Advanced Synthesis & Catalysis

Very Important Publication

DOI: 10.1002/adsc.201500639

Robust Silver(I) Catalyst for the Carboxylative Cyclization of Propargylic Alcohols with Carbon Dioxide under Ambient Conditions

Qing-Wen Song[a] and Liang-Nian He[a,*]

[a] State Key Laboratory and Institute of Elemento-Organic Chemistry, Collaborative Innovation Center of Chemical Science and Engineering, Nankai University, Tianjin 300071, People's Republic of China
Fax: (+86)-22-2350-3878; phone: (+86)-22-2350-3878; e-mail: heln@nankai.edu.cn

Received: July 3, 2015; Revised: November 11, 2015; Published online: December 17, 2015

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201500639.

Abstract: Inspired by the bulkier bis(triphenylphosphine)–silver cation-induced mechanism of propargylic alcohols and carbon dioxide through the alkyl carbonate intermediate, a robust dual-component catalytic system consisting of silver acetate and tetraheptylammonium bromide was rationally developed for the synthesis of α-methylene cyclic carbonates under ambient conditions without employing any additional organic base and ligand. This is one of the most effective catalysts reported to date for this conversion, with a very high turnover number of up to 6024, probably due to the synergistic effect of Lewis basic and Lewis acidic species for the activation of both propargylic alcohol and carbon dioxide by the formation of the alkyl carbonate with a bulkier counterion. Notably, this catalyst also worked well for the carboxylative cyclization of propargylic amines with carbon dioxide with the highest turnover number of 544.

Keywords: bulky cations; carbon dioxide; reaction mechanism; silver catalysis; synthetic methods

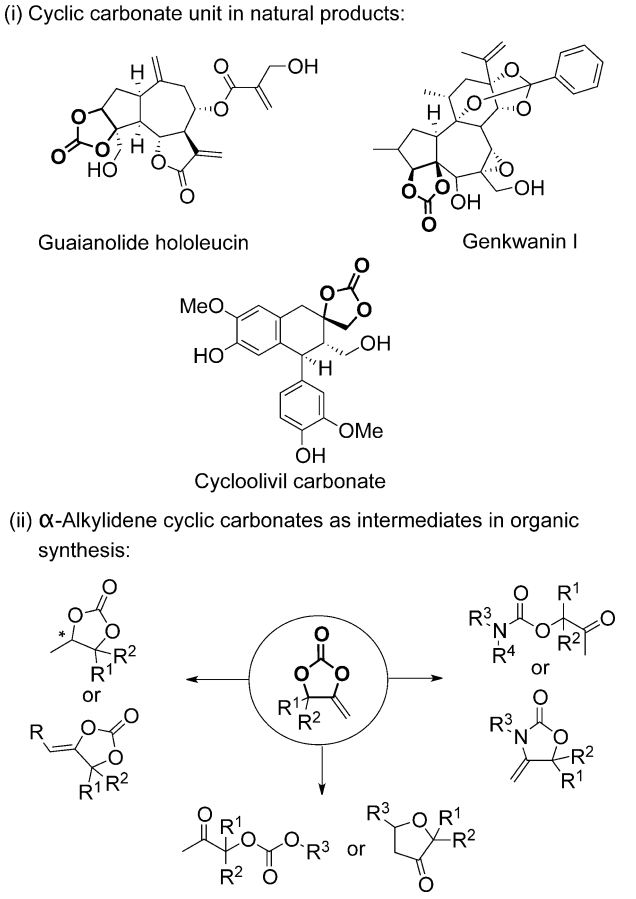
Introduction

The chemical conversion of carbon dioxide (CO_2) has evoked great interest in the past decades.[1] Compared with toxic phosgene and CO, CO_2 can be regarded as an abundant, easily available, environmentally friendly and renewable C_1 building block for organic synthesis. In this regard, great progress has been made in catalytic conversion of CO_2 with small-ring compounds, unsaturated compounds, hydrogen, amines and so on, resulting in the formation of C–C, C–O and C–N bonds.[2] However, its inherent thermodynamic stability and kinetic inertness hinder the development of efficient catalysts for CO_2 functionalization. Generally, active organometallic reagents, and/or nucleophiles and high pressure/temperature are required for the incorporation of CO_2 into organic products.[3] Although significant achievements have been made, chemical conversion of CO_2 at atmospheric pressure and room temperature remains a great challenge.

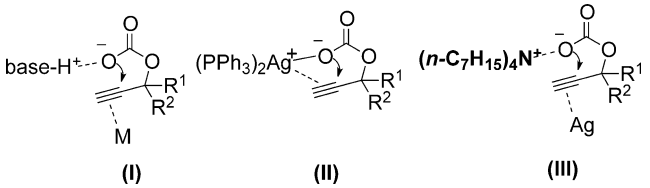
As is well-known, α-alkylidene cyclic carbonates are an important class of heterocyclic frameworks in natural products with potential bioactivities and also find wide applications in organic synthesis as shown in Scheme 1.[4]

In this aspect, the carboxylative cyclization of propargylic alcohols with CO_2 is one of the most promising and eco-friendly routes to α-alkylidene cyclic carbonates.[5] However, most of the published methods pose some drawbacks, in particular, the requirement of higher CO_2 pressure and use of stoichiometric amounts of additional base. Accordingly, the development of an efficient catalyst for CO_2 conversion under mild reaction conditions could be still highly desirable in both industry and academia.[6]

Only if we understand the underlying principles of the chemical transformation can highly effective catalytic systems be designed. The alkyl carbonate intermediate (**I**) was usually postulated in the two-component "metal-base"-catalyzed reaction of propargylic alcohols with CO_2 (Scheme 2, **I**).[5a,d] In this context, we envisioned that higher CO_2 pressure and reaction temperature are still indispensable presumably because the strong interaction between the base-H^+ and $HC{\equiv}CC(R^1R^2)OCO_2^-$ species reduces the nucleophilicity of alkyl carbonic anion (**I**). Most recently, we have successfully developed an efficient single-component catalyst, i.e., $[(PPh_3)_2Ag]_2CO_3$, which enables



Scheme 1. Applications of α-alkylidene cyclic carbonates.



Scheme 2. Activation modes involving a two-component "metal + base" catalytic system (base = tertiary amine) (**I**), a single-component bifunctional catalyst (**II**), and a bulkier $(n\text{-}C_7H_{15})_4N^+$-inspired intermediate (**III**) in this work.

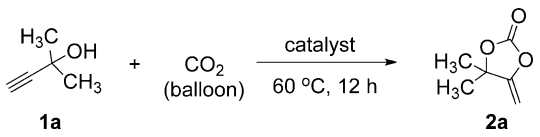
the reaction to perform smoothly under ambient conditions[5k] through the formation of intermediate (**II**) (Scheme 2).

The bulkier cation $[(Ph_3P)_2Ag(I)]^+$ can stabilize the carbonic anion and enhance the nucleophilicity of alkyl carbonate intermediate in comparison with the base-H^+ species. We hypothesized that an ideal catalytic system would be a kind of bifunctional one with both Lewis acidic and Lewis basic sites in combination with the bulkier cation. Herein we disclose a robust catalytic system consisting of $(n\text{-}C_7H_{15})_4NBr$ and AgOAc for the synthesis of α-alkylidene cyclic carbonates with a high turnover number (TON), presumably going through the proposed intermediate (**III**) (Scheme 2). This is a thermodynamically favourable step[7] and thus provides an attractive access to various organic carbonates without utilization of any base and ligand under solvent-free conditions.

Results and Discussion

2-Methylbut-3-yn-2-ol (**1a**) was chosen as the model substrate to optimize the reaction conditions, as summarized in Table 1. Various silver(I) compounds capable of activating the carbon-carbon triple bond were investigated in combination with quaternary ammonium salts. Initially, several easily available salts such as KOAc, $(n\text{-}C_7H_{15})_4NBr$, $(n\text{-}C_7H_{15})_4NOAc$ and AgOAc

Table 1. Optimization of the reaction conditions for the carboxylative cyclization of **1a** with CO_2.[a]



Entry	Catalyst	Co-Catalyst	Yield [%][b]
1	KOAc	–	0
2	$(n\text{-}C_7H_{15})_4NBr$	–	0
3	$(n\text{-}C_7H_{15})_4NOAc$	–	0
4	AgOAc	–	0
5	Ag_2O	$(n\text{-}C_7H_{15})_4NBr$	45
6	Ag_2CO_3	$(n\text{-}C_7H_{15})_4NBr$	25
7	AgOAc	$(n\text{-}C_7H_{15})_4NBr$	89
8	$AgNO_3$	$(n\text{-}C_7H_{15})_4NBr$	0
9	AgBr	$(n\text{-}C_7H_{15})_4NBr$	0
10	KOAc	$(n\text{-}C_7H_{15})_4NBr$	0
11	AgBr	$(n\text{-}C_7H_{15})_4NOAc$	<1
12	AgOAc	$(n\text{-}C_7H_{15})_4NOAc$	65
13	AgOAc	$(CH_3)_4NBr$	6
14	AgOAc	$(C_2H_5)_4NBr$	22
15	AgOAc	$(n\text{-}C_4H_9)_4NBr$	85
16	AgOAc	$n\text{-}C_{16}H_{33}(CH_3)_3NBr$	16
17	AgOAc	$PhCH_2(C_2H_5)_3NBr$	64
18	AgOAc	$(n\text{-}C_4H_9)_4NCl$	83
19	AgOAc	$(n\text{-}C_4H_9)_4PBr$	85
20[c]	AgOAc	$(n\text{-}C_7H_{15})_4NBr$	96
21[d]	AgOAc	$(n\text{-}C_7H_{15})_4NBr$	27
22[e]	AgOAc	$(n\text{-}C_7H_{15})_4NBr$	98

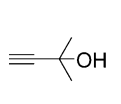
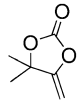
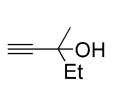
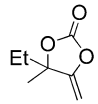
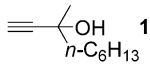
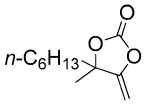
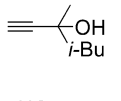
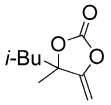
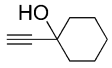
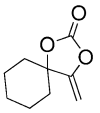
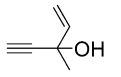
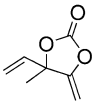
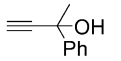
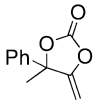
[a] Unless otherwise specified, all the reactions were performed with **1a** (0.421 g, 5 mmol), Cat. (1 mol%), Co-Cat. (1 mol%), neat, CO_2 balloon, 60 °C, 12 h.
[b] Determined by ^1H NMR with 1,1,2,2-tetrachloroethane as the internal standard.
[c] $(n\text{-}C_7H_{15})_4NBr$ (29.4 mg, 1.2 mol%).
[d] AgOAc (24.8 mg, 3 mol%), $(n\text{-}C_7H_{15})_4NBr$ (88.2 mg, 3.6 mol%), 25 °C.
[e] AgOAc (42 mg, 5 mol%), $(n\text{-}C_7H_{15})_4NBr$ (147 mg, 6 mol%), 25 °C.

were found to have no catalytic activity under neat conditions (Table 1, entries 1–4). Gratifyingly, a two-component system consisting of 1 mol% Ag_2O and $(n\text{-}C_7H_{15})_4NBr$ gave α-alkylidene cyclic carbonate **2a** in 45% yield (entry 5). Ag_2CO_3 displayed a lower activity than Ag_2O under otherwise identical conditions (entry 6 *vs.* 5). In previous studies, AgOAc in combination with a basic nitrogen ligand was highly effective for internal propargylic alcohols[5e] but showed low activity for terminal propargylic alcohols.[5k] Interestingly, AgOAc and $(n\text{-}C_7H_{15})_4NBr$ in this study displayed excellent activity, affording **2a** in 89% yield (entry 7). However, an acidic silver salt, for example, $AgNO_3$ or AgBr, was ineffective (entries 8 and 9), suggesting a crucial role of the anion in proton transfer. It is also worth mentioning that KOAc instead of AgOAc showed no activity, indicating that activation of the carbon-carbon triple bond could be a prequisite for the reaction (entry 10 *vs.* 7). On the other hand, insoluble AgBr was inactive (entry 11). In contrast, soluble AgOAc performed well (entry 12).

Furthermore, several quaternary ammonium salts were investigated as co-catalysts (entries 13–18). As a result, the yield of **2a** increased in the order $(CH_3)_4N^+ < (C_2H_5)_4N^+ < (n\text{-}C_4H_9)_4N^+ < (n\text{-}C_7H_{15})_4N^+$ (entries 13–15 and 7). In addition, the unsymmetrical tetraalkylammonium cation bearing one longer alkyl showed better performance than that with a less bulky cation evidently (entries 16, 17 *vs.* 13, 14). The bulkier tetraheptylammonium cation might form looser ion pairs with alkyl carbonic anion, as supported by a DFT study (see the Supporting Information, Figure S1), and thus can enhance the nucleophilicity of the alkyl carbonic anion, being in agreement with the published results.[8] On the other hand, $(n\text{-}C_4H_9)_4NCl$ and $(n\text{-}C_4H_9)_4PBr$ were found to have comparable activity with $(n\text{-}C_4H_9)_4NBr$ (entry 18, 19 *vs.* 7). A further improved result was obtained by using 1.2 mol% $(n\text{-}C_7H_{15})_4NBr$ (entry 20 *vs.* 7). Interestingly, the reaction could proceed smoothly even at room temperature. On further elevating the catalyst loading, **2a** was obtained almost quantitatively (entries 21 and 22).

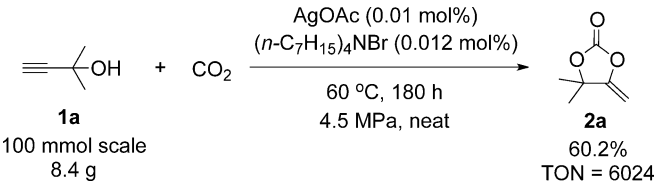
Having established the optimized reaction conditions, we next examined the substrate scope of this carboxylative cyclization as listed in Table 2. Terminal propargylic alcohols with both alkyl and aryl substituents at the propargylic position (**1a–1g**) underwent the reaction smoothly with CO_2 at atmospheric pressure to afford the corresponding α-alkylidene cyclic carbonates (**2a–2g**) in excellent yields. Herein, two procedures were employed as indicated in Table 2. As a result, both protocols (low catalytic loading or low temperature) were effective. Propargylic alcohols with $n\text{-}C_6H_{13}$, cyclohexyl, vinyl and phenyl substituents showed relatively poor reactivity especially at room temperature. Yet, such a problem could be surmounted by increasing the catalyst amount and prolonging the reaction time.

Table 2. Substrate scope.[a]

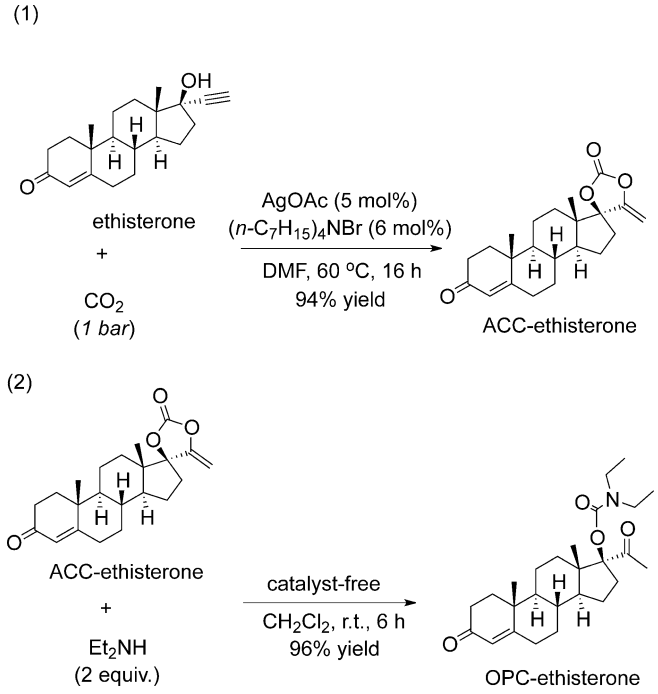
Entry	Substrate		Product			Yield [%][b]
1		**1a**		**2a**	**A**	96 (95[c])
					B	98
2		**1b**		**2b**	**A**	99
					B	98
3		**1c**		**2c**	**A**	90[d]
4		**1d**		**2d**	**A**	96
					B	>99
5		**1e**		**2e**	**A**	88
					B	98[e]
6		**1f**		**2f**	**A**	90
					B	91[e]
7		**1g**		**2g**	**A**	67[f]

[a] *Reaction conditions for protocol **A**:* **1** (2.5 mmol), AgOAc (4.2 mg, 1 mol%), $(n\text{-}C_7H_{15})_4NBr$ (14.7 mg, 1.2 mol%) at 60 °C; *protocol **B**:* **1** (2.5 mmol), AgOAc (21.0 mg, 5 mol%), $(n\text{-}C_7H_{15})_4NBr$ (73.5 mg, 6 mol%) at 25 °C for 12 h.
[b] NMR yield.
[c] Isolated yield.
[d] AgOAc (8.3 mg, 2 mol%), $(n\text{-}C_7H_{15})_4NBr$ (29.4 mg, 2.4 mol%), 48 h.
[e] AgOAc (42 mg, 10 mol%), $(n\text{-}C_7H_{15})_4NBr$ (147 mg, 12 mol%), 24 h.
[f] 36 h.

To further validate the efficaciousness of this methodology, a gram-scale experiment was performed with a lower catalyst amount as depicted in Scheme 3. To our delighted, over 60% **2a** yield was obtained with a high TON of up to 6024.



Scheme 3. Evaluation of the catalytic activity.



Scheme 4. Structure modifications of ethisterone.

Ethisterone is the first orally active progestin.[9] The structural modification of ethisterone could be interesting due to its significance for pharmaceutical chemistry.[10] The present AgOAc/(n-$C_7H_{15})_4$NBr-catalyzed carboxylative cyclization of propargylic alcohol with CO_2 was also applied to the synthesis of a complicated molecule with several functional groups such as ethisterone (Scheme 4, step 1) to afford the ACC-ethisterone (α-alkylene cyclic carbonate ethisterone) with retention of the configuration. The configuration of ACC-ethisterone was unambiguously confirmed by single-crystal X-ray analysis (Figure 1).[11] In addition, β-oxopropylcarbamate-modified ethisterone (OPC-ethisterone) was also successfully prepared through a ring-opening amination (Scheme 4, step 2).

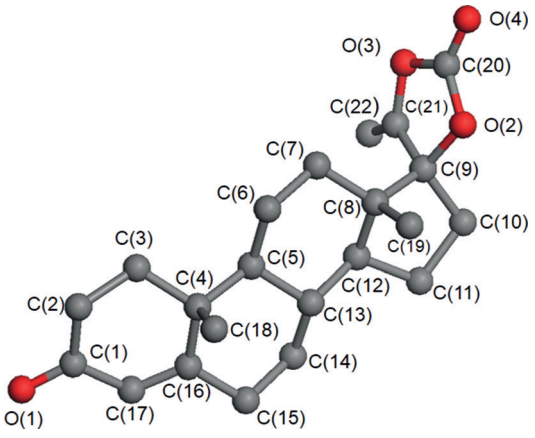


Figure 1. X-ray crystal structure of ACC-ethisterone. Hydrogen atoms are omitted for clarity.

The catalytic role of AgOAc/(n-$C_7H_{15})_4$NBr was further elucidated. The interaction of propargylic alcohol **1a** with CO_2 was monitored by ^{1}H and ^{13}C NMR techniques (Figure 2). The proton signal of the hydroxy group in **1a** became broad and was shifted from $\delta = 2.66$ to 5.93 ppm (Figure 2a and b), suggesting hydrogen bond formation between the acetic group and **1a**,[12] resulting in activation of propargylic alcohol, and thus enhancement of the nucleophilicity of the hydroxy group. As seen in Figure 2c and d, changes in carbon peaks could be attributed to the interaction of the silver salt with the carbon-carbon triple bond, leading to the activation of propargylic alcohol.[13]

A tentative mechanism for the AgOAc/(n-$C_7H_{15})_4$NBr-catalyzed fixation of atmospheric CO_2 with propargylic alcohols is illustrated in Scheme 5. Initially, the propargylic alcohol reacts with CO_2 to generate the propargylic carbonate intermediate in which CO_2 is activated by a hydroxy group[6a] with the aid of AgOAc and (n-$C_7H_{15})_4$NBr. Notably, the bulkier cation, i.e., ($n$$C_7H_{15})_4N^+$ plays a key role in stabilizing the carbonic anion and enhancing the nucleophilicity of the carbonate intermediate. Then, an intramolecular nucleophilic cyclization proceeds at the silver(I)-activated C≡C bond, followed by protonation with regeneration of the catalytic species.

The synthesis of oxazolidinones through the carboxylative cyclization of propargylic amines and CO_2 is one of the most attractive synthetic methods.[14,6f] To futher display the effectiveness of the present catalytic system, the carboxylative cyclization of propargylic amines with CO_2 was further examined (Scheme 6). To our delight, the current protocol was efficiently performed to give oxazolidinones **4a–4c** with almost quantitative yields even at ambient conditions. In the case of **3c**, the TON reached up to 544 which is the highest among the reported results to date.

Conclusions

In summary, we have established an elegant protocol for expeditious chemical fixation of atmospheric CO_2 to generate various α-alkylidene cyclic carbonates or oxazolidinones under ambient conditions. On the basis of a mechanistic understanding of the bulkier cation [$(Ph_3P)_2$Ag(I)]$^+$-catalyzed carboxylative cyclization of propargylic alcohols with CO_2, the robust dual-activation catalyst system, i.e., AgOAc/(n-$C_7H_{15})_4$NBr, which could simultaneously activate CO_2, a carbon-carbon triple bond, and a nucleophile (alcohols, amines etc.), was successfully developed. Taking the carboxylative cyclization of 2-methylbut-3-yn-2-ol

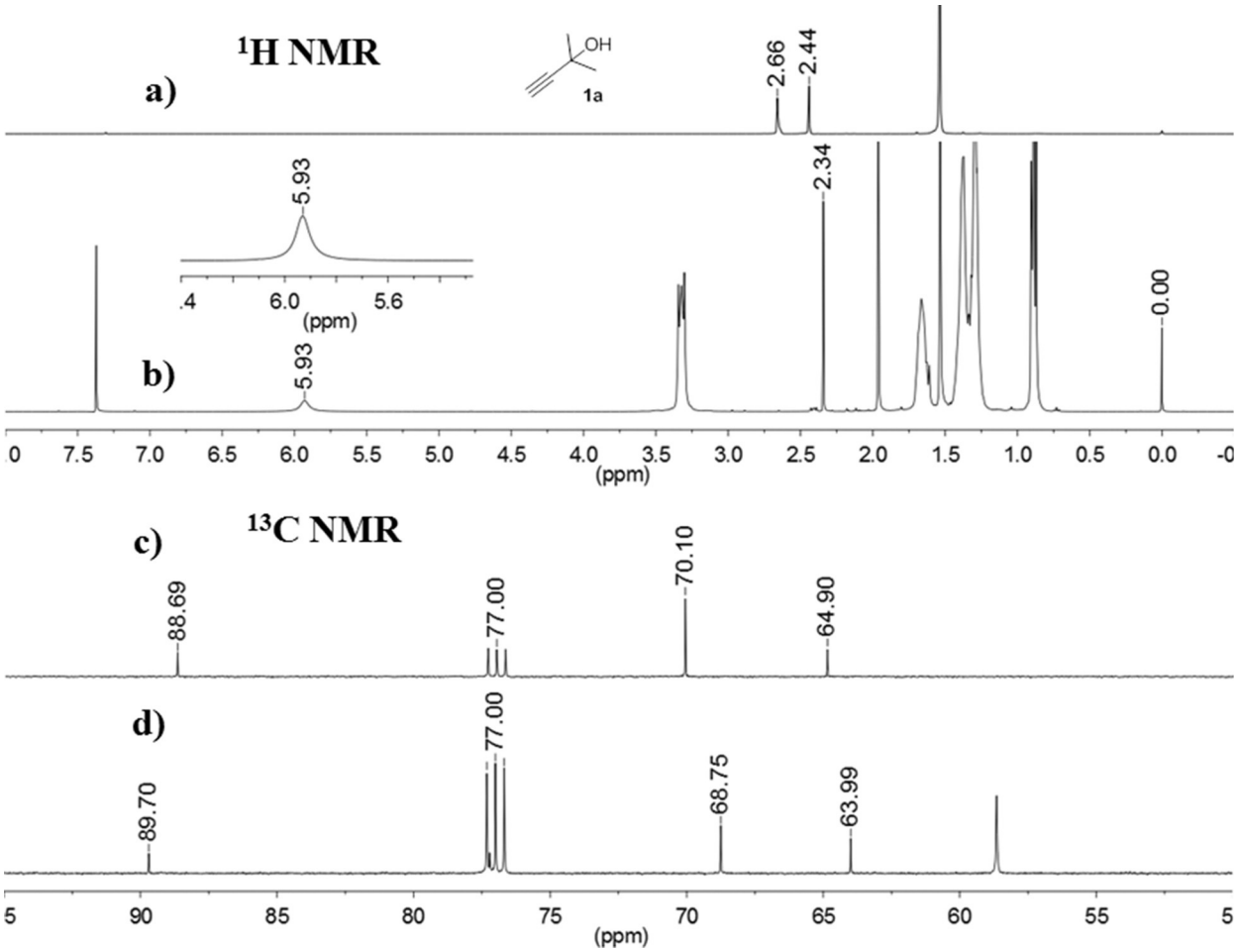
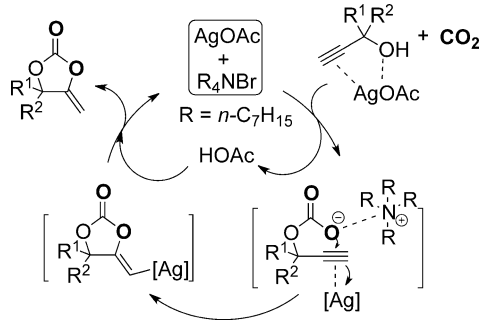
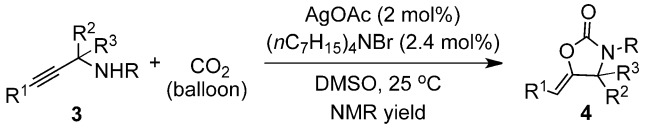


Figure 2. ^{1}H, ^{13}C NMR spectroscopic study: a, c for propargylic alcohol **1a** and b, d for a mixture of **1a**/AgOAc/(n-$C_7H_{15})_4$NBr: **1a** (0.1 mmol), AgOAc (1 equiv.), (n-$C_7H_{15})_4$NBr (1 equiv.) in $CDCl_3$ (0.6 mL).



Scheme 5. Plausible reaction mechanism.



3a: R^1 = Ph, R^2 = Ph, R^3 = H, R = n-Bu; **4a;** 94% (12 h)
3b: R^1 = H, R^2 = CH_3, R^3 = CH_3, R = Bn; **4b;** 99% (6 h)
3c: R^1 = H, R^2 = H, R^3 = H, R = Bn; **4c;** 99% (3 h)
3c: (0.1 mol% cat., 1 atm CO_2, 60 °C, 48 h, **4c** 54%, TON up to 544)

Scheme 6. AgOAc/(n-$C_7H_{15})_4$NBr-promoted chemical fixation of CO_2 with propargylic amines.

with CO_2 as an example, a TON of up to 6024 was achieved. This clean approach represents a promising strategy for the development of the highly efficient chemical conversion of CO_2 to produce valuable chemicals at atmospheric pressure.

Experimental Section

General Procedure for the Synthesis of α-Alkylidene Cyclic Carbonates

Taking the carboxylative cyclization of 2-methylbut-3-yn-2-ol with CO_2 as an example: a 10-mL Schlenk tube equipped with a stirrer bar was charged with AgOAc (4.2 mg, 1 mol%), (n-$C_7H_{15})_4$NBr (14.7 mg, 1.2 mol%), and **1a** (211 mg, 2.5 mmol) under neat conditions. Next, the Schlenk tube was attached to a balloon filled with CO_2 (99.99% purity). Then, the reaction mixture was stirred at 60 °C for 12 h [or protocol B: AgOAc (21 mg, 5 mol%), (n-$C_7H_{15})_4$NBr (74 mg, 6 mol%), 25 °C]. On carefully releasing the CO_2 after the reaction, the mixture was washed with $CHCl_3$ (1 mL). The organic phase was analyzed by ^{1}H NMR

with 1,1,2,2-tetrachloroethane as the internal standard or concentrated under vacuum and purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1–20:1) to give the pure product. Note: 1 mmol ethisterone was used for the reaction in Scheme 4.

4,4-Dimethyl-5-methylene-1,3-dioxolan-2-one (2a): yield: 321 mg (95%); colourless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.75–4.31 (dd, J = 4.0 Hz, 2H, CH_2), 1.59 (s, 6H, $2CH_3$); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 158.6, 151.2 (C=O), 85.2, 84.6, 27.5; MS (EI, 70 eV): m/z (%) = 128.10 (2.81), 85.10 (6.49), 84.10 (100), 83.10 (3.54), 69.10 (48.16); IR (neat): ν = 3023, 2991, 1825, 1687, 1271, 1086, 1032, 856 cm^{-1}.

4-Ethyl-4-methyl-5-methylene-1,3-dioxolan-2-one (2b): yield: 354 mg (97%); colourless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.80 (d, J = 4.0 Hz, 1H), 4.26 (d, J = 4.0 Hz, 1H), 1.94–1.70 (m, 2H), 1.57 (s, 3H), 0.97 (t, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 157.2, 151.4, 87.5, 85.4, 33.1, 25.7, 7.1; GC-MS (EI, 70 eV): m/z (%) = 143.10 (6), 113.05 (16), 98.10 (30), 83.05 (75), 70.10 (100).

4-Hexyl-4-methyl-5-methylene-1,3-dioxolan-2-one (2c): yield: 498 mg (90%); colourless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.77 (d, J = 4.0 Hz, 1H), 4.26 (d, J = 4.0 Hz, 1H), 1.89–1.64 (m, 2H), 1.57 (s, 3H), 1.26–1.37 (m, 8H), 0.86 (t, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 157.7, 151.5, 87.2, 85.4, 40.4, 31.4, 28.9, 26.3, 22.8, 22.4, 13.9; GC-MS (EI, 70 eV) m/z (%) = 199.15 ([M+H]$^+$, 2), 139.2 (13), 112.15 (35), 111.15 (51), 97.10 (68), 85.10 (30), 84.10 (45), 83.10 (72), 82.10 (29), 72.10 (75), 70.15 (93), 69.10 (100).

4-Isobutyl-4-methyl-5-methylene-1,3-dioxolan-2-one (2d): yield: 428 mg (96%); colourless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.79–4.26 (dd, 2H), 1.87–1.62 (m, 3H), 1.57 (s, 3H), 0.96 (6H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 158.1, 151.4, 87.3, 85.5, 48.3, 26.9, 24.2, 23.8, 23.5; GC-MS (EI, 70 eV) m/z (%) = 114.10 (8), 113.10 (8), 111.15 (19), 84.15 (37), 83.15 (15), 70.10 (10), 69.10 (100).

4-Methylene-1,3-dioxaspiro[4.5]decan-2-one (2e): yield: 423 mg (87%); colourless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.73 (d, J = 4.0 Hz, 1H), 4.28 (d, J = 4.0 Hz, 1H), 1.98–1.95 (m, 2H), 1.70–1.59 (m, 7H), 1.34–1.20 (m, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 158.4, 151.2, 86.2, 85.3, 36.2, 24.0, 21.4; GC-MS (EI, 70 eV): m/z (%) = 124.10 (9), 109.10 (15), 95.10 (15), 82.10 (49), 81.15 (50), 80.10 (20), 67.10 (100).

4-Methyl-5-methylene-4-vinyl-1,3-dioxolan-2-one (2f): yield: 356 mg (89%); colourless oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.96–5.89 (m, 1H), 5.48–5.29 (dd, 2H), 4.85–4.33 (dd, 2H), 1.67 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 156.0, 151.0, 136.0, 116.5, 87.2, 85.7, 25.5; GC-MS (EI, 70 eV): m/z (%) = 96.15 (16), 95.15 (50), 81.10 (51), 68.10 (39), 67.10 (100).

4-Methyl-5-methylene-4-phenyl-1,3-dioxolan-2-one (2g): yield: 471 mg (67%); greenish-yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.49–7.47 (m, 2H), 7.44–7.38 (m, 3H), 4.95 (d, J = 4.0 Hz, 1H), 4.48 (d, J = 4.0 Hz, 1H), 1.97 (s, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 157.2, 151.0, 139.1, 129.0, 128.8, 124.5, 88.1, 87.0, 27.3; GC-MS (EI, 70 eV): m/z (%) = 146.10 (13), 131.10 (19), 118.15 (100), 117.15 (82), 103.10 (52), 78.10 (32), 77.10 (43).

ACC-ethisterone: yield: 337 mg (94%); colourless crystals [acetone/hexane = 1:5 v/v]; mp 170–171 °C; IR (KBr): ν = 2971, 2944, 2912, 2859, 1820, 1677, 1458, 1291, 1260, 1133, 1037, 1027, 864 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.67 (s, 1H), 4.87 (d, J = 3.6 Hz, 1H), 4.31 (d, J = 4.0 Hz, 1H), 2.90–2.82 (1H), 2.43–2.29 (5H), 2.15–2.00 (m, 2H), 1.92–1.89 (1H), 1.77–1.51 (6H), 1.45–1.39 (2H), 1.34–1.26 (1H), 1.20 (s, 3H), 1.14–1.06 (1H), 1.02 (s, 3H), 0.95–0.90 (1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 199.0, 170.0, 157.5, 151.2, 123.9, 96.6, 89.0, 52.9, 48.3, 35.5, 35.4, 34.0, 33.7, 32.3, 31.2, 30.8, 22.7, 20.0, 17.2, 14.1; HR-MS (ESI): m/z = 379.1879, calcd. for $C_{22}H_{28}NaO_4^+$ [M+Na]$^+$: 379.1880.

OPC-ethisterone: yield: 408 mg (96%); white solid; mp. 169–170 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.71 (s, 1H), 3.38–3.29 (m, 2H), 3.28–3.18 (m, 1H), 2.80–2.72 (m, 1H), 2.41–2.24 (4H), 2.08 (s, 3H), 2.00–1.95 (m, 1H), 1.87–1.76 (m, 3H), 1.69–1.56 (m, 5H), 1.49–1.32 (m, 4H), 1.20 (t, J = 6.8 Hz, J = 7.2 Hz, 3H), 1.17 (s, 3H), 1.12 (t, J = 7.2 Hz, J = 6.8 Hz, 3H), 1.05 (s, 3H), 0.97–0.84 (m, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 208.8, 199.3, 170.7, 155.3, 124.0, 95.4, 52.9, 47.1, 47.0, 42.1, 41.6, 38.4, 35.7, 35.6, 33.9, 33.2, 32.7, 31.4, 27.1, 24.7, 20.6, 17.3, 15.4, 14.3, 13.6; HR-MS (ESI): m/z = 452.2772, calcd. for $C_{26}H_{39}NNaO_4^+$ [M+Na]$^+$: 452.2771.

General Procedure for the Synthesis of Oxazolidinones

Taking the carboxylative cyclization of *N*-benzylprop-2-yn-1-amine and CO_2 as an example: a 10-mL Schlenk tube equipped with a stirrer bar was charged with AgOAc (1.7 mg, 2 mol%), (n-C_7H_{15})$_4$NBr (5.9 mg, 2.4 mol%), *N*-benzylprop-2-yn-1-amine (72.6 mg, 0.5 mmol) and DMSO (0.3 mL). Next, the Schlenk tube was attached to a balloon filled with CO_2. Then, the reaction mixture was stirred at 25 °C for the preset time. The CO_2 was carefully released after the reaction. The organic phase was analyzed by ^{1}H NMR with 1,1,2,2-tetrachloroethane as the internal standard or concentrated under vacuum and purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1–5:1) to give the pure product.

5-Benzylidene-3-butyl-4-phenyloxazolidin-2-one (4a): yield: 141 mg (94%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.39–7.27 (m, 5H), 4.76–4.74 (1H), 4.47 (s, 2H), 4.25–4.23 (1H), 4.03–4.02 (2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 155.6, 148.9, 134.9, 129.0, 128.23, 128.15, 86.8, 47.8, 47.2; GC-MS (EI, 70 eV): m/z (%) = 189.20 (13.18), 92.15 (15.37), 91.15 (100), 65.10 (11.34).

3-Benzyl-4,4-dimethyl-5-methyleneoxazolidin-2-one (4b): yield: 112 mg (97%); light brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.33–7.27 (m, 5H), 4.66 (1H), 4.45 (s, 2H), 4.22 (1H), 1.30 (6H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 160.7, 154.8, 137.6, 128.6, 127.72, 127.69, 84.1, 61.5, 44.0, 27.6; GC-MS (EI, 70 eV): m/z (%) = 217.25 (4.67), 202.20 (19.34), 132.20 (7.04), 91.15 (100), 65.10 (8.80).

3-Benzyl-5-methyleneoxazolidin-2-one (4c): yield: 94 mg (98%); light brown oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.39–7.27 (m, 5H), 4.76–4.74 (1H), 4.47 (s, 2H), 4.25–4.23 (1H), 4.03–4.02 (2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 155.6, 148.9, 134.9, 129.0, 128.23, 128.15, 86.8, 47.8, 47.2; GC-MS (EI, 70 eV): m/z (%) = 189.20 (13.18), 92.15 (15.37), 91.15 (100), 65.10 (11.34).

Acknowledgements

This work was supported by funds from the National Natural Sciences Foundation of China, Specialized Research Fund for the Doctoral Program of Higher Education (20130031110013), MOE Innovation Team of China (IRT13022) and the "111" Project of Ministry of Education of China (project No. B06005).

References

[1] a) P. H. Abelson, *Science* **2000**, *289*, 1293–1293; b) D. W. Keith, *Science* **2009**, *325*, 1654–1655; c) C. S. Song, *Catal. Today* **2006**, *115*, 2–32; d) I. Omae, *Catal. Today* **2006**, *115*, 33–52; e) M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.* **2014**, *114*, 1709–1742.

[2] a) T. Sakakura, J. C. Cho, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365–2387; b) S. N. Riduan, Y. G. Zhang, *Dalton Trans.* **2010**, *39*, 3347–3357; c) W. Wang, S. P. Wang, X. B. Ma, J. L. Gong, *Chem. Soc. Rev.* **2011**, *40*, 3703–3727; d) M. Peters, B. Kçhler, W. Kuckshinrichs, W. Leitner, P. Markewitz, T. E. Müller, *ChemSusChem* **2011**, *4*, 1216–1240; e) K. Huang, C. L. Sun, Z. J. Shi, *Chem. Soc. Rev.* **2011**, *40*, 2435–2452; f) Z. Z. Yang, L. N. He, J. Gao, A. H. Liu, B. Yu, *Energy Environ. Sci.* **2012**, *5*, 6602–6639; g) Y. Tsuj, T. Fujihara, *Chem. Commun.* **2012**, *48*, 9956–9964; h) Q. W. Song, Y. N. Zhao, L. N. He, J. Gao, Z. Z. Yang, *Curr. Catal.* **2012**, *1*, 107–124; i) Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun.* **2015**, *6*, 5933, doi: 10.1038/ncomms6933.

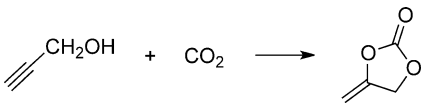
[3] a) L. N. He, J. Q. Wang, J. L. Wang, *Pure Appl. Chem.* **2009**, *81*, 2069–2080; b) X. Yin, J. R. Moss, *Coord. Chem. Rev.* **1999**, *181*, 27–60; c) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann, F. E. Kühn, *Angew. Chem.* **2011**, *123*, 8662–8690; *Angew. Chem. Int. Ed.* **2011**, *50*, 8510–8537.

[4] a) K. Ohe, H. Matsuda, T. Ishihara, S. Ogoshi, N. Chatani, S. Murai, *J. Org. Chem.* **1993**, *58*, 1173–1177; b) K. Ohe, H. Matsuda, T. Morimoto, S. Ogoshi, N. Chatani, S. Murai, *J. Am. Chem. Soc.* **1994**, *116*, 4125–4126; c) V. Besse, F. Camara, C. Voirin, R. Auvergne, S. Caillol, B. Boutevin, *Polym. Chem.* **2013**, *4*, 4545–4561, and the references cited therein; d) H. Zhang, H. B. Liu, J. M. Yue, *Chem. Rev.* **2014**, *114*, 883–898, and the references cited therein.

[5] For reports on thecarboxylative cyclization of propargylic alcohols with CO_2, see: a) Y. Inoue, J. Ishikawa, M. Taniguchi, H. Hashimoto, *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1204–1206; b) J. Fournier, C. Bruneau, P. H. Dixneuf, *Tetrahedron Lett.* **1989**, *30*, 3981–3982; c) Y. L. Gu, F. Shi, Y. Q. Deng, *J. Org. Chem.* **2004**, *69*, 391–394; d) W. Yamada, Y. Sugawara, H. M. Cheng, T. Ikeno, T. Yamada, *Eur. J. Org. Chem.* **2007**, *2007*, 2604–2607; e) S. Yoshida, K. Fukui, S. Kikuchi, T. Yamada, *J. Am. Chem. Soc.* **2010**, *132*, 4072–4073; f) Y. Kayaki, M. Yamamoto, T. Ikariya, *Angew. Chem.* **2009**, *121*, 4258–4261; *Angew. Chem. Int. Ed.* **2009**, *48*, 4194–4197; g) N. D. Cà, B. Gabriele, G. Ruffolo, L. Veltri, T. Zanetta, M. Costa, *Adv. Synth. Catal.* **2011**, *353*, 133–146; h) X. D. Tang, C. R. Qi, H. T. He, H. F. Jiang, Y. W. Ren, G. Q. Yuan, *Adv. Synth. Catal.* **2013**, *355*, 2019–2028; i) Q. W. Song, B. Yu, X. D. Li, R. Ma, Z. F. Diao, R. G. Li, W. Li, L. N. He, *Green Chem.* **2014**, *16*, 1633–1638; j) Y. B. Wang, D. S. Sun, H. Zhou, W. Z. Zhang, X. B. Lu, *Green Chem.* **2014**, *16*, 2266–2272; k) Q. W. Song, W. Q. Chen, R. Ma, A. Yu, Q. Y. Li, Y. Chang, L. N. He, *ChemSusChem* **2015**, *8*, 821–827.

[6] For typical examples of fixing atmospheric pressure of CO_2, see: a) S. Minakata, I. Sasaki, T. Ide, *Angew. Chem.* **2010**, *122*, 1331–1333; *Angew. Chem. Int. Ed.* **2010**, *49*, 1309–1311; b) H. Mizuno, J. Takaya, N. Iwasawa, *J. Am. Chem. Soc.* **2011**, *133*, 1251–1253; c) T. Kimura, K. Kamata, N. Mizuno, *Angew. Chem.* **2012**, *124*, 6804–6807; *Angew. Chem. Int. Ed.* **2012**, *51*, 6700–6703; d) L. Zhang, J. Cheng, B. Carry, Z. Hou, *J. Am. Chem. Soc.* **2012**, *134*, 14314–14317; e) Y. F. Zhao, B. Yu, Z. Z. Yang, H. Y. Zhang, L. D. Hao, X. Gao, Z. M. Liu, *Angew. Chem.* **2014**, *126*, 6032–6035; *Angew. Chem. Int. Ed.* **2014**, *53*, 5922–5925; f) J. Hu, J. Ma, Q. Zhu, Z. Zhang, C. Wu, B. X. Han, *Angew. Chem.* **2015**, *127*, 5489–5493; *Angew. Chem. Int. Ed.* **2015**, *54*, 5399–5403.

[7] Simplified reaction model as follows calculated by the B3LYP/6–311++g(d) method in DFT calculations: $\Delta H = -19.26\ kcal\,mol^{-1}$, $\Delta G = -4.38\ kcal\,mol^{-1}$. For details, see the Supporting Information.



[8] a) T. Ema, Y. Miyazaki, S. Koyama, Y. Yano, T. Sakai, *Chem. Commun.* **2012**, *48*, 4489–4491; b) T. Ema, Y. Miyazaki, J. Shimonishi, C. Maeda, J. Hasegawa, *J. Am. Chem. Soc.* **2014**, *136*, 15270–15279; the analogous strategy was also applied in earlier reports, see: c) S. H. Szczepankiewicz, C. M. Ippolito, B. P. Santora, T. J. Van de Ven, G. A. Ippolito, L. Fronckowiak, F. Wiatrowski, T. Power, M. Kozik, *Inorg. Chem.* **1998**, *37*, 4344–4352; d) K. Uemura, T. Kawaguchi, H. Takayama, A. Nakamura, Y. Inoue, *J. Mol. Catal. A Chem.* **1999**, *139*, 1–9; e) T. Ishikawa, T. Mizuta, K. Hagiwara, T. Aikawa, T. Kudo, S. Saito, *J. Org. Chem.* **2003**, *68*, 3702–3705.

[9] For a review, see: A. B. Forinash, S. L. Evans, *Pharmacotherapy* **2003**, *23*, 1573–1591.

[10] a) P. M. Levine, K. Imberg, M. J. Garabedian, K. Kirshenbaum, *J. Am. Chem. Soc.* **2012**, *134*, 6912–6915; b) H. Hofmeister, K. Annen, H. Laurent, H. Wiechert, *Angew. Chem.* **1984**, *96*, 720–722; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 727–729; c) Z. H. Liu, J. Q. Liu, L. Zhang, P. Q. Liao, J. N. Song, X. H. Bi, *Angew. Chem.* **2014**, *126*, 5409–5413; *Angew. Chem. Int. Ed.* **2014**, *53*, 5305–5309.

[11] CCDC 1043515 (ACC-ethisterone) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[12] For typical examples on activation of the nucleophile (NH group) by acetic-based catalyst-catalyzed CO_2 conversion, see: a) B. Yu, H. Y. Zhang, Y. F. Zhao, S. Chen, J. L. Xu, L. D. Hao, Z. M. Liu, *ACS Catal.* **2013**,

3, 2076–2082; b) W. J. Lu, J. Ma, J. Y. Hu, J. L. Song, Z. F. Zhang, G. Y. Yang, B. X. Han, *Green Chem.* **2014**, *16*, 221–225.

[13] The carbon peaks shifted apparently in the position of C≡C [from $\delta = (88.69$ and $70.10)$ to $(89.70$ and $68.75)$ ppm] and propargylic position (from $\delta = 64.90$ to 63.99 ppm), mainly due to the electronic effect of the activation of hydroxy and silver towards the unsaturated bond. The CH_3 ($\delta = 1.54$ ppm) group was unaffected. Other unlabelled peaks were assigned as follows: (n-$C_7H_{15})_4NOAc$, ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 3.32$ (t, $J = 8.4$ Hz, 8H, 4 -CH_2-N), 1.90 (s, 3H, CH_3COO), 1.61 (m, 8H, 4 -CH_2-), 1.27 (m, 32H, 16 -CH_2-), 0.82 (t, $J = 6.6$ Hz, 12H, 4 CH_3-); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 176.5$, 58.9, 31.4, 28.7, 26.3, 25.2, 22.3, 22.1, 13.9.

[14] For the recent reports on the synthesis of oxazolidinone derivatives from propargylic amines and CO_2, see: a) M. Feroci, M. Orsini, G. Sotgiu, L. Rossi, A. Inesi, *J. Org. Chem.* **2005**, *70*, 7795–7798; b) Y. Kayaki, M. Yamamoto, T. Suzuki, T. Ikariya, *Green Chem.* **2006**, *8*, 1019–1021; c) S. Yoshida, K. Fukui, S. Kikuchi, T. Yamada, *Chem. Lett.* **2009**, *38*, 786–787; d) M. Yoshida, T. Mizuguchi, K. Shishido, *Chem. Eur. J.* **2012**, *18*, 15578–15581; e) Y. Takeda, S. Okumura, S. Tone, I. Sasaki, S. Minakata, *Org. Lett.* **2012**, *14*, 4874–4877; f) S. Hase, Y. Kayaki, T. Ikariya, *Organometallics* **2013**, *32*, 5285–5288; g) K.-i. Fujita, J. Sato, K. Inoue, T. Tsuchimoto, H. Yasuda, *Tetrahedron Lett.* **2014**, *55*, 3013–3016.

