ChemPubSoc Europe

DOI: 10.1002/cssc.201600470

CHEMSUSCHEM Communications

Thermodynamically Favorable Synthesis of 2-Oxazolidinones through Silver-Catalyzed Reaction of Propargylic Alcohols, CO_2, and 2-Aminoethanols

Qing-Wen Song,[a, c] Zhi-Hua Zhou,[a] Mei-Yan Wang,[a] Kan Zhang,[c] Ping Liu,[c] Jia-Yao Xun,[c] and Liang-Nian He*[a, b]

Development of catalytic routes to incorporate CO_2 into carbonyl compounds at mild conditions remains attractive and challenging. Herein, a one-pot three-component cascade reaction of terminal propargylic alcohols, CO_2, and 2-aminoethanols through Ag^I-based catalysis is reported for the synthesis of carbonyl compounds through C–O/C–N bond formation. This thermodynamically favorable route can be ingeniously regulated to afford a wide range of 2-oxazolidinones along with concurrent production of α-hydroxyl ketone derivatives in excellent yields and selectivity. Preliminary mechanistic studies indicate that such a process proceeds through successive formation of α-alkylidene cyclic carbonate, β-oxopropylcarbamate, and 2-oxazolidinones.

Carbon dioxide, representing an abundant, safe, easily available, and renewable carbon resource, is attractive as an environmentally friendly feedstock for manufacturing commodity chemicals, fuels, and materials.[1] In commercial processes, chemical utilization of CO_2 as green carbonyl source is of great significance as an alternative to the CO and phosgene process for the synthesis of value-added products, such as carbonates, polycarbonates, polyurethanes, urea, and urethane through C–O and C–N bond formation.[2] In this respect, 2-oxazolidinones, among the most important heterocyclic compounds, are playing a significant role as chemical intermediates[3] and chiral auxiliaries[4] in organic synthesis and as antibacterial drugs[5] in pharmaceutical chemistry. In recent years, many environmentally benign synthetic processes attracted considerable attention to provide better methods for the synthesis of various oxazolidinones, such as carboxylative cyclization of propargylic amines and CO_2,[6] three-component reaction of propargylic alcohols, primary amines, and CO_2,[7] condensation of amino alcohols and CO_2,[8] and other convenient paths.[9] Although considerable progress has been made, the exploration of effective and economical catalytic processes using CO_2 as a feedstock under mild reaction conditions could be still highly desirable; this represent a significant and challenging area in both catalysis and sustainable chemistry.

β-Oxopropylcarbamate[10] and 1,3-oxazolidin-2-one[3–5] motifs are widely available compounds in synthetic and pharmaceutical chemistry. Generally, they are prepared through the reaction of propargylic alcohols, aliphatic amines, and CO_2 (Scheme 1 a, b). Notably, the formation of β-oxopropylcarbamate and oxazolidinone scaffolds depends on the structure of the amine (primary[7] and secondary[10]) employed. Considering the attractiveness of effective and convenient routes, we became interested in developing an alternative efficacious methodology for the conversion of CO_2 into more valuable chemicals using dual nucleophilic reagents. In this context, we hypothesized that a hydroxyl group as the second nucleophilic species can be attached to the reactive β-oxopropylcarbamate intermediate through a three-component reaction leading to simultaneous generation of two types of carbonyl compounds (Scheme 1 c). As part of our continuing studies on CO_2 chemistry associated with propargylic alcohols,[7d,10d] we herein present an unprecedented thermodynamically favored ($\Delta G = -22.39$ kcal mol$^{-1} < 0$; for detailed DFT calculation see the Supporting Information, Tables S1 and S2) one-pot process to synthesize 2-oxazolidinones and α-hydroxyl ketones[11] from terminal propargylic alcohols, CO_2, and 2-aminoethanols. As a result, the thermodynamic limitation of the condensation reaction of 2-aminoalcohol and CO_2 ($\Delta G = 2.75$ kcal mol$^{-1} > 0$, see Table S1 and S2 in the Supporting Information) is circumvented by avoiding the dehydration step.

To begin with, the individual reaction of 2-(benzylamino)-ethanol (**1 a**) and α-alkylidene cyclic carbonate (**IM-a**) was performed to identify the catalytic conditions to realize the goal (Table 1). We initially focused on silver compounds as catalyst due to their high activity towards various alkynes.[12]

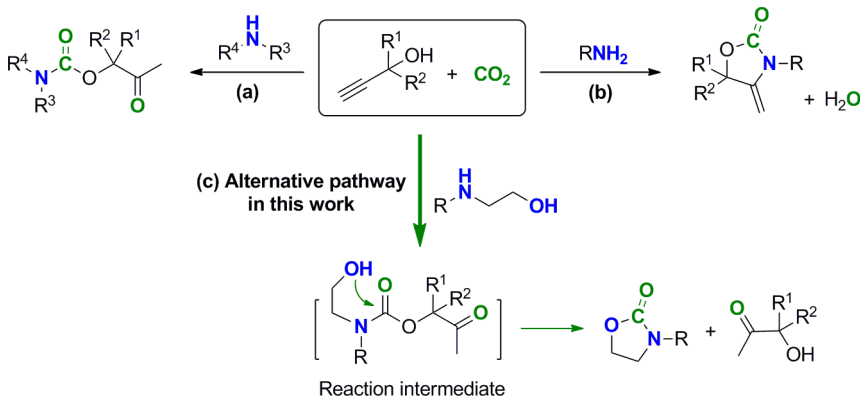
The reaction of **1 a** and **IM-a** did not occur for 2 h in the absence of any catalyst at room temperature (Table 1, entry 1). A relatively high temperature or Ag catalyst rendered the reaction to give the β-oxopropylcarbamate intermediate **IM-b** (entries 2 and 3, 60 °C), presumably because the nucleophilicity of the amine species in **IM-a** is reduced by the formation of hydrogen bonds through strong interaction between the hydrox-

[a] Dr. Q.-W. Song, Z.-H. Zhou, M.-Y. Wang, Prof. L.-N. He
State Key Laboratory and Institute of Elemento-Organic Chemistry
Nankai University
Tianjin, 300071 (P.R. China)
E-mail: heln@nankai.edu.cn

[b] Prof. L.-N. He
Collaborative Innovation Center of Chemical Science and Engineering
Nankai University
Tianjin, 300071 (P.R. China)

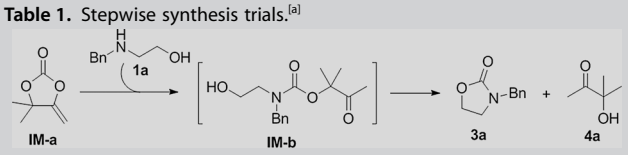
[c] Dr. Q.-W. Song, K. Zhang, Dr. P. Liu, J.-Y. Xun
State Key Laboratory of Coal Conversion
Institute of Coal Chemistry
Chinese Academy of Sciences
Taiyuan, 030001 (P. R. China)

Supporting Information for this article can be found under: http://dx.doi.org/10.1002/cssc.201600470.



Scheme 1. CO_2 conversion with propargylic alcohols and amines. Path a: the reaction of propargylic alcohols, CO_2, and secondary amines to afford β-oxopropylcarbamates; path b: the reaction of propargylic alcohols, CO_2, and primary amines to form vinyl oxazolidinones; path c: three-component cascade reaction of terminal propargylic alcohols, CO_2, and 2-aminoethanols.

Table 1. Stepwise synthesis trials.[a]



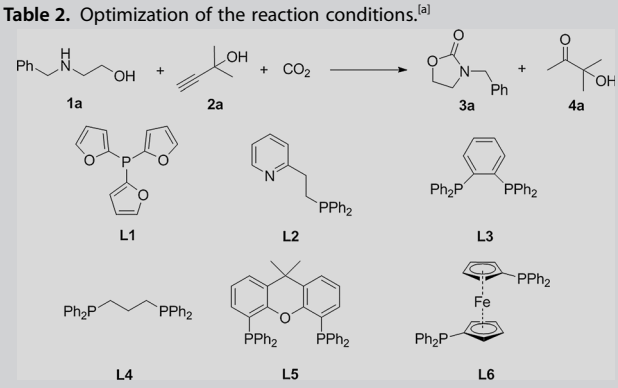
Entry	Ag catalyst	Additive	Yield[b] [%] IM-b	3a	4a
1[c]	–	–	0	0	0
2	–	–	47	0	0
3	Ag_2CO_3	–	49	1	1
4	Ag_2CO_3	PPh_3	94	5	5
5[d]	Ag_2CO_3	PPh_3	46	30	29

[a] Reaction conditions: **1a** (75.6 mg, 0.5 mmol), **IM-a** (64.0 mg, 0.5 mmol), Ag_2CO_3 (10 mol%), PPh_3 (40 mol%), $CHCl_3$ (1 mL), 60 °C, 2 h, yields of **IM-b**, **3a** and **4a** are related to **1a**. [b] Determined by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard. [c] 25 °C. [d] 24 h.

yl and amino groups, which was supported by a ^1H NMR study (Supporting Information, Figure S1). Interestingly, a basic silver complex, for example Ag_2CO_3/PPh_3, allowed the reaction to proceed further to form 3-benzyloxazolidin-2-one (**3a**) and 3-hydroxy-3-methylbutan-2-one (**4a**) (entries 4, 5). On the other hand, we also found that the bifunctional Ag_2CO_3/PPh_3 system promoted the carboxylative cyclization of propargylic alcohols with CO_2 to afford α-alkylidene cyclic carbonates.[10d]

Encouraged by these results, we then continued our studies by exploring the simultaneous formation of **3a** and **4a** from **1a** and 2-methylbut-3-yn-2-ol (**2a**) with CO_2 under 1 MPa CO_2 at 60 °C for 12 h (Table 2). Several representative silver compounds as π-Lewis acid capable of activating C–C triple bond were primarily screened (entries 1–6). Silver compounds such as AgOAc, Ag_2O, and Ag_2CO_3 with stronger alkalinity displayed a slightly higher activity than AgCl, $AgBF_4$, and $AgNO_3$ under otherwise identical conditions (entries 4–6 vs 1–3). Particularly, the Ag_2CO_3/PPh_3 system gave the best result with a 17% yield of **3a** as well as 16% yield of α-hydroxyl ketone **4a** (entry 6). On the other hand, Ag_2CO_3 itself was found to be ineffective

Table 2. Optimization of the reaction conditions.[a]



Entry	Catalyst	Additive	Solvent	Yield [%] 3a[b]	4a[b]
1	AgCl	PPh_3	CH_3CN	1	1
2	$AgBF_4$	PPh_3	CH_3CN	2	2
3	$AgNO_3$	PPh_3	CH_3CN	6	6
4	AgOAc	PPh_3	CH_3CN	11	10
5	Ag_2O	PPh_3	CH_3CN	10	10
6	Ag_2CO_3	PPh_3	CH_3CN	17	16
7	Ag_2CO_3	–	CH_3CN	0	0
8	Ag_2CO_3	**L1**	CH_3CN	0	0
9	Ag_2CO_3	**L2**	CH_3CN	9	8
10	Ag_2CO_3	PCy_3	CH_3CN	12	11
11	Ag_2CO_3	**L3**	CH_3CN	1	1
12	Ag_2CO_3	**L4**	CH_3CN	7	6
13	Ag_2CO_3	**L5**	CH_3CN	22	22
14	Ag_2CO_3	**L6**	CH_3CN	9	9
15	Ag_2CO_3	DBU	CH_3CN	14	14
16	Ag_2CO_3	2,2′-Bipy	CH_3CN	0	0
17	Ag_2CO_3	**L5**	$CHCl_3$	37	35
18	Ag_2CO_3	**L5**	CH_2Cl_2	17	15
19	Ag_2CO_3	**L5**	DMF	0	0
20[c]	Ag_2CO_3	**L5**	$CHCl_3$	64	62
21[c,d]	Ag_2CO_3	**L5**	$CHCl_3$	77	76
22[c,d,e]	Ag_2CO_3	**L5**	$CHCl_3$	92	90

[a] Unless otherwise specified, all the reactions were performed with **1a** (75.6 mg, 0.5 mmol), **2a** (42.1 mg, 1 equiv.), $[Ag^+]$ (5 mol%), additive (10 mol%), CO_2 (1 MPa), 60 °C, solvent (1 mL), 12 h, yields of **3a** and **4a** are related to **1a**. [b] Determined by ^1H NMR analysis by using 1,1,2,2-tetrachloroethane as an internal standard. [c] Ag_2CO_3 (5 mol%). [d] **2a** (63.2 mg, 1.5 equiv.). [e] 18 h.

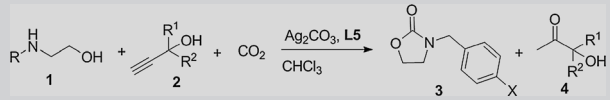
(entry 7), suggesting a $[(PPh_3)_2Ag]_2CO_3$-catalyzed process, which was verified in previous studies.[10d,13]

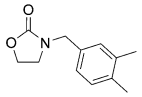
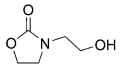
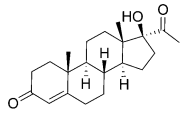
To promote the catalytic efficiency, several typical additives in Table 2 including monophosphine {such as tri(furan-2-yl)-phosphine (**L1**), 2-[2-(diphenylphosphino)ethyl]pyridine (**L2**), tricyclohexylphosphine (PCy_3)} and bidentate phosphine ligands[(e.g., 1,2-bis(diphenylphosphanyl)benzene (Dppbz, **L3**); 1,3-bis(diphenylphosphino)propane (Dppp, **L4**); 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos, **L5**); 1,1′-bis(diphenylphosphino)ferrocene (Dppf, **L6**)] were evaluated (entries 8–14). Especially, bidentate phosphine **L5** was found to the best and gave the desired product **3a** in 22% yield (entry 13). As seen from entry 15, a N-containing organic base (e.g., 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)] was also effective with a slightly lower efficiency than PPh_3 (entry 15 vs. 6). However, 2,2′-bipyridine (2,2′-Bipy) showed no activity (entry 16). Moreover, various reaction conditions involving the solvent, **2a** loading, and reaction time were also examined in the presence of ligand **L5** (entries 17–22). As illustrated by the results, the solvent effect is conspicuous, probably acting on the stability of the active silver complex. Clearly, using $CHCl_3$ as solvent gave the most promising result with 37% yield of **3a** (entry 17). Modulating the ratio of **1a** to **2a** and prolonging the reaction time, excellent results were obtained (entries 21, 22).

With the suitable catalytic conditions in hand, we next explored the scope of the three-component reaction. As shown in Table 3, the reactions of a wide range of aliphatic- and aromatic-substituted 2-aminoethanols proceeded smoothly. Benzyl-substituted 2-aminoalcohols with electron-donating group at the aromatic ring performed well, giving rise to the desired products, that is, 2-oxazolinones (**3**) and α-hydroxyl ketones (**4**), in high yields (entries 1–3). Nevertheless, benzyl-substituted 2-aminoethanols with electron-withdrawing group showed a slight reduction in reactivity, and an increased reaction time was required for improved yield (entries 4, 5). Presumably, the electron-withdrawing chloro and nitro groups could slow down the ammonolysis rate. Interestingly, bis(2-ethanolamine), which was generally reported to exhibit poor reactivity in the literature,[8c] was also successfully transformed into ethoxy 2-oxazolidinone (**3g**) in 73% yield (entry 7). What is more, propargylic alcohols **2b**–**2e** with alkyl or phenyl substituents at the propargylic position were also effective, yielding the corresponding 2-oxazolidinone **3a** and α-hydroxyl ketones **4b**–**4e** in moderate to good yields (entries 8–11).

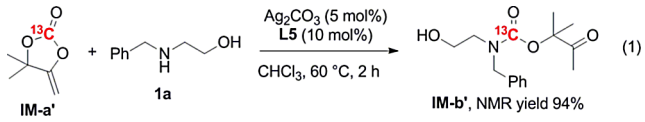
To confirm the reaction pathway, a two-component reaction of $^{13}C_{carbonyl}$-labeled α-alkylidene cyclic carbonate **IM-a'** and 2-aminoethanol **1a** was run as shown in Equation (1). To our delight, β-oxopropylcarbamate **IM-b'** was obtained in excellent yield. The structure of $^{13}C_{carbonyl}$-labeled **IM-b'** was unambiguously confirmed by ^{13}C NMR spectroscopy and high-resolution (HR)MS (Figures 1, S2, and S3). On the other hand, carbonyl shift of the ketone part in **IM-b** was found to be 206.5 ppm in the ^{13}C NMR spectrum (Supporting Information). These results support the ammonolysis pathway, being consistent with previous analogous mechanism of α-alkylidene cyclic carbonate **IM-a** with amines.[7,10]

Table 3. Substrate scope.[a]



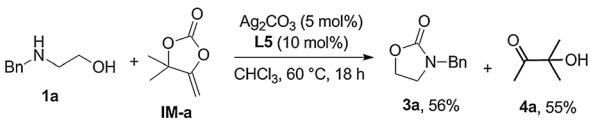
Entry	Product **3**	Product **4**	Yield[b] [%] **3**	**4**
1	X = H, **3a**	$R^1 = R^2$ = Me, **4a**	92(90[c])	90(85[c])
2	X = Me, **3b**	$R^1 = R^2$ = Me, **4a**	91	90
3	X = MeO, **3c**	$R^1 = R^2$ = Me, **4a**	84	84
4	X = Cl, **3d**	$R^1 = R^2$ = Me, **4a**	57(70[c,d])	57
5	X = NO_2, **3e**	$R^1 = R^2$ = Me, **4a**	33(40[c,d])	31
6		$R^1 = R^2$ = Me, **4a**	89	89
7		$R^1 = R^2$ = Me, **4a**	73	71
8[e]	X = H, **3a**	R^1 = Me, R^2 = Et, **4b**	80	79
9[e]	X = H, **3a**	$R^1 = R^2 = -(CH_2)_5-$, **4c**	83	57
10[e]	X = H, **3a**	R^1 = Me, R^2 = Ph, **4d**	84	85
11	X = H, **3a**		47[c]	47[c]

[a] Reactions were carried out with 0.5 mmol **1**, 0.75 mmol **2**, 5 mol% Ag_2CO_3, 10 mol% **L5** (5 mol%, relative to **1**) under 1.0 MPa CO_2 at 60 °C in $CHCl_3$ (1.0 mL) for 18 h, yields of **3** and **4** are related to **1**. [b] Determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. [c] Isolated yield. [d] 48 h. [e] 24 h.



(1)

To obtain further insight into the reaction mechanism, we also performed individual reactions of α-alkylidene cyclic carbonate with 2-aminoethanols. As seen from the results, 2-aminoethanol **1a** reacted with α-alkylidene cyclic carbonate **IM-a** smoothly to yield the desired product 2-oxazolidinone **3a** along with co-product α-hydroxyl ketone **4a** [Eq. (2)]. Accordingly, the synthesis likely occurs through a reaction sequence of ammonolysis and subsequent intramolecular cyclization.



(2)

A plausible reaction mechanism is proposed (Scheme 2) on the basis of the above results. The carboxylative cyclization of propargylic alcohol **2** with CO_2 initially affords the α-alkylidene cyclic carbonate intermediate **IM-A** through silver catalysis, which then proceeds via a nucleophilic ring-opening reaction with the 2-aminoethanol to generate the corresponding β-oxopropylcarbamate **IM-B**. The hydroxyl group as nucleophilic

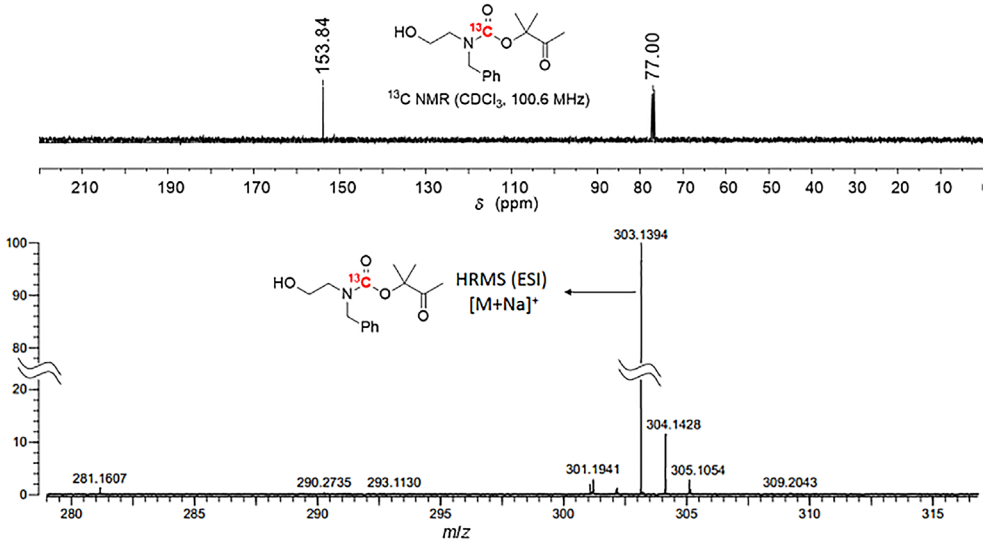
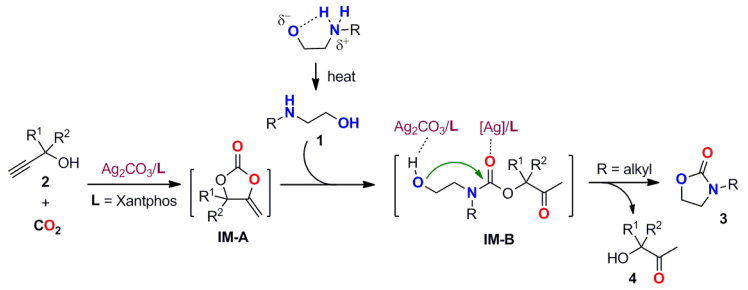


Figure 1. ^{13}C NMR (top) analysis and HRMS (bottom) of the $^{13}C_{carbonyl}$-labeled intermediate.



Scheme 2. Plausible reaction mechanism.

species in the intermediate **IM-B** can also be activated by the basic silver complex. Subsequently, an intramolecular nucleophilic cyclization takes place to yield 2-oxazolidinone **3** and concurrently form α-hydroxyl ketone **4**.

In summary, an unprecedented three-component protocol using terminal propargylic alcohols, CO_2, and 2-aminoethanols through Ag^I catalysis was established for the efficient chemical fixation of CO_2 to prepare various 2-oxazolidinone and α-hydroxyl ketone scaffolds in excellent yields and selectivity under mild conditions. This one-pot approach produces valuable carbonyl compounds at high productivity, in which CO_2 acts as a dual carbonyl reagent with high atom economy. In other words, the thermodynamic limitation in the condensation reaction of 2-aminoalcohols and CO_2 is circumvented by employing this thermodynamically feasible three-component approach through avoidance of the dehydration step. NMR investigations and DFT calculations of the reaction mechanism revealed that such a three-component reaction proceeds through the successive formation of α-alkylidene cyclic carbonate and β-oxopropylcarbamate. Further studies on potential applications and mechanistic understanding are underway.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China, National key research and development project (2016YFA0602900), and the Foundation of State Key Laboratory of Coal Conversion (Grant No. J16-17-902-2), Specialized Research Fund for the Doctoral Program of Higher Education (project 20130031110013), MOE Innovation Team (IRT13022) of China and the "111" Project of Ministry of Education of China (project No. B06005).

Keywords: carbon dioxide fixation · heterocycles · homogeneous catalysis · multicomponent reaction · synthetic methods

[1] Selected reviews: a) M. Peters, B. Kohler, W. Kuckshinrichs, W. Leitner, P. Markewitz, T. E. Müller, *ChemSusChem* **2011**, *4*, 1216 – 1240; b) M. He, Y. Sun, B. Han, *Angew. Chem. Int. Ed.* **2013**, *52*, 9620 – 9633; *Angew. Chem.* **2013**, *125*, 9798 – 9812; c) M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.* **2014**, *114*, 1709 – 1742; d) C. Maeda, Y. Miyazaki, T. Ema, *Catal. Sci. Technol.* **2014**, *4*, 1482 – 1497; e) B. Yu, L. N. He, *ChemSusChem* **2015**, *8*, 52 – 62.

[2] Reviews: a) X. B. Lu, D. J. Darensbourg, *Chem. Soc. Rev.* **2012**, *41*, 1462 – 1484; b) Z. Z. Yang, L. N. He, J. Gao, A. H. Liu, B. Yu, *Energy Environ. Sci.* **2012**, *5*, 6602 – 6639; c) N. Kielland, C. J. Whiteoak, A. W. Kleij, *Adv. Synth. Catal.* **2013**, *355*, 2115 – 2138; d) Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun.* **2015**, *6*, 5933.

[3] a) R. Roers, G. L. Verdine, *Tetrahedron Lett.* **2001**, *42*, 3563 – 3565; b) M. L. Leroux, T. Le Gall, C. Mioskowski, *Tetrahedron: Asymmetry* **2001**, *12*, 1817 – 1823.

[4] a) D. A. Evans, M. D. Ennis, T. Le, N. Mandel, G. Mandel, *J. Am. Chem. Soc.* **1984**, *106*, 1154 – 1156; b) D. A. Evans, K. T. Chapman, J. Bisaha, *J. Am. Chem. Soc.* **1988**, *110*, 1238 – 1256.

[5] J. V. N. Vara Prasad, *Curr. Opin. Microbiol.* **2007**, *10*, 454 – 460.

[6] For selected 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) S. Yoshida, K. Fukui, S. Kikuchi, T. Yamada, *Chem. Lett.* **2009**, *38*, 786 – 787; c) M. Yoshida, T. Mizuguchi, K. Shishido, *Chem. Eur. J.* **2012**, *18*, 15578 – 15581; d) S. Hase, Y. Kayaki, T. Ikariya, *Organometallics* **2013**, *32*, 5285 – 5288; e) J.

Hu, J. Ma, Q. Zhu, Z. Zhang, C. Wu, B. X. Han, *Angew. Chem. Int. Ed.* **2015**, *54*, 5399 – 5403; *Angew. Chem.* **2015**, *127*, 5489 – 5493.

[7] For recent examples of the synthesis of 2-oxazolidinone derivatives, see: a) Y. L. Gu, Q. H. Zhang, Z. Y. Duan, J. Zhang, S. G. Zhang, Y. Q. Deng, *J. Org. Chem.* **2005**, *70*, 7376 – 7380; b) H.-F. Jiang, J.-W. Zhao, *Tetrahedron Lett.* **2009**, *50*, 60 – 62; c) 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.

[8] For typical reports on reactions of 2-aminoethanols and CO_2, see: a) K.-i. Tominaga, Y. Sasaki, *Synlett* **2002**, 0307 – 0309; b) C. J. Dinsmore, S. P. Mercer, *Org. Lett.* **2004**, *6*, 2885 – 2888; c) S.-i. Fujita, H. Kanamaru, H. Senboku, M. Arai, *Int. J. Mol. Sci.* **2006**, *7*, 438 – 450; d) J. Paz, C. Pérez-Balado, B. Iglesias, L. Muñoz, *Synlett* **2009**, 395 – 398; e) J. Paz, C. Pérez-Balado, B. Iglesias, L. Muñoz, *J. Org. Chem.* **2010**, *75*, 3037 – 3046; f) R. Juárez, P. Concepcion, A. Corma, H. Garcia, *Chem. Commun.* **2010**, *46*, 4181 – 4183; g) S. Pulla, C. M. Felton, Y. Gartia, P. Ramidi, A. Ghosh, *ACS Sustainable Chem. Eng.* **2013**, *1*, 309 – 312; h) M. Tamura, M. Honda, K. Noro, Y. Nakagawa, K. Tomishige, *J. Catal.* **2013**, *305*, 191 – 203; i) Y. Takada, S. W. Foo, Y. Yamazaki, S. Saito, *RSC Adv.* **2014**, *4*, 50851 – 50857; j) J. R. Khusnutdinova, J. A. Garg, D. Milstein, *ACS Catal.* **2015**, *5*, 2416 – 2422.

[9] a) H. Zhou, Y. M. Wang, W. Z. Zhang, J. P. Qu, X. B. Lu, *Green Chem.* **2011**, *13*, 644 – 650; b) D. Adhikari, A. W. Miller, M.-H. Baik, S. T. Nguyen, *Chem. Sci.* **2015**, *6*, 1293 – 1300; c) B.-S. Wang, E. H. M. Elageed, D.-W. Zhang, S.-J. Yang, S. Wu, G.-R. Zhang, G.-H. Gao, *ChemCatChem* **2014**, *6*, 278 – 283.

[10] For selected examples of the synthesis of β-oxopropylcarbamates, see: a) H.-S. Kim, J.-W. Kim, S.-C. Kwon, S.-C. Shim, T.-J. Kim, *J. Organomet. Chem.* **1997**, *545 – 546*, 337 – 344; b) Q. Zhang, F. Shi, Y. Gu, J. Yang, Y. Deng, *Tetrahedron Lett.* **2005**, *46*, 5907 – 5911; c) C.-R. Qi, H.-F. Jiang, *Green Chem.* **2007**, *9*, 1284 – 1286; d) Q. W. Song, W. Q. Chen, R. Ma, A. Yu, Q. Y. Li, Y. Chang, L. N. He, *ChemSusChem* **2015**, *8*, 821 – 827.

[11] For α-hydroxyl ketones synthesis from hydration reaction of propargylic alcohols, see: a) H. He, C. Qi, X. Hu, Y. Guan, H. Jiang, *Green Chem.* **2014**, *16*, 3729 – 3733; b) Y. Zhao, Z. Yang, B. Yu, H. Zhang, H. Xu, L. Hao, B. Han, Z. Liu, *Chem. Sci.* **2015**, *6*, 2297 – 2301. For other methods for α-hydroxyl ketones synthesis, see Figure S4 in the Supporting Information.

[12] For examples of silver-promoted activation of alkynes, see: a) X.-Q. Yao, C.-J. Li, *Org. Lett.* **2005**, *7*, 4395 – 4398; b) J. Liu, Z. Fang, Q. Zhang, Q. Liu, X. Bi, *Angew. Chem. Int. Ed.* **2013**, *52*, 6953 – 6957; *Angew. Chem.* **2013**, *125*, 7091 – 7095; c) F. Li, J. Nie, L. Sun, Y. Zheng, J.-A. Ma, *Angew. Chem. Int. Ed.* **2013**, *52*, 6255 – 6258; *Angew. Chem.* **2013**, *125*, 6375 – 6378; d) C. He, S. Guo, J. Ke, J. Hao, H. Xu, H. Chen, A. Lei, *J. Am. Chem. Soc.* **2012**, *134*, 5766 – 5769.

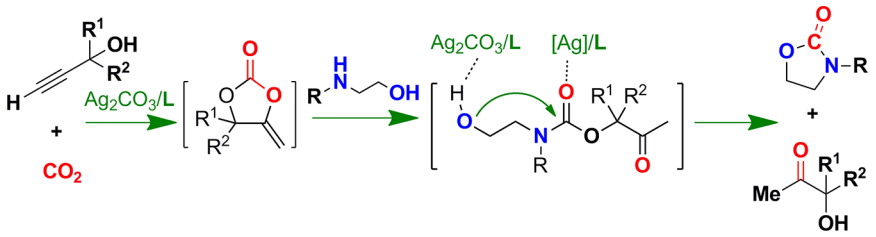
[13] G. A. Bowmaker, Effendy, J. V. Hanna, P. C. Healy, S. P. King, C. Pettinari, B. W. Skelton, A. H. White, *Dalton Trans.* **2011**, *40*, 7210 – 7218.

Received: April 11, 2016
Revised: May 12, 2016
Published online on ■■ ▮▮, 0000

*Q.-W. Song, Z.-H. Zhou, M.-Y. Wang, K. Zhang, P. Liu, J.-Y. Xun, L.-N. He**

■■ – ■■

Thermodynamically Favorable Synthesis of 2-Oxazolidinones through Silver-Catalyzed Reaction of Propargylic Alcohols, CO_2, and 2-Aminoethanols



Three in a pot: A thermodynamically feasible pathway for CO_2 conversion is successfully performed to concurrently synthesize 2-oxazolidinones and α-hydroxyl ketones through a three-component reaction of propargylic alcohols, CO_2, and 2-aminoalcohols. As a consequence, the thermodynamic limitation for the condensation reaction of 2-aminoalcohols and CO_2 is circumvented by avoiding the dehydration step.