

Efficient chemical fixation of CO₂ promoted by a bifunctional Ag₂WO₄/Ph₃P system†

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An efficient heterogeneous silver-catalyzed reaction for construction of the α -methylene cyclic carbonate motif was developed through carboxylative assembly of propargyl alcohols and CO₂. Such a CO₂ fixation protocol proceeded smoothly with only 1 mol% of Ag₂WO₄ and 2 mol% of PPh₃ as well as atmospheric CO₂ at room temperature under solvent-free conditions, in an environmentally benign and low energy manner along with an easy operating procedure. Notably, up to 98% isolated yields of carbonates could be attained with exclusive chemo-selectivity. In addition, the dual activation capacity of Ag₂WO₄ towards both the propargylic substrate and CO₂ is based on which cooperative catalytic mechanism by the silver cation and the tungstate anion is proposed. Recycling trials on carboxylative cyclization of propargyl alcohols and CO₂ illustrate that the catalyst can be reused at least 4 times with retention of high catalytic activity and selectivity. Especially, it allows the direct and effective application in the one-pot synthesis of various oxazolidinones bearing exocyclic alkenes and carbamates in moderate to high yields upon the alternative introduction of primary or secondary amines.

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Introduction

With increasing awareness of the ever-growing CO₂ level in the atmosphere, great efforts have been devoted to development of strategies towards the reduction of CO₂ emissions.¹ The chemical fixation of CO₂ is highly attractive and effective as a straightforward method to recycle CO₂ into value-added products due to the great potential of CO₂ as an abundant, non-toxic, easily available and renewable C₁ building block in organic synthesis.² However, only a small proportion of the total abundance of CO₂ is currently being consumed for chemical production due to its low reactivity as a result of its high thermodynamic stability and kinetic inertness. Consequently, vigorous nucleophiles like Grignard reagents and organolithium reagents, high-energy starting materials such as small ring compounds and organometallic reagents, or drastic reaction conditions are commonly required for reactions involving CO₂.³ Despite the significant advances in the past few decades, converting CO₂ into readily usable chemicals still

remains a daunting challenge presumably due to limitations existing in those known processes such as tedious reaction procedures, harsh reaction conditions, or low yields.⁴ Therefore, development of effective methodologies using CO₂ as a feedstock under mild conditions particularly low pressure of CO₂ (ideally at 1 atm) could be still highly desirable.

One of the most promising examples of CO₂ fixation is carboxylative cyclization of propargyl alcohols with CO₂ to access α -alkylidene cyclic carbonates, which stands for an important class of heterocyclic compounds with a wide range of applications in organic synthesis (Scheme 1).⁵ In this context, numerous catalytic systems including Ru,⁶ Pd,⁷ Co,⁸ Cu,⁹ Ag,¹⁰ Fe,¹¹ phosphines,¹² N-heterocyclic carbenes (NHC),¹³ K₂CO₃/crown ethers,¹⁴ bicyclic guanidines,¹⁵ silver-NHC complexes,¹⁶ or N-heterocyclic olefin/CO₂ adducts¹⁷ have been developed. Moreover, reactions conducted in ionic liquids¹⁸ or using the electrochemical method¹⁹ have also been reported. However, those procedures pose a number of drawbacks, in particular, use of complicated catalysts,

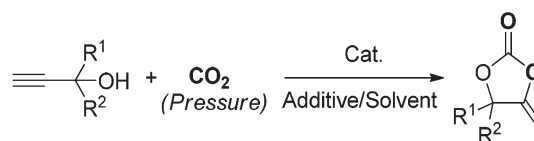
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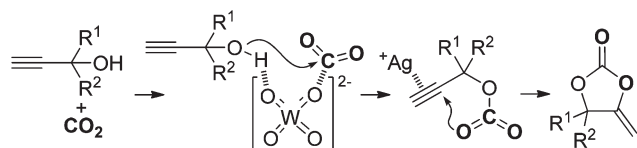
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Scheme 1 Chemical fixation of CO₂ into α -alkylidene cyclic carbonates.



Scheme 2 Chemical fixation of CO₂ through the dual activation pathway.

requirement of higher CO₂ pressure and avoidance of moisture. These challenges can be surmounted, to our delight, through the rational design of a high performance catalytic system. Consequently, a robust catalytic system is believed to be essential to find novel protocols for chemical fixation of CO₂ to value-added products in a cost-effective, practically viable, and environmentally benign manner.

Silver salts are widely employed as activators of the C≡C triple bond in organic synthesis.²⁰ For the reaction of propargyl alcohols with CO₂, the Yamada group¹⁰ and the Jiang group¹⁶ have developed a silver-based procedure for the synthesis of the α-alkylidene cyclic carbonates from CO₂. However, a stoichiometric amount of the base or high CO₂ pressure was required in those Ag-catalyzed systems. On the other hand, Mizuno *et al.*²¹ reported that [WO₄]²⁻ could activate a CO₂ molecule by forming the [WO₄]²⁻/CO₂ adduct, which thus could allow the CO₂ transformation to proceed smoothly under mild conditions. In this context, we envisaged that a novel bifunctional catalytic species containing Ag⁺ and [WO₄]²⁻, *i.e.* Ag₂WO₄, could be particularly efficient for the reaction of propargylic alcohols with CO₂. The [WO₄]²⁻ anion would activate both CO₂ and the O–H bond of propargylic alcohol,^{21a} which could favor the generation of the carboxylate intermediate. The carboxylate intermediate would then be trapped by the silver-activated C≡C triple bond to afford the stable α-alkylidene cyclic carbonate as shown in Scheme 2.

Herein, we would like to report Ag₂WO₄/Ph₃P as a highly efficient and robust bifunctional catalyst system for chemical fixation of atmospheric CO₂ with propargyl alcohols to provide α-alkylidene cyclic carbonates under neutral solvent-free conditions. Notably, this catalytic system was also proved to be effective for the three-component coupling reaction of propargylic alcohols, amines and CO₂. The present system can eliminate the need for large quantities of caustic base or flammable organic solvents.

Results and discussion

Several metal compounds were initially investigated for the reaction of 2-methylbut-3-yn-2-ol (**1a**), as the model substrate under a CO₂ balloon without a solvent at 50 °C for 6 h (Table 1). The reaction without a catalyst and an additive was carried out only to recover the starting material quantitatively (entry 1, Table 1). The catalysts such as DBU, Ph₃P, and CuCl were demonstrated to be ineffective under the given conditions (entries 2–4). Different silver salts like AgNO₃, AgOAc, Ag₂WO₄,

Table 1 Ag(I)-catalyzed reaction of propargyl alcohol **1a** with CO₂^a

Entry	Catalyst	Additive	Time/h	Yield ^b /%
1	—	—	6	0
2	DBU	—	6	0
3	Ph ₃ P	—	6	0
4	CuCl	—	6	0
5	AgNO ₃	Ph ₃ P	6	0
6	AgOAc	Ph ₃ P	6	<1
7	Ag ₂ WO ₄	Ph ₃ P	6	45
8	AgI	Ph ₃ P	6	0
9	Ag ₂ WO ₄	DBU	6	2
10	Ag ₂ WO ₄	2,2'-Bipyridine	6	0
11	Ag ₂ WO ₄	TMEDA	6	0
12 ^c	Ag ₂ WO ₄	Ph ₃ P	3	85
13 ^c	Ag ₂ WO ₄	L1	3	0
14 ^c	Ag ₂ WO ₄	L2	3	<1
15 ^c	Ag ₂ WO ₄	L3	3	82
16	Ag ₂ WO ₄	Ph ₃ P	12	>99
17 ^d	Ag ₂ WO ₄	Ph ₃ P	12	98
18 ^e	Ag ₂ WO ₄	Ph ₃ P	12	82
19 ^f	Ag ₂ WO ₄	Ph ₃ P	6	>99
20 ^g	Ag ₂ WO ₄	Ph ₃ P	6	>99

^a Unless otherwise specified, the reactions were performed with 2-methylbut-3-yn-2-ol (0.421 g, 5.0 mmol), [Ag⁺] or other catalysts (2 mol%), additive (2 mol%), CO₂ balloon, 50 °C. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; TMEDA = tetramethylethylenediamine. ^b GC yields were given using biphenyl as the internal standard. ^c Additive (1 mol%), 0.3 MPa. ^d 25 °C. ^e Ag₂WO₄ (16.3 mg, 0.7 mol%), Ph₃P (18.4 mg, 1.4 mol%). ^f 0.5 MPa. ^g Ag₂WO₄ (58.0 mg, 2.5 mol%), Ph₃P (65.5 mg, 5 mol%).

and AgI were also screened in the presence of Ph₃P as an additive (entries 5–8). Gratifyingly, the α-alkylidene cyclic carbonates **2a** were obtained in a yield of 45% by employing 1 mol% of Ag₂WO₄ in conjunction with 2 mol% of Ph₃P at 50 °C for 6 h (entry 7). The results encouraged us to further optimize the reaction conditions by using Ag₂WO₄ as a catalyst. The reaction did not occur using DBU, 2,2'-bipyridine, or TMEDA as an additive (entries 9–11). Then several bidentate phosphine ligands were screened under 0.3 MPa of CO₂ (entries 13–15). Those results show that **L1** and **L2** were not effective, whereas **L3** gave 82% yield of the target product. Gratifyingly, a simple Ag₂WO₄/Ph₃P catalytic system gave 85% yield of **2a** by increasing CO₂ to 0.3 MPa (entry 12). Based on this result, a quantitative yield was successfully reached in the presence of 0.1 MPa CO₂ at 50 °C or 25 °C by further prolonging the reaction time to 12 h (entries 16 and 17). With lower loading of the catalyst, the reaction at 50 °C for 12 h afforded **2a** in a yield of 82% (entry 18). Furthermore, it was found that higher CO₂ pressure or catalyst loading was needed for the full conversion in 6 h (entries 19 and 20).

Table 2 Carboxylative cyclization of propargyl alcohols with CO₂^a

Entry	Substrate	Product	t/h	Yield ^b /%
1			12	96
2			12	97
3			12	90 98 ^c
4			12	96
5			12	94
6			24	0
7 ^d			24	35
8 ^d			36	82
9			12	78 89 ^c

^a Unless otherwise specified, the reactions were performed with **1** (5.0 mmol), Ag₂WO₄ (23.2 mg, 1 mol%), Ph₃P (26.2 mg, 2 mol%), 25 °C. ^b Isolated yield. ^c 50 °C. ^d 1 MPa of CO₂ and 80 °C were used.

Subsequently, the substrate scope of this reaction was investigated under 0.1 MPa of CO₂ at 25 °C (Table 2). Propargyl alcohols with a variety of alkyl and aryl substituents at the propargylic position (**1a–1e**) were effective substrates to give the corresponding carbonates **2a–2e** in good to excellent yields even under the conditions of atmospheric CO₂ (entries 1–5, Table 2), whereas 1-isopropyl propargyl alcohol lost reactivity

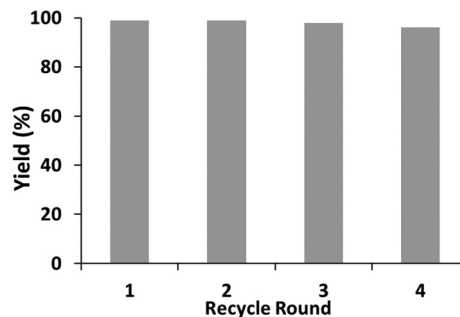
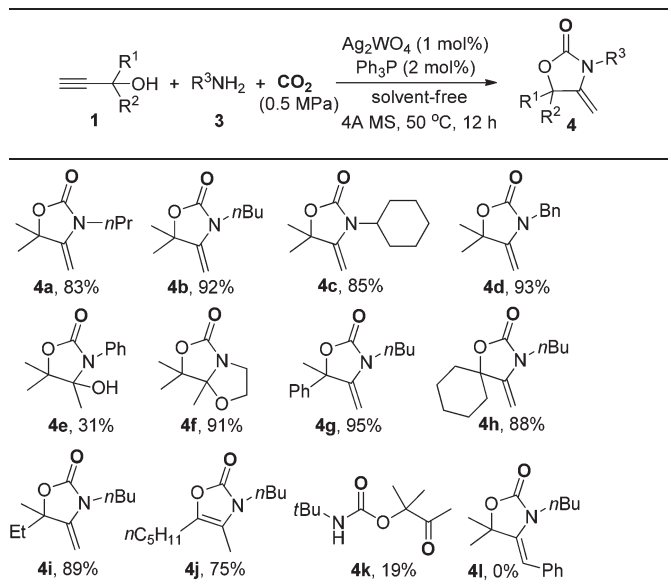


Fig. 1 Catalyst recycling for the carboxylation of **1a** with CO₂ (0.5 MPa) at 50 °C for 6 h.

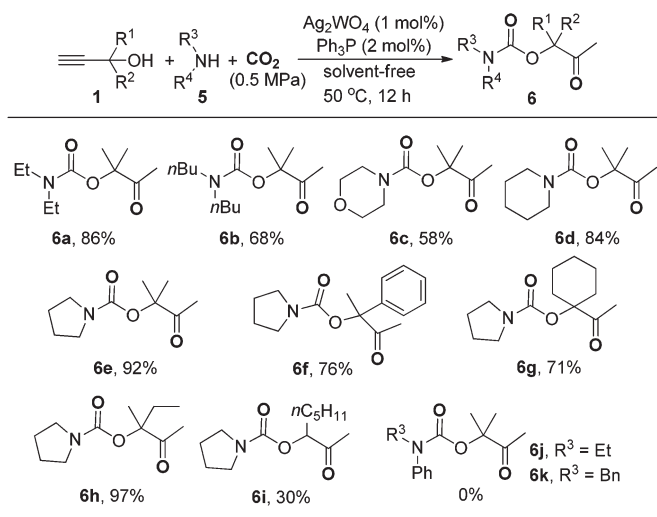
(entry 6), and 1,1-cyclopentylene showed low activity (entry 7), probably due to the steric hindrance and ring strain. The internal propargyl alcohol **1h** required higher CO₂ pressure (1 MPa) and temperature (80 °C) to afford the corresponding carbonate in 82% yield after 36 h (entry 8). However, the secondary alcohol **1i** failed in giving the cyclic carbonate but the subsequent alcoholysis product **2i** was formed (entry 9).

Notably, the reaction of propargyl alcohol **1a** with CO₂ (0.5 MPa) at 50 °C was continuously run to investigate the constancy of the catalyst activity. In each cycle, the heterogeneous catalyst could be easily separated by extraction with hexane. After drying with nitrogen, the catalyst was reused for the next run. As shown in Fig. 1, the catalyst can be reused at least 4 times without significant loss of catalytic activity.

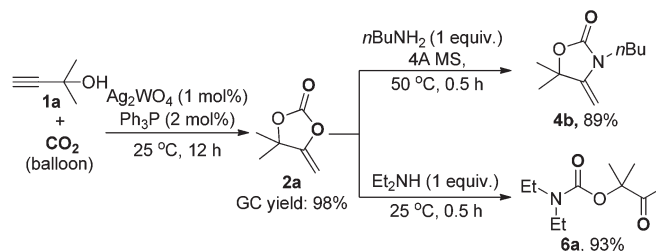
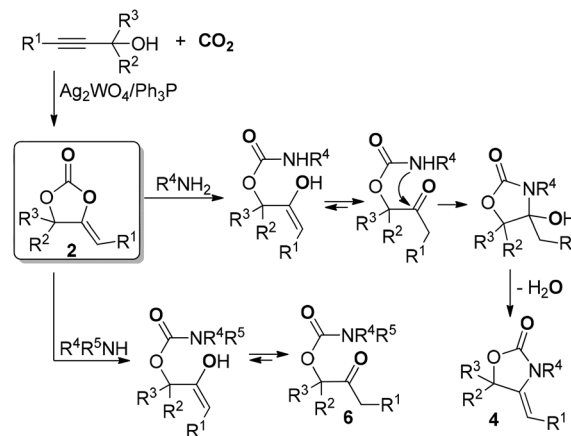
The successful transformation of propargyl alcohols to α -alkylidene cyclic carbonates through CO₂ fixation under extremely mild conditions prompted us to expand potential applications of this Ag₂WO₄/Ph₃P system to the synthesis of α -alkylidene cyclic carbamates *via* the three-component reaction^{15,22} of propargylic alcohols, primary amines and CO₂ under mild conditions as listed in Table 3. Pleasingly, the transformation was performed smoothly with the catalysis of Ag₂WO₄ in the presence of 0.5 MPa CO₂ at 50 °C for 12 h. When 1,1-dimethylpropargylic alcohol was used, and amines bearing *n*-propyl, *n*-butyl, cyclohexyl, and benzyl groups respectively were subjected to the reaction conditions, the 5-methyleneoxazo-lidin-2-one derivatives (**4a–4d**) were obtained in good to excellent yields. In the case of aniline, the undehydrated product **4e** was afforded in 31% yield. Interestingly, another five-membered ring was constructed *via* intramolecular dehydration to furnish **4f** in 91% yield by employing ethanolamine as a substrate. Reactions of propargylic alcohols with a range of substituents including 1-methyl, 1-ethyl, 1-phenyl, and 1-*n*-pentyl groups gave the desired products (**4g–4i**). Moreover, the steric hindrance of the tertiary butyl group of the amine significantly diminishes the reactivity of the carbamate species, which failed to provide the intramolecular cycloaddition product but β -oxopropylcarbamate **4k** was formed. Disappointingly, the corresponding carbamate **4l** was not obtained with internal propargyl alcohol as a starting material.

Table 3 Three-component reaction of propargylic alcohols, primary amines and CO₂^a

^a Unless otherwise stated, the reactions were conducted on a 5 mmol scale of propargylic alcohol and amine with Ag₂WO₄ (23.2 mg, 1 mol%) and Ph₃P (26.2 mg, 2 mol%) under 0.5 MPa of CO₂ at 50 °C for 12 h. Isolated yield was given.

**Scheme 3** The Ag₂WO₄/Ph₃P-catalyzed three-component reaction of propargylic alcohols, secondary amines and CO₂. Isolated yield was given.

Similarly, secondary amines were also applicable to the three-component reaction under identical reaction conditions, which afforded β-oxopropylcarbamates as products.^{11,22a,23} Various representative β-oxopropylcarbamates synthesized are depicted in Scheme 3. In most cases, the reaction was performed with an approximately equimolar amount of reactants and proceeded to completion within 12 h at 50 °C. Aliphatic propargylic alcohols, including 1,1-dimethyl propargylic

**Scheme 4** Stepwise synthesis of typical oxazolidinone and β-oxopropylcarbamate.**Scheme 5** Proposed mechanism for the Ag₂WO₄/Ph₃P-catalyzed three-component reactions.

alcohol, 1-methyl-1-phenyl propargylic alcohol, 1-ethyl-1-methyl propargylic alcohol, and 1-ethynylcyclohexanol, were also found to be good substrates. Both cyclic and linear secondary aliphatic amines afforded the corresponding product with good to excellent yields. Unfortunately, the reaction using the aromatic amines cannot furnish the desired products.

Although we are quite confident that the oxazolidinone generated from the three-component coupling reaction between propargylic alcohols, primary amines and CO₂ proceeds *via* a tandem aminolysis of α-alkylidene cyclic carbonates/intramolecular cyclization,^{22c,23b} the individual steps of this process were further examined as depicted in Scheme 4. In the absence of the amine, the expected carbonates 2a were produced in 98% GC yield under the reaction conditions. Subsequently, equimolar primary and secondary amines were added into the reaction mixture, respectively. The corresponding products 4b and 6a were isolated in reasonable yields after 0.5 h.

Consequently, a plausible mechanism of the Ag₂WO₄/Ph₃P-catalyzed three-component reactions is proposed as illustrated in Scheme 5. The carboxylative cyclization of the propargyl alcohol with CO₂ affords the carbonate 2 as an intermediate, which then undergoes a nucleophilic attack by a primary or secondary amine to generate the carbamate species. In the presence of a secondary amine, the corresponding

β -oxopropylcarbamate **6** can be obtained *via* tautomerization. In the case of a primary amine, further intramolecular nucleophilic attack followed by dehydration affords the oxazolidinone **4**.

Conclusions

In summary, we have described a sustainable and cost-competitive catalytic process promoted by the $\text{Ag}_2\text{WO}_4/\text{PPh}_3$ system for efficient chemical fixation of CO_2 to produce α -alkylidene cyclic carbonates, α -alkylidene cyclic carbamates, and β -oxopropylcarbamates under mild conditions, respectively. The scope of the reaction is broad, with a variety of propargylic alcohols undergoing carboxylative cyclization. Moreover, the three-component reactions of propargylic alcohols, amines and CO_2 are also well performed with this protocol. In addition, this procedure can eliminate the need for large quantities of caustic base and flammable organic solvents, yielding the strategy to prepare value-added α -alkylidene cyclic carbonates, α -alkylidene cyclic carbamates, and β -oxopropylcarbamates from both environmental and economical points of view. Importantly, the catalytic system is not sensitive to air and minor moisture, which may enhance the possibility of fixation of CO_2 . Such findings may be of great interest for developing alternative access to chemical fixation of CO_2 with the preparation of the CO_2 -based products under mild conditions.

Experimental section

General procedure for the synthesis of α -alkylidene cyclic carbonates **2a**: Ag_2WO_4 (23.2 mg, 1 mol%), PPh_3 (26.2 mg, 2 mol%), and propargylic alcohols (5 mmol) were added to a Schlenk tube equipped with a magnetic stir bar. A CO_2 balloon was consecutively introduced. Then the mixture was stirred at 25 °C for the desired time. Upon completion, the mixture was diluted with *n*-hexane (3 × 5 mL). The organic phase was collected and then purified by column chromatography on silica gel using petroleum ether–ethyl acetate as an eluent to give the desired products. The solid residue in the tube was Ag_2WO_4 , which could be used directly in the next run. **2a** was obtained as a colourless oil. ^1H NMR (CDCl_3 , 400 MHz) δ 4.75 (d, J = 4.0 Hz, 1H), 4.31 (d, J = 4.0 Hz, 1H), 1.59 (s, 6H) ppm. ^{13}C NMR (CDCl_3 , 100.6 MHz) δ 158.6 (C=O), 151.2, 85.2, 84.6, 27.5 ppm. 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).

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Notes and references

- (a) P. H. Abelson, *Science*, 2000, **289**, 1293; (b) D. W. Keith, *Science*, 2009, **325**, 1654–1655; (c) C. Federsel, R. Jackstell and M. Beller, *Angew. Chem., Int. Ed.*, 2010, **49**, 6254–6257; (d) A.-H. Liu, R. Ma, C. Song, Z.-Z. Yang, A. Yu, Y. Cai, L.-N. He, Y.-N. Zhao, B. Yu and Q.-W. Song, *Angew. Chem., Int. Ed.*, 2012, **51**, 11306–11310.
- (a) D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388–2410; (b) J. Louie, *Curr. Org. Chem.*, 2005, **9**, 605–623; (c) S. N. Riduan and Y. Zhang, *Dalton Trans.*, 2010, **39**, 3347–3357; (d) X. Yin and J. R. Moss, *Coord. Chem. Rev.*, 1999, **181**, 27–60; (e) Z.-Z. Yang, Y.-N. Zhao and L.-N. He, *RSC Adv.*, 2011, **1**, 545–567; (f) L.-N. He, J.-Q. Wang and J.-L. Wang, *Pure Appl. Chem.*, 2009, **81**, 2069–2080.
- For reviews on chemical fixation of CO_2 , see: (a) T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365–2387; (b) M. Cokoja, C. Bruckmeier, B. Rieger, W. A. Herrmann and F. E. Kühn, *Angew. Chem., Int. Ed.*, 2011, **50**, 8510–8537; (c) K. Huang, C.-L. Sun and Z.-J. Shi, *Chem. Soc. Rev.*, 2011, **40**, 2435–2452; (d) Y. Tsuji and T. Fujihara, *Chem. Commun.*, 2012, **48**, 9956–9964; (e) W.-Z. Zhang and X.-B. Lu, *Chin. J. Catal.*, 2012, **33**, 745–756; (f) Z.-Z. Yang, L.-N. He, J. Gao, A.-H. Liu and B. Yu, *Energy Environ. Sci.*, 2012, **5**, 6602–6639.
- (a) G. Centi, E. A. Quadrelli and S. Perathoner, *Energy Environ. Sci.*, 2013, **6**, 1711–1731; (b) P. Markewitz, W. Kuckshinrichs, W. Leitner, J. Linssen, P. Zapp, R. Bongartz, A. Schreiber and T. E. Muller, *Energy Environ. Sci.*, 2012, **5**, 7281–7305.
- A few reports on the transformation of α -alkylidene cyclic carbonates, see: (a) Y. Inoue, K. Matsushita, I. F. Yen and S. Imaizumi, *Chem. Lett.*, 1991, **20**, 1377–1378; (b) K. Ohe, H. Matsuda, T. Ishihara, S. Ogoshi, N. Chatani and S. Murai, *J. Org. Chem.*, 1993, **58**, 1173–1177; (c) K. Ohe, H. Matsuda, T. Morimoto, S. Ogoshi, N. Chatani and S. Murai, *J. Am. Chem. Soc.*, 1994, **116**, 4125–4126; (d) M. Yoshida and M. Ihara, *Angew. Chem., Int. Ed.*, 2001, **40**, 616–619.
- C. Bruneau and P. H. Dixneuf, *J. Mol. Catal.*, 1992, **74**, 97–107.
- K. Iritani, N. Yanagihara and K. Utimoto, *J. Org. Chem.*, 1986, **51**, 5499–5501.
- Y. Inoue, J. Ishikawa, M. Taniguchi and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 1204–1206.
- (a) H.-S. Kim, J.-W. Kim, S.-C. Kwon, S.-C. Shim and T.-J. Kim, *J. Organomet. Chem.*, 1997, **545–546**, 337–344; (b) H.-F. Jiang, A.-Z. Wang, H.-L. Liu and C.-R. Qi, *Eur. J. Org. Chem.*, 2008, 2309–2312.
- (a) S. Kikuchi, S. Yoshida, Y. Sugawara, W. Yamada, K. Sekine, I. Iwakura, T. Ikeno, T. Yamada and H.-M. Cheng, *Bull. Chem. Soc. Jpn.*, 2011, **84**, 698–717; (b) W. Yamada, Y. Sugawara, H. M. Cheng, T. Ikeno and T. Yamada, *Eur. J. Org. Chem.*, 2007, 2604–2607.
- T.-J. Kim, K.-H. Kwon, S.-C. Kwon, J.-O. Baeg, S.-C. Shim and D.-H. Lee, *J. Organomet. Chem.*, 1990, **389**, 205–217.

- 12 (a) J. M. Joumier, J. Fournier, C. Bruneau and P. H. Dixneuf, *J. Chem. Soc., Perkin Trans. 1*, 1991, 3271–3274; (b) Y. Kayaki, M. Yamamoto and T. Ikariya, *J. Org. Chem.*, 2007, **72**, 647–649.
- 13 Y. Kayaki, M. Yamamoto and T. Ikariya, *Angew. Chem., Int. Ed.*, 2009, **48**, 4194–4197.
- 14 K. Uemura, T. Kawaguchi, H. Takayama, A. Nakamura and Y. Inoue, *J. Mol. Catal. A: Chem.*, 1999, **139**, 1–9.
- 15 N. D. Ca, B. Gabriele, G. Ruffolo, L. Veltri, T. Zanetta and M. Costa, *Adv. Synth. Catal.*, 2011, **353**, 133–146.
- 16 X. Tang, C. Qi, H. He, H. Jiang, Y. Ren and G. Yuan, *Adv. Synth. Catal.*, 2013, **355**, 2019–2028.
- 17 Y.-B. Wang, Y.-M. Wang, W.-Z. Zhang and X.-B. Lu, *J. Am. Chem. Soc.*, 2013, **135**, 11996–12003.
- 18 Y. L. Gu, F. Shi and Y. Q. Deng, *J. Org. Chem.*, 2004, **69**, 391–394.
- 19 G.-Q. Yuan, G.-J. Zhu, X.-Y. Chang, C.-R. Qi and H.-F. Jiang, *Tetrahedron*, 2010, **66**, 9981–9985.
- 20 For examples of silver-promoted activation of alkynes, see: (a) U. Halbes-Letinois, J.-M. Weibel and P. Pale, *Chem. Soc. Rev.*, 2007, **36**, 759–769; (b) X.-Q. Yao and C.-J. Li, *Org. Lett.*, 2005, **7**, 4395–4398; (c) J. Liu, Z. Fang, Q. Zhang, Q. Liu and X. Bi, *Angew. Chem., Int. Ed.*, 2013, **52**, 6953–6957; (d) M. Gao, C. He, H. Chen, R. Bai, B. Cheng and A. Lei, *Angew. Chem., Int. Ed.*, 2013, **52**, 6958–6961; (e) F. Li, J. Nie, L. Sun, Y. Zheng and J.-A. Ma, *Angew. Chem., Int. Ed.*, 2013, **52**, 6255–6258; (f) C. He, S. Guo, J. Ke, J. Hao, H. Xu, H. Chen and A. Lei, *J. Am. Chem. Soc.*, 2012, **134**, 5766–5769; (g) X. Zhang, W. Z. Zhang, X. Ren, L. L. Zhang and X. B. Lu, *Org. Lett.*, 2011, **13**, 2402–2405.
- 21 (a) T. Kimura, K. Kamata and N. Mizuno, *Angew. Chem., Int. Ed.*, 2012, **51**, 6700–6703; (b) T. Kimura, H. Sunaba, K. Kamata and N. Mizuno, *Inorg. Chem.*, 2012, **51**, 13001–13008.
- 22 For selected examples of the synthesis of N-substituted 4-methylene-2-oxazolidinones, see: (a) Y. L. Gu, Q. H. Zhang, Z. Y. Duan, J. Zhang, S. G. Zhang and Y. Q. Deng, *J. Org. Chem.*, 2005, **70**, 7376–7380; (b) H. Jiang, J. Zhao and A. Wang, *Synthesis*, 2008, 763–769; (c) Y. Sasaki and P. H. Dixneuf, *J. Org. Chem.*, 1987, **52**, 4389–4391.
- 23 Chemical fixation of CO₂ into β-oxopropylcarbamates, see: (a) Q. Zhang, F. Shi, Y. Gu, J. Yang and Y. Deng, *Tetrahedron Lett.*, 2005, **46**, 5907–5911; (b) C.-R. Qi and H.-F. Jiang, *Green Chem.*, 2007, **9**, 1284–1286; (c) H.-S. Kim, J.-W. Kim, S.-C. Kwon, S.-C. Shim and T.-J. Kim, *J. Organomet. Chem.*, 1997, **545–546**, 337–344.