molecules

MDPI

Article

Silver-Catalyzed Decarboxylative Acylation of Isocyanides Accesses to α-Ketoamides with Air as a Sole Oxidant

Jia Xu †, Xue Li †, Xing-Yu Chen, Yu-Ting He, Jie Lei, Zhong-Zhu Chen * and Zhi-Gang Xu *

College of Pharmacy, National & Local Joint Engineering Research Center of Targeted and Innovative Therapeutics, IATTI, Chongqing University of Arts and Sciences, Chongqing 402160, China; xujia_0907@163.com (J.X.); lixue91jlsp@sina.com (X.L.); faith0909@163.com (X.-Y.C.); jjjxu_92@126.com (Y.-T.H.); jlei0916@163.com (J.L.)

* Correspondence: 18883138277@163.com (Z.-Z.C.); xzg@cqwu.edu.cn (Z.-G.X.)

† These authors contributed equally to this work.

Abstract: α-Ketoamide moieties, as privileged units, may represent a valuable option to develop compounds with favorable biological activities, such as low toxicity, promising PK and drug-like properties. An efficient silver-catalyzed decarboxylative acylation of α-oxocarboxylic acids with isocyanides was developed to derivatize the α-ketoamide functional group via a multicomponent reaction (MCR) cascade sequence in one pot. A series of α-ketoamides was synthesized with three components of isocyanides, aromatic α-oxocarboxylic acid analogues and water in moderate yields. Based on the research, the silver-catalyzed decarboxylative acylation confirmed that an oxygen atom of the amide moiety was derived from the water and air as a sole oxidant for the whole process.

Keywords: silver catalyst; decarboxylation; air oxidation; isocyanide; α-ketoamide

check for updates

Citation: Xu, J.; Li, X.; Chen, X.-Y.; He, Y.-T.; Lei, J.; Chen, Z.-Z.; Xu, Z.-G. Silver-Catalyzed Decarboxylative Acylation of Isocyanides Accesses to α-Ketoamides with Air as a Sole Oxidant. *Molecules* **2023**, *28*, 5342. https://doi.org/10.3390/molecules28145342

Academic Editor: M. Concepción Gimeno

Received: 21 June 2023
Revised: 7 July 2023
Accepted: 8 July 2023
Published: 11 July 2023

Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

1. Introduction

α-Ketoamides are privileged units and widely exist in biologically relevant molecules, natural products, pharmaceuticals and other functional materials [1,2]. The α-ketoamide functional group is also a key part of market drugs and drug candidates with favorable biological activities, promising PK and low toxicity, thus helping to face biological targets of increased complexity [3–5]. The favorable biological activities of α-ketoamides have been deeply exploited by modifying their structural rigidity or by conferring their capacity to increase hydrogen bonds, leading to the improvement of their pharmaceutical profile. Through continuing modification, their peculiar properties make α-ketoamides a privileged structure in medicinal chemistry that has led to the development of a wide array of compounds that have shown a variety of pharmacological activities [6–8]. In recent years, medicinal chemists have constantly exploited α-ketoamides to modify molecules with clinical potential, primarily as sedative/hypnotics, anxiolytics, antitumorals, antibacterials, antivirals and antiprions. For instance, their derivatives are essential constituents in inhibitors, agonist and bioactive compounds (Figure 1) [1–8]. Furthermore, the α-ketoamides' moiety also serves as a versatile and valuable intermediate and synthon that provides the gateway to access a variety of useful scaffolds in a number of functional group transformations and total syntheses. Owing to their importance and broad applications, numerous synthetic methods for the preparation of α-ketoamides have been developed over the past few decades [9–16].

Recently, transition metal-catalyzed decarboxylative transformations of α-oxocarboxylic acids have gained considerable attention due to their advantages of broad functional group compatibility, readily available feedstocks, simple operations and moderate to good yields [17–24]. Through the great efforts chemists have made, strategies have been established, and a direct approach was found to afford the acyl group. Prompted by these results, a decarboxylative acyl group insertion into the useful synthons to provide

N-monosubstituted α-ketoamides was developed. For example, Wang's group developed direct a copper-catalyzed decarboxylative acylation to generate α-ketoamides [25]. This cross-coupling reaction was performed between the acyl C-H of formamides and α-oxocarboxylic acids using 2 equiv. of DTBP as the oxidant and 2 equiv. of PivOH as an additive (Scheme 1A). Patel and coworkers reported palladium-catalyzed chemoselective insertion into organic cyanamides via decarboxylation. Meanwhile, 2 equiv. of $(NH_4)_2S_2O_8$ is necessary to directly access α-ketoamides (Scheme 1B) [26]. Although these impressive contributions had been made, more efficient and practical catalytic systems for the synthesis of α-ketoamide are still highly attractive and in demand.

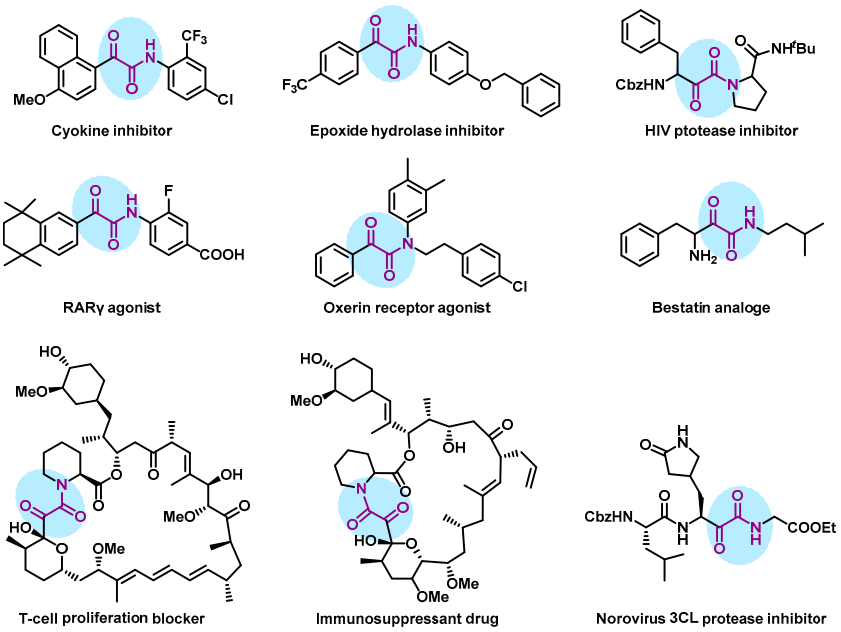
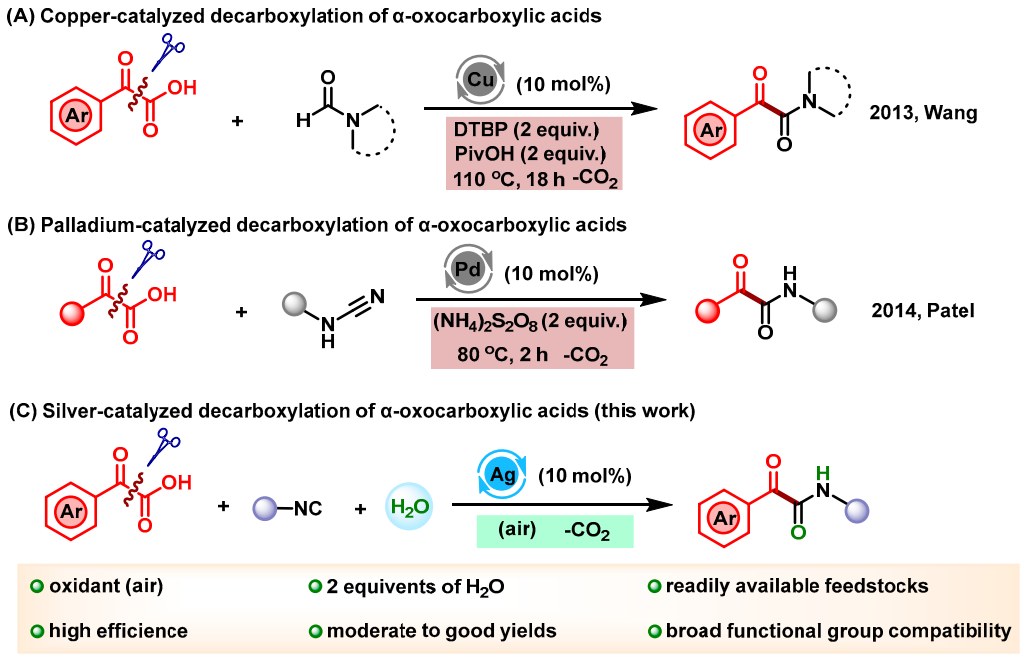


Figure 1. Biologically active compounds containing an α-ketoamides functional group.



Scheme 1. Previous transition metal-catalyzed decarboxylation of α-oxocarboxylic acids for the construction of α-ketoamides. (**A**): Coppercatalyzed decarboxylation [25]; (**B**): Palladiumcatalyzed decarboxylation [26]; (**C**): This work.

In the last 30 years, chemists have become more and more preoccupied about "green" sequences of reactions to produce a myriad of high-value chemicals [27]. So, atmospheric molecular oxygen is an ideal sequence because it is safe and free [28]. Neither transition metal-catalyzed decarboxylation for the synthesis of α-ketoamides has used oxygen as an oxidant. The development of alternative sustainable routes from commercially available starting materials and oxygen to access α-ketoamides is highly warranted. Isocyanides represent one of the most important and versatile synthons due to their unique electronic and structural characteristics. Moreover, isocyanide-based multicomponent reaction rapidly facilitated complex molecules in one pot from simple starting materials with remarkable synthetic efficiency and high-atom economy [29–33]. Based on the continuous interests in silver-catalyzed organic reactions of isocyanide and the Hunsdiecker reaction [34–36], we attempted to develop an alternative transition metal-catalyzed decarboxylation to construct α-ketoamides with isocyanide using air as the only oxidant. Herein, we report an efficient and practical silver-catalyzed decarboxylation to rapidly facilitate α-ketoamides using air as the sole oxidant (Scheme 1C). The importance of the given chemistry is threefold: (a) operation simplicity; (b) avoided additional oxidant (without stoichiometric peroxide or persulfide; (c) suppressed competitive reaction to achieve precise synthesis (no oxazole by-products were observed).

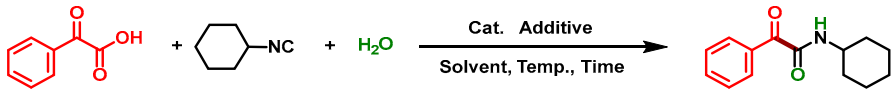
2. Results

To begin our investigation for silver-catalyzed decarboxylation to synthesize α-ketoamides, phenylglyoxylic acid and isocyanocyclohexane were selected as the model substrates in a solvent of acetonitrile (MeCN). In the screening of silver salts (Table 1, entries 1–6), we rapidly found that AgOTf was a powerful catalyst to afford α-ketoamides with a yield of 70%. To increase the conversion of final product **4a**, solvents were evaluated, such as *N*,*N*-dimethylformamide (DMF), 1,4-dioxane, 1,2-dichloroethane (DCE), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF) and toluene (entries 7–12). Among the screened solvents, DCE led to a higher yield of 82%. When the reaction was performed at 100 °C for 1 h, **4a** was isolated with a yield of 87% (entry 13). Fortunately, prolonging the reaction time to 2 h delivered α-ketoamide **4a** with the highest yield of 89% (entry 15). To the best of our knowledge, a stoichiometric oxidant was necessary to direct the silver-catalyzed decarboxylation of α-oxocarboxylic acids. Switching our attention to oxidants of $PhI(OAc)_2$, $K_2S_2O_8$ and oxone, diminished yields of **4a** were found. Therefore, oxygen was considered as the ideal oxidant in our protocol. To confirm the efficiency of the silver catalyst, the other transition metals were also investigated. None of them afforded the desired product **4a** with a satisfactory yield (entries 19–21). When optimizing the amount of water, we found that a 2.0 equiv. of water was more suitable to our system. Thus, the optimized reaction conditions of the three-component, one-pot reaction were determined to be: "**1a** (0.3 mmol), **2a** (0.3 mmol), **3** (2.0 equiv.) with 10 mol% AgOTf as catalyst by using DCE under 100 °C for 2 h."

After establishing the optimal reaction conditions, we set out to explore the substrate generality of the silver-catalyzed decarboxylative acylation of isocyanides to access α-ketoamides. Various phenylglyoxylic acids and isocyanides were subjected to this one-pot decarboxylative process, as the results show in Scheme 2, and the high tolerance of substituents on the substrates was observed. Under standard reaction conditions, the desired product **4a** was isolated with a yield of 89% and unequivocally confirmed by X-ray crystallography (CCDC 2267589). Specifically, the reaction worked well not only with aliphatic isocyanides but also with aromatic isocyanides. Despite the steric effect of isocyanides, the transformations for synthesizing α-ketoamides using 1,1,3,3-tetramethylbutyl isocyanide or *tert*-butyl isocyanide as an amide source did not decrease the reaction yields (**4c**, 89%; **4d**, 89%; **4e**, 88%). As the literature reported [37], the reaction with α-oxocarboxylic acids and toluenesulfonylmethyl isocyanide (TosMIC) was notably prone to giving the corresponding 5-phenyloxazole. Under optimal reaction conditions, the starting materials were directly converted to compound **4f** with a 90% yield. The aromatic

isocyanides of 2,6-dimethylphenyl isocyanide, 2-chloro-6-methylphenyl isocyanide and 2-isocyanonaphthalene, 4-methoxyphenyl isocyanide, 4-bromophenyl isocyanide and 4-chlorophenyl isocyanide afforded desired compounds in a good yield ranging from 79% to 86%. To expeditiously expand chemical diversity and to reach novel chemical space, α-oxo-1,3-benzodioxole-5-acetic acid was employed using as an acyl source. Various isocyanides were subjected to the standard conditions; comparatively, α-oxocarboxylic acid analogues containing electron-donating group generated lower yields of final products (**4o**–**4x**). Similar results were found for the substrates of 2-thiopheneglyoxylic acid and 2-furanglyoxylic acid, as the corresponding starting reagents were converted into the desired α-ketoamides with moderate yields (**4y**–**4ac**, 49–61%). Unfortunately, alkyl α-oxocarboxylic acid could not be tolerated in sliver-catalyzed decarboxylation with air as the sole oxidant, as depicted in Scheme 2 (**4ad**–**4af**).

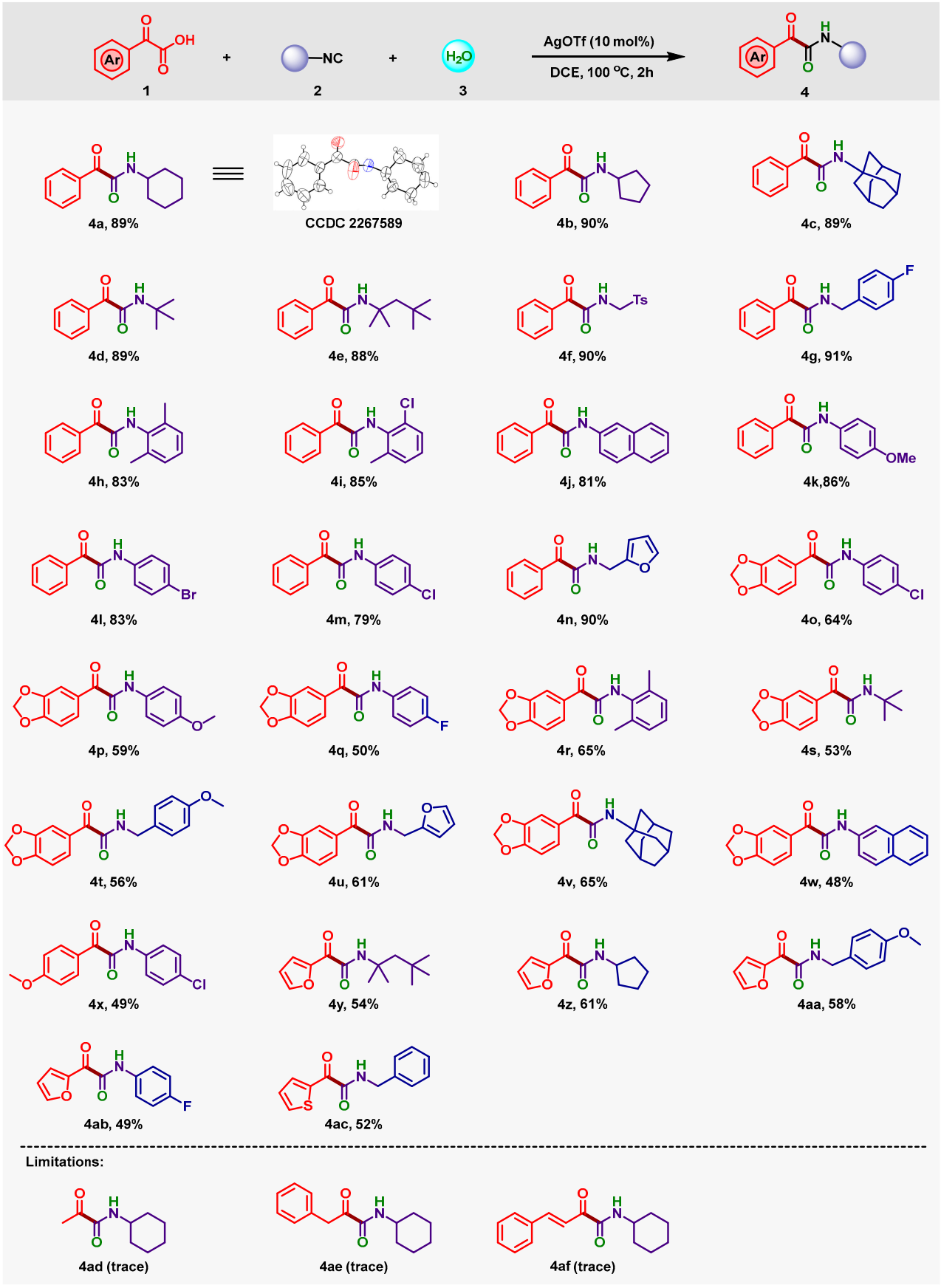
Table 1. Optimization of the reaction conditions [a].



1a 2a 3 4a

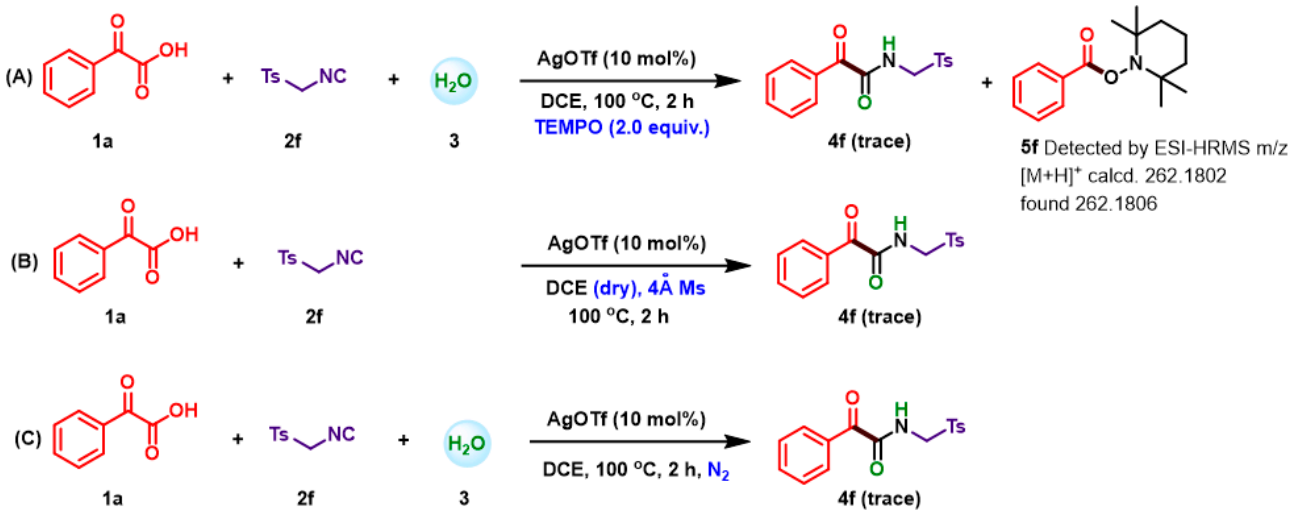
Entry	Cat.	Additive	Solvent	Temp. (°C)	Time (h)	Yield (%) [b]
1	Ag_2CO_3	-	MeCN	80	1	62
2	$AgBF_4$	-	MeCN	80	1	56
3	AgOAc	-	MeCN	80	1	59
4	Ag_2O	-	MeCN	80	1	51
5	AgOTf	-	MeCN	80	1	70
6	$AgNTf_2$	-	MeCN	80	1	54
7	AgOTf	-	DMF	80	1	47
8	AgOTf	-	1,4-Dioxane	80	1	79
9	AgOTf	-	DCE	80	1	82
10	AgOTf	-	DMSO	80	1	61
11	AgOTf	-	THF	80	1	33
12	AgOTf	-	Toluene	80	1	28
13	AgOTf	-	DCE	100	1	87
14	AgOTf	-	DCE	120	1	86
15	AgOTf	-	DCE	100	2	89
16 [c]	AgOTf	$PhI(OAc)_2$	DCE	100	2	85
17 [d]	AgOTf	$K_2S_2O_8$	DCE	100	2	88
18 [e]	AgOTf	Oxone	DCE	100	2	76
19	$Pd(OAc)_2$	-	DCE	100	2	23
20	$CuBr_2$	-	DCE	100	2	18
21	$FeCl_2$	-	DCE	100	2	31
22 [f]	AgOTf	-	DCE	100	2	73
23 [g]	AgOTf	-	DCE	100	2	67

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.3 mmol), **3** (2.0 equiv.) and catalyst (10 mol%) in solvent (2.0 mL). [b] Isolated yield. [c] 2.0 equiv. of $PhI(OAc)_2$. [d] 2.0 equiv. of $K_2S_2O_8$. [e] 2.0 equiv. of oxone. [f] 1.0 equiv. of water. [g] 3.0 equiv. of water.



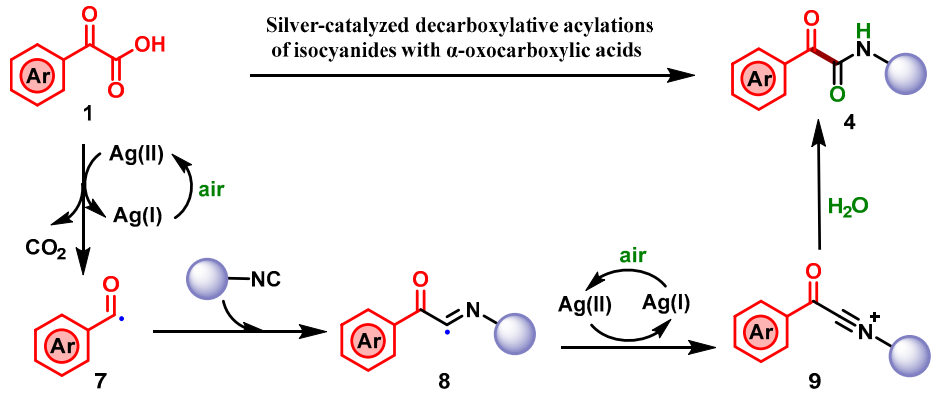
Scheme 2. Silver-catalyzed decarboxylation substrate scope.

As relative studies have reported, decarboxylation with α-keto acids as an acyl source always undergoes a radical process [25,26]. To further verify the possibility, 2.0 equiv. of TEMPO (common radical scavenger) was added into the mixture of phenylglyoxylic acid, TosMIC and water. The formation of α-ketoamide **4f** was dramatically inhibited. Unsurprisingly, TEMPO-adduct **5f** was observed by ESI-HRMS under standard reaction conditions (Scheme 3A). To clarify the mechanism by which isocyanide was used as an amide source, the model reaction was performed in the absence of water, and a trace amount of **4f** was obtained (Scheme 3B). The reaction was performed under a nitrogen atmosphere (Scheme 3C). As the results show, oxygen was essential to start the decarboxylation of α-keto acids. The results indicate that AgOTf was oxidized by oxygen to generate Ag(II) species.



Scheme 3. Control experiments. (**A**): TEMPO (2.0 equiv.) was added; (**B**): In the absence of water; (**C**): Under N_2.

Based on the control experiments and previous reports, the possible reaction mechanism was elucidated in Scheme 4. First, the decarboxylation of α-keto acids was initiated by AgOTf that was oxidized by air. Subsequently, the acyl radical was formed by releasing 1 mole of CO_2. Then, isocyanide trapped the in situ-generated radical species **7** to furnish the important intermediate **8**. Finally, the final compound was generated by the nucleophilic attack of H_2O on the nitrilium intermediate **9**. It could be found that acyl radical was a key intermediate to afford the final product. When α-ketoacids were directly conjugated with aromatic groups, aromatic radicals were formed which were more stable than aliphatic radicals. That is why aliphatic α-oxocarboxylic acids could not proceed well under standard reaction conditions.



Scheme 4. Possible reaction mechanism.

3. Materials and Methods

3.1. Analytical Techniques

^{1}H and ^{13}C NMR were recorded on a Bruker 400 spectrometer. ^{1}H NMR data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (Hz), relative intensity. ^{13}C NMR data are reported as follows: chemical shift in ppm (δ). LC/MS analyses were performed on a Shimadzu-2020 LC-MS instrument using the following conditions: Shim-pack VP-ODS C18 column (reverse phase, 150 × 4.6 mm); a linear gradient from 10% water and 90% acetonitrile to 75% acetonitrile and 25% water over 6.0 min; flow rate of 0.5 mL/min; UV photodiode array detection from 200 to 400 nm. High-resolution mass spectra (HRMS) were recorded on a Q Exactive hybrid quadrupole-Orbitrap mass spectrometer (Thermo Scientific) with an ESI source of 140,000 fwhm, AGC target set to 1×10^{6}, and a scan range of 100–1000 m/z. The raw data were deconvoluted using an Xcalibur 4.1. UV-VIS spectrophotometer TU-1950. The products were purified by Biotage Isolera™ Spektra Systems and hexane/EtOAc solvent systems. All reagents and solvents were obtained from commercial sources and used without further purification.

3.2. Synthetic Procedures for the Synthesis of Compound **4**

α-Oxocarboxylic acids (0.3 mmol), isocyanide (0.3 mmol), water (2.0 equiv.), and AgOTf (10 mol%) were mixed in DCE (2.0 mL). The reaction mixture was performed in a 5.0 mL microwave vial and stirred at 100 °C for 2 h. After completion, the reaction mixture was monitored by TLC, and the solvent was removed and extracted with ethyl acetate. Then, the organic phase was dried through Mg_2SO_4 and concentrated. The residue was purified by silica gel column chromatography using a gradient of ethyl acetate/hexane (0–100%) to afford the relative targeted product **4**.

N-Cyclohexyl-2-oxo-2-phenylacetamide (**4a**). White solid (89%), R_f = 0.30 (n-hexane/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.3 Hz, 2H), 7.66–7.61 (m, 1H), 7.49 (t, J = 7.6 Hz, 2H), 6.99 (s, 1H), 3.96–3.80 (m, 1H), 2.06–1.96 (m, 2H), 1.83–1.62 (m, 4H), 1.47–1.37 (m, 2H), 1.31–1.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.15, 160.86, 134.32, 133.45, 131.22, 128.46, 48.49, 32.73, 25.43, 24.76. HRMS (ESI) calcd for $C_{14}H_{18}NO_2^+$ ($[M + H]^+$) 232.1332, Found 232.1336.

N-Cyclopentyl-2-oxo-2-phenylacetamide (**4b**). White solid (90%), R_f = 0.30 (n-hexane/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 7.4 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.8 Hz, 2H), 6.97 (s, 1H), 4.27–4.17 (m, 1H), 2.03–1.96 (m, 2H), 1.70–1.63 (m, 2H), 1.61–1.56 (m, 2H), 1.49–1.41 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.99, 161.31, 134.32, 133.44, 131.24, 128.46, 51.22, 32.96, 23.81. HRMS (ESI) calcd for $C_{13}H_{16}NO_2^+$ ($[M + H]^+$) 218.1176, Found 218.1177.

N-(Adamantan-1-yl)-2-oxo-2-phenylacetamide (**4c**). White solid (89%), R_f = 0.33 (n-hexane/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29–8.25 (m, 2H), 7.59–7.53 (m, 1H), 7.46–7.39 (m, 2H), 6.84 (s, 1H), 2.09 (s, 9H), 1.70 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.61, 160.94, 134.11, 133.41, 131.20, 131.10, 128.34, 128.26, 52.35, 41.07, 40.98, 36.23, 36.15, 29.35, 29.27. HRMS (ESI) calcd for $C_{18}H_{22}NO_2^+$ ($[M + H]^+$) 284.1645, Found 284.1645.

N-(*tert*-Butyl)-2-oxo-2-phenylacetamide (**4d**). White solid (89%), R_f = 0.33 (n-hexane/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27–8.20 (m, 2H), 7.56–7.49 (m, 1H), 7.39 (t, J = 7.7 Hz, 2H), 6.86 (s, 1H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.60, 161.13, 134.16, 133.41, 131.22, 128.39, 51.68, 28.40. HRMS (ESI) calcd for $C_{12}H_{16}NO_2^+$ ($[M + H]^+$) 206.1176, Found 206.1177.

2-Oxo-2-phenyl-*N*-(2,4,4-trimethylpentan-2-yl)acetamide (**4e**). White solid (88%), R_f = 0.33 (n-hexane/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28–8.20 (m, 2H), 7.53 (dd, J = 10.6, 4.3 Hz, 1H), 7.39 (t, J = 7.8 Hz, 2H), 6.94 (s, 1H), 1.76 (s, 2H), 1.44 (s, 6H), 0.97 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.58, 160.73, 134.12, 133.43, 131.26, 128.37, 55.52, 51.71, 31.72, 31.45, 28.74. HRMS (ESI) calcd for $C_{12}H_{16}NO_2^+$ ($[M + H]^+$) 262.1802, Found 262.1806.

2-Oxo-2-phenyl-*N*-(tosylmethyl)acetamide (**4f**). White solid (90%), R_f = 0.20 (n-hexane/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.1 Hz, 2H), 7.83 (d, J = 8.3 Hz, 2H), 7.66–7.62 (m, 1H), 7.45 (t, J = 7.8 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 4.80 (d, J = 7.0 Hz, 2H), 2.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 186.03, 160.82, 145.71, 134.93, 133.43, 132.51, 131.09, 130.11, 129.67, 129.08, 128.59, 126.53, 60.00, 21.74. HRMS (ESI) calcd for $C_{12}H_{16}NO_2^+$ ([M + H]$^+$) 318.0795, Found 318.0796.

N-(4-Fluorobenzyl)-2-oxo-2-phenylacetamide (**4g**). A white solid (90%), R_f = 0.25 (n-hexane/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49–8.30 (m, 2H), 7.70–7.60 (m, 1H), 7.50 (t, J = 7.8 Hz, 3H), 7.39–7.30 (m, 2H), 7.13–6.99 (m, 2H), 4.55 (d, J = 6.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.51, 163.59, 161.59, 161.14, 134.58, 133.24, 133.00, 132.97, 131.26, 129.71, 129.63, 128.57, 115.85, 115.63, 42.77. HRMS (ESI) calcd for $C_{15}H_{13}FNO_2^+$ ([M + H]$^+$) 258.0925. Found:258.0928.

N-(2,6-Dimethylphenyl)-2-oxo-2-phenylacetamide (**4h**). White solid (83%), R_f = 0.25 (n-hexane/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50–8.38 (m, 3H), 7.69 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 7.21–7.14 (m, 3H), 2.33 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.72, 159.86, 135.15, 134.69, 133.23, 132.46, 131.40, 128.65, 128.40, 127.81, 18.52. HRMS (ESI) calcd for $C_{16}H_{16}NO_2^+$ ([M + H]$^+$) 254.1176, Found 254.1180.

N-(2-Chloro-6-methylphenyl)-2-oxo-2-phenylacetamide (**4i**). White solid (85%), R_f = 0.25 (n-hexane/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.46–8.40 (m, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 7.35 (dd, J = 6.7, 2.6 Hz, 1H), 7.25–7.17 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.06, 159.66, 137.77, 134.71, 133.12, 131.41, 129.39, 128.64, 128.42, 127.32, 19.05. HRMS (ESI) calcd for $C_{15}H_{13}ClNO_2^+$ ([M + H]$^+$) 274.0629, Found 274.0631.

N-(Naphthalen-2-yl)-2-oxo-2-phenylacetamide (**4j**). White solid (81%), R_f = 0.20 (n-hexane/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.41–8.35 (m, 3H), 7.79 (dd, J = 8.4, 3.6 Hz, 2H), 7.75 (d, J = 8.0 Hz, 1H), 7.60 (t, J = 7.4 Hz, 1H), 7.53 (dd, J = 8.8, 2.1 Hz, 1H), 7.46 (t, J = 6.0 Hz, 2H), 7.44–7.41 (m, 1H), 7.40–7.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.32, 159.00, 134.68, 134.05, 133.77, 133.15, 131.54, 131.13, 129.13, 128.60, 127.89, 127.67, 126.80, 125.59, 119.53, 117.14. HRMS (ESI) calcd for $C_{18}H_{14}NO_2^+$ ([M + H]$^+$) 276.1019, Found 276.1020.

N-(4-Methoxyphenyl)-2-oxo-2-phenylacetamide (**4k**). White solid (86%), R_f = 0.25 (n-hexane/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.48–8.41 (m, 2H), 7.70–7.62 (m, 3H), 7.53 (t, J = 7.8 Hz, 2H), 6.98–6.93 (m, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.61, 158.68, 157.12, 134.54, 133.26, 131.46, 129.83, 128.54, 121.53, 114.41, 55.51. HRMS (ESI) calcd for C15H14NO3+ ([M + H]+) 256.0968, Found 256.0971.

N-(4-Bromophenyl)-2-oxo-2-phenylacetamide (**4l**). White solid (83%), Rf = 0.20 (n-hexane/EtOAc, 8:2). 1H NMR (400 MHz, CDCl3) δ 8.92 (s, 1H), 8.38–8.29 (m, 2H), 7.61–7.57 (m, 1H), 7.56–7.51 (m, 2H), 7.46–7.41 (m, 4H). 13C NMR (100 MHz, CDCl3) δ 187.05, 158.80, 135.73, 134.83, 132.91, 132.27, 131.51, 128.65, 121.46, 118.10. HRMS (ESI) calcd for C14H11BrNO2+ ([M + H]+) 303.9968, Found 303.9968.

N-(4-Chlorophenyl)-2-oxo-2-phenylacetamide (**4m**). White solid (79%), Rf = 0.20 (n-hexane/EtOAc, 8:2). 1H NMR (400 MHz, CDCl3) δ 8.92 (s, 1H), 8.33 (d, J = 8.1 Hz, 2H), 7.62–7.56 (m, 3H), 7.44 (t, J = 7.8 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H). 13C NMR (100 MHz, CDCl3) δ 187.08, 158.79, 135.22, 134.83, 132.93, 131.51, 130.42, 129.33, 128.65, 121.15. HRMS (ESI) calcd for C14H11ClNO2+ ([M + H]+) 260.0473, Found 260.0475.

N-(Furan-2-ylmethyl)-2-oxo-2-phenylacetamide (**4n**). White solid (90%), Rf = 0.30 (n-hexane/EtOAc, 8:2). 1H NMR (400 MHz, CDCl3) δ 8.38 (dd, J = 8.2, 0.9 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.58–7.38 (m, 4H), 6.50–6.20 (m, 2H), 4.61 (d, J = 5.9 Hz, 2H). 13C NMR (100 MHz, CDCl3) δ 187.34, 161.42, 150.14, 142.63, 134.52, 133.27, 131.27, 128.55, 110.57, 108.12, 36.39. HRMS (ESI) calcd for C13H12NO3+ ([M + H]+) 230.0812, Found 230.0813.

2-(Benzo[*d*][1,3]dioxol-5-yl)-*N*-(4-chlorophenyl)-2-oxoacetamide (**4o**). White solid (64%), Rf = 0.30 (n-hexane/EtOAc, 7:3). 1H NMR (400 MHz, CDCl3) δ 8.93 (s, 1H), 8.22 (dd, J = 8.3, 1.6 Hz, 1H), 7.80 (d, J = 1.6 Hz, 1H), 7.60–7.55 (m, 2H), 7.30–7.27 (m, 2H), 6.85 (d, J = 8.3 Hz, 1H), 6.02 (s, 2H). 13C NMR (100 MHz, CDCl3) δ 159.16, 153.58, 148.16, 135.30, 130.33, 129.58, 129.30, 127.34, 121.12, 110.61, 108.28, 102.14. HRMS (ESI) calcd for C15H11ClNO4+ ([M + H]+) 304.0371, Found 304.0375.

2-(Benzo[*d*][1,3]dioxol-5-yl)-*N*-(4-methoxyphenyl)-2-oxoacetamide (**4p**). White solid (59%), Rf = 0.30 (n-hexane/EtOAc, 7:3). 1H NMR (400 MHz, CDCl3) δ 8.82 (s, 1H), 8.22 (dd, J = 8.3, 1.7 Hz, 1H), 7.80 (d, J = 1.6 Hz, 1H), 7.56–7.51 (m, 2H), 6.88–6.82 (m, 3H), 6.01 (s, 2H), 3.75 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 185.06, 159.05, 157.03, 153.34, 148.06, 129.88, 129.44, 127.77, 121.51, 114.37, 110.63, 108.21, 102.07, 55.52. HRMS (ESI) calcd for C16H14NO5+ ([M + H]+) 300.0866, Found 300.0870.

2-(Benzo[*d*][1,3]dioxol-5-yl)-*N*-(4-fluorophenyl)-2-oxoacetamide (**4q**). White solid (50%), Rf = 0.30 (n-hexane/EtOAc, 7:3). 1H NMR (400 MHz, CDCl3) δ 8.91 (s, 1H), 8.21 (dd, J = 8.3, 1.7 Hz, 1H), 7.79 (d, J = 1.6 Hz, 1H), 7.58 (dd, J = 9.1, 4.7 Hz, 2H), 7.01 (t, J = 8.7 Hz, 2H), 6.83 (d, J = 8.3 Hz, 1H), 6.01 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.70, 159.17, 153.49, 148.12, 132.81, 129.51, 127.58, 121.70, 121.62, 116.07, 115.85, 110.60, 108.25, 102.12. HRMS (ESI) calcd for $C_{15}H_{11}FNO_4^+$ ([M + H]$^+$) 288.0667, Found 288.0670.

2-(Benzo[*d*][1,3]dioxol-5-yl)-*N*-(2,6-dimethylphenyl)-2-oxoacetamide (**4r**). White solid (65%), Rf = 0.30 (n-hexane/EtOAc, 7:3). 1H NMR (400 MHz, CDCl3) δ 9.02 (s, 1H), 7.49 (dd, J = 8.2, 1.7 Hz, 1H), 7.35 (s, 1H), 7.17 (s, 1H), 7.09 (d, J = 7.2 Hz, 2H), 6.86 (d, J = 8.1 Hz, 1H), 6.04 (s, 2H), 2.16 (s, 6H). 13C NMR (100 MHz, CDCl3) δ 168.03, 161.91, 154.00, 148.88, 136.39, 131.16, 129.90, 128.86, 127.76, 108.58, 108.36, 102.47, 18.01. HRMS (ESI) calcd for C17H16NO4+ ([M + H]+) 298.1074, Found 298.1077.

2-(Benzo[*d*][1,3]dioxol-5-yl)-*N*-(tert-butyl)-2-oxoacetamide (**4s**). White solid (53%), Rf = 0.30 (n-hexane/EtOAc, 8:2). 1H NMR (400 MHz, CDCl3) δ 8.17–8.09 (m, 1H), 7.74 (t, J = 3.3 Hz, 1H), 6.97 (s, 1H), 6.85 (dd, J = 8.3, 3.9 Hz, 1H), 6.04 (s, 2H), 1.44 (s, 9H). 13C NMR (100 MHz, CDCl3) δ 186.21, 161.54, 152.92, 147.89, 128.97, 127.89, 110.37, 108.01, 101.95, 51.60, 28.36. HRMS (ESI) calcd for C13H16NO4+ ([M + H]+) 250.1074. Found 250.1076.

2-(Benzo[*d*][1,3]dioxol-5-yl)-*N*-(4-methoxybenzyl)-2-oxoacetamide (**4t**). White solid (56%), Rf = 0.35 (n-hexane/EtOAc, 7:3). 1H NMR (400 MHz, CDCl3) δ 8.22 (dd, J = 8.3, 1.7 Hz, 1H), 7.81 (d, J = 1.6 Hz, 1H), 7.40 (s, 1H), 7.32–7.21 (m, 2H), 6.94–6.84 (m, 3H), 6.08 (s, 2H), 4.50 (d, J = 6.0 Hz, 2H), 3.82 (s, 3H). 13C NMR (100 MHz, CDCl3) δ 185.24, 161.85, 159.27, 153.18, 148.02, 129.29, 129.13, 127.95, 114.23, 110.35, 108.14, 102.01, 55.32, 42.97. HRMS (ESI) calcd for C17H16NO5+ ([M + H]+) 314.1023, Found 314.1024.

2-(Benzo[*d*][1,3]dioxol-5-yl)-*N*-(furan-2-ylmethyl)-2-oxoacetamide (**4u**). White solid (61%), Rf = 0.30 (n-hexane/EtOAc, 8:2). 1H NMR (400 MHz, CDCl3) δ 8.24 (dd, J = 8.3, 1.7 Hz, 1H), 7.83 (d, J = 1.6 Hz, 1H), 7.47 (s, 1H), 7.42 (dd, J = 1.8, 0.7 Hz, 1H), 6.91 (d, J = 8.3 Hz, 1H), 6.38–6.33 (m, 2H), 6.10 (s, 2H), 4.59 (d, J = 5.9 Hz, 2H). 13C NMR (100 MHz, CDCl3) δ 184.89, 161.74, 153.27, 150.17, 148.05, 142.61, 129.21, 127.84, 110.55, 110.35, 108.18, 108.07, 102.05, 36.38. HRMS (ESI) calcd for C14H12NO4+ ([M + H]+) 274.0710, Found 274.0713.

N-(Adamantan-1-yl)-2-(benzo[*d*][1,3]dioxol-5-yl)-2-oxoacetamide (**4v**). White solid (65%), Rf = 0.30 (n-hexane/EtOAc, 8:2). 1H NMR (400 MHz, CDCl3) δ 8.16 (dd, J = 8.3, 1.7 Hz, 1H), 7.78 (d, J = 1.6 Hz, 1H), 6.86 (t, J = 10.2 Hz, 2H), 6.07 (s, 2H), 2.12 (t, J = 8.3 Hz, 9H), 1.73 (s, 6H). 13C NMR (100 MHz, CDCl3) δ 186.25, 161.18, 152.91, 147.90, 129.02, 127.96, 110.47, 108.02, 101.95, 52.32, 41.10, 36.25, 29.35. HRMS (ESI) calcd for C19H22NO4+ ([M + H]+) 328.1543, Found 328.1544.

2-(Benzo[*d*][1,3]dioxol-5-yl)-*N*-(naphthalen-2-yl)-2-oxoacetamide (**4w**). White solid (48%), Rf = 0.30 (n-hexane/EtOAc, 7:3). 1H NMR (400 MHz, CDCl3) δ 9.19 (s, 1H), 8.44 (d, J = 1.7 Hz, 1H), 8.36 (dd, J = 8.3, 1.7 Hz, 1H), 7.93 (d, J = 1.5 Hz, 1H), 7.86 (dd, J = 15.7, 8.3 Hz, 3H), 7.61 (dd, J = 8.8, 2.1 Hz, 1H), 7.55–7.44 (m, 2H), 6.95 (d, J = 8.3 Hz, 1H), 6.11 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.76, 159.40, 153.46, 148.13, 134.12, 133.76, 131.08, 129.55, 129.09, 127.88, 127.67, 126.77, 125.54, 119.56, 117.06, 110.67, 108.26, 102.12. HRMS (ESI) calcd for $C_{19}H_{14}NO_4^+$ ([M + H]$^+$) 320.0917, Found 320.0917.

N-(4-Chlorophenyl)-2-(4-methoxyphenyl)-2-oxoacetamide (**4x**). White solid (49%), R_f = 0.30 (n-hexane/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.46–8.41 (m, 2H), 7.61–7.57 (m, 2H), 7.31–7.27 (m, 2H), 6.93–6.89 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.82, 165.07, 159.40, 135.37, 134.34, 130.25, 129.28, 125.97, 121.11, 114.02, 55.65. HRMS (ESI) calcd for $C_{15}H_{13}ClNO_3^+$ ([M + H]$^+$) 290.0578. Found 290.0580.

2-(Furan-2-yl)-2-oxo-*N*-(2,4,4-trimethylpentan-2-yl)acetamide (**4y**). White solid (54%), R_f = 0.30 (n-hexane/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 3.6 Hz, 1H), 7.67 (d, J = 1.0 Hz, 1H), 7.16 (s, 1H), 6.54 (dd, J = 3.6, 1.6 Hz, 1H), 1.73 (s, 2H), 1.42 (s, 6H), 0.95 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.70, 159.05, 149.46, 149.18, 126.76, 113.08, 55.39, 51.70, 31.71, 31.42, 28.68. HRMS (ESI) calcd for $C_{14}H_{22}NO_3^+$ ([M + H]$^+$) 252.1594, Found 252.1596.

N-Cyclopentyl-2-(furan-2-yl)-2-oxoacetamide (**4z**). White solid (61%), R_f = 0.30 (n-hexane/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 3.6 Hz, 1H), 7.78 (d, J = 0.9 Hz, 1H), 7.27 (s, 1H), 6.65 (dd, J = 3.6, 1.5 Hz, 1H), 4.36–4.21 (m, 1H), 2.11–2.03 (m, 2H), 1.80–1.66 (m, 4H), 1.59–1.50 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.87, 159.66, 149.52, 149.30, 126.87, 113.13, 51.17, 32.87, 23.81. HRMS (ESI) calcd for $C_{11}H_{14}NO_3^+$ ([M + H]$^+$) 208.0968, Found 208.0970.

2-(Furan-2-yl)-*N*-(4-methoxybenzyl)-2-oxoacetamide (**4aa**). White solid (58%), R_f = 0.30 (n-hexane/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 3.6 Hz, 1H), 7.78 (d, J = 0.8 Hz, 1H), 7.62 (s, 1H), 7.27 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 6.65 (dd, J = 3.5, 1.5 Hz, 1H), 4.50 (d, J = 6.0 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.61, 159.91, 159.33, 149.52, 149.42, 129.30, 129.08, 126.92, 114.26, 113.17, 55.32, 42.94. HRMS (ESI) calcd for $C_{14}H_{14}NO_4^+$ ([M + H]$^+$) 260.0917, Found 260.0918.

N-(4-Fluorophenyl)-2-(furan-2-yl)-2-oxoacetamide (**4ab**). White solid (49%), R_f = 0.30 (n-hexane/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.31 (d, J = 3.7 Hz, 1H), 7.92–7.80 (m, 1H), 7.78–7.64 (m, 2H), 7.15–7.11 (m, 2H), 6.71 (dd, J = 3.7, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.38, 161.21, 158.77, 157.53, 149.84, 127.51, 121.78, 121.70, 116.14, 115.91, 113.41. HRMS (ESI) calcd for $C_{12}H_9FNO_3^+$ ([M + H]$^+$) 234.0561, Found 234.0564.

N-Benzyl-2-oxo-2-(thiophen-2-yl)acetamide (**4ac**). White solid (52%), R_f = 0.30 (n-hexane/EtOAc, 8:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.08 (s, 1H), 7.80 (d, J = 4.9 Hz, 1H), 7.66 (d, J = 3.7 Hz, 1H), 7.32 (d, J = 7.1 Hz, 2H), 7.28–7.21 (m, 3H), 7.11 (t, J = 4.4 Hz, 1H), 4.94 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.67, 167.29, 162.34, 139.21, 138.28, 137.31, 135.52, 129.07, 128.71, 128.69, 128.06, 43.27. HRMS (ESI) calcd for $C_{13}H_{12}NO_2S^+$ ([M + H]$^+$) 246.0583, Found 246.0585.

The results of the X-ray diffraction analysis for compound **4a** were deposited with the Cambridge Crystallographic Data Centre (CCDC 2267589) (Supplementary Materials).

4. Conclusions

In summary, we uncovered a one-pot MCR of silver-catalyzed decarboxylative acylation with α-oxocarboxylic acids, isocyanides and water. A series of α-ketoamides was synthesized, with air as the sole oxidant participating in the decarboxylative process. The control experiments confirmed that the oxygen atom of the amide moiety was derived from water. Notably, transition metal-catalyzed decarboxylation using oxygen as oxidants for the synthesis of α-ketoamides has not been well explored to date. And isocyanides, as one of the most important and versatile synthons, could achieve decarboxylative acylation but not directly acylated with carboxylic acid. The available data suggest that the introduction of cheap, handily accessible α-oxocarboxylic acids into decarboxylative acylation reactions might exhibit a powerful alternative to synthesize drug-like α-ketoamides.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules28145342/s1, Figures S1–S58: Selected ^{1}H and ^{13}C NMR spectra of the prepared compounds; Table S1: Control experiments for reagents. In addition, crystallographic information on compound **4a** (CCDC 2267589) are provided in the supporting information.

Author Contributions: Conceptualization, Z.-Z.C. and Z.-G.X.; methodology, J.X., X.-Y.C. and Y.-T.H.; formal analysis, J.X. and X.L.; investigation, Y.-T.H. and X.L.; writing-original draft preparation, J.L. and Z.-G.X.; visualization, X.L., X.-Y.C., J.L. and Y.-T.H.; supervision, Z.-Z.C. and Z.-G.X. All authors approved the final version. All authors have read and agreed to the published version of the manuscript.

Funding: This research was founded by the Science and Technology Research Program of Chongqing Municipal Education Commission (KJQN202201302, KJQN202101340 and KJZD-M201801301) the Natural Science Foundation Project of CQ CSTSC (cstc2021ycjh-bgzxm0163, cstc2020jcyj-msxmX0849 and cstc2021jcyj-bshX0242) and Chongqing University of Arts and Sciences: Program for Talents Introduction (R2022YX07, R2021FYX05 and P2022YX10).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors would like to thank H.-Z. Liu for obtaining the LC/MS, HRMS and NMR data.

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

Sample Availability: Not applicable.

References

1. Cai, W.; Qiao, X.; Zhang, H.; Li, B.; Guo, J.; Zhang, L.; Chen, W.-W.; Zhao, B. Asymmetric biomimetic transamination of α-keto amides to peptides. *Nat. Commun.* **2021**, *12*, 5174–5182. [CrossRef] [PubMed]
2. Wang, J.; Liang, B.; Chen, Y.; Chan, J.F.-W.; Yuan, S.; Ye, H.; Nie, L.; Zhou, J.; Wu, Y.; Wu, M.; et al. A new class of α-ketoamide derivatives with potent anticancer and anti-SARS-CoV-2 activities. *Eur. J. Med. Chem.* **2021**, *215*, 113267–113286. [CrossRef]
3. Zhou, J.; Mock, E.D.; Martella, A.; Kantae, V.; Di, X.Y.; Burggraaff, L.; Baggelaar, M.P.; Al-Ayed, K.; Bakker, A.; Florea, B.I.; et al. Activity-based protein profiling identifies α-ketoamides as inhibitors for Phospholipase A2 Group XVI. *ACS Chem. Biol.* **2019**, *14*, 164–169. [CrossRef] [PubMed]
4. Kumar, D.; Vemula, S.R.; Cook, G.R. Recent advances in catalytic synthesis of α-ketoamides. *ACS Catal.* **2016**, *6*, 4920–4945. [CrossRef]
5. Zhang, L.; Lin, D.; Kusov, Y.; Nian, Y.; Ma, Q.; Wang, J.; von Brunn, A.; Leyssen, P.; Lanko, K.; Neyts, J.; et al. Alpha-ketoamides as broad-spectrum inhibitors of coronavirus and enterovirus replication Structurebased design, synthesis, and activity assessment. *J. Med. Chem.* **2020**, *63*, 4562–4578. [CrossRef] [PubMed]
6. Robello, M.; Barresi, E.; Baglini, E.; Salerno, S.; Taliani, S.; Settimo, F.D. The alpha keto amide moiety as a privileged motif in medicinal chemistry: Current insights and emerging opportunities. *J. Med. Chem.* **2021**, *64*, 3508–3545. [CrossRef]
7. Zhou, J.; Mock, E.D.; Ayed, K.A.; Di, X.Y.; Kantae, V.; Burggraaff, L.; Stevens, A.; Martella, A.; Mohr, F.; Jiang, M.; et al. Structure-activity relationship studies of α-ketoamides as inhibitors of the phospholipase A and acyltransferase (PLAAT) enzyme family. *J. Med. Chem.* **2020**, *63*, 9340–9359. [CrossRef]
8. Risi, C.D.; Pollini, G.P.; Zanirato, V. Recent developments in general methodologies for the synthesis of α-ketoamides. *Chem. Rev.* **2016**, *116*, 3241–3305. [CrossRef]
9. Lv, Y.; Bao, P.; Yue, H.; Li, J.-S.; Wei, W. Visible-light-mediated metal-free decarboxylative acylations of isocyanides with α-oxocarboxylic acids and water leading to α-ketoamides. *Green Chem.* **2019**, *21*, 6051–6055. [CrossRef]
10. Zhao, F.; Meng, N.; Sun, T.; Wen, J.; Zhao, X.; Wei, W. Metal-free electrochemical synthesis of α-ketoamides via decarboxylative coupling of α-keto acids with isocyanides and water. *Org. Chem. Front.* **2021**, *8*, 6508–6514. [CrossRef]
11. Zhao, Y.; Meng, X.; Cai, C.; Wang, L.; Gong, H. Synthesis of α-ketoamides via electrochemical decarboxylative acylation of isocyanides using α-ketoacids as an acyl source. *Asian J. Org. Chem.* **2022**, *11*, 43–47. [CrossRef]
12. Papanikos, A.; Rademann, J.; Meldal, M. α-Ketocarbonyl Peptides: A General Approach to Reactive Resin-Bound Intermediates in the Synthesis of Peptide Isosteres for Protease Inhibitor Screening on Solid Support. *J. Am. Chem. Soc.* **2001**, *123*, 2176–2181. [CrossRef] [PubMed]
13. Li, P.-G.; Zhu, H.; Fan, M.; Yan, C.; Shi, K.; Chi, X.-W.; Zou, L.-H. Copper-catalyzed coupling of anthranils and α-keto acids: Direct synthesis of α-ketoamides. *Org. Biomol. Chem.* **2019**, *17*, 5902–5907. [CrossRef]
14. Zhang, X.; Yang, W.; Wang, L. Silver-catalyzed amidation of benzoylformic acids with tertiary amines *via* selective carbon–nitrogen bond cleavage. *Org. Biomol. Chem.* **2013**, *11*, 3649–3654. [CrossRef]
15. Wang, H.; Guo, L.-N.; Duan, X.-H. Copper-catalyzed oxidative condensation of α-oxocarboxylic acids with formamides: Synthesis of α-ketoamides. *Org. Biomol. Chem.* **2013**, *11*, 4573–4576. [CrossRef] [PubMed]
16. Lai, M.; Wu, Z.; Wang, Y.; Zheng, Y.; Zhao, M. Selective synthesis of aryl thioamides and aryl-α-ketoamides from α-oxocarboxylic acids and tetraalkylthiuram disulfides: An unexpected chemoselectivity from aryl sulfonyl chlorides. *Org. Chem. Front.* **2019**, *6*, 506–511. [CrossRef]
17. Rodríguez, N.; Goossen, L.J. Decarboxylative coupling reactions: A modern strategy for C–C-bond formation. *Chem. Soc. Rev.* **2011**, *40*, 5030–5048. [CrossRef]
18. Weaver, J.D.; Recio, A.; Grenning, A.J.; Tunge, J.A. Transition metal-catalyzed decarboxylative allylation and benzylation reactions. *Chem. Rev.* **2011**, *111*, 1846–1913. [CrossRef]

19. Wang, Q.; Zhang, X.; Fan, X. Synthesis of 2-aminobenzophenones through acylation of anilines with α-oxocarboxylic acids assisted by *tert*-butyl nitrite. *Org. Biomol. Chem.* **2018**, *16*, 7737–7747. [CrossRef]
20. Zou, H.-X.; Li, Y.; Yang, Y.; Li, J.-H.; Xiang, J. Silver-catalyzed decarboxylative couplings of acids and anhydrides: An entry to 1,2-diketones and aryl-substituted ethanes. *Adv. Synth. Catal.* **2018**, *360*, 1439–1443. [CrossRef]
21. Katiyar, S.; Kumara, A.; Sashidhara, K.V. Silver-catalyzed decarboxylative cyclization for the synthesis of substituted pyrazoles from 1,2-diaza-1,3-dienes and a-keto acids. *Chem. Commun.* **2022**, *58*, 7297–7300. [CrossRef] [PubMed]
22. Zeng, X.; Liu, C.; Wang, X.; Zhang, J.; Wang, X.; Hu, Y. Silver-catalyzed decarboxylative acylation of quinoxalin-2(1*H*)-ones with α-oxo-carboxylic acids. *Org. Biomol. Chem.* **2017**, *15*, 8929–8935. [CrossRef] [PubMed]
23. Wu, S.; Yu, H.; Hu, Q.; Yang, Q.; Xu, S.; Liu, T. Silver-catalyzed decarboxylative crosscoupling of α-keto acids with alkenes giving approach to chalcones. *Tetrahedron Lett.* **2017**, *58*, 4763–4765. [CrossRef]
24. Wang, J.; Liu, X.; Wu, Z.; Li, F.; Qin, T.; Zhang, S.; Kong, W.; Liu, L. Silver-catalyzed decarboxylative C–H functionalization of cyclic aldimines with aliphatic carboxylic acids. *Chin. Chem. Lett.* **2021**, *32*, 2777–2781. [CrossRef]
25. Li, D.; Wang, M.; Liu, J.; Zhao, Q.; Wang, L. Cu(II)-catalyzed decarboxylative acylation of acyl C–H of formamides with a-oxocarboxylic acids leading to α-ketoamides. *Chem. Commun.* **2013**, *49*, 3640–3642. [CrossRef] [PubMed]
26. Guin, S.; Rout, S.K.; Gogoi, A.; Ali, W.; Patel, B.K. A palladium(II)-catalyzed synthesis of α-ketoamides via chemoselective aroyl addition to cyanamides. *Adv. Synth. Catal.* **2014**, *356*, 2559–2565. [CrossRef]
27. Cioc, R.C.; Ruijter, E.; Orru, R.V.A. Multicomponent reactions: Advanced tools for sustainable organic synthesis. *Green Chem.* **2014**, *16*, 2958–2975. [CrossRef]
28. Campbell, A.N.; Stahl, S.S. Overcoming the "oxidant problem": Strategies to use O_2 as the oxidant in organometallic C–H oxidation reactions catalyzed by Pd (and Cu). *Acc. Chem. Res.* **2012**, *45*, 851–863. [CrossRef]
29. Leonardi, G.; Truscello, A.; Mondrone, G.G.; Sebastiano, R. A facile synthesis in aqueous medium of 3-hydroxy-2-pyrone from aldaric acids or their derivatives. *Results Chem.* **2022**, *4*, 100280–100284. [CrossRef]
30. Panday, S.K. Advances in the mitsunobu reaction: An excellent organic protocol with versatile applications. *Mini Rev. Org. Chem.* **2019**, *16*, 127–140. [CrossRef]
31. Shekuti, R.K.; Tangalipalli, S.; Dhonthulachitty, C.; Kothakapu, S.R.; Annapurna, P.D.; Neella, C.K. *N*-Benzoyl-4-dimethylaminopyridinium chloride: A Lewis base adduct for efficient poly and monobenzoylation. *ChemistrySelect* **2022**, *7*, e202202636.
32. Tavakoli, S.D.; Prieto-Araujo, E.; Sánchez-Sánchez, E.; Gomis-Bellmunt, O. Methodology for interaction identification in modular multi-level converter-based HVDC systems. *ISA Trans.* **2022**, *126*, 300–315. [CrossRef]
33. Lei, J.; Ding, Y.; Zhou, H.; Gao, X.-Y.; Cao, Y.-H.; Tang, D.-Y.; Li, H.; Xu, Z.-G.; Chen, Z.-Z. Practical synthesis of quinolone drugs via a novel TsCl-mediated domino reaction sequence. *Green Chem.* **2022**, *24*, 5755–5759. [CrossRef]
34. Lei, J.; Xu, J.; Luo, Y.-F.; Li, J.; Wang, J.-Y.; Li, H.; Xu, Z.-G.; Chen, Z.-Z. A novel isocyanide/Ag_2CO_3-promoted addition of heteroatoms to alkynes under mild conditions. *Org. Chem. Front.* **2023**, *10*, 786–792. [CrossRef]
35. Wang, Z.; Zhu, L.; Yin, F.; Su, Z.; Li, Z.; Li, C. Silver-catalyzed decarboxylative chlorination of aliphatic carboxylic acids. *J. Am. Chem. Soc.* **2012**, *134*, 4258–4263. [CrossRef]
36. Varenikov, A.; Shapiro, E.; Gandelman, M. Decarboxylative halogenation of organic compounds. *Chem. Rev.* **2021**, *121*, 412–484. [CrossRef] [PubMed]
37. Zhang, L.; Xu, M.; Liu, J.; Zhang, X.-M. Tandem cycloaddition–decarboxylation of α-keto acid and isocyanide under oxidant-free conditions towards monosubstituted oxazoles. *RSC Adv.* **2016**, *6*, 73450–73453. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.