecular cyclization step (via transition state TS3–4). It is clear from Figure 3 that the intramolecular cyclization step was still the rate-determining step which is the same as the amino-activated mechanism. In addition, a Noesy experiment was performed in order to examine the configuration of the product. As shown in the partial assignment of the ^1H NMR spectrum of the compound 2e (Figure S5), the signal assigned to 1 only showed obvious correlation with the signal of 2 in Noesy NMR spectrum, which provided the evidence for the Z-isomer structure of the product. This experimental result was in good agreement with our calculation result.



Scheme 3. The CO_2-activated mechanism for the carboxylative cyclization reactions of propargylic amines with CO_2 catalyzed by TEOA.

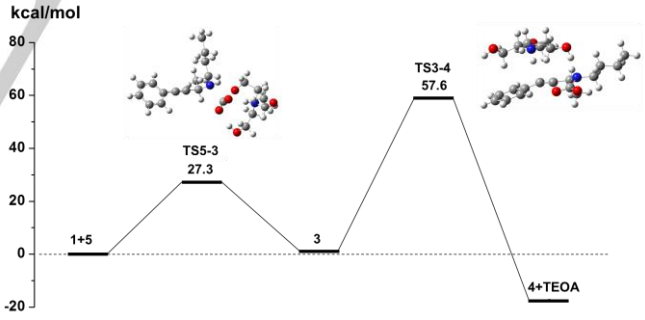


Figure 3. Free energy profiles of the CO_2-activated pathway for the carboxylative cyclization of propargylic amines with CO_2 catalyzed by TEOA.

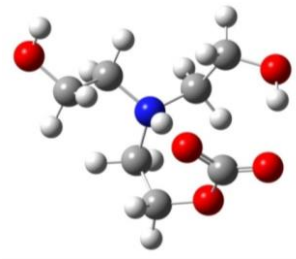


Figure 4. Optimized geometry for the zwitterionic ammonium carbonate adduct composed by CO_2 and TEOA.

By comparing the energy barrier of the both mechanisms, it can be concluded that the CO_2-activated mechanism had a lower energy barrier in the first step, and thus was more favorable than the amino-activated mechanism. This suggests that the formation of ring-shaped carbonate intermediate could decrease the activation energy for the formation of intermediate 3 , so that the reaction can proceed more easily. This made the point that the formation of ring-shaped carbonate intermediate might play an important role in the catalysis of the reaction. As we known, primary and secondary amines can form ammonium carbamates with CO_2, which are more stable than carbonate. This will potentially decrease the attack ability of N atom of propargylic amine on carbamates and have a negative effect on the reaction. Therefore, the catalytic activity of MEA and DEA for this carboxylative cyclization reaction is lower than that of tertiary amines, as shown in Table 1. When the TEOAs have more hydroxyl groups and smaller steric hindrance, the best catalytic activity has been found for the reaction among these tertiary amines (Table 1).

Conclusions

In summary, among the alkanolamines catalysts investigated, TEOA was found to display the best catalytic performance for the reactions of CO_2 with propargylic amine, and a series of desired products were synthesized in good to excellent yields. Additionally, TEOA could be easily regenerated and reused without obvious loss in its activity. The mechanistic studies revealed that CO_2 was activated by TEOA to form unstable ring-shaped carbonate intermediate. This carbonate intermediate could decrease the activation energy for the formation of intermediate 3, so that the reaction can proceed more easily. Considering the fact that TEOA is a cheap, biodegradable, commercially available and recyclable catalyst, we expect that more applications can be found for it in the transformation of CO_2 under mild conditions.

Experimental Section

Chemicals

CO_2 was supplied by Beijing Analytical Instrument Factory with a purity of 99.999%. The deuterated solvents (DMSO-d_6, $CDCl_3$) were provided by Cambridge Isotope Laboratories, Inc. All chemicals were of analytical grade and used as received. The propargylic amine substrates were synthesized by following the procedures described in literature[31].

General procedure for the synthesis of α-alkylidene cyclic carbonates

In a 20 mL Schlenk flask, propargylic amine (1.0 mmol) and the indicated amount of the catalyst were added. The air in the reactor was replaced by bubbling of CO_2. Then the reaction mixture was stirred at 90 °C for 12 h under the desired CO_2 pressure. After the reaction was finished, the product was extracted with n-hexane, leaving the catalyst alone in the reactor. The crude mixture was purified by silica gel column chromatography (EtOAc : petroleum ether = 1:20) to obtain the desired 2-oxazolidinone. The catalyst was recovered by drying under vacuum and reused in the next run.

Characterization of the products

^1H and ^{13}C NMR analyses of the purified products were conducted in $CDCl_3$ on a Bruker Avance III HD 600 spectrometer (600 MHz for ^1H NMR and 150 MHz for ^{13}C NMR), and the results are consistent with the previous reported experimental results[15].

Compound 2a. Light yellow oil; ^1H NMR (600 MHz, $CDCl_3$): δ=7.581 (d, *J* = 7.26 Hz, 2 H), 7.326 (t, *J* = 7.62 Hz, 2 H), 7.203 (t, *J* =7.44 Hz, 1 H), 5.465 (d, *J* = 1.74 Hz, 1 H), 4.524 (t, *J* = 1.8 Hz, 1 H), 3.633-3.582 (m, 1 H), 3.047-3.000 (m, 1 H), 1.886-1.826 (m, 1 H), 1.712−1.655 (m, 1 H), 1.622-1.520 (m, 2 H), 1.417-1.348 (m, 4 H), 0.958 (t, *J* = 7.32 Hz, 6 H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ =155.17, 147.00, 133.62, 128.48, 128.28, 126.75, 102.32, 58.40, 41.13, 34.43, 29.26, 19.92, 15.84, 13.91, 13.68 ppm.

Compound 2b. Colorless oil; ^1H NMR (600 MHz, $CDCl_3$): δ=7.592 (d, *J* = 1.2 Hz, 1 H), 7.579 (s, 1 H), 7.341-7.315 (m, 2 H), 7.219-7.194 (m, 1 H), 5.462 (d, *J* = 1.74 Hz, 1 H), 4.559-4.543 (m, 1H), 3.641-3.590 (m, 1 H), 3.040-2.993 (m, 1 H), 1.962-1.913 (m, 1H), 1.771-1.729 (m, 1 H), 1.629-1.529 (m, 3 H), 0.959 (t, *J* = 7.38Hz, 3 H), 0.902 (t, *J* = 7.32 Hz, 3 H) ppm ^{13}C NMR (150 MHz, $CDCl_3$): δ= 155.29, 146.61, 133.62, 128.48, 128.28, 126.73, 102.35, 59.00, 41.06, 29.23, 24.90, 19.93, 13.68 ppm.

Compound 2c. Colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ=7.589 (d, *J* = 7.6 Hz, 2 H), 7.329 (t, *J* = 7.2 Hz, 2 H), 7.208 (t, *J* = 7.2Hz, 1 H), 5.476 (d *J* = 2.0 Hz, 1 H), 4.556-4.503 (m, 1 H), 3.583-3.507 (m, 1 H), 3.174-3.104 (m, 1 H), 1.645-1.512 (m, 2 H), 1.475 (d, *J* = 6.4 Hz, 3 H), 1.400-1.340 (m 2 H), 0.960 (t, *J* = 7.2 Hz, 3 H), 0.902 (t, *J* = 7.32 Hz, 3 H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=154.80, 148.60,133.56, 128.49, 128.26, 126.80, 102.08, 54.65, 41.26, 29.36, 19.93, 19.74, 13.71 ppm.

Compound 2d. Colorless oil; ^1H NMR (600 MHz, $CDCl_3$): δ=7.591 (d, *J* = 7.56 Hz, 2 H), 7.328 (t, *J* = 7.44 Hz, 2 H), 7.210 (t, *J* =8.76 Hz, 1 H), 5.486 (s, 1 H), 4.306 (s, 1 H), 3.679-3.629 (m, 1 H), 3.075-3.030 (m, 1 H) 2.159-2.126 (m, 1 H), 1.631-1.538 (m, 2 H), 1.375-1.341 (m, 2 H), 1.099 (d, *J* = 6.96 Hz, 3 H), 0.955 (t, *J* = 7.26Hz, 3 H), 0.920 (d, *J* = 6.72 Hz, 3 H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 155.35, 145.02, 133.57, 128.47 126.85, 104.20, 63.71, 41.37, 30.20, 29.18, 19.91, 17.52, 15.44, 13.68 ppm.

Compound 2e. Light yellow oil; ^1H NMR (600 MHz, $CDCl_3$): δ =7.594-7.579 (m, 2 H), 7.335-7.309 (m, 2 H), 7.212-7.184 (m, 1 H), 5.452 (s, 1 H), 3.205 (t, *J* = 7.92 Hz, 2 H), 1.686-1.634 (m, 2 H), 1.493 (s, 6 H), 1.371-1.334 (m, 2 H), 0.958 (t, *J* = 7.38 Hz, 3 H)ppm; ^{13}C NMR (150 MHz $CDCl_3$): δ = 154.19, 153.51, 133.68, 128.46, 128.28, 126.71, 100.38, 62.17, 40.41, 31.52, 27.61, 20.24, 13.75 ppm.

Compound 2g. Colorless oil; ^1H NMR (600 MHz, $CDCl_3$): δ =7.480 (d, *J* = 7.8 Hz, 2 H), 7.136 (d, *J* = 7.8 Hz, 2 H), 5.428 (d, J = 1.2 Hz, 1 H), 4.545-4.530 (m, 1 H), 3.635-3.585 (m, 1 H), 3.032-2.986 (m, 1 H), 2.334 (s, 3 H), 1.949-1.904 (m, 1 H), 1.754-1.712 (m, 1 H), 1.612-1.532 (m, 2 H), 1.398-1.347 (m, 2 H), 0.956 (t, *J* = 7.2 Hz, 3 H), 0.891 (t, *J* = 7.2 Hz, 3 H)ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ =155.44, 145.84, 136.56, 130.79, 129.18, 128.21, 102.29, 58.98, 41.05, 29.24, 24.92, 21.21, 19.94, 13.69, 6.49 ppm.

Compound 2h. Light yellow oil; ^1H NMR (600 MHz, $CDCl_3$): δ =7.589 (d, *J* = 7.38 Hz, 2 H), 7.326 (t, *J* = 7.68 Hz, 2 H), 7.204 (t, *J* =14.82 Hz, 1 H), 5.466 (d, *J* = 1.68 Hz, 1 H), 4.531-4.516 (m, 1 H), 3.618-3.568 (m, 1 H), 3.042-2.996 (m, 1 H), 1.884-1.825 (m, 1 H), 1.712-1.655 (m, 1 H), 1.638-1.588 (m, 1 H), 1.449-1.383 (m, 1 H), 1.349-1.310 (m, 7 H), 0.956 (t, *J* = 7.32 Hz, 3 H), 0.905-0.882 (m, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ =

155.16, 147.02, 133.63, 128.48, 128.28, 126.75, 102.30, 58.41, 41.42, 34.43, 31.41, 27.19, 26.37, 22.53, 15.84, 13.99, 13.91 ppm.

Compound 2i. Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ =7.396-7.305 (m, 3 H), 7.271 (d, *J* = 7.8 Hz, 2 H), 4.755-4.735 (dd, *J*= 2.40 Hz, *J* = 2.80 Hz, 1 H), 4.472 (s, 2 H), 4.251-4.232 (m, 1 H), 4.023(t, *J* = 7.2 Hz, 2 H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ =155.66, 148.93, 134.96, 128.99, 128.27, 128.19, 86.81, 47.86, 47.23 ppm.

Theoretical methods

Density functional theory (DFT) calculations were performed by GAUSSIAN 09 D.01 program packages[39]. All the structures were optimized at B3LYP/6-31G* level. Vibrational frequency calculations at the same level of theory were performed to verify that a local minimum has no imaginary frequency and each transition state has only one single imaginary frequency. The lowest-energy conformers were obtained by comparing the single point energy of different structures. To obtain the relative free energies, single-point energy calculations for all of the species studied were performed at B3LYP/6-311+G(d,p) level. Intrinsic reaction coordinate (IRC) calculations were also performed to make sure that each transition state calculated indeed connects two relevant minima.

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[1] T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, **2007**, *107*, 2365-2387.
[2] G. Cui, J. Wang and S. Zhang, *Chem. Soc. Rev.*, **2016**, *45,* 4307-4339.
[3] Y. Kayaki, M. Yamamoto and T. Ikariya, *Angew. Chem. Int. Ed.*, **2009**, *48,* 4194-4197.
[4] B. Yu, Z. Yang, Y. Zhao, L. Hao, H. Zhang, X. Gao, B. Han and Z. Liu, *Chem.Eur. J.,* **2016**, *22,* 1097-1102.
[5] X. Sun, Q. Zhu, X. Kang, H. Liu, Q. Qian, Z. Zhang and B. Han, *Angew. Chem. Int. Ed.*, **2016**, *55,* 6771-6775.
[6] J. A. Kozak, J. Wu, X. Su, F. Simeon, T. A. Hatton and T. F. Jamison, *J. Am. Chem. Soc.*, **2013**, *135,* 18497-18501.
[7] J. Hu, J. Ma, Q. Zhu, Q. Qian, H. Han, Q. Mei and B. Han, *Green Chem.*, **2016**, *18*, 382-385.
[8] L. Hao, Y. Zhao, B. Yu, Z. Yang, H. Zhang, B. Han, X. Gao and Z. Liu, *ACS Catal.*, **2015**, *5*, 4989-4993.
[9] X. H. Liu, J. G. Ma, Z. Niu, G. M. Yang and P. Cheng, *Angew. Chem. Int. Ed.* , **2015**, *54*, 988-991.
[10] Y. Masuda, N. Ishida and M. Murakami, *J. Am. Chem. Soc.*, **2015**, *137,* 14063-14066.
[11] M. R. Barbachyn and C. W. Ford, *Angew. Chem. Int. Ed.* , **2003**, *42,* 2010-2023.
[12] T. A. M. a. G. D. Wright, *Chem. Rev.*, **2005**, *105,* 529-542.
[13] M. Wang, Q. Song, R. Ma, J. Xie and L. He, *Green Chem.*, **2016**, *18,* 282-287.
[14] D. Teffahi, S. Hocine and C.-J. Li, *Lett. Org. Chem.*, **2012**, *9,* 585-593.
[15] Y. Zhao, J. Qiu, L. Tian, Z. Li, M. Fan and J. Wang, *ACS Sustain. Chem. Eng.*, **2016**, *4*, 5553-5560.
[16] G. P. C. Alessia Bacchi, Mirco Costa, Bartolo Gabriele,Carlo Righib and Giuseppe Salerno, *Chem. Commun.*, **1997**, *16,* 1209-1210.
[17] M. S. a. Y.-M. Shen, *J. Org. Chem.*, **2002**, *67,* 16-21.
[18] H. Jiang and J. Zhao, *Tetrahedron Lett.*, **2009**, *50*, 60-62.
[19] K. Sekine and T. Yamada, *Chem. Soc. Rev.*, **2016**. *45,* 4524-4532
[20] W. Yamada, Y. Sugawara, H.-M. Cheng, T. Ikeno and T. Yamada, *Eur. J. Org. Chem.*, **2007**, *16*, 2604–2607
[21] S. Kikuchi, S. Yoshida, Y. Sugawara, W. Yamada, H.-M. Cheng, K. Fukui, K. Sekine, I. Iwakura, T. Ikeno and T. Yamada, *Bull. Chem. Soc. Jpn.*, **2011**, *84,* 698-717.
[22] S. Yoshida, K. Fukui, S. Kikuchi and T. Yamada, *Chem. Lett.*, **2009**, *38,* 786-787.
[23] Q. W. Song, Z. H. Zhou, H. Yin and L. N. He, *ChemSusChem*, **2015**, *8,* 3967-3972.
[24] T.-a. Mitsudo, Y. Hori, Y. Yamakawa and Y. Watanabe, *Tetrahedron lett.*, **1987**, *28,* 4417-4418.
[25] S. Hase, Y. Kayaki and T. Ikariya, *Organometallics*, **2013**, *32,* 5285-5288.
[26] K.-i. Fujita, K. Inoue, J. Sato, T. Tsuchimoto and H. Yasuda, *Tetrahedron*, **2016**, *72,* 1205-1212.
[27] K.-i. Fujita, J. Sato, K. Inoue, T. Tsuchimoto and H. Yasuda, *Tetrahedron Lett.*, **2014**, *55,* 3013-3016.
[28] M. Costa, G. P. Chiusoli, D. Taffurelli and G. Dalmonego, *J. Chem. Soc.. Perkin trans. I*, **1998**, 1541-1546.
[29] R. Nicholls, S. Kaufhold and B. N. Nguyen, *Catal. Sci. Technol.*, **2014**, *4,* 3458-3462.
[30] K.-i. Fujita, A. Fujii, J. Sato, S.-y. Onozawa and H. Yasuda, *Tetrahedron Lett.*, **2016**, *57,* 1282-1284.
[31] J. Hu, J. Ma, Q. Zhu, Z. Zhang, C. Wu and B. Han, *Angew. Chem. Int. Ed.*, **2015**, *54,* 5399-5403.
[32] D. d. B. Guerra-Neto, L. Ferreira-Pinto, W. M. Giufrida, M. S. Zabaloy, L. Cardozo-Filho and O. Chiavone-Filho, *J. Chem. Eng. Data*, **2014**, *59,* 3319-3323.
[33] A. Khoraamabadi-zad, M. Azadmanesh, R. Karamian, M. Asadbegy and M. Akbari, *RSC Adv.*, **2014**, *4*, 47721-47725.
[34] M.-D. Cheng, A. R. Caparanga, A. N. Soriano and M.-H. Li, *J. Chem. Therm..*, **2010**, *42,* 342-347.
[35] G. T. Rochelle, *Science*, **2009**, *325,* 1652-1654.
[36] C. Chatterjee and A. Sen, *J. Mater. Chem. A*, **2015**, *3*, 5642-5647.
[37] J. E. Rainbolt, P. K. Koech, C. R. Yonker, F. Zheng, D. Main, M. L. Weaver, J. C. Linehan and D. J. Heldebrant, *Energy Environ. Sci.*, **2011**, *4* 480-484.
[38] P. G. Jessop, D. J. Heldebrant, L Xiaowant, C. A. Eckert and C. L. Liotta, *Nature*. **2005**, *436,* 1102-1102
[39] M. J. T. Frisch, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A. et al., *Gaussian 09, Revision D.01*, Wallingford, CT, Gaussian, Inc, **2009**.

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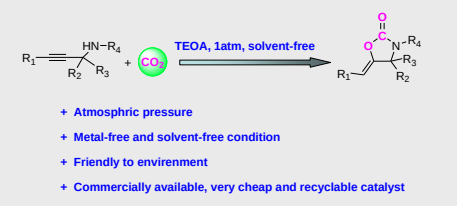

Triethanolamine (TEOA), as a low-cost and biodegradable catalyst, could efficiently promote the conversion of CO_2 with propargylic amine at atmospheric pressure.

*Yuling Zhao, Jikuan Qiu , Zhiyong Li, Huiyong Wang, Maohong Fan, Jianji Wang**

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An Experimental and Theoretical Study on the Unexpected Catalytic Activity of Triethanolamine for the Carboxylative Cyclization of Propargylic Amines with CO_2