



Article

Multifunctional Biomass-Based Ionic Liquids/CuCl-Catalyzed CO₂-Promoted Hydration of Propargylic Alcohols: A Green Synthesis of α -Hydroxy Ketones

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Abstract: α -Hydroxy ketones are a class of vital organic skeletons that generally exist in a variety of natural products and high-value chemicals. However, the traditional synthetic route for their production involves toxic Hg salts and corrosive H₂SO₄ as catalysts, resulting in harsh conditions and the undesired side reaction of Meyer–Schuster rearrangement. In this study, CO₂-promoted hydration of propargylic alcohols was achieved for the synthesis of various α -hydroxy ketones. Notably, this process was catalyzed using an environmentally friendly and cost-effective biomass-based ionic liquids/CuCl system, which effectively eliminated the side reaction. The ionic liquids utilized in this system are derived from natural biomass materials, which exhibited recyclability and catalytic activity under 1 bar of CO₂ pressure without volatile organic solvents or additives. Evaluation of the green metrics revealed the superiority of this CuCl/ionic liquid system in terms of environmental sustainability. Further mechanistic investigation attributed the excellent performance to the ionic liquid component, which exhibited multifunctionality in activating substrates, CO₂ and the Cu component.

Keywords: ionic liquid; CO₂; biomass; catalysis; α -hydroxy ketones



Citation: Yuan, Y.; Zhang, S.; Duan, K.; Xu, Y.; Guo, K.; Chen, C.; Chaemchuen, S.; Cao, D.; Verpoort, F. Multifunctional Biomass-Based Ionic Liquids/CuCl-Catalyzed CO₂-Promoted Hydration of Propargylic Alcohols: A Green Synthesis of α -Hydroxy Ketones. *Int. J. Mol. Sci.* **2024**, *25*, 1937. <https://doi.org/10.3390/ijms25031937>

Academic Editor: Ilya Nifant'ev

Received: 2 January 2024

Revised: 31 January 2024

Accepted: 3 February 2024

Published: 5 February 2024



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1. Introduction

Nowadays, the excessive emission of CO₂ has led to a range of environmental and social problems such as global warming, glaciers melting and sea levels rising [1–4]. As a result, the effective and efficient management of CO₂ has become an urgent concern for scientists and engineers. From the perspective of synthetic chemistry, CO₂ is regarded as an ideal substitute for traditional phosgene and carbon monoxide [5–8] due to its wide availability, low cost, easy accessibility, non-toxicity and environmental friendliness [9]. This has prompted the exploration of CO₂ for the production of fine chemicals, as it holds the potential to not only create economic value but also mitigate the greenhouse effect [10]. However, due to the thermodynamic stability and kinetic inertness of CO₂, its effective activation still remains a significant challenge. Consequently, the exploration of effective catalysts for CO₂ activation and the designation of feasible reaction routes for CO₂ conversion have accordingly emerged as critical focal points in the pursuit of CO₂ utilization.

In recent years, considerable progress has been achieved in this area [11–19], including effective routes for utilizing CO₂ in the production of methyl urea, urea, salicylic acid,

organic carbonate, methanol, polycarbonate, etc. Among them, α -hydroxy ketones are crucial organic skeletons that generally exist in a variety of natural products and are frequently used as synthetic precursors for high-value chemicals [20,21]. The hydration of propargyl alcohols was an ideal method for the production of α -hydroxy ketones due to its 100% atom economy and the accessibility of diverse starting materials. However, the direct hydration of propargyl alcohols typically required catalysts involving strong acids like H_2SO_4 [22,23] and rare, toxic metal salts such as Au [24–34], Ag [35–40] and Ru [41], which resulted in harsh conditions and the undesired side reaction of the Meyer–Schuster rearrangement [42]. Based on this, the indirect hydration of propargyl alcohols has emerged, in which the cyclization of CO_2 and propargyl alcohols firstly occurred to obtain the α -alkylidene cyclic carbonates, followed by an in situ hydration of these carbonates to give the desired α -hydroxy ketones [43]. This CO_2 -promoted indirect hydration generally proceeded under basic conditions, thus eliminating the Meyer–Schuster rearrangement in essence. Moreover, the reaction conditions were relatively milder than those for the direct process and thus have attracted great attention from researchers and engineers.

Over the past decade, numerous catalysts have been investigated for this CO_2 -promoted indirect hydration. In 2014, Jiang et al. introduced a $\text{AgOAc}/1,8\text{-diazabicyclo}[5.4.0]\text{undec-7-ene}$ (DBU) system, which successfully catalyzed this CO_2 -promoted hydration of internal and terminal propargyl alcohols, yielding the target products in high yield [44]. However, this system necessitated a high loading of Ag salts, traditional volatile solvents and strong bases. Moreover, its working pressure reached 20 bar of CO_2 . In 2015, Liu et al. presented a range of task-specific ionic liquids (ILs) for this hydration, operating effectively under 1 to 10 bar of pressure and offering a recycling and reusing ability [45]. In 2019, He et al. developed a $\text{Cu}_2\text{O}/\text{DBU}$ catalytic system composed of Cu_2O (20 mol%), DBU (50 mol%) and phosphine ligands (20 mol%), which efficiently converted various types of terminal propargyl alcohols into the corresponding target products in CH_3CN under 1 bar of CO_2 [46]. In 2020, Yuan et al. developed a AgOAc/ILs system for this reaction, which operated under atmospheric CO_2 pressure and solvent-free conditions to produce α -hydroxy ketones [47]. Furthermore, they established a Zn-based catalytic system that exhibited excellent catalytic activity for the target reaction under simulated flue gases, with the Zn species generated from pigment wastes [48]. More recently, two heterogeneous catalysts, namely a silver-anchored porous aromatic framework catalyst (Ag@PAF-DAB) and an amino-functionalized organic polymer Cu@Co-PIL-N4 loaded with highly dispersed CuI , have also been reported [49,50].

In the context of the aforementioned work, IL-involved systems have emerged as pivotal roles. ILs are composed of anions and cations with melting points below 100°C , which have been widely applied in CO_2 capture and catalytic conversion due to their advantages of designability, stability and catalytic activity [51]. However, the utilization of ILs for the CO_2 -promoted hydration of propargyl alcohols remains relatively uncommon and costly to date. Furthermore, some IL catalysts still required elevated CO_2 pressure to reach high activity, which largely limited their further applications.

Biomass compounds are natural organic substances such as cellulose, wood chips and fructose. Nowadays, these materials have been utilized in numerous emerging areas due to their greenness, abundance, renewability, etc. [52,53]. These compounds can be further disassembled into biomass-based platform compounds [54,55], such as the 12 biomass molecules of succinic acid, 2,5-furan dicarboxylic acid, 3-hydroxypropionic acid, itaconic acid and levulinic acid, proposed by the US Department of Energy [56]. These derived compounds typically contain carboxylic or hydroxyl groups, indicating their great potential for ionization and application as the anions of ILs. Importantly, ILs containing carboxylic or hydroxyl ions have been proven to exhibit significant interaction with CO_2 molecules [57]. As a result, the biomass-based ILs have the potential to demonstrate catalytic activity for CO_2 capture and activation. In addition, these ILs are derived from biomass, which indicates their economical, renewable and eco-friendly nature, aligning with the requirements of modern green and sustainable development.

Herein, a series of biomass-based ILs were designed and synthesized, which were further combined with the economical CuCl for the catalysis of the CO₂-promoted hydration reaction of propargyl alcohols. Particularly, this catalytic system worked under 0.1 MPa of CO₂ with a low metal loading of CuCl (1 mol%) without any traditional organic solvents or ligands. Further evaluation of the green metrics revealed the superiority of this CuCl/IL system in terms of environmental sustainability.

2. Results

In this section, the catalytic performance of various biomass-based ILs for the CO₂-promoted reaction was investigated, with the employment of 2-methyl-3-butyn-2-ol (**1a**) as the initial substrate (Table 1). The screening of ILs commenced with the blank experiments, demonstrating that the reaction could not proceed without catalysts (entry 1). Subsequently, it was observed that neither the metal salts nor the ILs alone could catalyze the target reaction (entries 2, 3). Notably, the absence of CO₂ hindered the target reaction, indicating the crucial role of CO₂ (entry 4). After the blank experiments, the investigation of the catalytic activity of different ILs was performed with the metal salt component fixed as CuCl. The screening was initially focused on the optimization of various anions (Figure 1), derived from levulinic acid (Lev), lactic acid (La), itaconic acid (ITa) and succinic acid (Sa). Experimental results revealed that [Lev] obtained the highest yield (entries 5–8), which was consequently identified as the optimal anion. Subsequently, the effects of cations (Figure 1) on the activity of ILs were explored, with the catalytic performance order revealed as [C₂C₁im] > [N₄₄₄₄] > [P₄₄₄₄] > [C₄C₁im] > [DBUH] > [DBNH] (entries 5, 9–13). The slight difference between [C₂C₁im] and [C₄C₁im] cations in catalytic activity can be attributed to the physical properties of the corresponding ILs. Generally, [C₄C₁im][Lev] exhibited higher viscosity than [C₂C₁im][Lev], resulting in a thicker reaction system that was more difficult to blend and stir. Consequently, the best choice of ILs was identified as [C₂C₁im][Lev]. With the optimal IL in hand, the metal salts in the catalytic system were further explored, which was mainly focused on economical Cu salts due to their inherent affinity to triple bonds, such as CuCl, CuBr, CuI, Cu₂O, Cu₂S, CuCl₂, Cu(OAc)₂, and CuSO₄ (entries 13–20). It was found that both Cu (I) and Cu (II) salts exhibited considerable catalytic activity towards the target reaction, with CuCl achieving the highest yield of 95% (entry 13). Consequently, the optimal catalytic system was determined as CuCl/[C₂C₁im][Lev].

After identifying the optimal catalytic system as CuCl/[C₂C₁im][Lev], the reaction conditions were subsequently explored (Table 2). The amount of [C₂C₁im][Lev] was gradually increased from 0.5 to 1 equiv., resulting in the highest yield of 95% (entries 1–3). A similar trend was observed for the amount of CuCl, with the yields increasing as the amount of CuCl rose from 0.25 to 1 mol%. (entries 3–6). Subsequent investigations focused on the reaction temperature. An increase in reaction temperature from 40 to 80 °C significantly improved the catalytic yield from 5% to 95%. However, at a higher temperature of 100 °C, the reaction could not proceed further, leading to the identification of 80 °C as the optimal temperature (entries 3, 7–9). Furthermore, the influence of reaction time was investigated, and the yield increased gradually as the reaction time extended (entries 3, 10–12). At a reaction time of 12 h, the yield of the product reached 95% (entry 3). Since the target reaction proceeded smoothly under 1 bar of CO₂, experiments for higher pressure were not performed. Consequently, the final reaction conditions were determined as CuCl (1 mol%), [C₂C₁im][Lev] (1 equiv.), 80 °C, CO₂ (0.1 MPa) and 12 h.

Table 1. Screening of catalytic systems ^a.

$$\text{1a} + \text{H}_2\text{O} \xrightarrow[\text{CO}_2 (0.1 \text{ MPa})]{\text{metal salts /ILs}} \text{2a}$$

Entry	Metal Salt	IL	Yield (%) ^b
1	- ^c	- ^d	0
2	CuCl	- ^d	0
3	- ^c	[C ₂ C ₁ im][Lev]	0
4 ^e	CuCl	[C ₂ C ₁ im][Lev]	0
5	CuCl	[N ₄₄₄₄][Lev]	94
6	CuCl	[N ₄₄₄₄] ₂ [ITa]	80
7	CuCl	[N ₄₄₄₄] ₂ [Sa]	88
8	CuCl	[N ₄₄₄₄][La]	74
9	CuCl	[P ₄₄₄₄][Lev]	87
10	CuCl	[DBUH][Lev]	75
11	CuCl	[DBNH][Lev]	47
12	CuCl	[C ₄ C ₁ im][Lev]	85
13	CuCl	[C ₂ C ₁ im][Lev]	95
14	CuBr	[C ₂ C ₁ im][Lev]	89
15	CuI	[C ₂ C ₁ im][Lev]	66
16	Cu ₂ O	[C ₂ C ₁ im][Lev]	86
17	Cu ₂ S	[C ₂ C ₁ im][Lev]	72
18	CuCl ₂	[C ₂ C ₁ im][Lev]	67
19	Cu(OAc) ₂	[C ₂ C ₁ im][Lev]	80
20	CuSO ₄	[C ₂ C ₁ im][Lev]	73

^a Conditions: metal salt (1 mol%), **1a** (2.5 mmol), H₂O (5 mmol), ILs (2.5 mmol), 80 °C, CO₂ (0.1 MPa), 12 h; ^b yields were determined via ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard; ^c without metal salt; ^d without IL; ^e absence of CO₂.

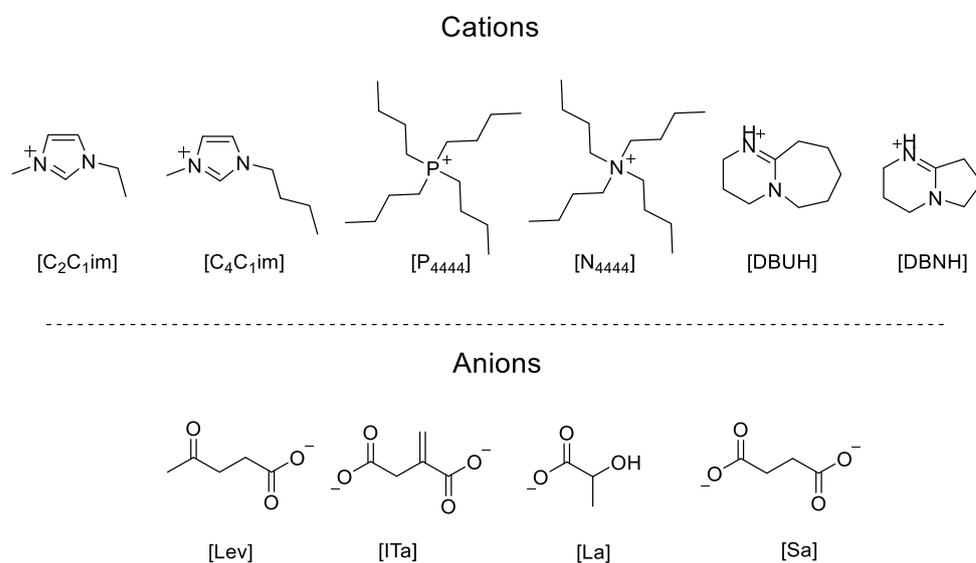
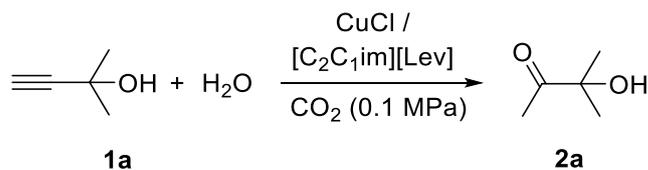
**Figure 1.** The cations and anions of the ILs.

Table 2. Screening of the reaction conditions ^a.

Entry	CuCl (mol %) ^c	IL (equiv.) ^c	Temperature (°C)	Time (h)	Yield (%) ^b
1	1	0.5	80	12	41
2	1	0.75	80	12	62
3	1	1	80	12	95
4	0.75	1	80	12	76
5	0.5	1	80	12	51
6	0.25	1	80	12	42
7	1	1	40	12	5
8	1	1	60	12	78
9	1	1	100	12	93
10	1	1	80	3	40
11	1	1	80	6	60
12	1	1	80	9	80

^a Reaction conditions: **1a** (2.5 mmol), H₂O (5 mmol), CO₂ (0.1 MPa). ^b Yields were determined via ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard. ^c Based on the amount of **1a**.

After determining the reaction conditions, the substrate scope of the CuCl/[C₂C₁im][Lev] system was explored (Table 3). The experimental results revealed that the majority of tertiary propargylic alcohols with various substituents effectively produced the corresponding products (**1a–1g**). Notably, the steric effects of the substituents significantly influenced the reactivity of substrates during the formation process of α-hydroxy ketones. Substrates with less sterically hindered substituted groups such as methyl and ethyl provided high yields of 85–95% within 12 h. However, for the propargylic alcohol **1g** containing a bulky phenyl group, the yield was only 33% under the same conditions, which could be improved via extending the reaction time. Additionally, attempts were made to react primary and secondary propargylic alcohols (**1h**, **1i**), but the corresponding products could not be produced. This might be attributed to the lack of gem-dialkyl effects in these substrates, resulting in the failure of cyclizing CO₂ and propargylic alcohol [58,59]. Subsequently, the recyclability of the CuCl/[C₂C₁im][Lev] system was investigated. After being recycled and reused three times, the catalytic system could still catalyze the target reaction to produce the α-hydroxy ketones with a yield of 90%, demonstrating its considerable stability and recyclability.

In addition to substrate scope and recyclability, the greenness of the reaction process is another important aspect of modern sustainable development, which can be quantified by utilizing the “green metrics”, including atom economy (AE), E-factor, carbon efficiency (CE), reaction mass efficiency (RME), mass intensity (MI) and mass productivity (MP) [60]. These well-defined and objective metrics provide quantitative standards for the greenness evaluation (Part 2, supporting information). In this context, the green metrics of the CuCl/[C₂C₁im][Lev] system and the calculable systems reported by other researchers were compared, based on the hydration of **1a** (Table 4). Upon evaluating a total of six green metrics, the CuCl/[C₂C₁im][Lev] system provided superior values in four aspects (AE, E-factor, MI, MP). This result indicated that the CuCl/[C₂C₁im][Lev]-catalyzed hydration of propargyl alcohols was a relatively greener process.

Table 3. Screening of the substrates ^a.

Reaction scheme: $\text{R}_1\text{C}(\text{OH})(\text{R}_2)\text{C}\equiv\text{C}\text{R}_3 + \text{H}_2\text{O} \xrightarrow[\text{CO}_2 (0.1 \text{ MPa})]{\text{CuCl, IL}} \text{R}_1\text{C}(\text{OH})(\text{R}_2)\text{C}(=\text{O})\text{R}_3$

	Substrate	Product	Time (h)	Yield (%) ^b
1a		2a:	12	95 (90 ^c)
1b		2b:	12	89
1c		2c:	12	87
1d		2d:	12	85
1e		2e:	12	81
1f		2f:	12 24	69 79
1g		2g:	12 36	33 73
1h		2h:	12	0
1i		2i:	12	0

^a Conditions: **1** (2.5 mmol), CuCl (1 mol%), H₂O (5 mmol), [C₂C₁im][Lev] (2.5 mmol), CO₂ (0.1 MPa), 80 °C; ^b yields were determined via ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard. ^c After 3 times of recycling and reuse.

Table 4. Comparison of the green metrics.

Ref.	Catalyst	Solvent	AE (%)	E-Factor (kg/kg)	CE (%)	RME (%)	MI (kg/kg)	MP (%)
2015 [45]	[Bu ₄ P][Im]	/	100	11.2	92	78.2	12.2	8.2
2019 [46]	Cu ₂ O/DBU cyclohexyldiphenylphosphine	CH ₃ CN	100	10.0	97	97.1	11.0	9.1
2021 [61]	[P ₄₄₄₄][2-OP]	/	100	4.9	83	83.0	5.9	16.9
2023 [49]	Silver-anchored porous aromatic framework	CH ₃ CN	100	17.7	99	86.3	18.7	5.4
this work	Ag@PAF-DAB CuCl/[C ₂ C ₁ im][Lev]	/	100	3.0	95	80.8	4.0	24.7

3. Discussion

3.1. Identification of Tandem Mechanism

Based on previous reports [47], the CO₂-promoted hydration of propargyl alcohols may proceed via a two-step tandem reaction mechanism. Substrates and CO₂ may first undergo cyclization to form α -alkylidene cyclic carbonates, followed by the in situ hydration of these carbonates with the release of CO₂ during the process. To investigate whether the CuCl/[C₂C₁im][Lev]-catalyzed reaction aligns with this proposed mechanism, a series of control experiments were conducted. Initially, **1a**, CO₂ and CuCl/[C₂C₁im][Lev] were introduced into the system under the optimal reaction conditions, with the omission of H₂O. After 12 h, the reaction was terminated, and the sample was analyzed using ¹H NMR. Comparing the spectrum of the reaction mixture with that of pure α -alkylidene cyclic carbonate, the characteristic peaks of α -alkylidene cyclic carbonates appeared on the spectrum of the reaction mixture (Figure 2a), indicating the generation of these carbonates in this process. Subsequently, the pure α -alkylidene cyclic carbonates were added with H₂O and allowed to react for 12 h under the catalysis of [C₂C₁im][Lev]. Upon completion of the reaction, the sample was analyzed using ¹H NMR. The result showed that the desired α -hydroxy ketones were successfully obtained (Figure 2b). These experiments demonstrated that the CuCl/[C₂C₁im][Lev]-catalyzed CO₂-promoted hydration of propargyl alcohols followed the proposed tandem reaction mechanism, and the ILs act as the pivotal catalyst for the hydration process.

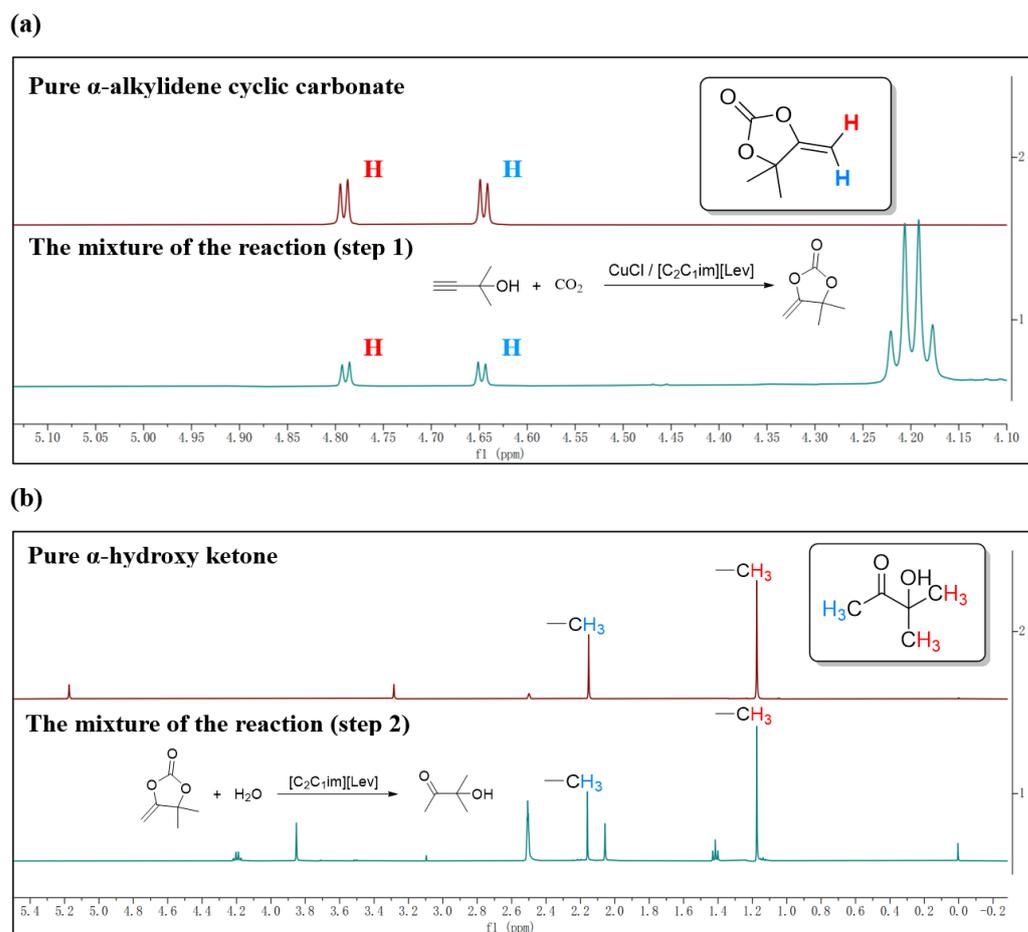


Figure 2. Comparison of ¹H NMR spectra: (a) pure α -alkylidene carbonates vs. mixture of step 1; (b) pure α -hydroxy ketones vs. mixture of step 2.

3.2. Activation of the Propargylic Alcohols

Upon identifying the tandem mechanism of the target reaction, the first cyclization step was further studied. In this step, the activation of the hydroxyl group in propargyl alcohols was quite crucial, which would initiate the whole catalytic process. Therefore, the investigation focused on identifying the component responsible for this crucial activation. Typically, this activation could be indicated via the shape and chemical shift of the hydroxyl signal peak in the ^1H NMR spectrum. For pure **1a**, the hydroxyl proton exhibited a distinct characteristic peak at $\delta = 5.29$ ppm (Figure 3a), indicating its inactivated state. However, upon the addition of DBU, a well-established organic base known for its effective hydroxyl group activation, the signal transformed into a broad peak with a different chemical shift (Figure 3b). This represented the activated state of the hydroxyl proton. Subsequently, the two components of the catalytic system were successively scrutinized. The addition of CuCl to **1a** did not produce any discernible change in the ^1H NMR results (Figure 3c), suggesting that CuCl was not capable of activating **1a**. Conversely, the combination of $[\text{C}_2\text{C}_1\text{im}][\text{Lev}]$ and **1a** led to a broad and shifted hydroxyl peak similar to that in the DBU/**1a** system (Figure 3d). This result implied that $[\text{C}_2\text{C}_1\text{im}][\text{Lev}]$ played a pivotal role in the activation of the hydroxyl group in **1a**.

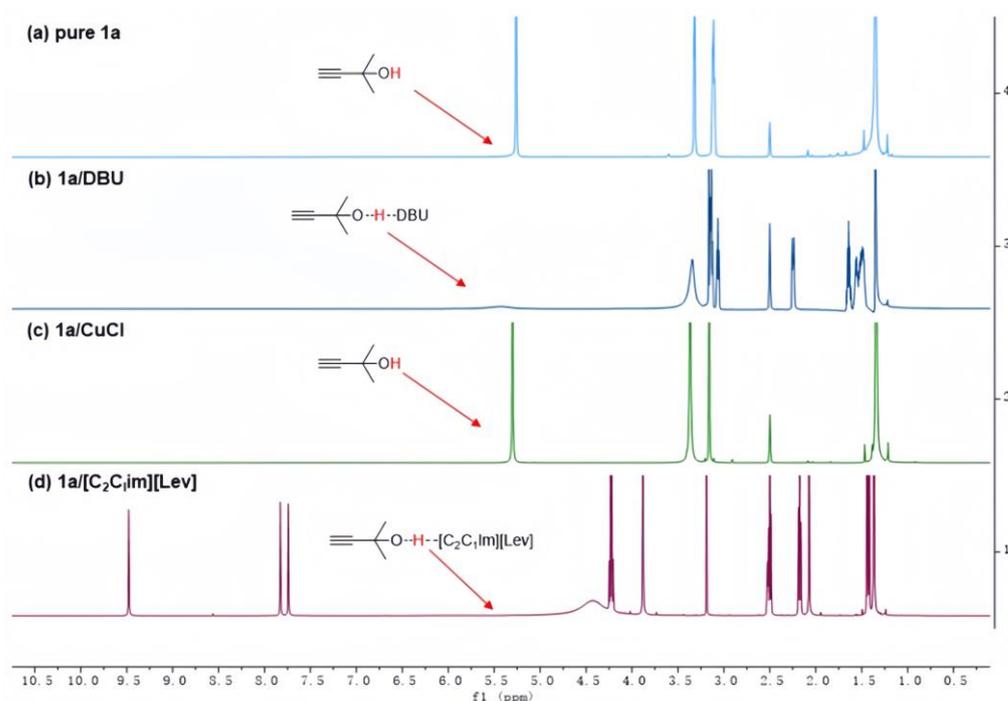
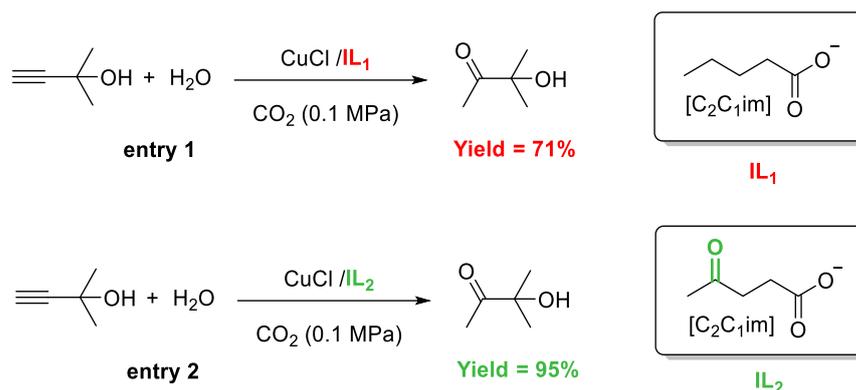


Figure 3. ^1H NMR of (a) pure **1a**, (b) **1a**/DBU (1:1), (c) **1a**/CuCl (1:1), (d) **1a**/[$\text{C}_2\text{C}_1\text{im}$][Lev] (1:1) in $\text{DMSO}-d_6$.

3.3. Generation of NHC- CO_2 Adducts

It has been reported that under basic conditions, imidazole compounds might interact with CO_2 , resulting in the generation of free N-heterocyclic carbenes (NHCs) that are capable of CO_2 capture and activation via the formation of NHC- CO_2 adducts (Scheme 1) [62,63]. In the aforementioned investigations, $[\text{C}_2\text{C}_1\text{im}][\text{Lev}]$ was identified to provide suitable basic conditions for the activation of the hydroxyl group. Therefore, subsequent exploration focused on whether this imidazole IL could produce NHC- CO_2 adducts. In this study, CO_2 was introduced into $[\text{C}_2\text{C}_1\text{im}][\text{Lev}]$, and the mixture was allowed to stir for 12 h. It could be observed that the solution became turbid gradually. Upon completion, the solution was analyzed using ^{13}C NMR. In the spectrum, a new signal peak at $\delta = 154.60$ ppm was observed (Figure 4a), which was consistent with the characteristic peak of CO_2 adducts reported in the literature [63], indicating the successful formation of NHC- CO_2 adducts.



Scheme 2. Parallel experiments employed IL₁ and IL₂. (Conditions: substrate: 2.5 mmol, CuCl: 1 mol%, H₂O: 5 mmol, IL: 2.5 mmol, CO₂: 0.1 MPa, 80 °C).

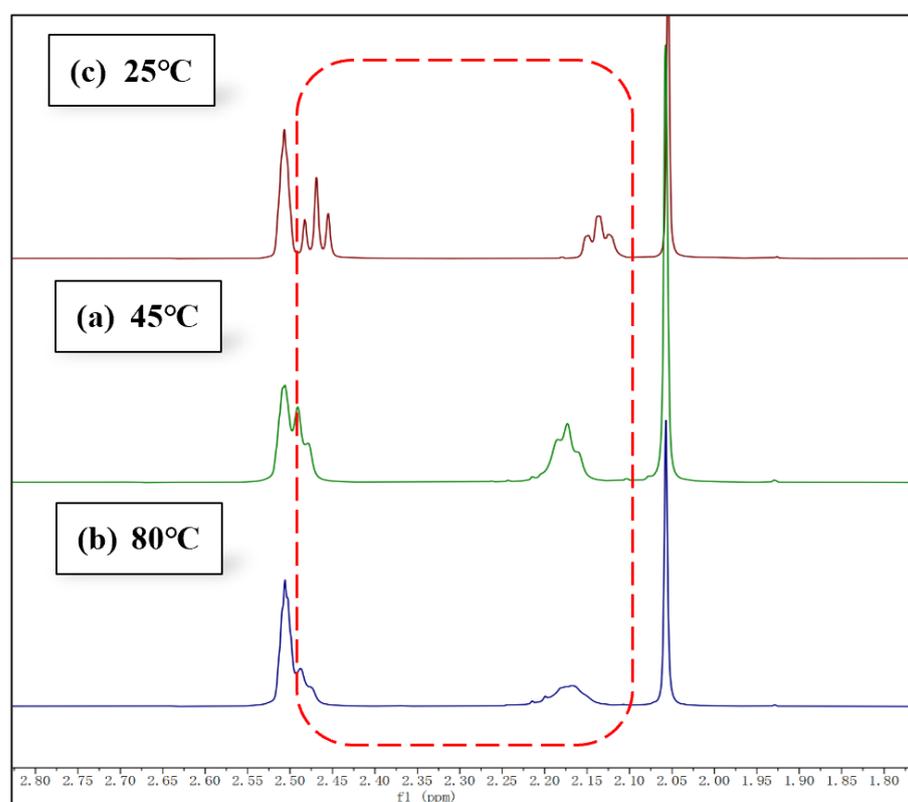
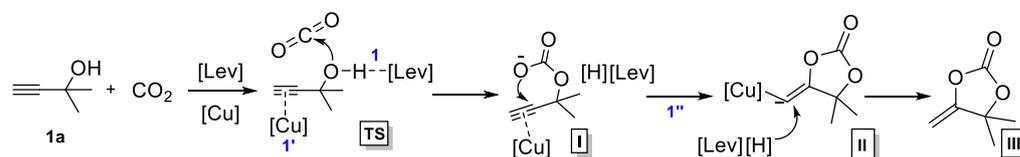


Figure 5. ¹H NMR for the mixture of CuCl and [C₂C₁im][Lev] at 25 °C (a), 45 °C (b), 80 °C (c).

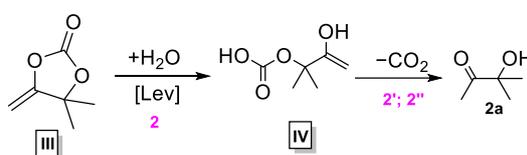
3.5. Proposed Mechanism for the Catalytic Process

Based on the aforementioned experiments and discussions [44,57,64–66], the following mechanism for the CO₂-promoted hydration of propargylic alcohols catalyzed via the CuCl/[C₂C₁im][Lev] system was proposed, which could be outlined in two steps (Scheme 3). Firstly, [Lev] activates the hydroxy group of **1a**, thereby enhancing the nucleophilicity of the hydroxy oxygen and facilitating its subsequent attack on the CO₂ molecule. Simultaneously, the Cu species coordinates with the unsaturated triple bond of **1a**, leading to the formation of the transition state (TS). In the next stage, the negative hydroxyl oxygen atom bonds with the positive carbon center of CO₂, incorporating the inert CO₂ molecule into the organic skeletons, resulting in the formation of intermediate I. Subsequently, the negative oxygen of the CO₂ moiety continues to attack the triple bond, activated via the Cu species, leading to intramolecular cyclization and the formation of intermediate II. Finally, the proton is transferred back to the organic skeletons, resulting in the generation

of the key α -alkylidene carbonate (intermediate **III**). In the second step, H_2O initiates a nucleophilic attack on intermediate **III** with the catalysis of the basic [Lev]. This leads to the ring-opening reaction and the generation of intermediate **IV**. Afterwards, this intermediate undergoes keto-enol isomerization, subsequently releasing the CO_2 molecule and yielding the final target product **2a**.



Step 1: 1: activation of the hydroxy group; 1': the Cu coordination; 1'': cyclization



Step 2: 2: ring-opening reaction; 2': keto-enol isomerization; 2'': release of CO_2

Scheme 3. Proposed catalytic mechanism of the $\text{CuCl}/[\text{C}_2\text{C}_1\text{im}][\text{Lev}]$ system.

4. Materials and Methods

The series of biomass-based ILs used in the experiments were synthesized according to the reported literature (Part 1, supporting information) [57,67,68]. Unless otherwise specified, all the propargyl alcohol substrates (98%) and biomass acids (95%) used in the experiments were purchased from Aladdin (Shanghai, China), TCI (Tokyo, Japan), Sigma-Aldrich (Shanghai, China), Macklin (Shanghai, China), Alfa (Shanghai, China), etc. and directly used without further purification and drying. The purity of the CO_2 used for purging and reacting was 99.9%, supplied by Wuhan Xiangyun Industry and Trade Co., Ltd., (Wuhan, China).

The ^1H NMR spectra were recorded on a Bruker Avance III HD 500 MHz spectrometer, with the internal standard TMS ($\delta = 0$ ppm) serving as the reference. Meanwhile, the ^{13}C NMR spectra were recorded at 126 MHz in CDCl_3 ($\delta = 77.23$ ppm) or $\text{DMSO}-d_6$ ($\delta = 39.50$ ppm), with the solvent peaks as the internal references. The data were given as chemical shifts (ppm) and coupling constants (Hz), respectively.

4.1. The CO_2 -Promoted Hydration of Propargylic Alcohols

CuCl (0.025 mmol), 1-ethyl-3-methylimidazolium levulinic ($[\text{C}_2\text{C}_1\text{im}][\text{Lev}]$, 2.5 mmol), propargylic alcohols (2.5 mmol) and H_2O (5 mmol) were added into a Schlenk tube. Subsequently, the system was purged three times with CO_2 and then stirred at 80°C under 0.1 MPa of CO_2 for the required time. When the reaction was completed, the mixture was extracted with diethyl ether (3×15 mL). The upper organic phases were concentrated under a vacuum to give the crude products, which were further purified via column chromatography on silica gel using petroleum ether/ethyl acetate (v/v , 100:1–20:1) as the eluent.

4.2. Procedures for Recycling the Catalytic System

After the reaction was completed, the mixture was extracted three times with diethyl ether (3×15 mL). The lower layer was then dried under a vacuum for 4 h to totally remove the residual solvents, reactants and products. After drying, the catalytic system could be reused for the next round.

5. Conclusions

In summary, a CuCl/[C₂C₁im][Lev] system was developed for the CO₂-promoted hydration of propargylic alcohols under 1 bar of CO₂ pressure without the use of organic volatile solvents or additives. The system demonstrated high activity, a wide substrate scope and significant recyclability. Notably, the catalytic process was identified as superior in terms of green metric evaluation. A comprehensive mechanistic investigation revealed that the exceptional performance of this system can be attributed to the triple function of the [C₂C₁im][Lev] component, which encompasses the activation of substrates, generation of NHC-CO₂ adducts and interaction with the Cu component.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ijms25031937/s1>.

Author Contributions: Conceptualization, Y.Y. and F.V.; methodology, S.Z.; software, K.D.; validation, Y.Y., S.Z. and K.D.; formal analysis, Y.X.; investigation, K.G.; resources, C.C.; data curation, S.C.; writing—original draft preparation, Y.Y.; writing—review and editing, F.V.; visualization, S.Z.; supervision, D.C. and F.V.; project administration, F.V.; funding acquisition, Y.Y. All authors have read and agreed to the published version of the manuscript.

Funding: The project was supported by the National Natural Science Foundation of China (no. 22102127).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article and Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Oerlemans, J. Glaciers as indicators of a carbon dioxide warming. *Nature* **1986**, *320*, 607–609. [[CrossRef](#)]
2. McNutt, M. Time's up, CO₂. *Science* **2019**, *365*, 411. [[CrossRef](#)] [[PubMed](#)]
3. Mac Dowell, N.; Reiner, D.M.; Haszeldine, R.S. Comparing approaches for carbon dioxide removal. *Joule* **2022**, *6*, 2233–2239. [[CrossRef](#)]
4. Frölicher, T.L.; Fischer, E.M.; Gruber, N. Marine heatwaves under global warming. *Nature* **2018**, *560*, 360–364. [[CrossRef](#)] [[PubMed](#)]
5. Yang, Z.-Z.; He, L.-N.; Gao, J.; Liu, A.-H.; Yu, B. Carbon dioxide utilization with C–N bond formation: Carbon dioxide capture and subsequent conversion. *Energy Environ. Sci.* **2012**, *5*, 6602–6639. [[CrossRef](#)]
6. Huang, K.; Sun, C.-L.; Shi, Z.-J. Transition-metal-catalyzed C–C bond formation through the fixation of carbon dioxide. *Chem. Soc. Rev.* **2011**, *40*, 2435–2452. [[CrossRef](#)] [[PubMed](#)]
7. He, M.; Sun, Y.; Han, B. Green Carbon Science: Scientific Basis for Integrating Carbon Resource Processing, Utilization, and Recycling. *Angew. Chem. Int. Ed.* **2013**, *52*, 9620–9633. [[CrossRef](#)]
8. Bao, J.; Yang, G.; Yoneyama, Y.; Tsubaki, N. Significant Advances in C1 Catalysis: Highly Efficient Catalysts and Catalytic Reactions. *ACS Catal.* **2019**, *9*, 3026–3053. [[CrossRef](#)]
9. Kleij, A.W.; North, M.; Urakawa, A. CO₂ Catalysis. *ChemSusChem* **2017**, *10*, 1036–1038. [[CrossRef](#)]
10. Mac Dowell, N.; Fennell, P.S.; Shah, N.; Maitland, G.C. The role of CO₂ capture and utilization in mitigating climate change. *Nat. Clim. Change* **2017**, *7*, 243–249. [[CrossRef](#)]
11. Hou, S.-L.; Dong, J.; Zhao, B. Formation of C–X Bonds in CO₂ Chemical Fixation Catalyzed by Metal–Organic Frameworks. *Adv. Mater.* **2020**, *32*, 1806163. [[CrossRef](#)]
12. Dabral, S.; Schaub, T. The Use of Carbon Dioxide (CO₂) as a Building Block in Organic Synthesis from an Industrial Perspective. *Adv. Synth. Catal.* **2019**, *361*, 223–246. [[CrossRef](#)]
13. Riemer, D.; Schilling, W.; Goetz, A.; Zhang, Y.; Gehrke, S.; Tkach, I.; Hollóczki, O.; Das, S. CO₂-Catalyzed Efficient Dehydrogenation of Amines with Detailed Mechanistic and Kinetic Studies. *ACS Catal.* **2018**, *8*, 11679–11687. [[CrossRef](#)]
14. Riemer, D.; Mandaviya, B.; Schilling, W.; Götz, A.C.; Kühl, T.; Finger, M.; Das, S. CO₂-Catalyzed Oxidation of Benzylic and Allylic Alcohols with DMSO. *ACS Catal.* **2018**, *8*, 3030–3034. [[CrossRef](#)]
15. Hirapara, P.; Riemer, D.; Hazra, N.; Gajera, J.; Finger, M.; Das, S. CO₂-assisted synthesis of non-symmetric α -diketones directly from aldehydes via C–C bond formation. *Green Chem.* **2017**, *19*, 5356–5360. [[CrossRef](#)]
16. Riemer, D.; Hirapara, P.; Das, S. Chemoselective Synthesis of Carbamates using CO₂ as Carbon Source. *ChemSusChem* **2016**, *9*, 1916–1920. [[CrossRef](#)] [[PubMed](#)]
17. Aresta, M.; Dibenedetto, A.; Angelini, A. Catalysis for the Valorization of Exhaust Carbon: From CO₂ to Chemicals, Materials, and Fuels. Technological Use of CO₂. *Chem. Rev.* **2014**, *114*, 1709–1742. [[CrossRef](#)] [[PubMed](#)]

18. Appel, A.M.; Bercaw, J.E.; Bocarsly, A.B.; Dobbek, H.; DuBois, D.L.; Dupuis, M.; Ferry, J.G.; Fujita, E.; Hille, R.; Kenis, P.J.A.; et al. Frontiers, Opportunities, and Challenges in Biochemical and Chemical Catalysis of CO₂ Fixation. *Chem. Rev.* **2013**, *113*, 6621–6658. [[CrossRef](#)] [[PubMed](#)]
19. Sakakura, T.; Choi, J.-C.; Yasuda, H. Transformation of Carbon Dioxide. *Chem. Rev.* **2007**, *107*, 2365–2387. [[CrossRef](#)]
20. Otto, A.; Grube, T.; Schiebahn, S.; Stolten, D. Closing the loop: Captured CO₂ as a feedstock in the chemical industry. *Energy Environ. Sci.* **2015**, *8*, 3283–3297. [[CrossRef](#)]
21. Yang, K.; Zhang, F.; Fang, T.; Li, C.; Li, W.; Song, Q. Passerini-type reaction of boronic acids enables α -hydroxyketones synthesis. *Nat. Commun.* **2021**, *12*, 441. [[CrossRef](#)]
22. Kutscheroff, M. Ueber die Einwirkung der Kohlenwasserstoffe der Acetylenreihe auf Quecksilberoxyd und dessen Salze. *Ber. Dtsch. Chem. Ges.* **1884**, *17*, 13–29. [[CrossRef](#)]
23. Kutscheroff, M. Ueber eine neue Methode direkter Addition von Wasser (Hydratation) an die Kohlenwasserstoffe der Acetylenreihe. *Ber. Dtsch. Chem. Ges.* **1881**, *14*, 1540–1542. [[CrossRef](#)]
24. Xing, Y.; Zhang, M.; Ciccarelli, S.; Lee, J.; Catano, B. AuIII-Catalyzed Formation of α -Halomethyl Ketones from Terminal Alkynes. *Eur. J. Org. Chem.* **2017**, *2017*, 781–785. [[CrossRef](#)]
25. Weerasiri, K.C.; Chen, D.; Wozniak, D.I.; Dobereiner, G.E. Internal Alkyne Regio- and Chemoselectivity using a Zwitterionic N-Heterocyclic Carbene Gold Catalyst in a Silver-Free Alkyne Hydration Reaction. *Adv. Synth. Catal.* **2016**, *358*, 4106–4113. [[CrossRef](#)]
26. Gatto, M.; Belanzoni, P.; Belpassi, L.; Biasiolo, L.; Del Zotto, A.; Tarantelli, F.; Zuccaccia, D. Solvent-, Silver-, and Acid-Free NHC-Au-X Catalyzed Hydration of Alkynes. The Pivotal Role of the Counterion. *ACS Catal.* **2016**, *6*, 7363–7376. [[CrossRef](#)]
27. Ebule, R.E.; Malhotra, D.; Hammond, G.B.; Xu, B. Ligand Effects in the Gold Catalyzed Hydration of Alkynes. *Adv. Synth. Catal.* **2016**, *358*, 1478–1481. [[CrossRef](#)]
28. Xu, Y.; Hu, X.; Shao, J.; Yang, G.; Wu, Y.; Zhang, Z. Hydration of alkynes at room temperature catalyzed by gold(i) isocyanide compounds. *Green Chem.* **2015**, *17*, 532–537. [[CrossRef](#)]
29. Liang, S.; Jasinski, J.; Hammond, G.B.; Xu, B. Supported Gold Nanoparticle-Catalyzed Hydration of Alkynes under Basic Conditions. *Org. Lett.* **2015**, *17*, 162–165. [[CrossRef](#)]
30. Ibrahim, H.; de Frémont, P.; Braunstein, P.; Théry, V.; Nauton, L.; Cisnetti, F.; Gautier, A. Water-Soluble Gold–N-Heterocyclic Carbene Complexes for the Catalytic Homogeneous Acid- and Silver-Free Hydration of Hydrophilic Alkynes. *Adv. Synth. Catal.* **2015**, *357*, 3893–3900. [[CrossRef](#)]
31. Chen, T.; Cai, C. Catalytic hydration of alkynes to ketones by a salen–gold(III) complex. *Catal. Commun.* **2015**, *65*, 102–104. [[CrossRef](#)]
32. Xie, L.; Wu, Y.; Yi, W.; Zhu, L.; Xiang, J.; He, W. Gold-Catalyzed Hydration of Haloalkynes to α -Halomethyl Ketones. *J. Org. Chem.* **2013**, *78*, 9190–9195. [[CrossRef](#)] [[PubMed](#)]
33. Oonishi, Y.; Gómez-Suárez, A.; Martin, A.R.; Nolan, S.P. Hydrophenoxylation of Alkynes by Cooperative Gold Catalysis. *Angew. Chem. Int. Ed.* **2013**, *52*, 9767–9771. [[CrossRef](#)] [[PubMed](#)]
34. Leyva, A.; Corma, A. Isolable Gold(I) Complexes Having One Low-Coordinating Ligand as Catalysts for the Selective Hydration of Substituted Alkynes at Room Temperature without Acidic Promoters. *J. Org. Chem.* **2009**, *74*, 2067–2074. [[CrossRef](#)] [[PubMed](#)]
35. Santhi, J.; Baire, B. Carbonyl Directed Regioselective Hydration of Alkynes under Ag-Catalysis. *ChemistrySelect* **2017**, *2*, 4338–4342. [[CrossRef](#)]
36. Dong, Q.; Li, N.; Qiu, R.; Wang, J.; Guo, C.; Xu, X. Silver-containing microemulsion as a high-efficient and recyclable catalytic system for hydration of alkynes. *J. Organomet. Chem.* **2015**, *799–800*, 122–127. [[CrossRef](#)]
37. Chen, Z.-W.; Ye, D.-N.; Ye, M.; Zhou, Z.-G.; Li, S.-H.; Liu, L.-X. AgF/TFA-promoted highly efficient synthesis of α -haloketones from haloalkynes. *Tetrahedron Lett.* **2014**, *55*, 1373–1375. [[CrossRef](#)]
38. Chen, Z.-W.; Ye, D.-N.; Qian, Y.-P.; Ye, M.; Liu, L.-X. Highly efficient AgBF₄-catalyzed synthesis of methyl ketones from terminal alkynes. *Tetrahedron* **2013**, *69*, 6116–6120. [[CrossRef](#)]
39. Venkateswara Rao, K.T.; Sai Prasad, P.S.; Lingaiah, N. Solvent-free hydration of alkynes over a heterogeneous silver exchanged silicotungstic acid catalyst. *Green Chem.* **2012**, *14*, 1507–1514. [[CrossRef](#)]
40. Das, R.; Chakraborty, D. AgOTf catalyzed hydration of terminal alkynes. *Appl. Organomet. Chem.* **2012**, *26*, 722–726. [[CrossRef](#)]
41. Grotjahn, D.B.; Lev, D.A. A General Bifunctional Catalyst for the Anti-Markovnikov Hydration of Terminal Alkynes to Aldehydes Gives Enzyme-Like Rate and Selectivity Enhancements. *J. Am. Chem. Soc.* **2004**, *126*, 12232–12233. [[CrossRef](#)]
42. Banerjee, S.; Ambegave, S.B.; Mule, R.D.; Senthilkumar, B.; Patil, N.T. Gold-Catalyzed Alkynylative Meyer–Schuster Rearrangement. *Org. Lett.* **2020**, *22*, 4792–4796. [[CrossRef](#)]
43. Yoshida, S.; Fukui, K.; Kikuchi, S.; Yamada, T. Silver-Catalyzed Enantioselective Carbon Dioxide Incorporation into Bispropargylic Alcohols. *J. Am. Chem. Soc.* **2010**, *132*, 4072–4073. [[CrossRef](#)] [[PubMed](#)]
44. He, H.; Qi, C.; Hu, X.; Guan, Y.; Jiang, H. Efficient synthesis of tertiary α -hydroxy ketones through CO₂-promoted regioselective hydration of propargylic alcohols. *Green Chem.* **2014**, *16*, 3729–3733. [[CrossRef](#)]
45. Zhao, Y.; Yang, Z.; Yu, B.; Zhang, H.; Xu, H.; Hao, L.; Han, B.; Liu, Z. Task-specific ionic liquid and CO₂-cocatalysed efficient hydration of propargylic alcohols to α -hydroxy ketones. *Chem. Sci.* **2015**, *6*, 2297–2301. [[CrossRef](#)] [[PubMed](#)]
46. Zhou, Z.-H.; Zhang, X.; Huang, Y.-F.; Chen, K.-H.; He, L.-N. Synthesis of α -hydroxy ketones by copper(I)-catalyzed hydration of propargylic alcohols: CO₂ as a cocatalyst under atmospheric pressure. *Chin. J. Catal.* **2019**, *40*, 1345–1351. [[CrossRef](#)]

47. Li, D.; Gong, Y.; Du, M.; Bu, C.; Chen, C.; Chaemcheun, S.; Hu, J.; Zhang, Y.; Yuan, Y.; Verpoort, F. CO₂-Promoted Hydration of Propargylic Alcohols: Green Synthesis of α -Hydroxy Ketones by an Efficient and Recyclable AgOAc/Ionic Liquid System. *ACS Sustain. Chem. Eng.* **2020**, *8*, 8148–8155. [[CrossRef](#)]
48. Zhang, Y.; Hu, J.; Xu, Y.; Yan, X.; Zhang, S.; Duan, K.; Chen, C.; Yuan, Y.; Verpoort, F. CO₂-induced dissolution of ZnO into ionic liquids and its catalytic application for the hydration of propargylic alcohols. *Appl. Catal. B* **2022**, *310*, 121270. [[CrossRef](#)]
49. Guo, X.-X.; Cai, Z.-T.; Muhammad, Y.; Zhang, F.-L.; Wei, R.-P.; Gao, L.-J.; Xiao, G.-M. Silver-anchored porous aromatic framework for efficient conversion of propargylic alcohols with CO₂ at ambient pressure. *Chin. Chem. Lett.* **2023**, *34*, 107740. [[CrossRef](#)]
50. Guo, X.; Zhang, F.; Muhammad, Y.; Yang, Z.; Wei, R.; Gao, L.; Xiao, G. Amino-functionalized organic polymer loaded with highly dispersed CuI for efficient catalytic conversion of CO₂ with PA. *Microporous Mesoporous Mater.* **2023**, *352*, 112507. [[CrossRef](#)]
51. Simon, N.M.; Zanatta, M.; dos Santos, F.P.; Corvo, M.C.; Cabrita, E.J.; Dupont, J. Carbon Dioxide Capture by Aqueous Ionic Liquid Solutions. *ChemSusChem* **2017**, *10*, 4927–4933. [[CrossRef](#)] [[PubMed](#)]
52. Zhao, H.-Y.; Dong, W.-X.; Deng, Y.; Chen, L.-F.; Zhao, C.-F.; Zhang, C.-L.; Zhou, J.; Qu, Y.-F.; Li, Y.-S.; Li, D.-J.; et al. Biomass-based biomimetic-oriented Janus nanoarchitecture for efficient heavy-metal enrichment and interfacial solar water sanitation. *Interdiscip. Mater.* **2022**, *1*, 537–547. [[CrossRef](#)]
53. Li, T.; Chen, C.; Brozena, A.H.; Zhu, J.Y.; Xu, L.; Driemeier, C.; Dai, J.; Rojas, O.J.; Isogai, A.; Wågberg, L.; et al. Developing fibrillated cellulose as a sustainable technological material. *Nature* **2021**, *590*, 47–56. [[CrossRef](#)] [[PubMed](#)]
54. Tiong, Y.W.; Yap, C.L.; Gan, S.; Yap, W.S.P. Conversion of Biomass and Its Derivatives to Levulinic Acid and Levulinate Esters via Ionic Liquids. *Ind. Eng. Chem. Res.* **2018**, *57*, 4749–4766. [[CrossRef](#)]
55. Bernardo, J.R.; Oliveira, M.C.; Fernandes, A.C. HReO₄ as highly efficient and selective catalyst for the conversion of carbohydrates into value added chemicals. *Mol. Catal.* **2019**, *465*, 87–94. [[CrossRef](#)]
56. Werpy, T.A.; Holladay, J.E.; White, J.F. *Top Value Added Chemicals From Biomass: I. Results of Screening for Potential Candidates from Sugars and Synthesis Gas*; National Renewable Energy Lab. (NREL): Golden, CO, USA, 2004.
57. Hu, Y.; Song, J.; Xie, C.; Wu, H.; Jiang, T.; Yang, G.; Han, B. Transformation of CO₂ into α -Alkylidene Csights into the levulinate-based ionic liquid class: By CuI and Ionic Liquid with Biomass-Derived Levulinate Anion. *ACS Sustain. Chem. Eng.* **2019**, *7*, 5614–5619. [[CrossRef](#)]
58. Grignard, B.; Ngassamtounzoua, C.; Gennen, S.; Gilbert, B.; Méreau, R.; Jerome, C.; Tassaing, T.; Detrembleur, C. Boosting the Catalytic Performance of Organic Salts for the Fast and Selective Synthesis of α -Alkylidene Cyclic Carbonates from Carbon Dioxide and Propargylic Alcohols. *ChemCatChem* **2018**, *10*, 2584–2592. [[CrossRef](#)]
59. Kayaki, Y.; Yamamoto, M.; Ikariya, T. Stereoselective Formation of α -Alkylidene Cyclic Carbonates via Carboxylative Cyclization of Propargyl Alcohols in Supercritical Carbon Dioxide. *J. Org. Chem.* **2007**, *72*, 647–649. [[CrossRef](#)]
60. Constable, D.J.C.; Curzons, A.D.; Cunningham, V.L. Metrics to ‘green’ chemistry—Which are the best? *Green Chem.* **2002**, *4*, 521–527. [[CrossRef](#)]
61. Tang, M.; Zhang, F.; Zhao, Y.; Wang, Y.; Ke, Z.; Li, R.; Zeng, W.; Han, B.; Liu, Z. A CO₂-mediated base catalysis approach for the hydration of triple bonds in ionic liquids. *Green Chem.* **2021**, *23*, 9870–9875. [[CrossRef](#)]
62. Kayaki, Y.; Yamamoto, M.; Ikariya, T. N-Heterocyclic Carbenes as Efficient Organocatalysts for CO₂ Fixation Reactions. *Angew. Chem. Int. Ed.* **2009**, *48*, 4194–4197. [[CrossRef](#)]
63. Gurau, G.; Rodríguez, H.; Kelley, S.P.; Janiczek, P.; Kalb, R.S.; Rogers, R.D. Demonstration of Chemisorption of Carbon Dioxide in 1,3-Dialkylimidazolium Acetate Ionic Liquids. *Angew. Chem. Int. Ed.* **2011**, *50*, 12024–12026. [[CrossRef](#)]
64. Zhao, Y.; Tian, L.; Qiu, J.; Li, Z.; Wang, H.; Cui, G.; Zhang, S.; Wang, J. Remarkable synergistic effect between copper(I) and ionic liquids for promoting chemical fixation of CO₂. *J. CO₂ Util.* **2017**, *22*, 374–381. [[CrossRef](#)]
65. Shi, G.; Zhai, R.; Li, H.; Wang, C. Highly efficient synthesis of alkylidene cyclic carbonates from low concentration CO₂ using hydroxyl and azolate dual functionalized ionic liquids. *Green Chem.* **2021**, *23*, 592–596. [[CrossRef](#)]
66. Ouyang, L.; Tang, X.; He, H.; Qi, C.; Xiong, W.; Ren, Y.; Jiang, H. Copper-Promoted Coupling of Carbon Dioxide and Propargylic Alcohols: Expansion of Substrate Scope and Trapping of Vinyl Copper Intermediate. *Adv. Synth. Catal.* **2015**, *357*, 2556–2565. [[CrossRef](#)]
67. Mezzetta, A.; Becherini, S.; Pretti, C.; Monni, G.; Casu, V.; Chiappe, C.; Guazzelli, L. Insights into the levulinate-based ionic liquid class: Synthesis, cellulose dissolution evaluation and ecotoxicity assessment. *New J. Chem.* **2019**, *43*, 13010–13019. [[CrossRef](#)]
68. Deng, L.; Yue, W.; Zhang, L.; Guo, Y.; Xie, H.; Zheng, Q.; Zou, G.; Chen, P. Biobased Protic Ionic Liquids as Sustainable Solvents for Wool Keratin/Cellulose Simultaneous Dissolution: Solution Properties and Composited Membrane Preparation. *ACS Sustain. Chem. Eng.* **2022**, *10*, 2158–2168. [[CrossRef](#)]

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