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Zhilian Wu,^{abc†} Lei Sun,^{b†} Qinggang Liu,^{bd} Xiaofeng Yang,^{*b} Xue Ye,^b Yancheng Hu,^b and Yanqiang

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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The fixation of CO₂ as carboxylic acid is a significant reaction for the C-C bond formation in organic synthesis. So far, other than C-H carboxylations using stoichiometric amounts of metals or organometallic reagents, great efforts have been devoted to develop new heterogeneous catalyst, while the catalytic performance of supported metal catalysts is not satisfactory. Here, a Schiff base modified silver catalyst is developed for the direct carboxylation of terminal alkynes with CO₂, enabling an efficient and green synthesis of valuable alkynyl carboxylic acids. The reaction can proceed smoothly at atmospheric pressure and low temperature (60 °C). Moreover, the silver-based catalyst, which was prepared by an in situ reduction route, can be facile prepared, easily recovered and reused for five times without a significant loss of activity due to the promoted stability by the Schiff-base on the support surface. In addition, the markedly negative influence of H₂O and solvent effect has also been discussed to this reaction system.

Huang*^b

The conversion and chemical fixation of CO_2 is presently a field of research with ever-increasing interest in virtue of environment, energy, and related social issues in the past decades.¹⁻³ Besides, CO_2 is an attractive C_1 building block in organic synthesis due to its intriguing features, such as nontoxic, renewable, inexpensive, and readily available. Great efforts have been devoted toward the efficient utilization of CO_2 by chemical methods.⁴⁻⁸ Among various CO_2 derivatives, alkynyl carboxylic acids are not only key structural motifs in numerous biologically active molecules,⁹⁻¹¹ but also versatile building blocks for the construction of coumarins, flavones, and alkynylarenes.¹²⁻¹⁵ Thus a variety of methods including the hydrolysis of alkynyl bromide and relative derivatives, oxidative carbonylation of alkynes, and reaction of alkynylmetal species with chloroformate have been developed towards their synthesis. Despite these advances, the exploration of an efficient alternative, that fulfils the principles of green chemistry, is still demanded.¹⁶ In this context, the direct carboxylation of terminal alkynes with CO₂ is definitely the simplest and most straightforward access to alkynyl carboxylic acids.¹⁷⁻²⁴

Several homogeneous catalytic systems have been reported in this research area,^{22, 25-28} however, the further application was severely impeded by either the recycling problems or the metal contamination of the products. To date, only a few of heterogeneous conversion was conducted by the supported silver catalysts for the direct carboxylation of terminal alkynes with CO₂ to produce alkynyl carboxylic acids.^{24, 29-31} However, the catalytic performance of supported metal catalysts is not satisfactory due to their poor yield of desired product, harsh reaction conditions, or difficult catalyst preparation. For example, Finashina's group recently reported that Ag/F-Al₂O₃ catalyst only gave a yield of 62.1% phenylpropiolic acid under 50 °C and 60 atm conditions. ²⁹ Bhaumik and his colleague found that AgNPs/Co-MOF catalyst demonstrated an improved catalytic efficiency,³⁰ but the complex synthetic route limits its further application. Therefore, the development of an efficient and robust heterogeneous catalyst featuring facile preparation for this type of reactions still remains a great challenge.

In situ reduction route is demonstrated as a green and facile method for the fabrication of highly dispersed metal clusters or nanoparticles over the support.³² For example, Bao's group recently disclosed that amino groups of APTES (aminopropyltriethoxylsilane)-modified mesoporous silica can be used to anchor formaldehyde as the reducing agent, on which silver precursor could be *in situ* reduced.³³ In particular, our group have successfully developed a method to synthesize a new type of Schiff base modified gold catalyst by one-pot aldimine condensation and the *in situ* autoreduction of a gold

^{a.} CAS Key Laboratory of Renewable Energy, Guangzhou Institute of Energy Conversion. Chinese Academy of Sciences. Guanazhou 510640 (PR China).

^{b.} State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China. E-mail: yangxf2003@dicp.ac.cn, yqhuang@dicp.ac.cn

^c University of Chinese Academy of Sciences, Beijing 100049 (PR China). ^d Laboratory of Advanced Materials and Catalytic Engineering, School of Chemistry,

Dalian University of Technology, Dalian 116024, China. † These authors contributed equally to this work and should be considered co-first authors.

[‡] Electronic Supplementary Information (ESI) available: Description of materials and methods, Table S1–S2 and Fig. S1–S13. See DOI: 10.1039/x0xx00000x

100 nm

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precursor,³⁴ and the catalyst can be served as an environmentfriendly and efficient catalyst for H₂ production from formic acid owing to its highly dispersed, small sized gold nanoparticles. Inspired by the previous reports, the functionalization of Schiff base over supported silver catalysts will result in a promoted metal dispersion and would offer great opportunity for the carboxylation of terminal alkynes with CO₂ to produce alkynyl carboxylic acids.

Herein, we present a general route to synthesize a novel Schiff base modified silver catalyst by the in situ reduction of silver precursor under ultrasonic conditions. Such Schiff base modified silver catalyst can act as a robust and green catalyst in the conversion of CO₂ under low temperature (60 °C) and atmospheric pressure (1.0 atm) conditions, and show excellent recyclability in the reactions.

The solid Schiff base was synthesized by one-pot aldimine condensation of (3-aminopropyl)-triethoxysilane (APTES) with HCHO. Briefly, a quantitative amount of HCHO solution (37%) was added into an aqueous solution of APTES with vigorous stirring at room temperature; after washing and drying, a precipitate was obtained as a metastable SiO₂ support (Scheme 1 A). Next, silver nanoparticles (NPs) were deposited on the support by direct reduction of the AgNO₃ precursor with metastable aminal on the SiO₂ support under ultrasonic conditions, followed by washing and drying to obtain the final Schiff base modified silver catalyst (supporting information, 1a-1d, Ag/Schiff-SiO₂, Scheme 1 B). 2a (supporting information, Ag/SiO₂) and **3a** (supporting information, Ag/Schiff-SiO₂) were developed as reference catalysts by a NaBH₄ reduction strategy.

The generated Schiff-SiO2 was confirmed by Fourier transform infrared spectroscopy (FTIR), in which a strong peak at 1660 cm⁻¹ ascribed to the stretched vibration of the C=N group of imine was observed (Figure S1). ²⁹Si CP-MAS NMR and ¹³C CP-MAS NMR spectra were also used to verify the evolution of the Schiff base during the whole preparation procedures. As demonstrated in the ²⁹Si CP-MAS NMR spectra the Si environments of T^2 (-60 ppm), T^3 (-67 ppm) and Si-O-



Scheme 1 The synthetic scheme employed for preparing Ag/Schiff-SiO₂ nano-composite.

b а 100 nm 100 nm d С

Figure 1 Element maps for the Ag/Schiff-SiO₂ sample (1c): a) TEM image; b) Si (green); c) O (cyan); d) Ag (red).

100 nm



Figure 2 TEM image of the Ag/SiO2-Schiff sample (1c; left) and size distribution of the Ag NPs in a sample of 1c (Ag NPs size: 6.3±1.9 nm) (right).

C₂H₅ groups (-50 ppm) were detected according to the NMR chemical shifts (Figure S2a), showing the APTES hydrolysis and condensation with HCHO to Schiff-SiO₂ solid material with some alkane-Si moieties retaining. In the ¹³C CP-MAS NMR spectra (Figure S2b), the sample of Schiff-SiO₂ showed resonance peaks of carbon chemical shifts at d = 163 and 78 ppm, which were assigned to the -N=C (C₁) Schiff base and aminal N-C-N (C₂), respectively, while the metastable aminal (C₂) may be further hydrolysed to -NHCH₂OH.^{34, 35} Powder Xray diffraction (PXRD) pattens in Figure S3 show that the asprepared catalysts (1a, 1b, 1c and 1d) showed no silver peaks, indicating finely distributed small Ag nanoparticles. The Ag nanoparticles in the catalyst of 1c-recycled may slightly aggregated in the reaction, which displayed by the poor characterized peaks of Ag (111). However, the catalysts of 2a

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Table 1 Synthesis of 3-phenylpropiolic acid from CO_2 and 1-ethynylbenzene^[a]

		0.	14 mol% cata 1.5 equiv. bas	alyst se Ho	сі /	<u> </u>	
<u>`</u> _/		CO ₂ —	solvent, t		(COOH
Entry	Cat.	Base	solvent	T/°C	t/h	Yield ^[b]	TON ^[c]
						/%	
1	None	Cs_2CO_3	DMSO	60	6	37	-
2	Schiff-	Cs_2CO_3	DMSO	60	6	36	_
	SiO ₂						
3	1c	Cs_2CO_3	DMSO	60	6	78	561
4	1c	Cs_2CO_3	DMSO	60	24	98	705
5	2a	Cs_2CO_3	DMSO	60	24	97	697
6	3a	Cs_2CO_3	DMSO	60	24	82	590
7	1a	Cs_2CO_3	DMSO	60	24	82	590
8	1b	Cs_2CO_3	DMSO	60	24	86	618
9	1d	Cs_2CO_3	DMSO	60	24	89	640
10	1c	NaOH	DMSO	60	24	1	7
11	1c	КОН	DMSO	60	24	3	22
12	1c	CsOH·	DMSO	60	24	1	7
		H₂O					
13	1c	Na_2CO_3	DMSO	60	24	2	14
14	1c	K_2CO_3	DMSO	60	24	23	165
15 ^[d]	1c	K_2CO_3	DMSO	60	24	39	280
17	1c	Cs_2CO_3	DMF	60	24	50	360
18	1c	Cs ₂ CO ₃	MeCN	60	24	7	50
19	1c	Cs_2CO_3	Dioxane	60	24	3	22
20	1c	Cs ₂ CO ₃	PC	60	24	23	165
21	1c	Cs ₂ CO ₃	DMSO	25	24	12	86
22	1c	Cs_2CO_3	DMSO	40	24	50	360
23	1c	Cs_2CO_3	DMSO	50	24	82	590
24	1c	Cs_2CO_3	DMSO	70	24	92	661

[a]Reaction conditions: 1-ethynylbenzene (1.0 mmol), catalyst (**1a** = 1.17 wt% Ag/Schiff-SiO₂, **1b** = 1.36 wt% Ag/Schiff-SiO₂, **1c** = 1.45 wt% Ag/Schiff-SiO₂, **1d** = 2.52 wt% Ag/Schiff-SiO₂, **2a** = 1.20 wt% Ag/ SiO₂, **3a** = 0.71 wt% Ag/Schiff-SiO₂, Ag: 1-ethynylbenzene = 1:719 mol mol⁻¹), Cs₂CO₃ (1.5 mmol), CO₂ (1.0 atm), 60 °C, solvent (5 mL), 24 h, unless otherwise noted. [b] Yield based on HPLC. [c] TON = (moles of product)/(moles of metal in the catalyst), unless otherwise noted. [d] 3.0 mmol CsCl was added to the reaction system.

and 3a sintered into bulk Ag particles, which indicated by sharp characterized peaks of Ag (111), Ag (200), Ag (220) and Ag (311). Correspondingly, X-ray photoelectron spectroscopy (XPS) results indicated that the Silver ions were successfully reduced to Ag (0) nanoparticles by the support of Schiff-SiO₂, and the charge states of silver nanoparticles almost with no change (Figure S9, Figure S11). Small fraction of Ag⁺¹ species in the XPS are likely to be the Ag₂O (Figure S9, Figure S11), because the Ag nanoparticles are easily to be oxidized in the air. Besides, the N species of -N=C and -NH-C groups in the 1crecycled were quite similar with the 1c (Figure S10, Figure S12). Catalysts 1 a, 1 b, 1 c, 1d, 2a, and 3a have Ag loadings of 1.17, 1.36, 1.45, 2.52, 1.20 and 0.71 wt%, respectively, as confirmed by inductively coupled plasma (ICP) analysis (Table S1). To further study the Ag/Schiff-SiO₂ catalysts, the morphology of the silver NPs deposited on the support of Schiff-SiO₂ was characterized by energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM). EDS images (Figure 1) showed that the Ag NPs were homogeneously distributed

DOI: 10.1039/C7GC00923B COMMUNICATION

sizes (6.3±1.9 nm) than those in 1a, 1b, and 1d. The catalytic activities of the Ag/Schiff-SiO₂ samples (1a-1d, **2a**, and **3a**) were then evaluated for the fixation of CO_2 with terminal alkynes into propiolic acids. In the initial research, the carboxylation of 1-ethynylbenzene was selected as a model reaction to explore the influence of various parameters on the reaction. Under the conditions of 60 $^{\circ}$ C, 1.0 atm of CO₂ and 6 h, reaction in DMSO only gave 37% and 36% yields in the absence of catalyst and in the presence of Schiff-SiO₂, respectively (Table 1, entry 1-2). If we added the Ag/Schiff-SiO₂ catalyst (1c) into the same reaction, the yield can be promoted to 78% (Table 1, entry 3). Up to 98% yield of the desired propiolic acid product was obtained with 0.14 mol% of catalyst 1c at ambient pressure in 24 h (Table 1, entry 4), and the catalyst 1c has the largest TON (705) compared with previous heterogeneous catalytic systems in table S2. As reference catalysts, Ag/SiO₂ (2a) was developed with NaBH₄ reduction strategy and Ag/Schiff-SiO₂ (3a) was developed with NaBH₄ reduction along with stirring strategy. Interestingly, 2a also can gave good yield (97%) (Table 1, entry 5), but after one cycle, the Ag loading of recycled 2a catalyst only owned half of the fresh one, while the recycled 1c catalyst almost possessed the same Ag loading, therefore the 2a catalyst shown very poor stability compared to 1c catalyst. While 3a catalyst only can gave relative poor yield (82%) (Table 1, entry 6), and it can be explained by PXRD results (PXRD; Figure S3). Besides, the support of Schiff-SiO₂ may be served as enhanced stability and a significant decrease in the propensity for loss of metals from the catalysts, during the reaction. Based on the above results, it can be deduced that the in situ autoreduction route is the best method to fabricate the nano-silver catalyst among the three strategies. Under the same reaction conditions, 1a, 1b, and 1d gave 82%, 86% and 89% of the desired product yields, respectively (Table 1, entries 7-9), and the catalytic activity decreased in the following order: 1c>1d>1b>1a, which was accordance with the TEM results. From the catalytic activity results of 1a-1d, it is demonstrated that the average size of Ag nanoparticles may be the main reason, which lead to catalytic performances of the all catalysts with different Ag loadings being different. Accordingly, a larger surface area of active sites is available for the substrates, and a better catalytic performance was achieved with 1c.

 $\rm Cs_2CO_3$ is one of the most commonly used bases for many organic reactions.³⁶ Here, $\rm Cs_2CO_3$ also performed as the best base for this carboxylation reaction of 1-ethynylbenzene with CO₂, which is consistent with the results in previous report.^{16, 19, 24, 37} Among those bases we screened, NaOH, KOH, CsOH·H₂O, Na₂CO₃, and K₂CO₃, only resulted in poor yields (Table 1, entries 10-14). Surprisingly, if we added 2 mmol CsCl into the reaction system of K₂CO₃, the yield can be elevated from 23% to 39% (Table 1, entries 14-15), and it was proved that Cs⁺ could promote the reaction.

In addition, the impact of the polar organic solvents is thoroughly investigated, and DMSO was confirmed to be the

DOI: 10.1039/C7GC00923B Green Chemistry



Figure 3 Effect of H₂O additive on the 3-phenylpropiolic acid yield and selectivity. Reaction conditions: catalyst 1c (1.45wt% Ag/Schiff-SiO₂, 10 mg), Cs₂CO₃ (1.5 mmol), 1-ethynylbenzene (1.0 mmol), CO₂ (1.0 atm), DMSO (5 mL), 60 °C, 24 h.

best solvent for this reaction. Under the conditions of 60 °C and 1.0 atm of CO₂, 98% yield was obtained in DMSO over catalyst **1c** (Table 1, entry 4). While 50%, 7%, 3%, and 23% yields was obtained in N,N-dimethylformamide (DMF), acetonitrile (MeCN), 1,4-dioxane (Dioxane) and propylene carbonate (PC), respectively (Table 1, entries 17-20). It was deduced that the greater polar solvent (DMSO) may be more beneficial for this heterogeneous reaction, similar result also can be found in the previous report.³⁸ The influence of temperature on the reaction was also studied, and 60 °C was proved to be the optimal temperature (Table 1, entry 4, 21-24).

Due to unique structure and properties, water have great impact on the reaction course,³⁹ which might lead to particular interactions, such as polarity, hydrophobic effect, hydrogen bonding and trans-phase interactions. Especially, some recent fundamental discoveries were proved that water could accelerate reactions under heterogeneous conditions.40-42 However, H₂O has markedly negative influence to our reaction system. When the reaction was conducted in the standard conditions, it was found that the H₂O additive is linearly related to the propiolic acid yield (Figure 3). It is worth to note that when 8 μ L H₂O was added into the reaction system, the 3phenylpropiolic acid yield was rapidly dropped from 98% to 56%. A control experiment was conducted by using 3phenylpropiolic acid (1.0 mmol) as starting reactant under the same conditions with CO_2 (1.0 atm) in DMSO (5 mL) with H_2O (8 µL) at 60 °C for 24 h. A mixture of alkynyl carboxylic acid and terminal alkyne (ratio is about 5 : 5) was obtained. Therefore, it is speculated that H₂O in the reaction system might facilitate decarboxylation reaction of alkynyl carboxylic acid.

So as to investigate the generality of the Ag/Schiff-SiO₂ catalyst (**1c**) in the carboxylation reaction, various typical terminal alkynes were explored (Table 2). Under the standard conditions: **1c** (0.14 mol% of Ag), 1.5 equivalents of Cs_2CO_3 , 5

Table 2 Substrate scope tests over the 1c catalyst^[a]

$$R \longrightarrow + CO_2 \xrightarrow{\begin{array}{c} 0.14 \text{ mol}\% \text{ 1c}, \\ 1.5 \text{ equiv. } Cs_2CO_3 \\ \hline DMSO, 60 \text{ °C}, 24 \text{ h} \end{array}} \xrightarrow{\begin{array}{c} \text{HCI}} R \longrightarrow COOH \end{array}$$

Entry 1	Alkyne	Product	Yield ^[b] /% 98
2	H3CO-	Н₃00-√СООН	92
3	F-	F	87
4	0 ₂ N-	02N-	93
5	s>=	SССООН	86
6		COOH	94
7		СООН	92

[a] Reaction conditions: alkyne (1.0 mmol), catalyst **1c** (1.45wt% Ag/Schiff-SiO₂, 10 mg), Cs₂CO₃ (1.5 mmol), CO₂ (1.0 atm), 60 °C, DMSO (5 mL), 24 h. [b] Isolated yields.

mL DMSO, 60 °C and 1.0 atm CO_2 , the corresponding carboxylation products were obtained in promising yields (86-98 %) when aromatic alkynes with either electron-donating group (Table 2, entry 2) or with electron-withdrawing groups (Table 2, entries 3-4). Even for an alkyne with a hetero aromatic ring group (Table 2, entry 5), a yield of 86% was achieved. Both the alkyl- or alkenyl-substituted terminal alkynes are amenable to the procedure, thus giving the corresponding alkynyl carboxylic acids in synthetically satisfactory yields of 94% and 92%, respectively (Table 2, entry 6-7).

As a heterogeneous catalyst, Ag/Schiff-SiO₂ could not only be facilely prepared, but also easily separated by centrifugation or filtration of the reaction mixture. As Shown in figure S4, the catalyst 1c maintained high activity under the optimized conditions, only slightly decreased activity was observed, which may be attributed to the nano Ag particle slightly aggregated in the reaction, and the decreased amount of catalyst during the regeneration process, it is deduced that the N species in Schiff-SiO₂ can effectively anchor Ag NPs. The PXRD pattern (Figure S3), TEM images (Figure S5) and XPS (Figure S11-S12) of the used Ag/Schiff-SiO₂ (1c) were almost the same as the fresh catalyst. In short, the Ag/Schiff-SiO₂ (1c) demonstrated robust stability and recyclability as a heterogeneous catalyst for the direct carboxylation of terminal alkynes with CO₂ to produce propiolic acids. The total TON for 1c in the beginning 5 runs was 3430, and the number would be further increased.



Scheme 2 Possible reaction mechanism for the Ag/Schiff-SiO2 catalyzed carboxylation of terminal alkyne.



Figure 4 Relative free energies of the energy barrier (ΔE) for the Ag₈catalyzed electrophilic attack step in DMF (black) and DMSO (red) solvents.

Based on our finding and some previous reports,^{24, 25} a possible mechanism over Ag/Schiff-SiO₂ (1c) was proposed and schematically depicted in Scheme 2. It is speculated that the silver NPs on Schiff-SiO₂ can coordinate to the terminal alkyne and be deprotonated by Cs₂CO₃ through acidifying the C-H bond to form a silveracetylide intermediate A, meanwhile, electrophilic attack from carbon dioxide to the coordinated acetylide to form the transition state **B**, subsequently to form the silver carboxylate C. In the presence of a large amount of Cs₂CO₃ and alkyne reactants, the transmetallation occurred quickly, and the generation of cesium carboxylate **D** and reformation of A was finished in a flash. After the mixture was acidified by concentrated HCl to pH=1 at low temperature, the carboxylic acid product E was obtained. The synergistic effect **Green Chemistry Accepted Manuscrip**

between silver NPs and Cs₂CO₃ enormously enhanced the catalytic activity of this nanocatalyst system.

As the key step in the reaction, the transition state **B** in the solvent was investigated by using density functional theory (DFT) calculations. In this step, the complex of deprotonated is considered as the reactant. Figure 4 displays the relative free energy profiles for the Ag8-catalyzed electrophilic attack with CO₂ in DMSO and DMF solvent, respectively. In DMSO, the deprotonation of phenylacetylene coordinates with CO2 over the alkynyl C=C triple bond by a moderate energy barrier of 15.1 kcal/mol (E_{DMSO}). Then the product is formed by the coordination of PhC=C-COO to Ag₈ cluster with an energy decreasing (-5.1 kcal/mol) against to the reactant. However, the same reactive path in DMF solvent exhibits an increase of 6.6% in the energy barrier (E_{DMF}=16.1 kcal/mol) comparing to the reaction in DMSO. The calculations indicate that the silver NPs could be an effective catalyst for the electrophilic attack process. Moreover, the greater polar solvent (DMSO) may be more beneficial for this heterogeneous reaction, which is in well consistent with our experimental findings.

Conclusions

In summary, a Schiff-base modified silver nano-composite catalyst is successfully synthesized and demonstrated to have robust activity for the direct carboxylation of terminal alkynes with CO₂ to produce valuable carboxylic acids. H₂O has markedly negative influence on this reaction system. The DFT calculations indicate that the silver NPs could be an effective catalyst for the electrophilic attack process. Moreover, the strongly polar solvent (DMSO) may be more beneficial for this heterogeneous reaction. The heterogeneous catalyst feature good catalytic activity, robust recyclability, and excellent substrate generality in the carboxylation of terminal alkynes with CO₂ under mild conditions. Potential applications of this catalyst in other areas can be anticipated, for instance, in organic synthesis, polymer, and particularly for the fixation of CO2 into chemicals and fuels. Tremendous efforts to elucidate the catalytic mechanism and to explore new efficient catalysts are still underway in our lab.

Acknowledgements

The authors acknowledge the financial support from the National Natural Science Foundation of China (21403218, 21476226, 21503125 & 21506204), China Ministry of Science and Technology under contact of 2016YFB0600902, Dalian Science Foundation for Distinguished Young Scholars (2016RJ04), the Youth Innovation Promotion Association CAS. The authors also appreciate valuable discussions with Dr Xiaohuan Liu, Dr Guangfeng Liang, and Miss Xiaoli Yang.

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A Schiff base modified silver catalyst for efficient and fixation of CO₂ as carboxylic acid at ambient pressure

Zhilian Wu,^{abc†} Lei Sun,^{b†} Qinggang Liu,^{bd} Xiaofeng Yang,^{*b} Xue Ye,^b Yancheng Hu,^b and Yanqiang Huang^{*b}

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A Schiff base modified silver catalyst is developed for the direct carboxylation of terminal alkynes with CO_2 , enabling an efficient and synthesis of valuable alkynyl carboxylic acids.