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## Cu-histidinyI catalysts for mild and efficient propargylic alcohol carboxylation with CO<sub>2</sub>

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### ABSTRACT

Propargylic alcohol cyclizing carboxylation with CO<sub>2</sub> at atmospheric pressure was catalyzed by a nanocluster, Cu(I)<sub>4</sub>(histidinyI)<sub>4</sub>Ga(I)I. excess His, abbreviated Cu-Ga, at 50 °C, providing α-alkylidene cyclic carbonates in good yields. The nanocluster Cu-Ga supported in ZIF-8, noted Cu-Ga/ZIF-8, heterogeneously catalyzed this cyclizing carboxylation of various terminal propargyl alcohols and was recycled five time without significant yield decrease.

### 1. Introduction

Given the essential role of Cu-histidine in all forms of life involving breathing [1] and as a therapeutic agent [2], we have envisaged searching the role of this well-known metal-ligand system as catalyst in key transformations. Here, we present preliminary results on the catalysis of CO<sub>2</sub> activation, an area that has been of considerable interest in this century [3–5].

Among the various recent CO<sub>2</sub> conversion approaches [3–7], its transformation to α-alkyl cyclic carbonates using propargylic alcohols has garnered much interest [8–13], as these cyclic carbonates serve as precursors toward various applications in organic synthesis, pesticides, agricultural products, and pharmaceutical industry [14]. Notably, bi-component catalysts containing both a base and a copper catalyst, such as Cu/DIPEA, have been reported to be particularly effective for this

transformation [15]. For recycling purpose, Metal-Organic Frameworks (MOFs) [13,16] and Covalent Organic Frameworks (COFs) are most often utilized [17] in metal catalysts, and Cu(I)-based MOFs have a notable proficiency in this reaction [18–24]. For instance, Zhao *et al.* introduced an effective [Cu<sub>4</sub>L<sub>4</sub>]-based MOF that catalyzed the cyclization of propargylic alcohols with CO<sub>2</sub> under mild conditions with the high turnover number (TON) of 14400 [13].

### 2. Results and discussion

In the present work, we report cyclizing carboxylation of propargyl alcohols in high yield and 5-time recycling without significant yield decrease with a catalyst, Cu-Ga/ZIF-8. First, the Cu-Ga catalyst was prepared by mixing CuI, GaBr<sub>3</sub>, and excess L-histidine (His) and triethylamine (TEA) and heating at 100 °C for 1 day under N<sub>2</sub>, then the

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<sup>1</sup> Both authors (YL and TW) contributed equally to this work.

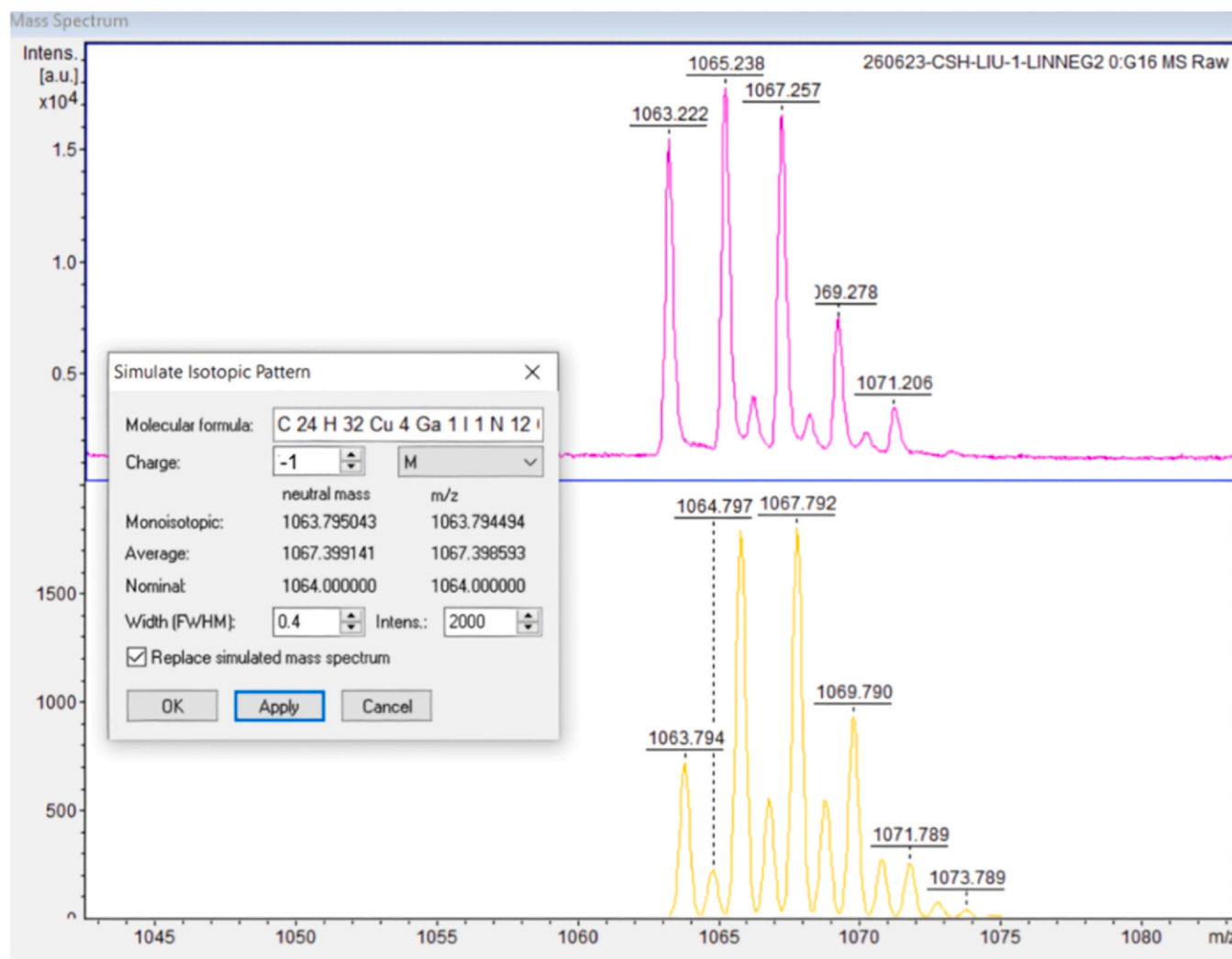


Fig. 1. Experimental (top) and simulated (bottom) isotopic pattern of  $\text{Cu}_4(\text{Histidinyl})_4\text{GaI}$ . For  $\text{Cu}_4(\text{His})_3\text{GaI}$  and  $\text{Cu}_4(\text{His})_3$ , see Figs. S1 and S2, respectively.

resulting mixture was washed with MeCN and dried providing a grey-blue solid, followed by support onto ZIF-8 by wet impregnation (see the Supporting Information, SI, page 2).

**MALDI-TOF mass spectrometry** of Cu-Ga provides three major sets of signal containing, each, essentially five isotopic distribution peaks separated by two units, due to the large abundance of two isotopes of copper,  $^{61}\text{Cu}$  and  $^{63}\text{Cu}$  and two isotopes of gallium,  $^{69}\text{Ga}$  and  $^{71}\text{Ga}$ . The “mother” peaks appear to be those of  $\text{Cu}_4(\text{histidinyl})_4\text{GaI}$  at 1063, 1065, 1067, 1069 and 1071 (Fig. 1).

In this MALDI TOF mass spectrum of Cu-Ga (Fig. 1 and S1-S3), there is also mostly a series of dominant peaks corresponding to  $\text{Cu}_4(\text{His})_3\text{GaI}$  at 913, 915, 917, 919 and 921, and a third series of peaks corresponding to  $\text{Cu}_4(\text{His})_3$  at 717, 719, 721, 723 and 725. The two latter sets of peaks seem to result from fragmentation of the “mother” species, then, rearrangement.

**Compared infrared spectra of histidine and Cu-Ga** (Fig. S4) indicating the prominent carboxylate stretching vibrations signals near  $1630\text{--}1560$  and  $1445\text{--}1340\text{ cm}^{-1}$ , which confirms the presence of the carboxylate group of the histidinyl ligands for  $\text{Cu}^{\text{I}}$  and  $\text{Ga}^{\text{I}}$ , and elemental analysis shows the presence of a large excess His (Table S1).

**$^1\text{H}$  NMR spectroscopy** of both solids, synthesized in the absence and presence of Ga (Fig. S5), showed that Cu and Ga do not perturb the diamagnetism, arguing for a catalyst formula with diamagnetic  $\text{Cu}^{\text{I}}$  and  $\text{Ga}^{\text{I}}$ . This oxidation state I for both metals is found in the XPS spectra. The corresponding high resolution narrow-range XPS analysis is shown in Fig. 2a-d for the constituent elements Cu, I, Ga, and O, respectively, and a full range XPS survey of Cu-Ga/ZIF-8 is presented in Fig. S7 and Table S2.

**XPS.** The narrow range of binding energy of Cu 2p in Fig. 2a clearly indicates two bands at 952.4 and 932.7 eV, reflecting the respective  $2p_{1/2}$  and  $2p_{3/2}$  orbitals. The lack of discernible signal at the asterisk shows that Cu exists in the form of  $\text{Cu}^{\text{I}}$ . Ga exists in the form of  $\text{Ga}^{\text{I}}$  and  $\text{Ga}^{\text{III}}$ ,  $\text{Ga}^{\text{I}}$  being dominant, as observed at 18.1 and 19.9 eV (Fig. 2c), respectively.  $\text{Ga}^{\text{I}}$  is apparently formed during cluster synthesis upon  $\text{Ga}^{\text{III}}$  reduction by  $\text{NET}_3$  facilitated by the high reaction temperature. As shown in Fig. 2(d), the XPS analysis of various O species is based on the peak deconvolution and comparison with the observed binding energies with standard reference. The O 1s spectrum is typically composed of multiple overlapping peaks corresponding to different oxygen species.

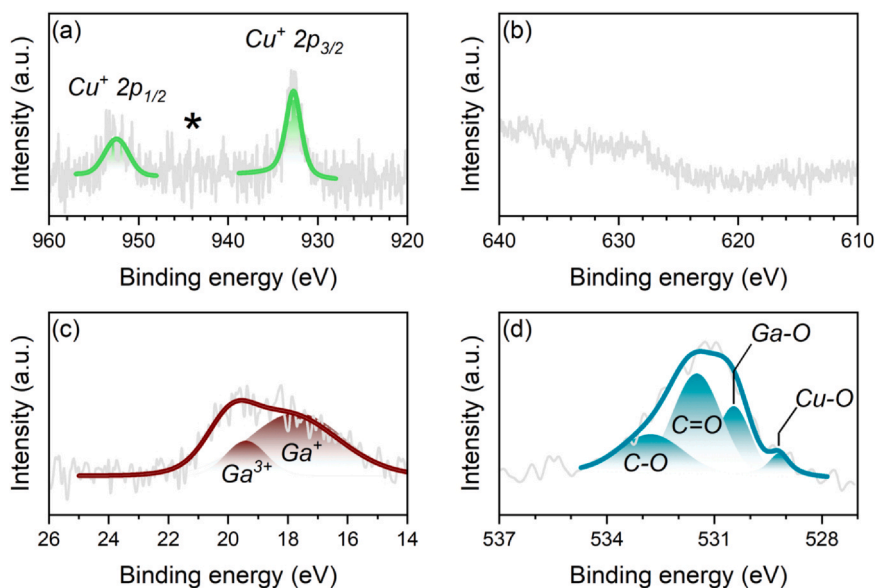


Fig. 2. XPS analysis of Cu(a), I(b), Ga(c) and O(d) of Cu-Ga/ZIF-8.

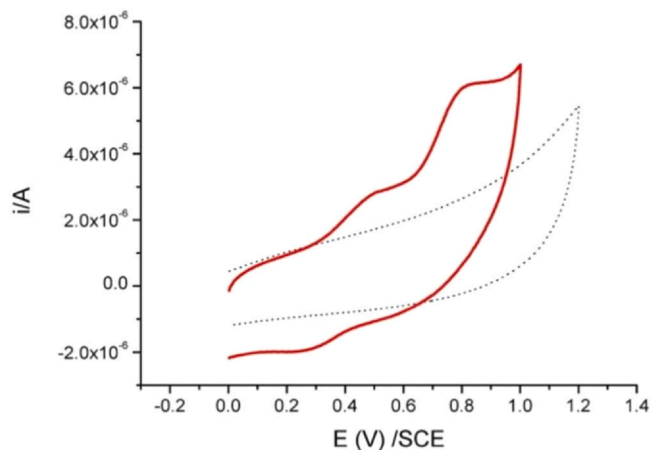


Fig. 3. Cyclic voltammogram of the cluster Cu-Ga in DMF with  $n\text{-Bu}_4\text{NBF}_4$  0.1 M as a supporting electrolyte at a scan rate of 0.1 V/s on a glassy carbon electrode.

Deconvolution of the spectrum using curve-fitting software allows separation of these peaks. Each peak represents a specific chemical environment of oxygen. By comparison with the observed binding energies with standard reference, for example, C-O appears around 532.8 eV, corresponding to oxygen bonded to carbon in hydroxyl or ether groups. The attribution for the O 1s component at 530.5 eV is in line with Ga-O as confirmed in relevant reference below Fig. S8.

The most notable features exhibited by the XPS analysis of the recycled catalyst (Fig. S8) are threefold. First, the emergence of a Zn-O coordination component that has a larger binding energy (1023.15 eV) than that of the Zn (II) found in ZIF-8 (1021.70 eV). This specific oxygen-coordinated Zn(II) is possibly due to the electronegativity of the oxygen present in several oxygen functional groups found in the

catalyst. Combined with the STEM-EDX analysis (Fig. S9), this interaction might induce morphological changes in the ZIF-8 structure. Second, the emergence of a satellite peak near the Cu  $2p_{1/2}$  region is attributable to a high coordination state of the Cu(I) ions. Third, the retention of the Ga-O component, which can be found in the O 1s spectrum. Relevant references are added under Fig. S8.

**Cyclic voltammetry** (Fig. 3) shows, upon anodic scanning, a quasi-reversible wave near 0.55 V system with a return cathodic wave near 0.3 V, the large, the scan-rate-dependant potential difference (0.25 V) between the oxidation and reduction waves being indicative of a slow electron transfer witnessing structural rearrangement (distortion) of a Cu cluster during anodic oxidation, yet showing stability of the oxidized cluster, at least at the electrochemical timescale (approx. 2 s). This type of behavior is characteristic of a late transition-metal cluster [25,26]. A second oxidation wave at  $E_p = 0.9$  V, irreversible could be assigned either to  $\text{Cu}_4$  or to Ga.

Altogether, the spectrometric observations converge to five monovalent metal atoms (4  $\text{Cu}^I$  and 1  $\text{Ga}^I$ ), four anionic histidyl ligands bonded to the metals through the carboxylate group, and one iodide ligand in the main structural motif. The structure most probably involves a tetrahedron of  $\text{Cu}^I$ , with histidyl ligands, either terminal or bridging Cu atoms in a more or less distorted cube, the cubic structure of  $(\text{Cu}^I)_4$ -derived MOFs being known [13]. It is difficult to anticipate the exact ligand coordination mode (chelation or bridging of one or more metals). Indeed, for instance, His is known to bind Cu through its imidazole, amino and carboxylate groups [27], though in the present case carboxylate binding the  $\text{Cu}^I$  centers appears obvious. On the other hand, the  $\text{Ga}^I$  atom seems to be linked to the  $\text{Cu}_4$  cluster via histidine ligand bridging and should ensure inter-cluster linkage. Additional His molecules give rise to weak coordination presumably resulting in the formation of a larger ensemble in a Cu-Ga nanoparticle (NP).

**HRTEM analysis** shows discernible rhombic dodecahedra morphology of ZIF-8 particles with an average size of 1.24  $\mu\text{m}$  as well as supported NPs with an average size of 3.69 nm (Fig. 4a, b). In Fig. 4a,

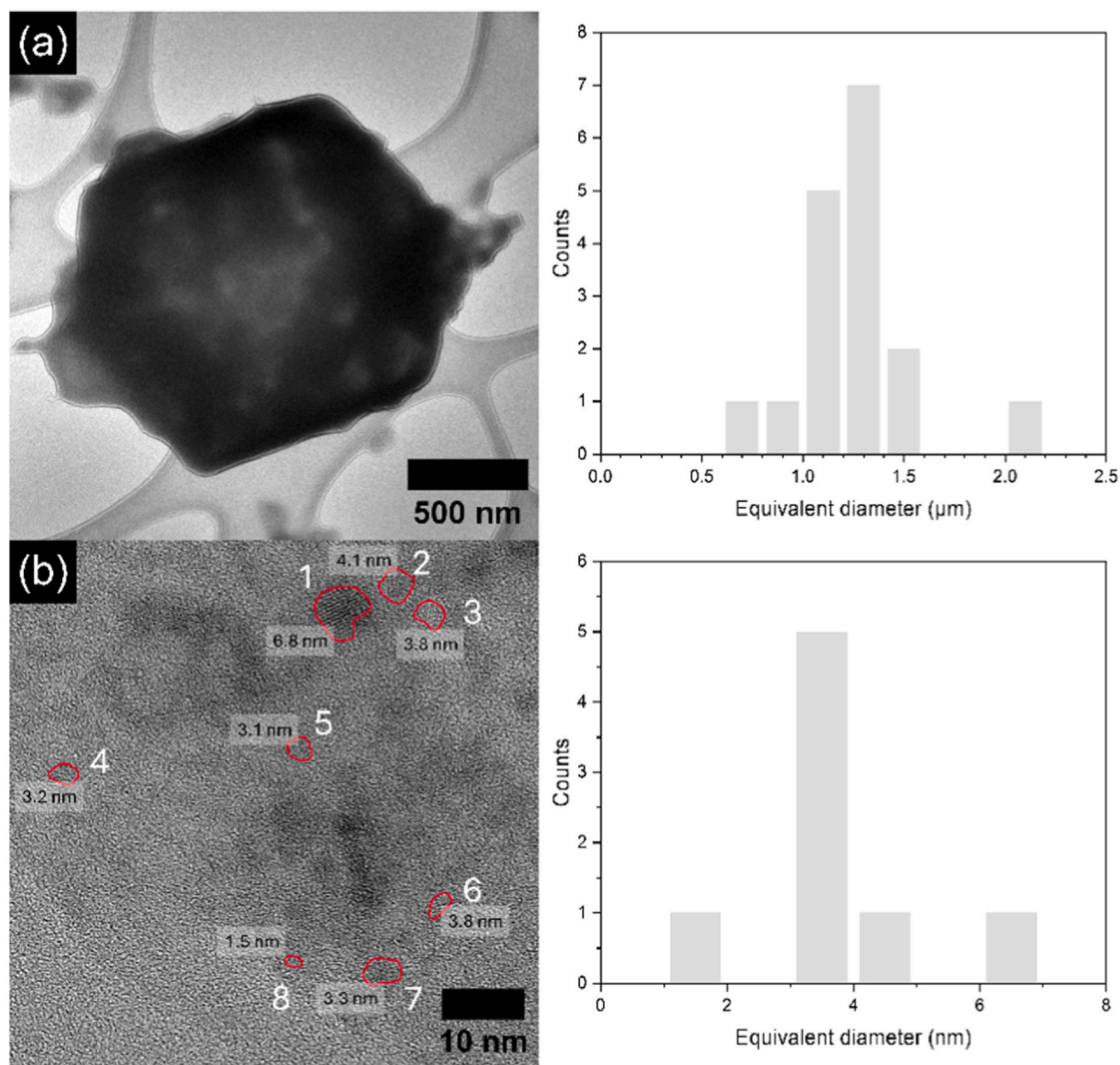


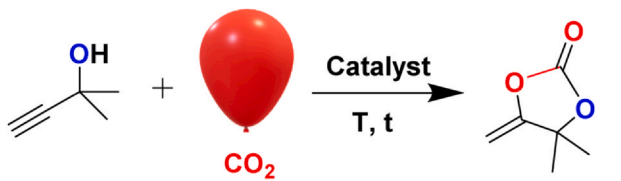
Fig. 4. TEM (a) and HRTEM (b) of Cu-Ga/ZIF-8 with corresponding size distributions of ZIF-8 particles and Cu-Ga clusters.

the morphology of ZIF-8 appears with relatively uniform and well-dispersed Cu-Ga clusters, in the darker-tone zone, encapsulated by the ZIF-8 shell. Additionally, in the HRTEM results (Fig. 4b), single crystalline grains were observed in several zones, facilitating estimates of lattice interplanar separation,  $d_{hkl}$ . Identified grains, number-labelled in Fig. 4b, exhibit a distribution of values within 1.16–2.97 Å.

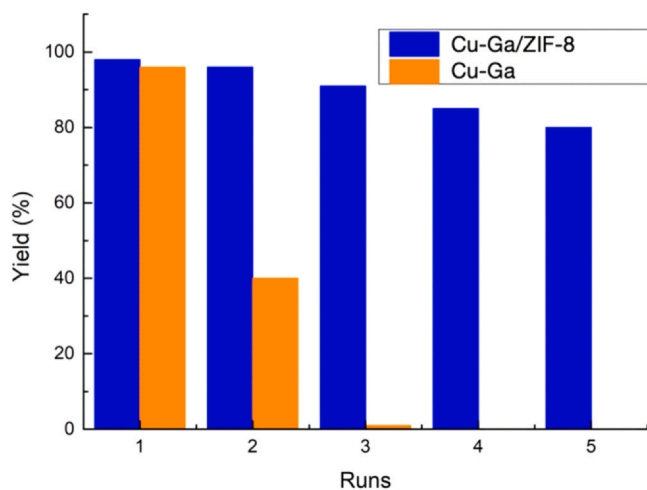
**Carboxylic cyclization of propargylic alcohols** was catalyzed by Cu-Ga/ZIF-8 using excess histidine and triethylamine (TEA) under 1 atm  $\text{CO}_2$  at 50 °C for 10 h. In order to optimize reaction conditions, 2-methyl-3-butyn-2-ol was chosen as the model substrate, the results are shown in Table 1. In the presence of either CuI, GaBr<sub>3</sub> or His as the catalyst, only trace of the product  $\alpha$ -alkylidene cyclic carbonates was obtained (Table 1, entries 1–5). In contrast, Cu-Ga/ZIF-8 showed

excellent catalytic activity, and the yield of the target product was 94 % at 80 °C (Table 1, entry 6), indicating that Cu-Ga/ZIF-8 exhibited highly efficient catalytic activity in carboxylic cyclization of propargylic alcohols. Then, the influence of temperature on carboxylic cyclization was examined upon temperature variation (Table 1, entries 6–8). The yield increased from 94 % to 98 % when the temperature decreased from 80 °C to 50 °C. Further decrease of the temperature from 50 °C to 40 °C led to yield decrease from 98 % to 87 %, indicating that 50 °C was the optimum reaction temperature. In addition, different reaction times were also examined (Table 1, entry 9 and 10), and the optimum reaction time was 12 h.

From Table 1, entry 1, it appears that catalysis of propargyl carboxylation is not working if only CuI is utilized as catalyst, and entries 6–12 show that catalysis is efficient if a Lewis acid is added as a

**Table 1**Control experiments of carboxylic cyclization of propargylic alcohols with CO<sub>2</sub>.<sup>a</sup>


Entry	Catalyst	T (°C)	t (h)	Yield (%) <sup>b</sup>
1	CuI	80	12	< 1
2	GaBr <sub>3</sub>	80	12	< 1
3	His	80	12	< 1
4	CuI + His	80	12	< 1
5	GaBr <sub>3</sub> + His	80	12	< 1
6	Cu-Ga/ZIF-8	80	12	94
7	Cu-Ga/ZIF-8	50	12	98
8	Cu-Ga/ZIF-8	40	12	87
9	Cu-Ga/ZIF-8	50	10	96
10	Cu-Ga/ZIF-8	50	3	28
11	Cu-Ga	50	12	96
12	CuI/ZIF-8	50	12	84

<sup>a</sup> Reaction conditions: 1 mmol substrate, 0.05 mmol catalyst Cu-Ga/ZIF-8, 1 bar CO<sub>2</sub>, 1 mL TEA.<sup>b</sup> The yields were determined by <sup>1</sup>H NMR with 1,1,2,2-tetrachloroethane as the internal standard.**Fig. 5.** Recyclability of Cu-Ga/ZIF-8 (Reaction conditions: 1 mmol substrate (2-methyl-3-butyn-2-ol), 0.05 mmol catalyst, 1 atm CO<sub>2</sub> balloon, 1 mL TEA).

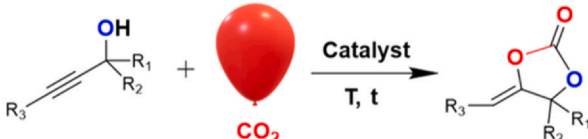
co-catalyst. Indeed, deprotonation of propargyl alcohol by the base is too difficult, if it is not assisted by a Lewis acid that activates the oxygen atom of propargyl alcohol. Binding of this oxygen atom by the Lewis acid provides it an oxonium character, rendering the propargyl alcohol easily deprotonated by the base for further continuation of the catalytic cycle (Scheme S1). Entries 11 and 12 of Table 1 show that either GaBr<sub>3</sub> or ZIF-8 can be efficiently used as co-catalyst, with a

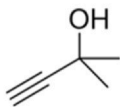
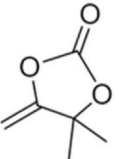
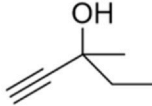
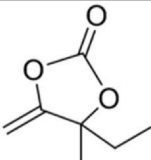
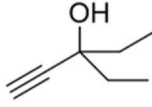
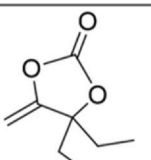
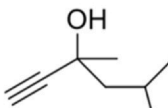
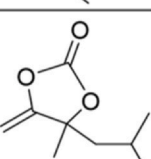
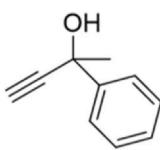
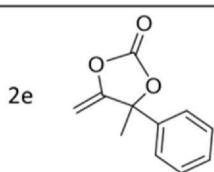
slight advantage for GaBr<sub>3</sub> (96 % yield of the targeted  $\alpha$ -alkylidene cyclic carbonate.) over ZIF-8 (84 % yield) under the same conditions (60 °C, 12 h). Entry 7 shows that the cumulative use of both of these Lewis acids in the same reaction as co-catalysts in addition to the Cu catalyst under these conditions leads to an even better yield of 98 %. Thus, there appears to be a possible synergistic effect between these catalyst components. The main advantage of the utilization of ZIF-8, however, in addition to this possible synergy, is that it immobilizes the catalyst, which affords an excellent recycling, whereas recycling of the Cu-Ga catalyst is poor in the absence of ZIF-8 (vide infra, Fig. 5). Actually, the use of the group 13 Lewis acids is quite prevalent [28], as well known with AlCl<sub>3</sub> for Friedel-Crafts reactions, by also with GaX<sub>3</sub> and InX<sub>3</sub>. For instance, Ga(OTf)<sub>3</sub> with Au as co-catalyst is commonly employed in processes like tandem intramolecular acetylene amination and inverse electron-demand Diels-Alder reactions [29,30]. In(OTf)<sub>3</sub> can promote the hydroalkylation [31], and in another report, cycloisomerization by Au-In(OTf)<sub>3</sub> reaches a quantitative yield in just 20 min, compared to AgOTf [32]. Lewis acids, like those based on Ga or In compounds, act as  $\pi$ -acids and can occasionally catalyze alkyne functionalization reactions independently [33,34]. Concerning the carboxylation of propargylic alcohols, Zhao's work stressed the use of In (III) as Lewis acid [13].

Encouraged by the efficient catalytic activity of Cu-Ga/ZIF-8 in CO<sub>2</sub> fixation of 2-methyl-3-butyn-2-ol, the generalization of the carboxylic cyclization of propargylic alcohols was further explored using several typical terminal propargylic alcohols with various substituents under the optimized reaction conditions, and the yields of the target products and the value of TOF and TON are summarized in Table 2. Delightfully, terminal propargylic alcohols with methyl, ethyl, isopropyl, tert-butyl, and phenyl substituents could efficiently generate corresponding product  $\alpha$ -alkylidene cyclic carbonates (Tables 2, 2a-2d) in high yields. The terminal propargylic alcohols with phenyl substituents (Tables 2, 1d) underwent the cyclization reaction with the double amount of Cu-Ga/ZIF-8 catalyst, resulting in rather low TON and TOF, because the steric hindrance partly inhibits the progress of the formation of the carboxylic cycles. In sum, the highest TOF value of Cu-Ga/ZIF-8 is 8.16, which is competitive among typical reported catalysts (Table S3).

**Recyclability of Cu-Ga/ZIF-8.** In order to investigate the recyclability of Cu-Ga/ZIF-8, this heterogeneous catalyst was collected after 12 h of reaction with 2-methyl-3-butyn-2-ol and re-used with the same model catalysis system for another 12 h. Cu-Ga without ZIF-8 and Cu-Ga/ZIF-8 were compared, and the data are gathered in Fig. 5. The Cu-Ga/ZIF-8 catalyst maintained its catalytic activity in the carboxylic cyclization of propargylic alcohols, showing minimal reduction even after five re-use cycles. In contrast, Cu-Ga without ZIF-8 faltered after just 3 runs, resulting in a dramatic decrease in yield to trace. This suggests that the Cu-Ga catalyst combined with ZIF-8 offers considerably greater stability than its counterpart without ZIF-8.

Based on the aforementioned results and information from the literature [13,22,28], the reaction mechanism with Cu-Ga/ZIF-8 as the catalyst appears to comprise both Cu<sup>I</sup> centers for alkyne activation and Ga<sup>I</sup> or Zn<sup>II</sup> Lewis acid site to facilitate the alcohol deprotonation by TEA (Scheme S1). The exact form of active Cu<sup>I</sup> must await further studies, however, because various Cu<sup>I</sup>-histidine or Cu<sup>I</sup>-histidiny species could be catalytically active.

**Table 2**Substrate scope for the carboxylic cyclization of propargylic alcohols with CO<sub>2</sub> catalyzed by Cu-Ga/ZIF-8.<sup>[a]</sup>


Substrate	Product	Yield(%) <sup>[b]</sup>	TON	TOF/h <sup>-1</sup>
1a 	2a 	98%	98	8.16
1b 	2b 	93%	93	7.75
1c 	2c 	94%	94	7.83
1d 	2d 	94%	94	7.83
1e 	2e 	80% <sup>[c]</sup>	40	3.33

[a] Reaction conditions: 1 mmol substrate, 0.05 mmol catalyst Cu-Ga/ZIF-8, 1 atm CO<sub>2</sub> balloon, 1 mL TEA. [b] The yields were determined by <sup>1</sup>H NMR with 1,1,2,2-tetrachloroethane as the internal standard. [c] Reaction conditions: 1 mmol substrate, 0.1 mmol catalyst, 1 atm CO<sub>2</sub> balloon, 1 mL TEA.

### 3. Conclusion

A new Cu-Ga/ZIF-8 heterogeneous catalyst was synthesized by mixing CuI, GaBr<sub>3</sub> and excess TEA and His at 100 °C, then adsorbing the catalyst inside ZIF-8 (as shown by TEM). XPS shows the presence of Cu<sup>I</sup> and Ga<sup>I</sup>, the latter resulting from the reduction of Ga<sup>III</sup>Br<sub>3</sub> by TEA at 100 °C, and <sup>1</sup>H NMR of Cu-Ga is consistent with a diamagnetic compound containing both Cu<sup>I</sup> and Ga<sup>I</sup>. The MALDI TOF mass spectrum of Cu-Ga shows a molecular peak corresponding to Cu<sub>4</sub>(histidinyI)<sub>4</sub>GaI and the IR confirms the presence of carboxylate ligands. The catalyst Cu-Ga/ZIF-8 forms a supramolecular 3-nm sized NPs, from TEM and HRTEM, including excess His, the role which in the catalysis will be examined in future studies.

The Cu-Ga catalyst exhibits high efficiency to convert CO<sub>2</sub> to α-alkylidene cyclic carbonate with propargylic alcohols at atmospheric pressure, with poor recyclability. On the other hand, when Cu-Ga is adsorbed inside ZIF-8, high yields and excellent recycling are obtained with the heterogeneous catalyst Cu-Ga/ZIF-8, and the reaction is extended with good yields to various terminal propargylic alcohols under mild conditions.

### CRediT authorship contribution statement

**Yue Liu:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Tiansheng Wang:** Writing – original draft, Validation, Methodology, Investigation, Formal analysis. **Guilherme Mateus Bousada:** Methodology, Investigation, Formal analysis. **Lionel Salmon:** Methodology, Formal analysis, Data curation. **Ahmed Subrati:** Writing – original draft, Validation, Software, Methodology, Investigation, Formal analysis. **Sergio Moya:** Writing – original draft, Methodology, Investigation, Funding acquisition. **Nathalie Daro:** Software, Investigation, Formal analysis, Data curation. **Philippe Hapiot:** Methodology, Investigation, Formal analysis, Data curation. **Jean-Luc Pozzo:** Validation, Methodology, Funding acquisition. **Haizhu Yu:** Writing – original draft, Validation, Funding acquisition. **Jean-René Hamon:** Writing – review & editing, Validation, Supervision, Project administration, Methodology, Funding acquisition. **Didier Astruc:** Writing – review & editing, Writing – original draft, Validation, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization..

## Data availability

Data will be made available on request.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Supplementary information

General data, syntheses of the catalysts, catalytic reactions,  $^1\text{H}$  and  $^{13}\text{C}$  NMR, IR, MALDI TOF and XPS spectra and data, elemental analysis of the catalysts, compared catalytic activity with those of reported catalysts, proposed catalytic mechanism, and  $^1\text{H}$  and  $^{13}\text{C}$  NMR of the carboxylation products,

## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.cocr.2025.100005](https://doi.org/10.1016/j.cocr.2025.100005).

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