An Efficient and Recyclable $AgNO_3$/Ionic Liquid System Catalyzed Atmospheric CO_2 Utilization: Simultaneous Synthesis of 2-Oxazolidinones and α-Hydroxyl Ketones

Minchen Du, Yanyan Gong, Chao Bu, Jia Hu, Yongxing Zhang, Cheng Chen, Somboon Chaemchuen, Ye Yuan, Francis Verpoort

PII: S0021-9517(20)30457-7
DOI: https://doi.org/10.1016/j.jcat.2020.11.011
Reference: YJCAT 13970

To appear in: *Journal of Catalysis*

Received Date: 1 September 2020
Revised Date: 6 November 2020
Accepted Date: 10 November 2020

Please cite this article as: M. Du, Y. Gong, C. Bu, J. Hu, Y. Zhang, C. Chen, S. Chaemchuen, Y. Yuan, F. Verpoort, An Efficient and Recyclable $AgNO_3$/Ionic Liquid System Catalyzed Atmospheric CO_2 Utilization: Simultaneous Synthesis of 2-Oxazolidinones and α-Hydroxyl Ketones, *Journal of Catalysis* (2020), doi: https://doi.org/10.1016/j.jcat.2020.11.011

An Efficient and Recyclable $AgNO_3$/Ionic Liquid System Catalyzed Atmospheric CO_2 Utilization: Simultaneous Synthesis of 2-Oxazolidinones and α-Hydroxyl Ketones

Minchen Du,[a,c] Yanyan Gong,[b] Chao Bu,[a,c] Jia Hu,[a,c] Yongxing Zhang,[a,c] Cheng Chen,[a] Somboon Chaemchuen,[a] Ye Yuan,*[a] Francis Verpoort*[a,c,d,e]

[a] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, P.R. China

[b] State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250353, P.R. China

[c] School of Material Science and Engineering, Wuhan University of Technology, Wuhan 430070, P.R. China

[d] National Research Tomsk Polytechnic University, Lenin Avenue 30, Tomsk 634050, Russian Federation

[e] Global Campus Songdo, Ghent University, 119 Songdomunhwa-Ro, Yeonsu-Gu, Incheon, Korea

Correspondence authors E-mail: fyyuanye@whut.edu.cn;francis.verpoort@ghent.ac.kr

Abstract

Oxazolidinones and α-hydroxyl ketones are two series of fine chemicals that have been generally utilized in biological, pharmaceutical, and synthetic chemistry. Herein, a $AgNO_3$/ionic liquid (IL) catalytic system was developed for the simultaneous synthesis of these compounds through the atom-economical three-component reactions of propargyl alcohols, 2-aminoethanols, and CO_2. Notably, this system behaved excellent catalytic activity with the lowermost metal loading of 0.25 mol%. Meanwhile, it is the first reported metal-catalyzed system that could efficiently work under atmospheric CO_2 pressure and be recycled at least five times. Evaluation of the green metrics proved the $AgNO_3$/IL-catalyzed processes to be relatively more sustainable and greener than the other Ag-catalyzed examples. Further mechanistic investigations revealed the derivative active species of N-heterocyclic carbene (NHC) silver complexes and CO_2 adducts generated during the process. Subsequently, their reactivity in this reaction was assessed for the first time, which was finally identified as beneficial for the catalytic activity.

Keywords

carbon dioxide utilization; silver catalysis; ionic liquid; multicomponent reaction; heterocycles

1. Introduction

With modern industry development, carbon dioxide (CO_2) has attracted more and more attention as its unignorable influence on the greenhouse effect [1-4]. While in the aspect of synthetic chemistry, CO_2 is considered as an ideal C1 source for its merits, such as nontoxicity, economy, renewability, and abundance [5-8]. Based on this, the transformation of CO_2 into organics has become a highly promising area in modern green and sustainable chemistry [9-12]. Up to now, numerous strategies have been developed to effectively utilize CO_2 for the synthesis of valuable chemicals [13-21] such as alcohols [22-25], carboxylic acids & esters [26-31], amides [32-36], carbonates [31, 37-51] and carbamates [52-56]. Among them, oxazolidinones and α-hydroxyl ketones have gained a lot of interest for their wide applications in biological, pharmaceutical, and synthetic chemistry [57]. For example, oxazolidinone skeletons exist in multitudinous drugs like linezolid, eperezolid, zolmitriptan, *etc.* [58] Meanwhile, they are applied to prepare chiral amino acids, dipeptide, (α,α)-di-substituted amine and other fine chemicals [59]. On the other hand, α-hydroxyl ketones such as HMPP (2-hydroxy-2-methylpropiophenone) and HCPK (1-hydroxycyclohexyl phenyl ketone) act as photo-initiators in the curing system of ultraviolet photosensitive resin [60, 61]. However, the traditional methods for preparing these two series of compounds still suffered from several drawbacks, such as harsh reaction conditions, low atom economy and harmful reagents such as phosgene [62], Hg salts, and H_2SO_4 [63-65]. These disadvantages limited their further utilization in modern green and sustainable industry.

Based on this, several pathways aimed to establish an economical and environmentally-friendly synthesis of oxazolidinones and α-hydroxyl ketones, including the cyclization of propargylamine with CO_2 [66-71], three-component reactions of propargyl alcohols/primary amine/CO_2 [72-76], direct condensation of

2-aminoalcohols with CO_2 [77-79], the cycloaddition of aziridines with CO_2 [80-83] for preparing oxazolidinones, and CO_2-cocatalysed hydration of propargyl alcohols [84-86], reduction of diketones or oxidation of diols [87], α-H oxidative hydroxylation of ketones [88] for producing α-hydroxyl ketones. In particular, the three-component reactions of propargyl alcohols, CO_2 and 2-aminoethanols attracted our interests because this strategy could simultaneously produce both oxazolidinones and α-hydroxyl ketones in a one-pot manner with 100% atom-economy under relatively mild and green conditions. In this area, He and co-workers [89] developed a silver salt/phosphine ligand catalytic system for this three-component cascade reaction in which 5 mol% of Ag_2CO_3 and 10 mol% of 9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene (Xantphos) were employed. This catalytic system could smoothly convert various substrates into the corresponding products under 1 MPa of CO_2 in $CHCl_3$. Subsequently, they reported a catalytic system consisting of 5 mol% Ag_2O and 30 mol% of 1,1,3,3-tetramethylguanidine (TMG) for this reaction, which could proceed successfully under 1 MPa of CO_2 in CH_3CN with a TON up to 1260 [90]. Further investigations showed that TMG could activate propargyl alcohols, 2-aminoethanols, and CO_2 remarkably. Furthermore, a Cu(I) system with considerable catalytic activity was also established [56]. Desired products could be obtained in the presence of 5 mol% CuI as the catalyst, 5 mol% 1,10-phen (1,10-phenanthroline) as the ligand and 10 mol% t-BuOK as additives under 0.5 MPa of CO_2. Very recently, a task-specific ionic liquid (IL), 1,5,7-triazabicylo[4.4.0]dec-5-ene trifluoroethanol ([TBDH][TFE]) was designed and synthesized through an anion-exchange resin, which could promote the cascade reaction under 0.1 MPa of CO_2 [91]. Although remarkable progress has been achieved, the existing systems still suffered from several drawbacks. For the most studied metal-catalyzed systems, which were considered to be potential for industrial applications due to their simple, stable and relatively economical components, high metal loadings, harsh reaction conditions, poor recyclability, usage of volatile solvents, additions of ligands and/or bases still blocked their practical utilizations. On the other hand, the only example of a metal-free strategy generally employed a commercially unavailable IL ([TBDH][TFE]), whose synthesis required a relatively rare organic base and anion-exchange resins. This also limited its large-scale applications in industry. Despite this, it was worth noting that these two strategies were complementary in certain aspects, which inspired us that the combination of these two strategies might create catalytic systems that brought in the dual merits from both metal- and metal-free systems.

Herein, we employed a commercially available and easily accessible ionic liquid, namely 1-ethyl-3-methylimidazolium acetate ($[C_2C_1im][OAc]$) together with $AgNO_3$ for the simultaneous synthesis of 2-oxazolidinones and α-hydroxyl ketones through the three-component reactions of propargyl alcohols, 2-aminoethanols, and CO_2 under atmospheric CO_2 pressure without any additives or traditional volatile solvents. Diverse desired products could be smoothly produced with a lowermost level of metal loading (0.25 mol%). Particularly, this catalytic system could be effectively recycled and reused, which also exhibited excellent metrics in the evaluation of its green and sustainable level.

2. Experimental details

2.1. Materials

Ag_2WO_4 and $AgSbF_6$ were obtained from Alfa Aesar and Macklin, respectively, while the other silver salts were obtained from Aladdin. $[C_2C_1im][OAc]$, $[C_4C_1im][OAc]$ and $[C_2C_1im][ClO_4]$ were purchased from Sigma-Aldrich, while other imidazole-derived ionic liquids and $[N_{4444}][OAc]$ were purchased from Aladdin. The CO_2 (99.999%) was supplied by Wuhan Xiangyun Industry and Trade Co., Ltd. 2-(Benzylamino)ethanol, diethanolamine, as well as all kinds of propargyl alcohols were purchased from Macklin. [DBUH]-derived ILs and other 2-aminoethanol derivatives were synthesized according to the reported literature [89-92]. The aromatic aldehydes and 2-aminoethanols utilized for the synthesis were purchased from Macklin. Raw materials of DBU, acetic acid, 1H-imidazole, and 2-methylimidazole were purchased from Aladdin. Drying agents (Na_2SO_4), $NaBH_4$, and the organic solvents (CH_3OH, CH_2Cl_2, Et_2O, petroleum ether, and ethyl acetate) used in the processes of reaction, extraction and purification were acquired from Sinopharm Chemical Reagent Co., Ltd. 1,3,5-Trimethoxybenzene used as the internal standard was obtained from Aladdin. Deuterated solvents used for NMR analysis were purchased from CIL (Cambridge Isotope Laboratories). All the above-mentioned materials were directly used without further purification.

2.2. General analytic methods

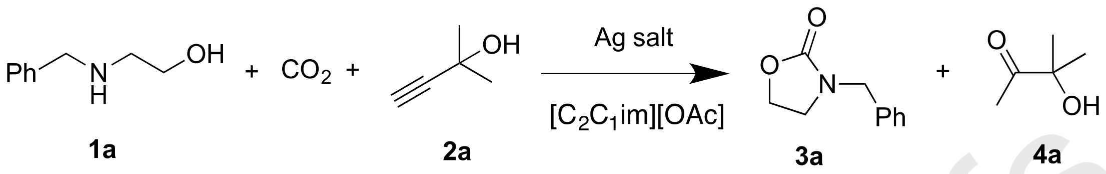
^{1}H NMR spectra were recorded on a Bruker Avance III HD 500 MHz spectrometer with internal standard TMS (δ = 0 ppm) as the reference. ^{13}C NMR spectra were recorded at 126 MHz in $CDCl_3$ (δ = 77.00 ppm) or DMSO-d_6 (δ = 39.90 ppm) with the solvent peaks as references. The data were given as chemical shifts (ppm) and coupling constants (Hz), respectively. HRMS was conducted using a Bruker Daltonics micro TOF-QII mass spectrometry instrument with the data of high-resolution mass given in per charge (m/z).

2.3. General procedures for the synthesis of 2-oxazolidinones and α-hydroxyl ketones

The synthesis of 2-oxazolidinones and α-hydroxyl ketones was performed in a 15 ml Schlenk tube. $AgNO_3$ (0.0125 mmol, 0.25 mol%), $[C_2C_1im][OAc]$ (6 mmol), 2-aminoethanols (5 mmol) and propargyl alcohols (7.5 mmol) were first added. Then the system was purged with CO_2 three times and the mixture was stirred at 60°C under 0.1 MPa of CO_2 for 12 h. Afterwards, the mixture was extracted with diethyl ether (5 × 10 mL) and the upper layers were collected and concentrated under vacuum to give the raw products, which were further purified by column chromatography on silica gel using petroleum ether/ethyl acetate (v/v, 5:1–1:1) as the eluent. When the recyclability of the catalytic system was investigated, the lower layer was recycled and reused directly for the next round after drying under vacuum at 60°C for 4 h.

3. Results and Discussion

Table 1. Screening of Ag salts in catalytic systems. [a, b]



Entry	[Ag] salts	Ionic liquids	Yields/%	
			3a	**4a**
1	/	/	/	/
2	$AgNO_3$	/	/	/
3	/	$[C_2C_1im][OAc]$	/	/
4	AgCl	$[C_2C_1im][OAc]$	76	74
5	AgBr	$[C_2C_1im][OAc]$	87	85
6	AgI	$[C_2C_1im][OAc]$	65	65
7	Ag_2CO_3	$[C_2C_1im][OAc]$	66	65
8	Ag_2WO_4	$[C_2C_1im][OAc]$	68	66
9	Ag_3PO_4	$[C_2C_1im][OAc]$	75	74
10	AgOAc	$[C_2C_1im][OAc]$	88	87
11	$AgNO_3$	$[C_2C_1im][OAc]$	94	93
12	$C_2AgF_3O_2$	$[C_2C_1im][OAc]$	74	73
13	Ag_2O	$[C_2C_1im][OAc]$	70	68
14	$AgPF_6$	$[C_2C_1im][OAc]$	39	36
15	$AgBF_4$	$[C_2C_1im][OAc]$	57	53

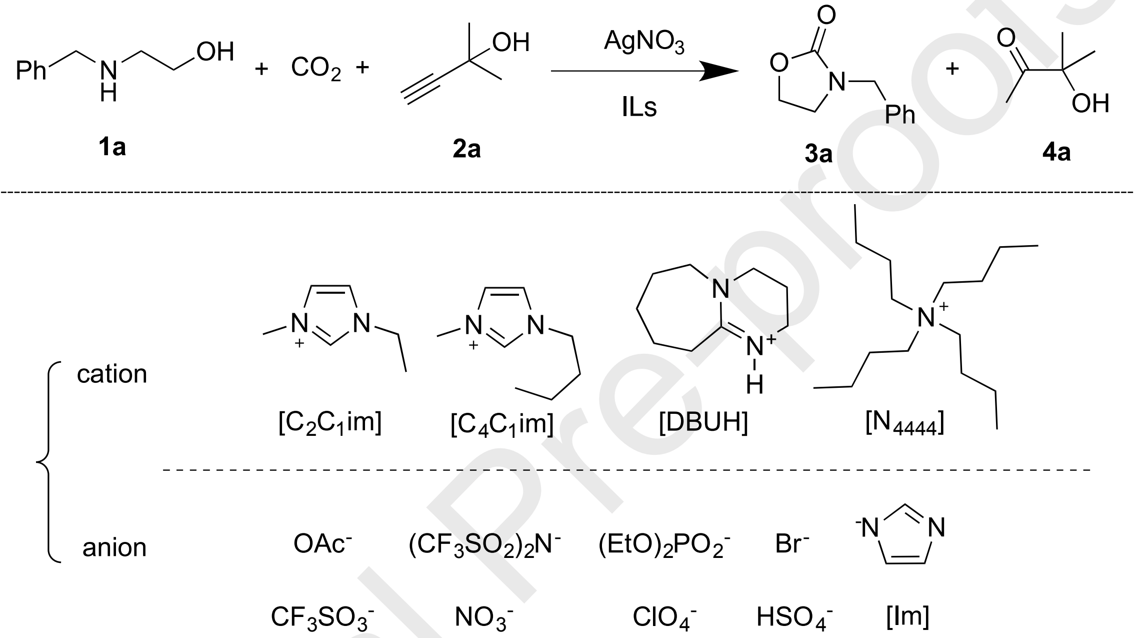
16	$AgSbF_6$	$[C_2C_1im][OAc]$	71	69

[a] Reaction conditions: [Ag] (0.0125 mmol, 0.25 mol% based on **1a**), $[C_2C_1im][OAc]$ (6 mmol), **1a** (5 mmol), **2a** (7.5 mmol), CO_2 (0.1 MPa), 60°C, 12 h.

[b] Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard based on **1a**.

The study initially proceeded by screening the optimal catalytic system of Ag salts and ILs in the reaction of 2-(benzylamino)ethanol (**1a**) and 2-methylbut-3-yn-2-ol (**2a**) under 0.1 MPa of CO_2 at 60°C for 12 h (Table 1). Firstly, a blank experiment showed that the reaction couldn't proceed without catalysts (entry 1). Similarly, the absence of any component in the catalytic system led to a failure of the reaction (entries 2-3). Satisfactorily, when introducing both Ag salts and ILs into the reaction, desired 2-oxazolidinone **3a** and α-hydroxyl ketone **4a** were eventually obtained (entry 4). Further investigations indicated that most of the silver salts including AgCl, AgBr, AgI, Ag_2CO_3, Ag_2WO_4, Ag_3PO_4, AgOAc, $AgNO_3$, $C_2AgF_3O_2$, Ag_2O, $AgPF_6$, $AgBF_4$ and $AgSbF_6$ could efficiently catalyze the reaction in combination with $[C_2C_1im][OAc]$ (entries 4-16). Among them, $AgNO_3$ exhibited the best catalytic performance for the three-component reaction (entry 11). These differences of Ag salts might be attributed to their negative anions which probably influenced their properties. For example, Ag salts like Ag_2O, Ag_2CO_3, *etc*. showed lower solubility and dissociation than AgOAc, $AgNO_3$, *etc*., which might be responsible for their relatively poor catalytic performances (entries 7, 13 *vs.* 10, 11). Additionally, the anions also affected the stability of the silver salts. $AgNO_3$ is considered to be relatively stable when exposed to the light, while $AgPF_6$ or $AgBF_4$ is quite easy to decompose under the same condition, thus possibly leading to the low yields (entries 14, 15 *vs.*11).

Table 2. Screening of ILs in catalytic systems. [a, b]



Entry	[Ag] salts	Ionic liquids	Yields/%	
			3a	**4a**
1	$AgNO_3$	$[C_2C_1im][OAc]$	94	93
			73[c]	70[c]
2	$AgNO_3$	$[C_2C_1im][NTf_2]$	7	4
3	$AgNO_3$	$[C_2C_1im][Et_2PO_4]$	43	42
4	$AgNO_3$	$[C_2C_1im]Br$	/	/
5	$AgNO_3$	$[C_2C_1im][OTf]$	5	6
6	$AgNO_3$	$[C_2C_1im][NO_3]$	5	6

7	$AgNO_3$	$[C_2C_1im][ClO_4]$	/	/
8	$AgNO_3$	$[C_2C_1im][HSO_4]$	/	/
9	$AgNO_3$	$[C_4C_1im][OAc]$	77	78
10	$AgNO_3$	[DBUH][OAc]	53 48 [c]	54 44 [c]
11	$AgNO_3$	[DBUH][Im]	33	36
12	$AgNO_3$	$[N_{4444}][OAc]$	23	20

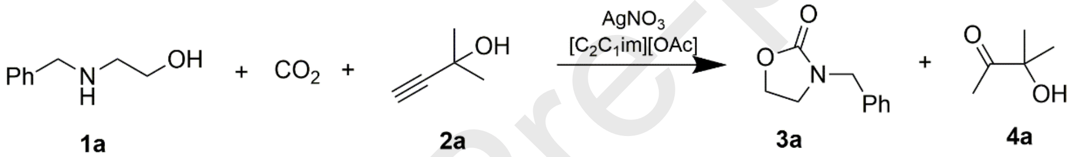
[a] Reaction conditions: $AgNO_3$ (0.0125 mmol, 0.25 mol% based on **1a**), ILs (6 mmol), **1a** (5 mmol), **2a** (7.5 mmol), CO_2 (0.1 MPa), 60°C, 12 h.

[b] Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard based on **1a**.

[c] 10 mL of CH_3CN was added.

Afterwards, the influences of different ionic liquids on the catalytic activity were examined (Table 2). First of all, the anion OAc^- in the $[C_2C_1im][OAc]$ IL was replaced respectively by $(CF_3SO_2)_2N^-$, $Et_2PO_4^-$, Br^-, $CF_3SO_3^-$, NO_3^-, ClO_4^-, and HSO_4^- (entries 2-8). It could be clearly observed that only the $Et_2PO_4^-$ gave a moderate yield of 42%. At the same time, other neutral or acidic anions behaved quite poor activity, indicating that the basic anions were more favorable and OAc^- exhibited superior activity for this reaction. Similar conclusions could also be obtained in the experiments of [DBUH]-derived ILs (entry 10 *vs.* 11). On the other hand, the cation of $[C_2C_1im][OAc]$ was replaced by a similar *n*-butyl substituted imidazole cation, resulting in a slight decrease of the yield (entry 9). Particularly, the catalytic performance of the [DBUH][OAc] was much lower than the imidazole-derived ILs (entry 10 *vs.* 1, 9). This was probably due to the fact that $[DBUH]^+$ cation is a H-bond donor, which can potentially interact with the partially deprotonated propargyl alcohol hence decrease its nucleophilicity and its interaction with CO_2. Besides, another acetate IL employing $[N_{4444}]^+$ as the cation also gave a poor result (entry 12). In conclusion, the system of $AgNO_3/[C_2C_1im][OAc]$ was proved to behave the optimal catalytic activity for this reaction.

Table 3. Screening of the optimal reaction conditions. [a, b]



Entry	$AgNO_3$ /mol% [c]	$[C_2C_1im][OAc]$ /equiv. [c]	Temperature /°C	**1a**:**2a**	Yields/%	
					3a	**4a**
1	0.10	1.2	60	1:1.5	69	70
2	0.25	1.2	60	1:1.5	94	93
3	0.50	1.2	60	1:1.5	93	90
4	1.00	1.2	60	1:1.5	94	91
5	0.25	0.6	60	1:1.5	71	73
6	0.25	0.9	60	1:1.5	89	86
7	0.25	1.5	60	1:1.5	86	83
8	0.25	1.2	25	1:1.5	/	/
9	0.25	1.2	40	1:1.5	31	32

10	0.25	1.2	80	1:1.5	95	91
11	0.25	1.2	60	1:1	69	70
12	0.25	1.2	60	1:1.2	80	79
13	0.25	1.2	60	1:2	91	90

[a] CO_2 (0.1 MPa), 12 h.

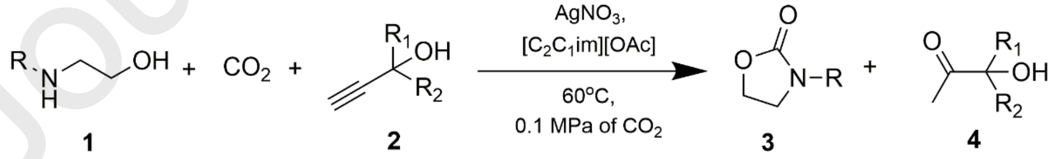
[b] Yields were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard based on **1a**.

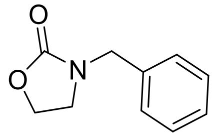
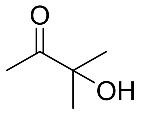
[c] Based on the amount of **1a**.

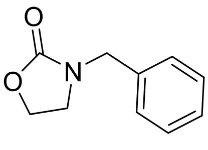
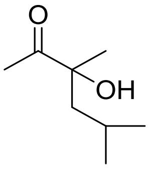
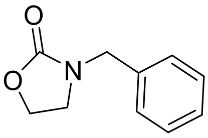
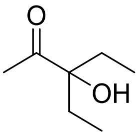
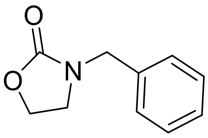
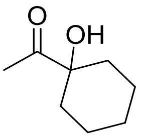
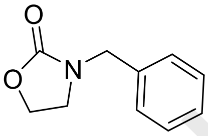
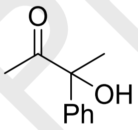
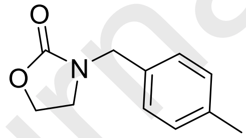
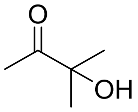
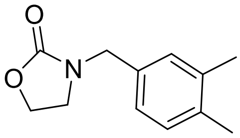
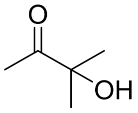
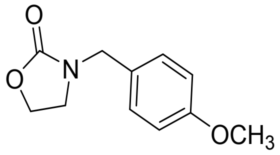
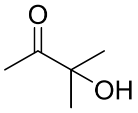
Considering the amounts of catalytic components, temperature, and the ratio of the substrates (**1a**: **2a**) might affect the reaction, these condition parameters were further screened (Table 3). Firstly, when the silver loading rose from 0.1 mol% to 0.25 mol%, the yield increased significantly. However, higher Ag loadings of 0.5 mol% and 1.0 mol% would not contribute more for the yield (entries 1-4), indicating 0.25 mol% of $AgNO_3$ was suitable for this reaction (entry 2 & Part 5.1 of supporting information). Similarly, the varying amounts of IL would influence the catalytic activity and the optimal amount was tuned as 1.2 equiv. of **1a** (entry 2 *vs.* entries 5-7 & Part 5.2 of supporting information). Subsequently, the influence of temperature was also studied. At room temperature, no reaction occurred. However, with an increase in temperature, the desired products would be successively obtained in rising yields. When the temperature reached 60°C, **3a** and **4a** could be produced in more than 90% yield. Although the higher temperature of 80°C would give a slightly better yield, we still selected 60°C as the best condition considering the energy-consumption and the volatility of α-hydroxyl ketones (entry 2 *vs.* entries 8-10). Surprisingly, changing the ratio of substrates would make a difference for the experimental result, which revealed that a higher equivalent of **2a** would help shift the equilibrium towards the desired products (entry 2 *vs.* entries 11-13). Finally, the optimal conditions were fixed as $AgNO_3$ (0.25 mol%)/$[C_2C_1im][OAc]$ (1.2 equiv. of **1a**) at 60°C under atmospheric CO_2 pressure with the ratio of 1:1.5 (**1a**:**2a**). Particularly, it is worth mentioning that this is the first report that could efficiently work under atmospheric CO_2 pressure for the metal-catalyzed systems. Meanwhile, 0.25 mol% is the lowest level of metal loading reported by far.

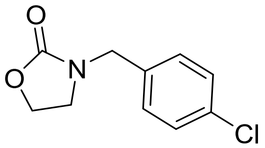
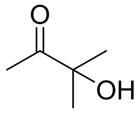
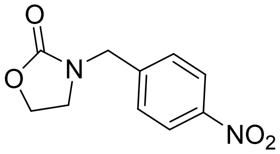
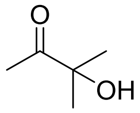
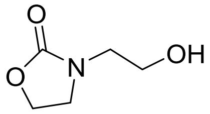
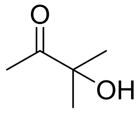
Based on the optimal catalytic system as well as its best reaction conditions, the scope of the substrates was explored afterwards, as shown in Table 4. Delightedly, various propargyl alcohols and 2-aminoethanols with diverse substituents could be smoothly converted into the desired oxazolidinones and α-hydroxyl ketones with the catalysis of the $AgNO_3/[C_2C_1im][OAc]$ system under 0.1 MPa of CO_2. Particularly, the structures of the propargyl alcohols greatly influenced the reactions, and high yields could be easily obtained in the cases of substrate **2** bearing less sterically hindered substituents (entries 1, 2, 3). While for those propargyl alcohols with bulky groups such as cyclohexyl or phenyl group, prolonged reaction time was required to reach the comparable yields (entries 4, 5). This might be because the bulky substituent group would hinder the effective nucleophilic attack of the adjacent hydroxyl oxygen on the carbon of the CO_2 molecule, thus leading to the lower reactivity of the corresponding propargyl alcohol. On the other hand, different 2-aminoethanols substituted by the benzyl or its derived groups also performed different reactivity. Electron-donating groups such as $-CH_3$ connected on the aromatic rings would facilitate the reactions while a specific electron-withdrawing group of $-NO_2$ largely limited the reactivity of the corresponding substrate (entries 6, 7 *vs.* 10). This was possibly because the electron-donating groups would increase the electron density of the benzene ring, thus might enhance the nucleophilicity of the nitrogen atom. While for the strong electron-withdrawing group such as O_2N- (entry 10), its electron effect would give an opposite impact. In addition, an alkyl substituted 2-aminoethanol **1g** was also tried and satisfactory yields of 2-oxazolidinones (94%) and α-hydroxyl ketones (95%) were smoothly obtained (entry 11). Finally, a gram-scale experiment of **1a** and **2a** was conducted under its optimal reaction conditions, in which the $AgNO_3/[C_2C_1im][OAc]$ system still gave satisfactory yields for grams of substrates (entry 1, condition c).

Table 4. Screening of the substrates. [a, b]



Entry	Product **3**	Product **4**	Time/h	Yield/%	
				3	**4**
1			12	94 93[c]	93 91[c]

	3a	**4a**			
2	 **3a**	 **4b**	24	94 90[d]	98 90[d]
3	 **3a**	 **4c**	24	90	85
4	 **3a**	 **4d**	36	95	93
5	 **3a**	 **4e**	36	89	91 84[d]
6	 **3b**	 **4a**	12	97 91[d]	97
7	 **3c**	 **4a**	18	94	90
8			18	98	97

	3d	**4a**			
9			12	97	92
	3e	**4a**			
10			24	25	22
	3f	**4a**			
11			24	94	95
	3g	**4a**			

---

[a] $AgNO_3$ (0.0125 mmol, 0.25 mol% based on **1a**), IL (6 mmol), 2-aminoethanols (**1**) (5 mmol), propargyl alcohols (**2**) (7.5 mmol).

[b] Yields were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard based on **1**.

[c] Gram-scale experiment: **1a** (10 mmol, 1.5122 g), **2a** (15 mmol, 1.2618 g), $AgNO_3$ (0.25 mol% based on **1a)**, IL (12 mmol, 2.0425 g).

[d] Isolated yield.

Having identified the excellent catalytic activity and the broad substrate scope of the $AgNO_3$/[C_2C_1im][OAc] system, we next studied its recyclability, which was treated as another key metric for evaluating its potential in practical applications. Herein, the recycling experiments of the $AgNO_3$/[C_2C_1im][OAc] system were performed using **1a** and **2a** as the model substrates. To our delight, this system could efficiently catalyze the three-component reaction at least 5 times with robust recyclability and reusability (as shown in Fig. 1& Part 4 of supporting information), which is the first report among the metal-catalyzed systems.

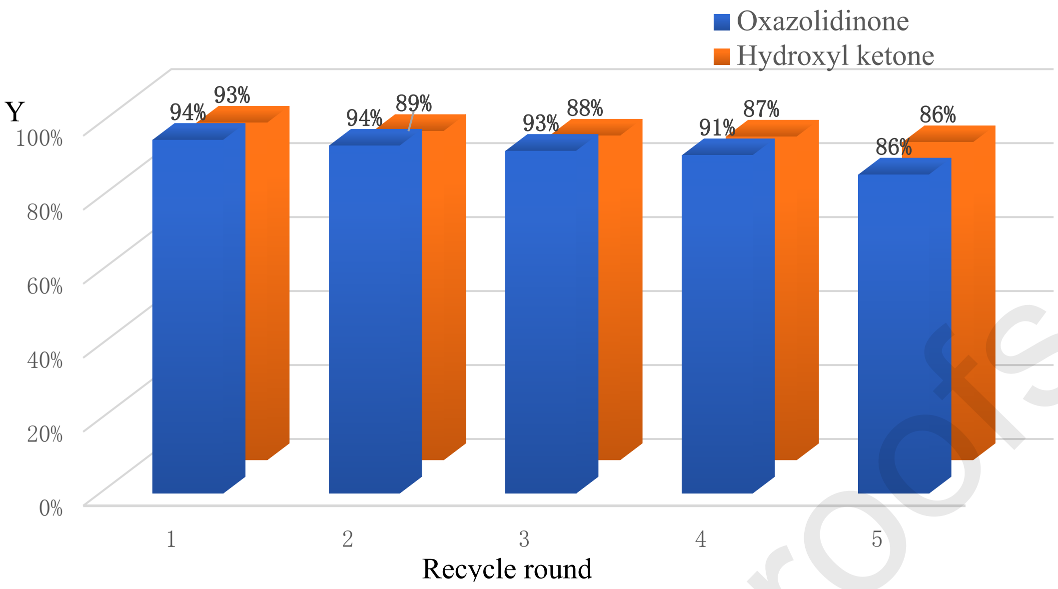
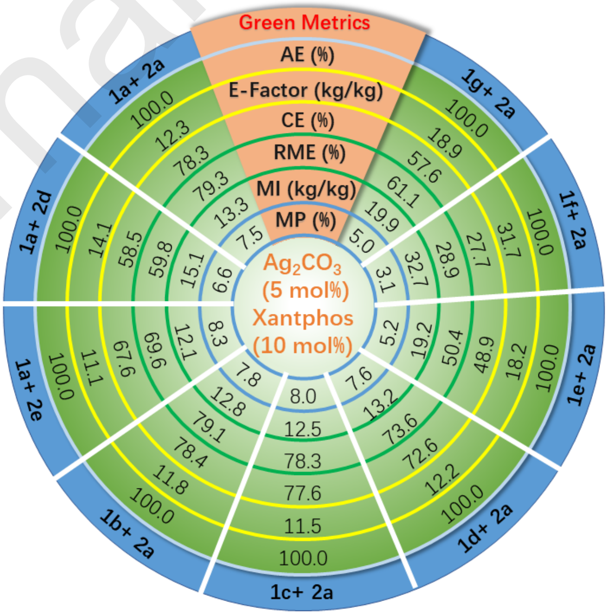


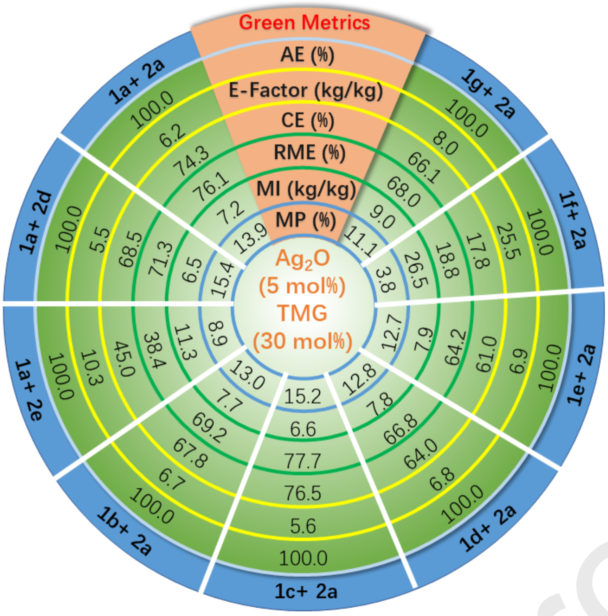
Fig. 1. Reusability of the $AgNO_3$/[C_2C_1im][OAc] system.

For the modern industry, the green and sustainable chemical process level have obtained more and more attention, which could be assessed by the quantitative green metrics [93, 94]. In order to evaluate the performance of the $AgNO_3$/[C_2C_1im][OAc] system in this aspect, several representative metrics were calculated for this system and other reported Ag-catalyzed systems based on several common substrates (as shown in Fig.2 & Part 2 of supporting information). Firstly, the atom economy (AE) values of all these processes were 100%, indicating the three-component reaction was a theoretically ideal way to produce oxazolidinones and hydroxyl ketones. However, AE is a theoretical number that disregards the substances that do not appear in the chemical equation (e.g., solvents or auxiliary chemicals). Therefore, the E-factor, which takes waste from all auxiliary components into account, was examined subsequently. To our delight, the E-factors of the $AgNO_3$/[C_2C_1im[OAc]-catalyzed processes showed much lower values than those of the references, implying these processes exhibited weaker negative effects on the environment. Subsequently, calculations of carbon efficiency (CE) and reaction mass efficiency (RME) were successively performed, in which the $AgNO_3$/[C_2C_1im][OAc]-catalyzed substrates gave higher values, indicating higher catalytic efficiency of the corresponding system. Finally, the metrics of mass intensity (MI) and mass productivity (MP) which reveal the relationship between product mass and total input mass, were also evaluated. The obtained data showed that the $AgNO_3$/[C_2C_1im][OAc]-catalyzed processes also exhibited better performances than the others in this assessment. These abovementioned calculation results proved the $AgNO_3$/[C_2C_1im][OAc]-catalyzed three-component reactions to be relatively more sustainable and greener than the other processes accomplished by the reported Ag-catalyzed systems.

(a)



(b)



(c)

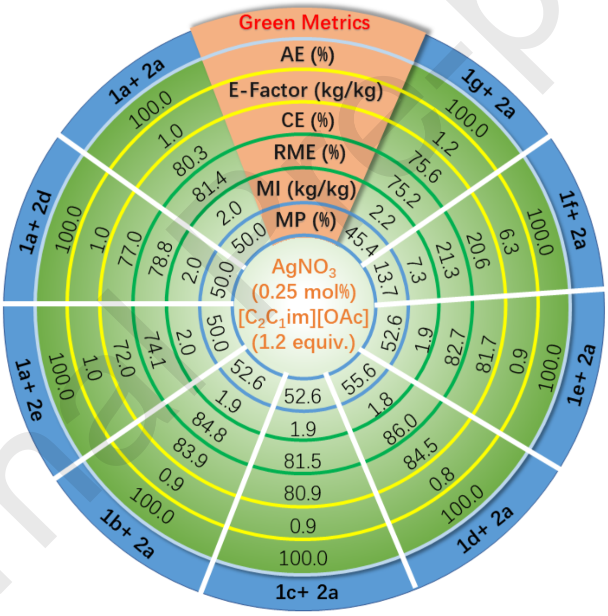


Fig. 2. Green metrics evaluation for the Ag-catalyzed systems.

(a. Ag$_2$CO$_3$/Xantphos system [89]; b. Ag$_2$O/TMG system [90]; c. this work)

4. Mechanistic investigation

4.1 Investigations on the activation of the hydroxyl protons in propargyl alcohols

Regarding the mechanism, it has been reported that the three-component reactions of propargyl alcohols, CO_2, and 2-aminoethanols are cascade reactions [56, 89-91], in which the cyclization between CO_2 and propargyl alcohols occurs first to generate the key intermediary α-alkylidene cyclic carbonates. Then, the carbonates react with 2-aminoethanols to give the final oxazolidinones and hydroxyl ketones through the nucleophilic ring-opening reaction (Fig. 3a). In the first cyclization step, the activation of the hydroxyl groups in propargyl alcohols is regarded as the crucial process, which initiates the vital bonding between CO_2 and substrates, thus introducing the inert CO_2 molecular into the catalytic process [45, 49, 90, 95]. Therefore, investigations on the components which could accomplish this activation are of great importance. Generally, this activation is achieved by forming the hydrogen bonds of the hydroxyl groups with certain basic species, which could be indicated by the shape and chemical shift of the hydroxyl proton signal in ^{1}H NMR [48, 96]. Therefore, Pure **2a**, the mixture of **2a** and the basic amine **1a** (1.5:1), **2a** and the basic IL $[C_2C_1im][OAc]$ (1.5:1.2), were prepared in DMSO-d_6 and directly checked by ^{1}H NMR (Fig. 3b). A sharp peak at $\delta = 5.31$ ppm could be observed in pure **2a**, representing the unactivated hydroxyl proton (Fig. 3b (1)). When **1a** was added, the peak remained sharp, revealing **1a** had no noticeable effect on the activation (Fig. 3b (2)). Nevertheless, in the mixture of **2a** and $[C_2C_1im][OAc]$, the hydroxyl proton was found to show a distinctively different signal which was broad and shifted from its previous position, implying the activation of the hydroxyl group was achieved in this system (Fig. 3b (3)). Consequently, the $[C_2C_1im][OAc]$ was the key component that could accomplish the activation of the hydroxyl group individually.

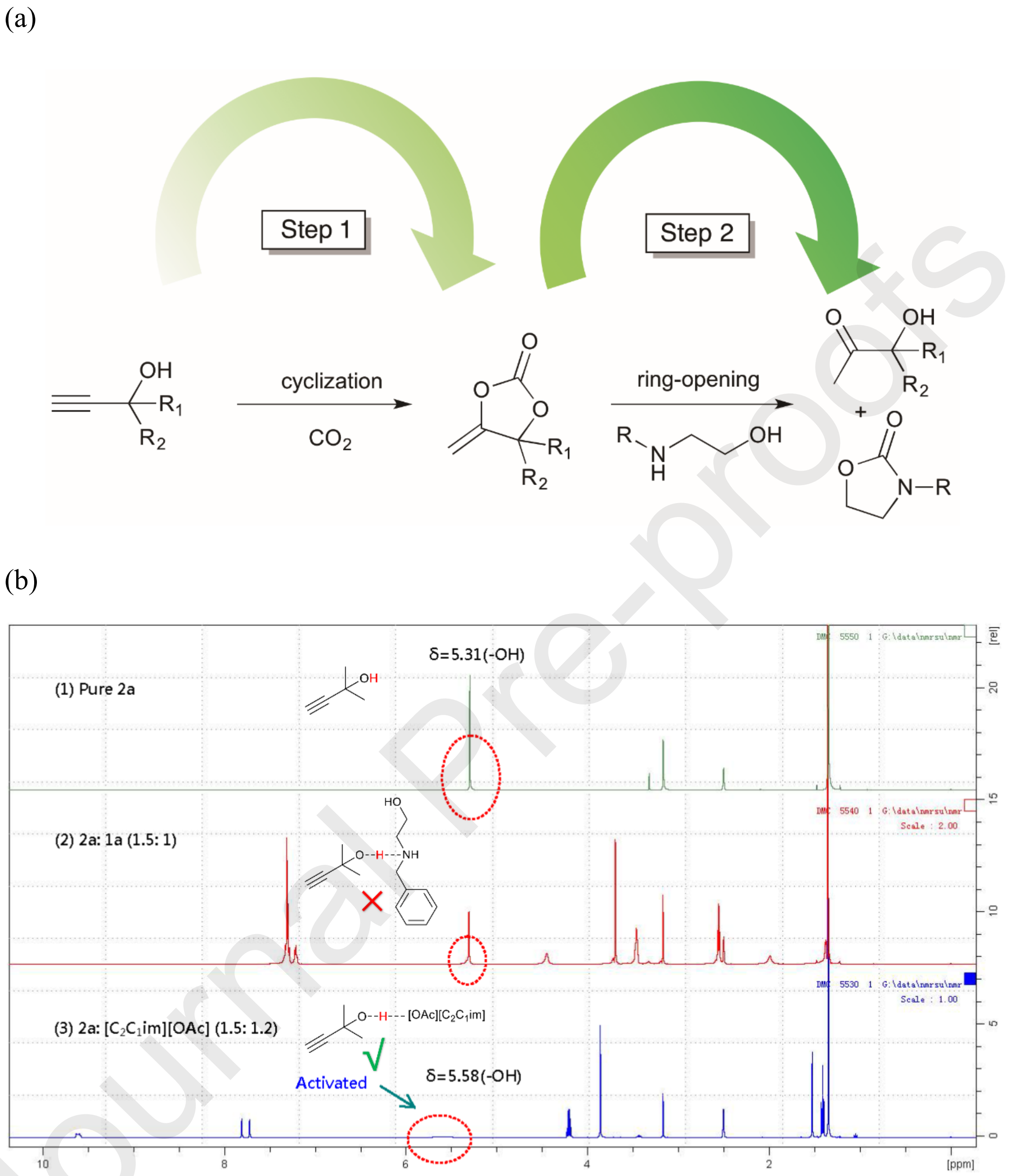
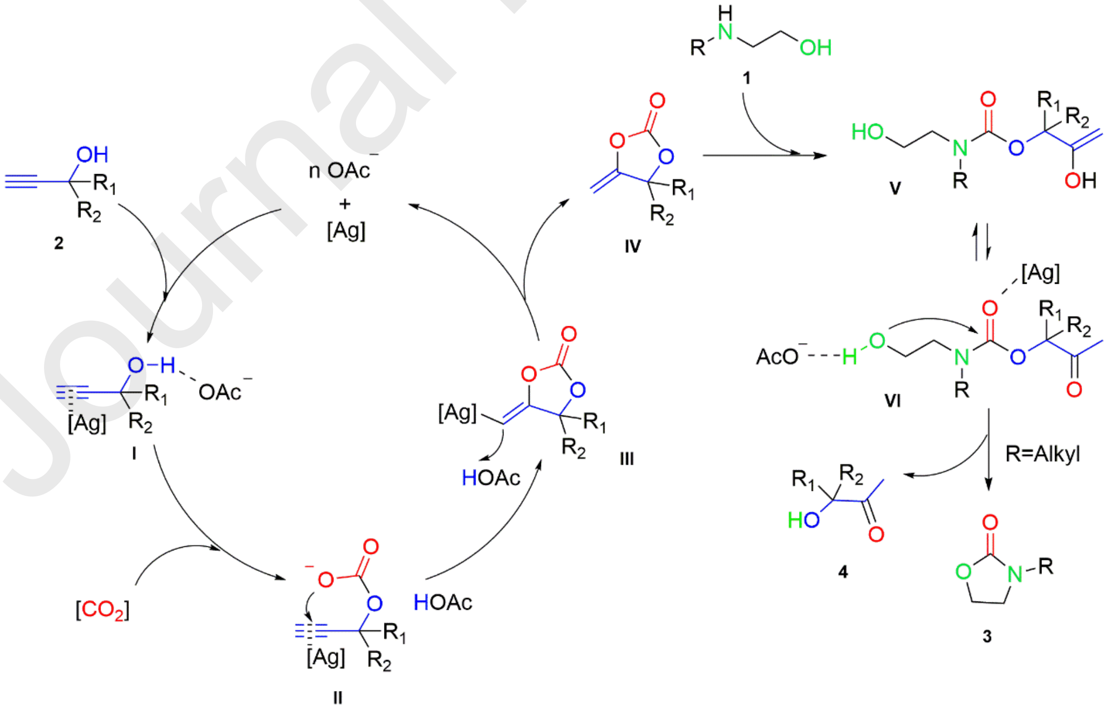


Fig. 3. (a) The cascade procedures for the three-component reactions of propargyl alcohols, CO_2 and 2-aminoethanols. (b) The activation of hydroxyl protons in propargyl alcohols.

4.2 Proposed catalytic mechanism of the $AgNO_3$/[C_2C_1im][OAc] system

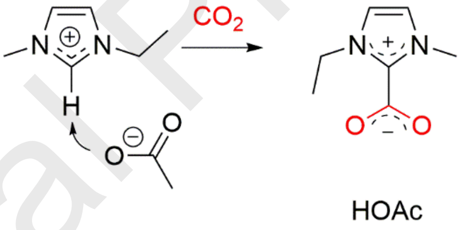
Subsequently, the catalytic cycle of $AgNO_3$/[C_2C_1im][OAc] system for the reaction was speculated, as shown in Scheme 1. Firstly, the basic acetate ion activates the hydroxyl group in substrate **2**, inducing its formation of the C-O bond with CO_2 (intermediate **II**). Subsequently, the Ag species activates the triple bond to promote the bonding of the oxygen anion to the carbon in the alkynyl group, resulting in the formation of a five-membered ring **III**. Then, the catalysts are released and the cyclic carbonate **IV** is produced. Afterwards, the nitrogen atom in substrate **1** attacks the carbonyl group of the carbonate **IV** to produce intermediate **V**, followed by the tautomerization of the enol to the ketone. Eventually, the corresponding oxazolidinone is formed through the intramolecular cyclization of intermediate **VI** with one hydroxyl ketone molecular released from the skeleton.



Scheme 1. Proposed catalytic mechanism of the $AgNO_3$/[C_2C_1im][OAc] system.

4.3 Exploration for the N-heterocyclic carbene-CO_2 (NHC-CO_2) adducts

Based on this general mechanism, we further explored more catalytic features of the $AgNO_3$/[C_2C_1im][OAc] system. It was worth noting that besides the general physical absorption of CO_2, this specific [C_2C_1im][OAc] IL might behave extra chemical absorption ability. When CO_2 was introduced into the [C_2C_1im][OAc] system in some cases, the OAc^- would take the protons from the imidazole rings and free NHC carbenes were generated in situ, which would capture and activate CO_2 by forming NHC-CO_2 adducts (Scheme 2) [97]. Herein, we explored whether this extra CO_2 source existed in the reaction and participated in the catalytic process.



Scheme 2. Generation of NHC-CO_2 adducts.

Following the reported literature [97], we first prepared the fresh NHC-CO_2 adducts in the corresponding IL by introducing CO_2 into the pure [C_2C_1im][OAc] for several hours. Once becoming unclear, the solution was degassed and sampled in DMSO-d_6 for ^{13}C NMR. A series of similar peaks (Fig. 4 (2), marked with red color and ▲) appeared close to the original peaks of [C_2C_1im][OAc] (Fig. 4 (1), marked with green color), representing the imidazole carbon signals of the NHC-CO_2. More importantly, a peak around δ = 154 ppm was clearly observed (Fig. 4 (2), 7*), which represented the extra carboxylic carbon of the NHC-CO_2. This peak could be used as the characteristic peak for the detection of the NHC-CO_2 [97]. Subsequently, we took the reaction mixture of **1a** and **2a** catalyzed by the $AgNO_3$/[C_2C_1im][OAc] system for ^{13}C NMR (Fig. 4 (3)). It could be clearly observed that the characteristic peak at δ = 154.22 ppm appeared, indicating the existence of the NHC-CO_2 adducts. Moreover, other peaks of the imidazole carbon signals of the NHC-CO_2 could also be successively found in this spectrum (Fig. 4 (2) *vs.* (3)). These results further confirmed the existence of the NHC-CO_2 adducts in the reaction process.

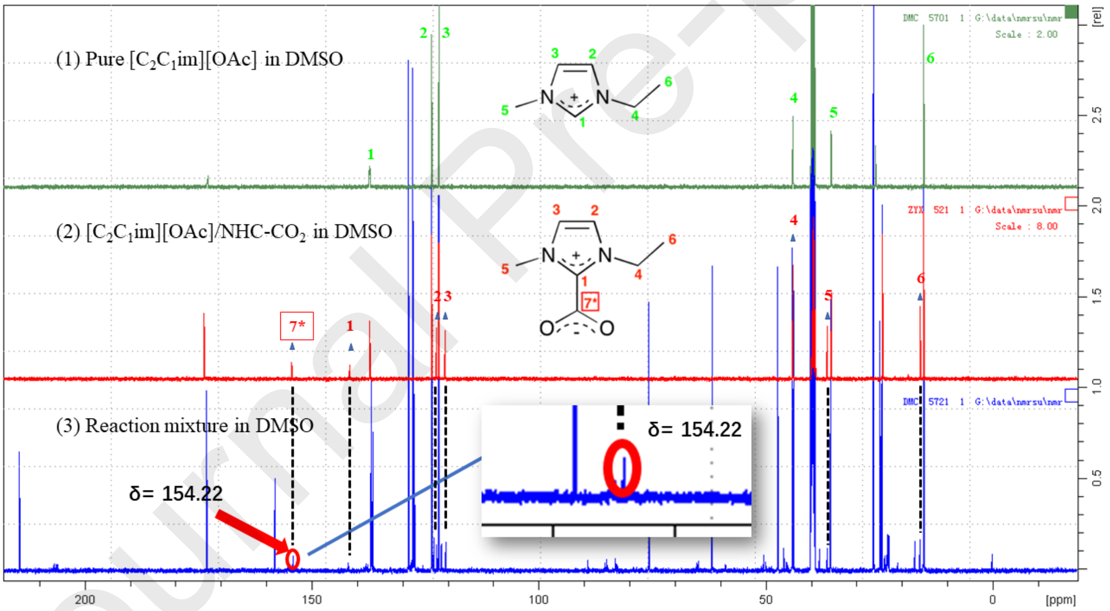


Fig. 4. The detection of NHC-CO_2 adducts.

Afterwards, **model reaction I** (Fig. 5 Model I) without CO_2 was performed to further explore the reactivity of this extra CO_2 source, in which the freshly prepared and degassed 3 mmol [C_2C_1im][OAc]/NHC-CO_2 mixture (containing 0.45 mmol of NHC-CO_2. Fig. S1 of Part 1.1, supporting information) was introduced instead of the normal [C_2C_1im][OAc]. After several hours, the reaction mixture was directly sampled for ^{13}C NMR. In the spectrum, the signals of **3a** could be clearly detected (Fig. S2 of Part 1.1, supporting information), indicating the NHC-CO_2 adducts might participate in the reaction individually without CO_2. Moreover, 17% of **3a** was obtained, namely 0.45 mmol of NHC-CO_2 was converted to 0.42 mmol of **3a**, revealing this transformation was almost stoichiometric. Subsequently, **model reactions II** and **III** (Fig.5 Model II *vs.* III) varied in the ILs (freshly prepared [C_2C_1im][OAc]/NHC-CO_2 *vs.* normal [C_2C_1im][OAc]) were conducted under 1 bar of CO_2 with the same amount of $AgNO_3$ and substrates. After 20 minutes, **model reaction II** that generating NHC-CO_2 in advance, gave a better yield than **model reaction III**. These results suggested that the existence of this extra CO_2 source was probably beneficial for the catalytic reaction.

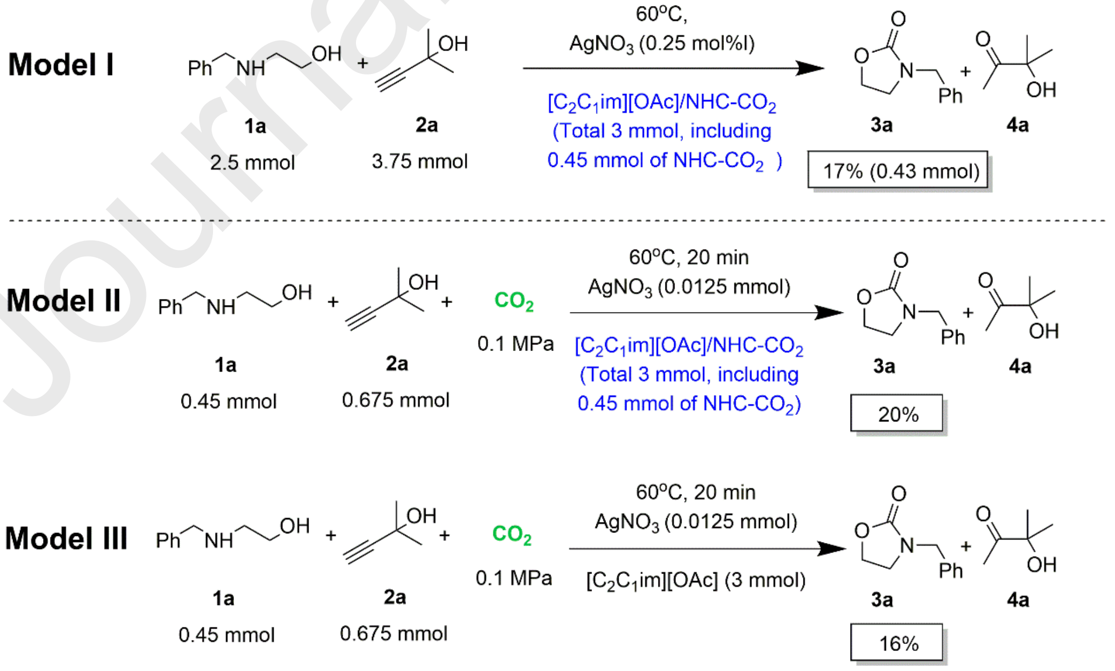
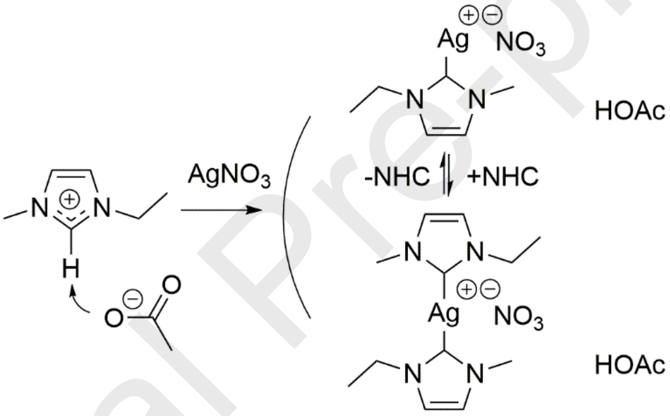


Fig. 5. Model reactions for the exploration of NHC-CO_2 adducts

4.4 Exploration for the NHC-Ag complexes

Having verified the existence of the NHC-CO_2 adducts as well as its reactivity, we were inspired to further investigate a similar hypothesis about the active Ag species. Similarly, we speculated that in this catalytic reaction, the $AgNO_3$ might combine with the imidazole rings assisted by the basic OAc^- anions (Scheme 3), giving the NHC-Ag complexes [29, 56, 86, 98, 99]. Herein, we successively explored the existence of the complexes as well as the catalytic activity.



Scheme 3. Generation of NHC-Ag complexes.

In order to explore the NHC-Ag complexes in the catalytic process, **model reaction IV** (Fig. 7 Model IV) was performed. Once the reaction was finished, the mixture was checked directly by HRMS. Obviously, the spectrum clearly showed two signals of 216.98911 and 327.07304, which were found to meet the calculated masses of the NHC-Ag complexes (Fig. 6). Other isotopic peaks generated due to the silver were also observed, which further confirmed the existence of the desired complexes.

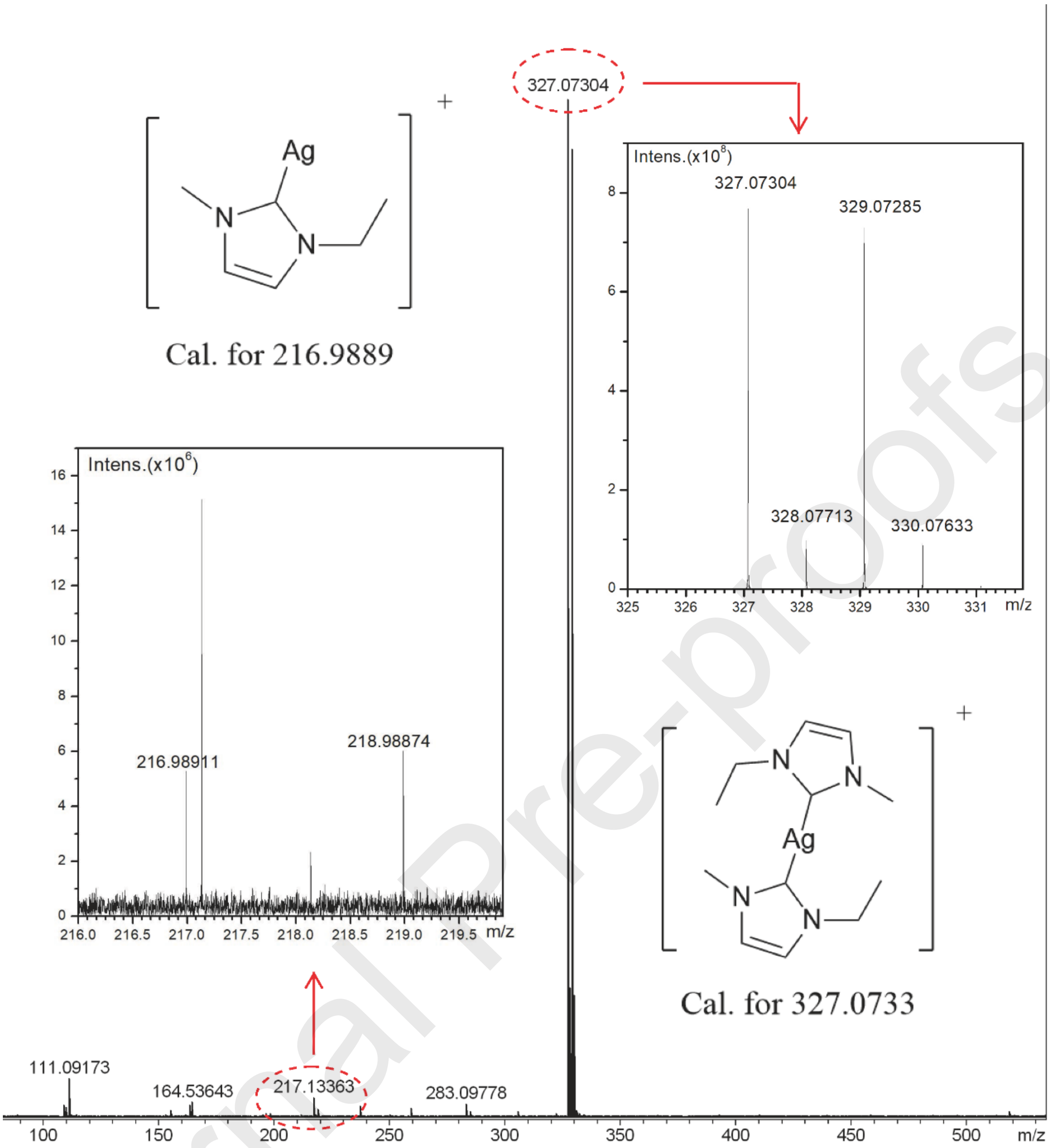
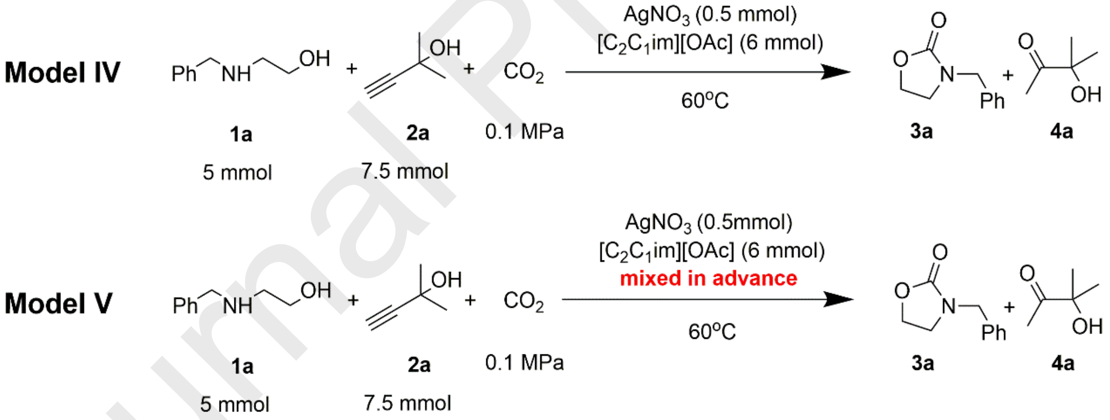


Fig. 6. Detection of the NHC-Ag complexes during the catalytic process.

Subsequently, we compared the catalytic activity of the NHC-Ag complexes with the normal AgNO$_3$ through the **model reaction IV** and **V** (Fig. 7a). Particularly for **V**, AgNO$_3$ and [C$_2$C$_1$im][OAc] were firstly mixed and stirred for several hours to in situ generate the desired NHC-Ag complexes, which could be indicated by the HRMS spectrum (Fig. S3 of Part 1.2, supporting information). Once finished, this mixture was directly used for **model reaction V**. Meanwhile, **model reaction IV** with the same amount of $AgNO_3$, $[C_2C_1im][OAc]$, substrate **1a** and **2a** under the same conditions were simultaneously started. Both of these reactions were monitored by ^1H NMR to respectively obtain their kinetic curves (Fig. 7b). Obviously, a higher conversion could be invariably obtained by **model reaction V** at any time of the reaction process, although the same amount of Ag source was employed. This result indicated that the NHC-Ag complexes were probably more active catalytic species than the normal $AgNO_3$. This might be one reason for the superior catalytic activity of the $AgNO_3/[C_2C_1im][OAc]$ system even with the lowermost Ag loading employed.

(a)



(b)

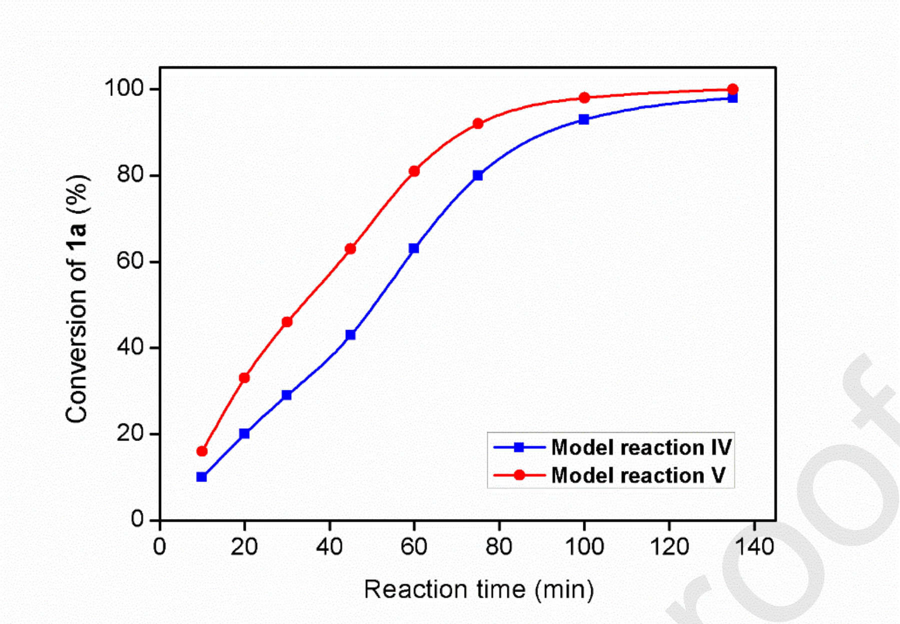


Fig. 7. (a) Model reactions for the exploration of NHC-Ag complexes;

(b) Kinetic curves (conversion *vs*. time) of two systems.

4. Conclusions

In summary, a $AgNO_3$/[C_2C_1im][OAc] catalytic system was developed for the three-component reactions of propargyl alcohols, CO_2, and 2-aminoethanols to simultaneously produce oxazolidinones and α-hydroxyl ketones. Numerous substrates bearing diverse substitutes could be efficiently converted into the desired products with the catalysis of the lowermost metal loading ever reported. Particularly, this system is considered to be the first example that could efficiently work under atmospheric CO_2 pressure, as well as the first report that could be recycled and reused at least five times among the metal-catalyzed systems. In evaluating the green metrics, this system exhibited a relatively greener and more sustainable level than the other Ag-catalyzed systems. Moreover, the components of this system are commercially available. These performances confirmed its excellent catalytic activity as well as the potential for practical applications. Furthermore, the mechanistic investigations verified the existence of two active species during the catalytic process, namely the NHC-Ag complexes and the NHC-CO_2 adducts. Subsequently, their reactivity in this reaction was evaluated for the first time, which was finally proved to be beneficial for the catalytic activity.

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.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 21950410754). We appreciate the Fundamental Research Funds for the Central Universities (No. 205201028, 205201026).

Appendix A. Supplementary data

Supplementary data associated with this article can be found.

References

[1] N. Mac Dowell, P.S. Fennell, N. Shah, G.C. Maitland, The role of CO_2 capture and utilization in mitigating climate change, Nature Climate Change, 7 (2017) 243-249. DOI: 10.1038/nclimate3231

[2] C.L. Quéré, R.M. Andrew, J.G. Canadell, S. Sitch, J.I. Korsbakken, G.P. Peters, A.C. Manning, T.A. Boden, P.P. Tans, R.A. Houghton, Global carbon budget 2016, Earth Syst. Sci. Data, 8 (2016) 605-649. DOI: 10.5194/essd-2016-51

[3] C. Federsel, R. Jackstell, M. Beller, State-of-the-art catalysts for hydrogenation of carbon dioxide, Angew. Chem. Int. Ed., 49 (2010) 6254-6257. DOI: 10.1002/anie.201000533

[4] E.S. Sanzperez, C.R. Murdock, S.A. Didas, C.W. Jones, Direct capture of CO_2 from ambient air, Chem. Rev., 116 (2016) 11840-11876. DOI: 10.1021/acs.chemrev.6b00173

[5] K. Huang, C.L. Sun, Z.J. Shi, Transition-metal-catalyzed C–C bond formation through the fixation of carbon dioxide, Chem. Soc. Rev., 40 (2011) 2435-2452. DOI: 10.1039/C0CS00129E

[6] M. He, Y. Sun, B. Han, Green carbon science: scientific basis for integrating carbon resource processing, utilization, and recycling, Angew. Chem. Int. Ed., 52 (2013) 9620-9633. DOI: 10.1002/anie.201209384

[7] Z. Yang, L. He, J. Gao, A. Liu, B. Yu, Carbon dioxide utilization with C–N bond formation: carbon dioxide capture and subsequent conversion, Energy Environ. Sci., 5 (2012) 6602-6639. DOI: 10.1039/C2EE02774G

[8] J. Bao, G.H. Yang, Y. Yoneyama, N. Tsubaki, Significant Advances in C1 Catalysis: Highly Efficient Catalysts and Catalytic Reactions, Acs Catalysis, 9 (2019) 3026-3053. DOI: 10.1021/acscatal.8b03924

[9] M.E. Boot-Handford, J.C. Abanades, E.J. Anthony, M.J. Blunt, S. Brandani, N. Mac Dowell, J.R. Fernández, M.-C. Ferrari, R. Gross, J.P. Hallett, Carbon capture and storage update, Energy Environ. Sci., 7 (2014) 130-189. DOI: 10.1039/c3ee42350f

[10] P.T.K. Nguyen, H.T.D. Nguyen, H.N. Nguyen, C.A. Trickett, Q.T. Ton, E. Gutierrez-Puebla, M.A. Monge, K.E. Cordova, F. Gandara, New Metal-Organic Frameworks for Chemical Fixation of CO_2, ACS Appl. Mater. Interfaces, 10 (2018) 733-744. DOI: 10.1021/acsami.7b16163

[11] J. Wei, Q. Ge, R. Yao, Z. Wen, C. Fang, L. Guo, H. Xu, J. Sun, Directly converting CO_2 into a gasoline fuel, Nat. Commun., 8 (2017) 15174. DOI: 10.1038/ncomms15174

[12] J. Artz, T.E. Muller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow, W. Leitner, Sustainable Conversion of Carbon Dioxide: An Integrated Review of Catalysis and Life Cycle Assessment, Chem. Rev., 118 (2018) 434-504. DOI: 10.1021/acs.chemrev.7b00435

[13] M. Aresta, A. Dibenedetto, A. Angelini, Catalysis for the valorization of exhaust carbon: from CO_2 to chemicals, materials, and fuels. Technological use of CO_2, Chem. Rev., 114 (2013) 1709-1742. DOI: 10.1021/cr4002758

[14] T. Sakakura, J.-C. Choi, H. Yasuda, Transformation of carbon dioxide, Chem.

Rev., 107 (2007) 2365-2387. DOI: 10.1021/cr068357u

[15] A.M. Appel, J.E. Bercaw, A.B. Bocarsly, H. Dobbek, D.L. Dubois, M. Dupuis, J.G. Ferry, E. Fujita, R. Hille, P.J.A. Kenis, Frontiers, Opportunities, and Challenges in Biochemical and Chemical Catalysis of CO_2 Fixation, Chem. Rev., 113 (2013) 6621-6658. DOI: 10.1021/cr300463y

[16] S.L. Hou, J. Dong, B. Zhao, Formation of C-X Bonds in CO_2 Chemical Fixation Catalyzed by Metal-Organic Frameworks, Adv. Mater., 32 (2020) 14. DOI: 10.1002/adma.201806163

[17] S. Dabral, T. Schaub, The Use of Carbon Dioxide (CO_2) as a Building Block in Organic Synthesis from an Industrial Perspective, Adv. Synth. Catal., 361 (2019) 223-246. DOI: 10.1002/adsc.201801215

[18] D. Riemer, B. Mandaviya, W. Schilling, A.C. Götz, T. Kühl, M. Finger, S. Das, CO_2-Catalyzed Oxidation of Benzylic and Allylic Alcohols with DMSO, ACS Catalysis, 8 (2018) 3030-3034. DOI: 10.1021/acscatal.7b04390

[19] D. Riemer, W. Schilling, A. Goetz, Y. Zhang, S. Gehrke, I. Tkach, O. Hollóczki, S. Das, CO_2-Catalyzed Efficient Dehydrogenation of Amines with Detailed Mechanistic and Kinetic Studies, ACS Catalysis, 8 (2018) 11679-11687. DOI: 10.1021/acscatal.8b03059

[20] P. Hirapara, D. Riemer, N. Hazra, J. Gajera, M. Finger, S. Das, CO_2-assisted synthesis of non-symmetric α-diketones directly from aldehydesviaC–C bond formation, Green Chem., 19 (2017) 5356-5360. DOI: 10.1039/c7gc02425h

[21] D. Riemer, P. Hirapara, S. Das, Chemoselective Synthesis of Carbamates using

CO_2 as Carbon Source, ChemSusChem, 9 (2016) 1916-1920. DOI: 10.1002/cssc.201600521

[22] J. Kothandaraman, R.A. Dagle, V.L. Dagle, S.D. Davidson, E.D. Walter, S.D. Burton, D.W. Hoyt, D.J. Heldebrant, Condensed-phase low temperature heterogeneous hydrogenation of CO_2 to methanol, Catal. Sci. Technol., 8 (2018) 5098-5103. DOI: 10.1039/c8cy00997j

[23] A. Goeppert, M. Czaun, J.-P. Jones, G.S. Prakash, G.A. Olah, Recycling of carbon dioxide to methanol and derived products–closing the loop, Chem. Soc. Rev., 43 (2014) 7995-8048. DOI: 10.1039/C4CS00122B

[24] S. Zhang, X. Liu, Z. Shao, H. Wang, Y. Sun, Direct CO_2 hydrogenation to ethanol over supported Co_2C catalysts: Studies on support effects and mechanism, J. Catal., 382 (2020) 86-96. DOI: 10.1016/j.jcat.2019.11.038

[25] Y. Lian, T. Fang, Y. Zhang, B. Liu, j. Li, Hydrogenation of CO_2 to alcohol species over $Co@Co_3O_4/C\text{-}N$ catalysts, J. Catal., 379 (2019) 46-51. DOI: 10.1016/j.jcat.2019.09.018

[26] B. Yu, Z.F. Diao, C.X. Guo, L.N. He, Carboxylation of olefins/alkynes with CO_2 to industrially relevant acrylic acid derivatives, J. CO_2 Util., 1 (2013) 60-68. DOI: 10.1016/j.jcou.2013.01.001

[27] Y. Yuan, C. Chen, C. Zeng, B. Mousavi, S. Chaemchuen, F. Verpoort, Carboxylation of Terminal Alkynes with Carbon Dioxide Catalyzed by an In Situ Ag_2O/N-Heterocyclic Carbene Precursor System, ChemCatChem, 9 (2017) 882-887. DOI: 10.1002/cctc.201601379

[28] F. Manjolinho, M. Arndt, K. Gooßen, L.J. Gooßen, Catalytic C–H Carboxylation of Terminal Alkynes with Carbon Dioxide, ACS Catalysis, 2 (2012) 2014-2021. DOI: 10.1021/cs300448v

[29] D. Yu, M.X. Tan, Y. Zhang, Carboxylation of Terminal Alkynes with Carbon Dioxide Catalyzed by Poly(N-Heterocyclic Carbene)-Supported Silver Nanoparticles, Adv. Synth. Catal., 354 (2012) 969-974. DOI: 10.1002/adsc.201100934

[30] L. Zhang, J. Cheng, B. Carry, Z. Hou, Catalytic boracarboxylation of alkynes with diborane and carbon dioxide by an N-heterocyclic carbene copper catalyst, J. Am. Chem. Soc., 134 (2012) 14314-14317. DOI: 10.1021/ja3063474

[31] A. Banerjee, G.R. Dick, T. Yoshino, M.W. Kanan, Carbon dioxide utilization via carbonate-promoted C–H carboxylation, Nature, 531 (2016) 215-219. DOI: 10.1038/nature17185

[32] C. Maeda, Y. Miyazaki, T. Ema, Recent progress in catalytic conversions of carbon dioxide, Catal. Sci. Technol., 4 (2014) 1482-1497. DOI: 10.1039/C3CY00993A

[33] Q. Liu, L. Wu, R. Jackstell, M. Beller, Using carbon dioxide as a building block in organic synthesis, Nat. Commun., 6 (2015) 5933. DOI: 10.1038/ncomms6933

[34] E. Blondiaux, J. Pouessel, T. Cantat, Carbon Dioxide Reduction to Methylamines under Metal-Free Conditions, Angew. Chem. Int. Ed., 53 (2014) 12186-12190. DOI: 10.1002/anie.201407357

[35] C.C. Chong, R. Kinjo, Hydrophosphination of CO_2 and Subsequent Formate Transfer in the 1,3,2-Diazaphospholene-Catalyzed N-Formylation of Amines, 10.1002/anie.201505244, 54 (2015) 12116-12120. DOI: 10.1002/anie.201505244

[36] X. Liu, X. Li, C. Qiao, L. He, Transition-Metal-Free Catalysis for the Reductive Functionalization of CO_2 with Amines, Synlett, 29 (2018) 548-555. DOI: 10.1055/s-0036-1591533

[37] A.-A.G. Shaikh, S. Sivaram, Organic carbonates, Chem. Rev., 96 (1996) 951-976. DOI: 10.1021/cr950067i

[38] T. Sakakura, K. Kohno, The synthesis of organic carbonates from carbon dioxide, Chem. Commun., (2009) 1312-1330. DOI: 10.1039/B819997C

[39] J. Sun, S.-i. Fujita, M. Arai, Development in the green synthesis of cyclic carbonate from carbon dioxide using ionic liquids, J. Organomet. Chem., 690 (2005) 3490-3497. DOI: 10.1016/j.jorganchem.2005.02.011

[40] A.J. Kamphuis, F. Picchioni, P.P. Pescarmona, CO_2-fixation into cyclic and polymeric carbonates: principles and applications, Green Chem., 21 (2019) 406-448. DOI: 10.1039/c8gc03086c

[41] S.L. Hou, J. Dong, X.L. Jiang, Z.H. Jiao, B. Zhao, A Noble-Metal-Free Metal-Organic Framework (MOF) Catalyst for the Highly Efficient Conversion of CO_2 with Propargylic Alcohols, Angew. Chem. Int. Ed., 58 (2019) 577-581. DOI: 10.1002/anie.201811506

[42] S. Chaemchuen, X. Xiao, M. Ghadamyari, B. Mousavi, N. Klomkliang, Y.

Yuan, F. Verpoort, Robust and efficient catalyst derived from bimetallic Zn/Co zeolitic imidazolate frameworks for CO_2 conversion, J. Catal., 370 (2019) 38-45. DOI: 10.1016/j.jcat.2018.11.027

[43] Y.Y. Gong, Y. Yuan, C. Chen, P. Zhang, J.C. Wang, S. Zhuiykov, S. Chaemchuen, F. Verpoort, Core-shell metal-organic frameworks and metal functionalization to access highest efficiency in catalytic carboxylation, J. Catal., 371 (2019) 106-115. DOI: 10.1016/j.jcat.2019.01.036

[44] Y.Y. Gong, Y. Yuan, C. Chen, P. Zhang, J.C. Wang, A. Khan, S. Zhuiykov, S. Chaemchuen, F. Verpoort, Enhancing catalytic performance via structure core-shell metal-organic frameworks, J. Catal., 375 (2019) 371-379. DOI: 10.1016/j.jcat.2019.06.031

[45] Y. Yuan, Y. Xie, C. Zeng, D.D. Song, S. Chaemchuen, C. Chen, F. Verpoort, A recyclable AgI/OAc- catalytic system for the efficient synthesis of alpha-alkylidene cyclic carbonates: carbon dioxide conversion at atmospheric pressure, Green Chem., 19 (2017) 2936-2940. DOI: 10.1039/c7gc00276a

[46] Y. Yuan, Y. Xie, C. Zeng, D.D. Song, S. Chaemchuen, C. Chen, F. Verpoort, A simple and robust AgI/KOAc catalytic system for the carboxylative assembly of propargyl alcohols and carbon dioxide at atmospheric pressure, Catal. Sci. Technol., 7 (2017) 2935-2939. DOI: 10.1039/c7cy00696a

[47] Y. Yuan, Y. Xie, D.D. Song, C. Zeng, S. Chaemchuen, C. Chen, F. Verpoort, One-pot carboxylative cyclization of propargylic alcohols and CO_2 catalysed by N-heterocyclic carbene/Ag systems, Appl. Organomet. Chem., 31 (2017) 6. DOI:

10.1002/aoc.3867

[48] Q.W. Song, L.N. He, Robust Silver(I) Catalyst for the Carboxylative Cyclization of Propargylic Alcohols with Carbon Dioxide under Ambient Conditions, Adv. Synth. Catal., 358 (2016) 1251-1258. DOI: 10.1002/adsc.201500639

[49] W. Yamada, Y. Sugawara, H.M. Cheng, T. Ikeno, T. Yamada, Silver-Catalyzed Incorporation of Carbon Dioxide into Propargylic Alcohols, Eur. J. Org. Chem., 2007 (2007) 2604-2607. DOI: 10.1002/ejoc.200700169

[50] J. Hu, J. Ma, L. Lu, Q. Qian, Z. Zhang, C. Xie, B. Han, Synthesis of Asymmetrical Organic Carbonates using CO_2 as a Feedstock in AgCl/Ionic Liquid System at Ambient Conditions, ChemSusChem, 10 (2017) 1292-1297. DOI: 10.1002/cssc.201601773

[51] X. Yu, Z. Yang, F. Zhang, Z. Liu, P. Yang, H. Zhang, B. Yu, Y. Zhao, Z. Liu, A Rose bengal-functionalized porous organic polymer for carboxylative cyclization of propargyl alcohols with CO_2, Chem. Commun. (Cambridge, U. K.), 55 (2019) 12475-12478. DOI: 10.1039/c9cc07043e

[52] W. Xiong, C. Qi, H. He, L. Ouyang, M. Zhang, H. Jiang, Base-Promoted Coupling of Carbon Dioxide, Amines, and N-Tosylhydrazones: A Novel and Versatile Approach to Carbamates, Angew. Chem. Int. Ed., 54 (2015) 3084-3087. DOI: 10.1002/anie.201410605

[53] D. Riemer, P. Hirapara, S. Das, Chemoselective synthesis of carbamates using CO_2 as carbon source, ChemSusChem, 9 (2016) 1916-1920. DOI:

10.1002/cssc.201600521

[54] S. Arshadi, E. Vessally, A. Hosseinian, S. Soleimani-amiri, L. Edjlali, Three-component coupling of CO_2, propargyl alcohols, and amines: An environmentally benign access to cyclic and acyclic carbamates (A Review), J. CO_2 Util., 21 (2017) 108-118. DOI: 10.1016/j.jcou.2017.07.008

[55] A. Hosseinian, S. Ahmadi, R. Mohammadi, A. Monfared, Z. Rahmani, Three-component reaction of amines, epoxides, and carbon dioxide: A straightforward route to organic carbamates, J. CO_2 Util., 27 (2018) 381-389. DOI: 10.1016/j.jcou.2018.08.013

[56] D. Song, D. Li, X. Xiao, C. Cheng, S. Chaemchuen, Y. Yuan, F. Verpoort, Synthesis of β-oxopropylcarbamates in a recyclable AgBr/ionic liquid catalytic system: An efficient assembly of CO_2 under ambient pressure, J. CO_2 Util., 27 (2018) 217-222. DOI: 10.1016/j.jcou.2018.07.021

[57] R. Roers, G.L. Verdine, Concise enantio-and diastereoselective synthesis of α-hydroxy-α-methyl-β-amino acids, Tetrahedron Lett., 42 (2001) 3563-3565. DOI: 10.1016/S0040-4039(01)00457-9

[58] J.V. Prasad, New oxazolidinones, Curr. Opin. Microbiol., 10 (2007) 454-460. DOI: 10.1016/j.mib.2007.08.001

[59] G. Zappia, P. Menendez, G. Delle Monache, D. Misiti, L. Nevola, B. Botta, The contribution of oxazolidinone frame to the biological activity of pharmaceutical drugs and natural products, Mini-Rev. Med. Chem., 7 (2007) 389-409. DOI: 10.2174/138955707780363783

[60] P. Hoyos, J.-V. Sinisterra, F. Molinari, A.s.R. Alcántara, P. Domínguez de María, Biocatalytic strategies for the asymmetric synthesis of α-hydroxy ketones, Acc. Chem. Res., 43 (2009) 288-299. DOI: 10.1021/ar900196n

[61] J. Segurola, N.S. Allen, M. Edge, A. McMahon, S. Wilson, Photoyellowing and discolouration of UV cured acrylated clear coatings systems: influence of photoinitiator type, Polym. Degrad. Stab., 64 (1999) 39-48. DOI: 10.1016/S0141-3910(98)00169-4

[62] T. Nishiyama, S. Matsui, F. Yamada, Synthesis and spectral behavior of 5-methyl-3-phenyl-1, 3-oxazolidin-2-ones using NMR, J. Heterocycl. Chem., 23 (1986) 1427-1429. DOI: 10.1002/jhet.5570230535

[63] H. Zhang, F. Huo, F. Liu, Z. Chen, J. Liu, S. Bo, Z. Zhen, L. Qiu, Synthesis and characterization of two novel second-order nonlinear optical chromophores based on julolidine donors with excellent electro-optic activity, RSC Adv., 6 (2016) 99743-99751. DOI: 10.1039/C6RA21814H

[64] M. Kutscheroff, Ueber eine neue Methode direkter Addition von Wasser (Hydratation) an die Kohlenwasserstoffe der Acetylenreihe, Eur. J. Inorg. Chem., 14 (1881) 1540-1542. DOI: 10.1002/cber.188101401320

[65] M. Kutscheroff, Ueber die Einwirkung der Kohlenwasserstoffe der Acetylenreihe auf Quecksilberoxyd und dessen Salze, Eur. J. Inorg. Chem., 17 (1884) 13-29. DOI: 10.1002/cber.18840170105

[66] M. Feroci, M. Orsini, G. Sotgiu, L. Rossi, A. Inesi, Electrochemically promoted C−N bond formation from acetylenic amines and CO_2. Synthesis of

5-methylene-1, 3-oxazolidin-2-ones, J. Org. Chem., 70 (2005) 7795-7798. DOI: 10.1021/jo0511804

[67] S. Yoshida, K. Fukui, S. Kikuchi, T. Yamada, Silver-catalyzed preparation of oxazolidinones from carbon dioxide and propargylic amines, Chem. Lett., 38 (2009) 786-787. DOI: 10.1246/cl.2009.786

[68] S. Hase, Y. Kayaki, T. Ikariya, NHC–Gold (I) complexes as effective catalysts for the carboxylative cyclization of propargylamines with carbon dioxide, Organometallics, 32 (2013) 5285-5288. DOI: 10.1021/om400949m

[69] J. Hu, J. Ma, Q. Zhu, Z. Zhang, C. Wu, B. Han, Transformation of Atmospheric CO_2 Catalyzed by Protic Ionic Liquids: Efficient Synthesis of 2‐Oxazolidinones, Angew. Chem. Int. Ed., 54 (2015) 5399-5403. DOI: 10.1002/anie.201411969

[70] M.Y. Wang, Q.W. Song, R. Ma, J.N. Xie, L.N. He, Efficient conversion of carbon dioxide at atmospheric pressure to 2-oxazolidinones promoted by bifunctional Cu(II)-substituted polyoxometalate-based ionic liquids, Green Chem., 18 (2016) 282-287. DOI: 10.1039/c5gc02311d

[71] X. Liu, M.Y. Wang, S.Y. Wang, Q. Wang, L.N. He, In Situ Generated Zinc (II) Catalyst for Incorporation of CO_2 into 2‐Oxazolidinones with Propargylic Amines at Atmospheric Pressure, ChemSusChem, 10 (2017) 1210-1216. DOI: 10.1002/cssc.201601469

[72] H.F. Jiang, J.W. Zhao, Silver-catalyzed activation of internal propargylic alcohols in supercritical carbon dioxide: efficient and eco-friendly synthesis of

4-alkylidene-1, 3-oxazolidin-2-ones, Tetrahedron Lett., 50 (2009) 60-62. DOI: 10.1016/j.tetlet.2008.10.078

[73] N.D. Ca', B. Gabriele, G. Ruffolo, L. Veltri, T. Zanetta, M. Costa, Effective guanidine‐catalyzed synthesis of carbonate and carbamate derivatives from propargyl alcohols in supercritical carbon dioxide, Adv. Synth. Catal., 353 (2011) 133-146. DOI: 10.1002/adsc.201000607

[74] Q.W. Song, B. Yu, X.D. Li, R. Ma, Z.F. Diao, R.G. Li, W. Li, L.N. He, Efficient chemical fixation of CO_2 promoted by a bifunctional Ag_2WO_4/Ph_3P system, Green Chem., 16 (2014) 1633-1638. DOI: 10.1039/C3GC42406E

[75] Y.B. Wang, Y.M. Wang, W.Z. Zhang, X.B. Lu, Fast CO_2 sequestration, activation, and catalytic transformation using N-heterocyclic olefins, J. Am. Chem. Soc., 135 (2013) 11996-12003. DOI: 10.1021/ja405114e

[76] Y. Gu, Q. Zhang, Z. Duan, J. Zhang, S. Zhang, Y. Deng, Ionic Liquid as an Efficient Promoting Medium for Fixation of Carbon Dioxide: A Clean Method for the Synthesis of 4-Methylene-1, 3-oxazolidin-2-ones from Propargylic Alcohols, Amines, and Carbon Dioxide Catalyzed by Cu(I) under Mild Conditions, J. Org. Chem., 70 (2005) 7376-7380. DOI: 10.1021/jo050802i

[77] S. Pulla, C.M. Felton, Y. Gartia, P. Ramidi, A. Ghosh, Synthesis of 2-oxazolidinones by direct condensation of 2-aminoalcohols with carbon dioxide using chlorostannoxanes, ACS Sustainable Chem. Eng., 1 (2013) 309-312. DOI: 10.1021/sc300077m

[78] M. Tamura, M. Honda, K. Noro, Y. Nakagawa, K. Tomishige, Heterogeneous

CeO_2-catalyzed selective synthesis of cyclic carbamates from CO_2 and aminoalcohols in acetonitrile solvent, J. Catal., 305 (2013) 191-203. DOI: 10.1016/j.jcat.2013.05.013

[79] Y. Takada, S.W. Foo, Y. Yamazaki, S. Saito, Catalytic fluoride triggers dehydrative oxazolidinone synthesis from CO_2, RSC Adv., 4 (2014) 50851-50857. DOI: 10.1039/C4RA09609F

[80] H. Zhou, Y.M. Wang, W.Z. Zhang, J.P. Qu, X.B. Lu, N-Heterocyclic carbene functionalized MCM-41 as an efficient catalyst for chemical fixation of carbon dioxide, Green Chem., 13 (2011) 644-650. DOI: 10.1039/C0GC00541J

[81] D. Adhikari, A.W. Miller, M.-H. Baik, S.T. Nguyen, Intramolecular ring-opening from a CO_2-derived nucleophile as the origin of selectivity for 5-substituted oxazolidinone from the (salen) Cr-catalyzed [aziridine+ CO_2] coupling, Chem. Sci., 6 (2015) 1293-1300. DOI: 10.1039/c4sc02785j

[82] B. Wang, E.H. Elageed, D. Zhang, S. Yang, S. Wu, G. Zhang, G. Gao, One-Pot conversion of carbon dioxide, ethylene oxide, and amines to 3-aryl-2-oxazolidinones catalyzed with binary ionic liquids, ChemCatChem, 6 (2014) 278-283. DOI: 10.1002/cctc.201300801

[83] X.D. Lang, L.N. He, Green catalytic process for cyclic carbonate synthesis from carbon dioxide under mild conditions, Chem. Rec., 16 (2016) 1337-1352. DOI: 10.1002/tcr.201500293

[84] H. He, C. Qi, X. Hu, Y. Guan, H. Jiang, Efficient synthesis of tertiary α-hydroxy ketones through CO_2-promoted regioselective hydration of

propargylic alcohols, Green Chem., 16 (2014) 3729-3733. DOI: 10.1039/C4GC00522H

[85] Y. Zhao, Z. Yang, B. Yu, H. Zhang, H. Xu, L. Hao, B. Han, Z. Liu, Task-specific ionic liquid and CO_2-cocatalysed efficient hydration of propargylic alcohols to α-hydroxy ketones, Chem. Sci., 6 (2015) 2297-2301. DOI: 10.1039/C5SC00040H

[86] D. Li, Y. Gong, M. Du, C. Bu, C. Chen, S. Chaemcheun, J. Hu, Y. Zhang, Y. Yuan, F. Verpoort, CO_2-Promoted Hydration of Propargylic Alcohols: Green Synthesis of α-Hydroxy Ketones by an Efficient and Recyclable AgOAc/Ionic Liquid System, ACS Sustainable Chem. Eng., 8 (2020) 8148-8155. DOI: 10.1021/acssuschemeng.9b07546

[87] N. Carrara, J.M. Badano, F. Coloma-Pascual, C. Vera, M. Quiroga, Hydrogenation of diacetyl over composite-supported egg-shell noble metal catalysts, Chem. Pap., 71 (2017) 1669-1683. DOI: 10.1007/s11696-017-0161-4

[88] A.K. El-Qisairi, H.A. Qaseer, Oxidation of ketone by palladium (II). α-Hydroxyketone synthesis catalyzed by a bimetallic palladium (II) complex, J. Organomet. Chem., 659 (2002) 50-55. DOI: 10.1016/S0022-328X(02)01691-1

[89] Q.W. Song, Z.H. Zhou, M.Y. Wang, K. Zhang, P. Liu, J.Y. Xun, L.N. He, Thermodynamically Favorable Synthesis of 2-Oxazolidinones through Silver-Catalyzed Reaction of Propargylic Alcohols, CO_2, and 2-Aminoethanols, ChemSusChem, 9 (2016) 2054-2058. DOI: 10.1002/cssc.201600470

[90] X.D. Li, Q.W. Song, X.D. Lang, Y. Chang, L.N. He, AgI/TMG-Promoted

Cascade Reaction of Propargyl Alcohols, Carbon Dioxide, and 2-Aminoethanols to 2-Oxazolidinones, ChemPhysChem, 18 (2017) 3182-3188. DOI: 10.1002/cphc.201700297

[91] S. Xia, Y. Song, X. Li, H. Li, L.N. He, Ionic Liquid-Promoted Three-Component Domino Reaction of Propargyl Alcohols, Carbon Dioxide and 2-Aminoethanols: A Thermodynamically Favorable Synthesis of 2-Oxazolidinones, Molecules, 23 (2018) 3033. DOI: 10.3390/molecules23113033

[92] J. Qiu, Y. Zhao, Z. Li, H. Wang, M. Fan, J. Wang, Efficient Ionic-Liquid-Promoted Chemical Fixation of CO_2 into α-Alkylidene Cyclic Carbonates, ChemSusChem, 10 (2017) 1120-1127. DOI: 10.1002/cssc.201601129

[93] D.J.C. Constable, A.D. Curzons, V.L. Cunningham, Metrics to ‘green’ chemistry—which are the best?, Green Chem., 4 (2002) 521-527. DOI: 10.1039/B206169B

[94] Sheldon, R. Arthur, Metrics of Green Chemistry and Sustainability: Past, Present, and Future, ACS Sustainable Chem. Eng., 6 (2018) 32-48. DOI: 10.1021/acssuschemeng.7b03505

[95] J. Hu, J. Ma, Q. Zhu, Q. Qian, H. Han, Q. Mei, B. Han, Zinc (II)-catalyzed reactions of carbon dioxide and propargylic alcohols to carbonates at room temperature, Green Chem., 18 (2016) 382-385. DOI: 10.1039/C5GC01870F

[96] Q.W. Song, W.Q. Chen, R. Ma, A. Yu, Q.Y. Li, Y. Chang, L.N. He, Bifunctional Silver (I) Complex-Catalyzed CO_2 Conversion at Ambient

Conditions: Synthesis of α-Methylene Cyclic Carbonates and Derivatives, ChemSusChem, 8 (2015) 821-827. DOI: 10.1002/cssc.201402921

[97] G. Gurau, H. Rodriguez, S.P. Kelley, P. Janiczek, R.S. Kalb, R.D. Rogers, Demonstration of chemisorption of carbon dioxide in 1,3-dialkylimidazolium acetate ionic liquids, Angew. Chem. Int. Ed., 50 (2011) 12024-12026. DOI: 10.1002/anie.201105198

[98] X. Tang, C. Qi, H. He, H. Jiang, Y. Ren, G. Yuan, Polystyrene-Supported N-Heterocyclic Carbene–Silver Complexes as Robust and Efficient Catalysts for the Reaction of Carbon Dioxide and Propargylic Alcohols, Adv. Synth. Catal., 355 (2013) 2019-2028. DOI: 10.1002/adsc.201300007

[99] S. Li, J. Sun, Z. Zhang, R. Xie, X. Fang, M. Zhou, Carboxylation of terminal alkynes with CO_2 using novel silver N-heterocyclic carbene complexes, Dalton Trans., 45 (2016) 10577-10584. DOI: 10.1039/C6DT01746K

Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights

- The metal loading employed in this $AgNO_3$/ionic liquid system is the lowest level by far.

- This $AgNO_3$/ionic liquid system could work efficiently under 1 bar of CO_2, which is the first report among the metal-catalyzed systems.

- This $AgNO_3$/ionic liquid system is the first example which could be recyclable and reused for at least 5 times among the metal-catalyzed systems.

- In the green metrics evaluation, the processes catalyzed by this $AgNO_3$/ionic liquid system behaved the best performance among the reported Ag-catalyzed cases.

- NHC-CO_2 adducts and NHC-Ag complexes were detected during the process. Their reactivity in this reaction was further assessed for the first time, which was finally proved to be beneficial for this reaction.