



Cite this: *Chem. Soc. Rev.*, 2016, 45, 4524

Received 4th December 2015

DOI: 10.1039/c5cs00895f

www.rsc.org/chemsocrev

## Silver-catalyzed carboxylation

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Silver-catalyzed reactions are some of the important methodologies in organic chemistry. Since 2007, a new application of silver catalysts has been emerging. For the sequential carboxylation and cyclization of alkyne derivatives, such as propargyl alcohols and amines, using carbon dioxide, silver catalysts show significant reactivity under mild conditions unlike other transition metals. These developments have received much attention for the effective utilization of carbon dioxide in organic chemistry to synthesize heterocyclic compounds. Related silver-catalyzed C–C bond forming reactions with carbon dioxide have also provided the synthetic methods of the corresponding carboxylic acid derivatives. In this review, the recent studies of the silver-catalyzed carboxylation reactions using carbon dioxide are described.

## Introduction

Silver catalysts are widely utilized in organic reactions as Lewis acids. For example, the silver-catalyzed cyclization reactions of alkyne or allene derivatives are the promising synthetic methods of heterocyclic compounds. The silver-catalyzed or -mediated reactions have been reviewed<sup>1–5</sup> and summarized in a book.<sup>6</sup> It has since been revealed that silver catalysts still have an additional potential to show unique reactivity in the sequential carboxylation and cyclization reaction using carbon dioxide during the synthesis of heterocyclic compounds.

Carbon dioxide is thermodynamically stable and much less reactive than other carbon derivatives due to its high oxidation

state. Therefore, strong nucleophiles or harsh reaction conditions were usually required when carbon dioxide is utilized in organic syntheses. For example, the Kolbe–Schmitt reaction, found in any organic chemistry textbook, requires high pressure carbon dioxide and high temperature, though the reaction has been employed for the commercial production of salicylic acid. Recently, carbon dioxide has been regarded as an appealing C1 resource due to its abundant supply from industries and easy handling.<sup>7</sup> Methods to transform carbon dioxide into high-value chemicals have been developed. The transition-metal-catalyzed carboxylation reactions of various carbon nucleophiles with C–C bond formation have been actively developed for the preparation of fine chemicals.<sup>8,9</sup>

Considering the carboxylation of simple alcohols or amines with carbon dioxide, these two reactions are in equilibrium. Therefore, the problem is that the corresponding carbonate

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Tohru Yamada was born in Hokkaido, Japan, in 1958. He received his PhD degree in 1987 from the University of Tokyo under the guidance of Professor Teruaki Mukaiyama. In 1987, he joined Mitsui Petrochemical Ind. Ltd. In 1997, he moved to Keio University and in 2002 was promoted to a professor of Chemistry Department. In 1992 he received the Chemical Society of Japan Award for Young Chemist, in 2003 and 2011 the BCSJ Award by the Chemical Society of Japan, and in 2010 the Nissan Chemical Industries Award for Novel Reaction & Method 2010 by Synthetic Organic Chemistry, Japan.



and carbamate produced easily return back to the starting material and carbon dioxide after quenching the reactions. The transformation of the unstable intermediates into a stable product is one of the reliable solutions of the problem. With respect to atom economy, the cyclization of unsaturated organic molecules is an important methodology. Though the sequential carboxylation and cyclization of propargyl alcohols and propargyl amines using carbon dioxide have been developed, harsh conditions (high temperature or high pressure carbon dioxide) were required and substrates were limited to terminal alkynes. In 2007, the silver catalyst made a major breakthrough in the cascade carboxylation and cyclization of propargyl alcohols and carbon dioxide. Related silver-catalyzed carboxylation reactions have also been achieved. In this review, the recent studies of the silver-catalyzed carboxylation using carbon dioxide are described.

## 1. Silver-catalyzed synthesis of cyclic carbonates

One of the reasonable synthetic approaches of cyclic carbonates is the cyclization of readily available propargyl alcohols and carbon dioxide from the viewpoint of atom economy. The reaction of propargyl alcohols and carbon dioxide was promoted by a transition metal, carbene and phosphine as the catalyst; however, these reported methods required harsh reaction conditions, such as high carbon dioxide pressure and high reaction temperature. Moreover, terminal alkynes were only applicable for these carbonate formations, and the internal alkynes afforded sluggish reactions.

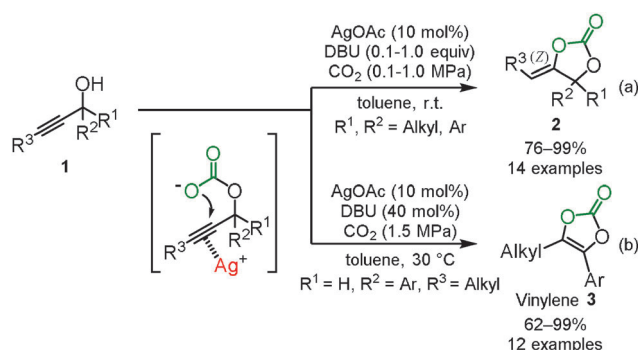
### 1.1 Silver-catalyzed sequential carboxylation and cyclization of propargyl alcohols

In 2007, we indeed reported the silver-catalyzed carboxylation and cyclization of propargyl alcohols **1** under mild reaction conditions (Scheme 1(a)).<sup>10</sup> The study indicated that the combined use of silver acetate and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was an efficient catalyst system for the incorporation of carbon dioxide into various propargyl alcohols **1** to afford the corresponding cyclic carbonates **2** in high-to-excellent yields, though other transition-metals including copper, gold, rhodium, mercury, platinum, and palladium were not effective at room temperature. It was also noted that this catalytic

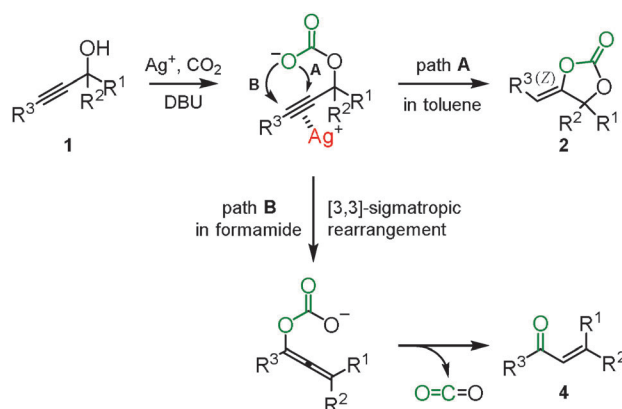
system could be applied to the aryl- and alkyl-substituted internal alkynes even under mild reaction conditions. The *exo*-alkenyl cyclic carbonates were obtained as the sole isomers and the geometry of the C–C double bond was confirmed to be the *Z* isomer by X-ray single crystal structure analysis or NOE. These results suggested that the silver catalyst activates the C–C triple bond from the opposite side of the carbonate to promote anti-addition through 5-*exo*-dig cyclization. This assumption was also supported by DFT calculations.<sup>11</sup> The outer-sphere attack is similar to the typical reactivity of the related gold(I) catalysts,<sup>12</sup> but only the silver catalyst is able to induce cyclization, and gold catalysis fails under these conditions.<sup>13</sup>

We recently found that when the secondary propargyl alcohols were employed under the present reaction conditions, the vinylene carbonates **3**, which are useful as prodrugs for drug-delivery systems and are used as electrolyte additives of lithium ion batteries, were produced.<sup>14</sup> These vinylene carbonates were produced after the isomerization of the *exo*-alkenyl cyclic carbonate (Scheme 1(b)).

In the reactions mentioned above, the silver-catalyzed reaction of propargyl alcohols with carbon dioxide selectively afforded the corresponding cyclic carbonates in a toluene solution (path A in Scheme 2), while in dichloromethane and chlorobenzene, the corresponding  $\alpha,\beta$ -unsaturated carbonyl compounds **4**, generated *via* a Meyer–Schuster type reaction, were detected along with the cyclic carbonate. We proposed the following reaction mechanism for  $\alpha,\beta$ -unsaturated carbonyl compounds: the  $\beta$ -carbon of propargyl alcohol would be alternatively attacked to promote the [3,3]-sigmatropic rearrangement into the allene-enolate. The  $\alpha,\beta$ -unsaturated carbonyl compounds would result from the release of carbon dioxide (path B in Scheme 2). It is reasonable to assume that the polarized structure with an elongated C–O bond in the carbonate intermediate would be stabilized in a polar solvent, thus enhancing the attack on the  $\beta$ -carbon in the activated propargyl alcohol. In fact, DMF and DMA solvents improved the selectivity toward the enone. Finally, it was found that formamide was the best choice to selectively obtain the corresponding enone. Various tertiary and secondary propargyl alcohols were efficiently converted into the corresponding  $\alpha,\beta$ -unsaturated carbonyl compounds in high yield using a

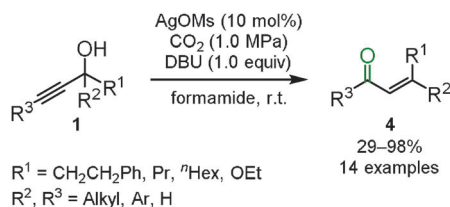


**Scheme 1** Silver-catalyzed incorporation of carbon dioxide into propargyl alcohols.



**Scheme 2** Postulated reaction mechanism of propargyl alcohols and carbon dioxide.





Scheme 3 Transformation of propargyl alcohols into enones.

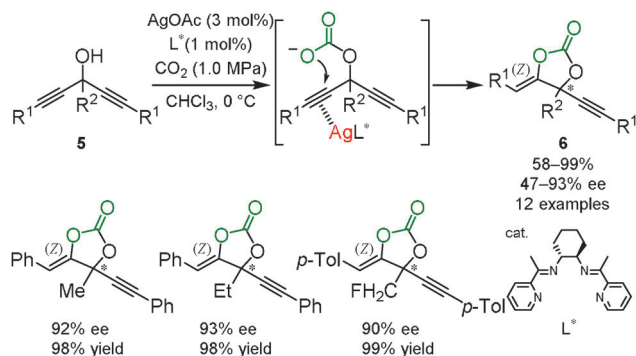
catalytic amount of silver methanesulfonate with DBU and carbon dioxide (Scheme 3).<sup>15</sup>

### 1.2 Silver-catalyzed asymmetric synthesis of cyclic carbonate

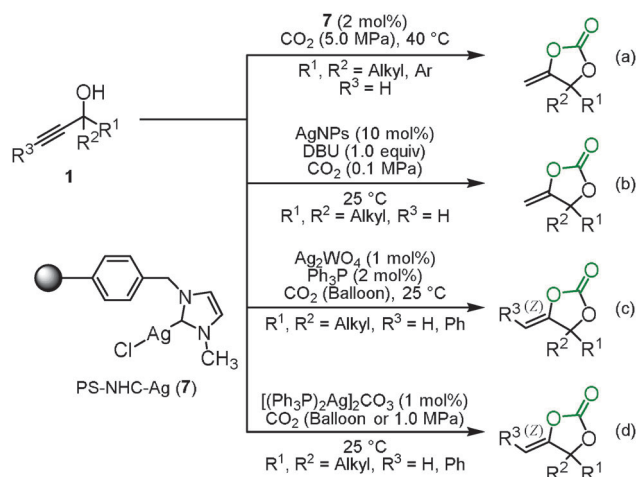
As described in Section 1.1, the silver ion activated the C–C triple bond as a  $\pi$ -Lewis acid. On the basis of this observation, an optically active silver catalyst, which is in rapid equilibrium between the two alkynes in bispropargyl alcohols **5**, was expected to selectively promote a nucleophilic attack on one of the C–C triple bonds with asymmetric desymmetrization. We developed the asymmetric carbon dioxide incorporation into bispropargyl alcohols with desymmetrization by the combination of silver acetate and the chiral Schiff base ligand **L\*** to afford the corresponding cyclic carbonates **6** with good-to-excellent enantiomeric excess (Scheme 4). We confirmed that (*S*)-cyclic carbonate was obtained in the reaction catalyzed by the complex with (*R,R*)-**L\*** based on a VCD measurement in combination with the corresponding spectra predicted by DFT calculations.<sup>16</sup>

### 1.3 Application for highly efficient silver catalysts

Highly efficient and reusable silver catalysts for the incorporation of carbon dioxide into propargyl alcohols were developed because a relatively large amount of the silver catalyst and a stoichiometric amount of DBU were required as mentioned in Section 1.1. The polystyrene-supported N-heterocyclic carbene silver complex **7** (PS-NHC-Ag) had a good catalytic activity and could be reused up to 15 times without considerable loss of its catalytic activity, though a high pressure of carbon dioxide was required (Scheme 5(a)).<sup>17</sup> In addition, Han and co-workers reported that silver nanoparticles (AgNPs) catalyzed the carboxylation and cyclization of propargyl alcohols and carbon dioxide and were recyclable at least 5 times (Scheme 5(b)).<sup>18</sup>



Scheme 4 Enantioselective cyclization of bispropargyl alcohols and carbon dioxide.



Scheme 5 Efficient silver catalysts for the carboxylation and cyclization of propargyl alcohols.

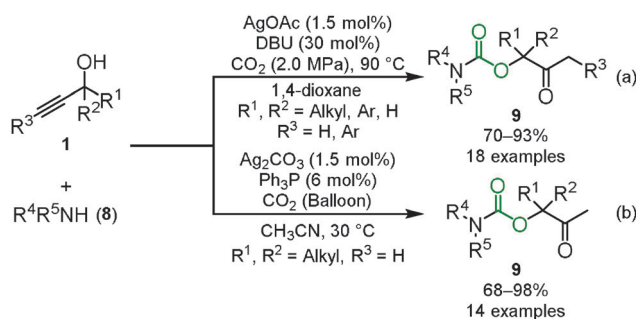
He's group achieved the reaction at a low catalyst loading of  $\text{Ag}_2\text{WO}_4$  and  $\text{Ph}_3\text{P}$  even under the balloon pressure of carbon dioxide. The activation of carbon dioxide by  $[\text{WO}_4]^{2-}$  was postulated to provide high efficiency (Scheme 5(c)).<sup>19</sup> He and co-workers also developed the reaction which was efficiently catalyzed by the silver complex  $[(\text{Ph}_3\text{P})_2\text{Ag}]_2\text{CO}_3$  without any organic base (Scheme 5(d)). Based on the monitoring of the reaction by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, they assumed that  $[(\text{Ph}_3\text{P})_2\text{Ag}]_2\text{CO}_3$  simultaneously activated the propargyl alcohol and carbon dioxide to effectively promote the reaction.<sup>20</sup>

One of the applications of carbon dioxide incorporation into propargyl alcohols is the three-component reaction. The reaction between propargyl alcohol, carbon dioxide and secondary amines **8** provided the corresponding carbamates **9** through the ring-opening reaction of the cyclic carbonate by secondary amines (Scheme 6).<sup>21</sup> In the case of primary amines **10**, intramolecular nucleophilic addition and dehydration produced the corresponding oxazolidinones **11** (Scheme 7).<sup>19</sup>

## 2. Transformation of amine derivatives

### 2.1 Propargyl amine

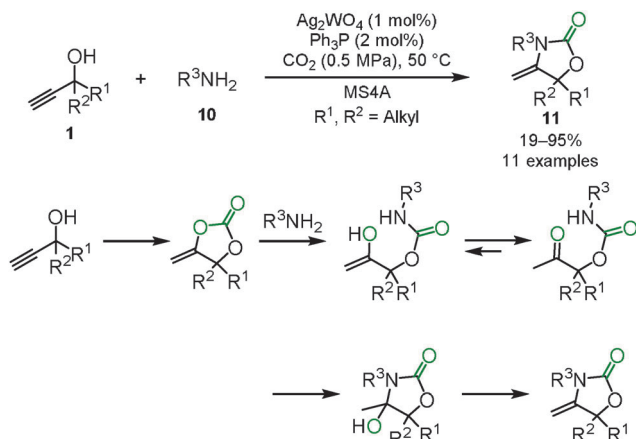
The oxazolidinone preparation from carbon dioxide is one of the most attractive synthetic methods. We reported that carbon



Scheme 6 Three-component reaction between propargyl alcohols, secondary amines and carbon dioxide.







**Scheme 7** Three-component reaction between propargyl alcohols, primary amines and carbon dioxide.

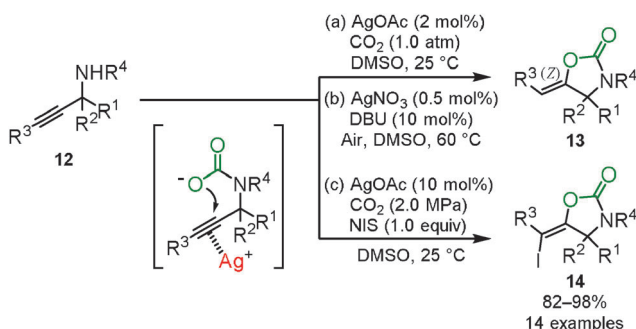
dioxide incorporation into various propargylic amines **12** proceeded to give the corresponding oxazolidinone derivatives **13** in high yields under mild reaction conditions, *i.e.*, 2 mol% of AgOAc and 1.0 atm of carbon dioxide (Scheme 8(a)).<sup>22</sup>

Yoshida and co-workers reported that the silver/DBU catalytic system promoted the fixation of carbon dioxide into propargyl amines even under atmospheric carbon dioxide (Scheme 8(b)). DBU was found to be necessary for the reaction. They proposed that the DBU–CO<sub>2</sub> adduct generated *in situ* from DBU and the atmospheric carbon dioxide promoted the reaction with the propargyl amine and carbon dioxide. This assumption was supported by the attempted reaction of propargyl amine and the DBU–CO<sub>2</sub> adduct.<sup>23</sup>

For the synthesis of high-valued compounds, the silver-catalyzed three-component reaction of propargylic amines, carbon dioxide, and *N*-iodosuccinimide was developed for the stereoselective synthesis of (*E*)-iodovinylloxazolidinones **14** which could be useful for the metal catalyzed coupling reactions (Scheme 8(c)).<sup>24</sup>

## 2.2 Benzoxazine-2-one from *o*-alkynylaniline and carbon dioxide

Benzoxazine-2-one derivatives **16** have attracted much attention as some of the most important heterocyclic structures in pharmaceutical science, but their synthesis methods were limited.



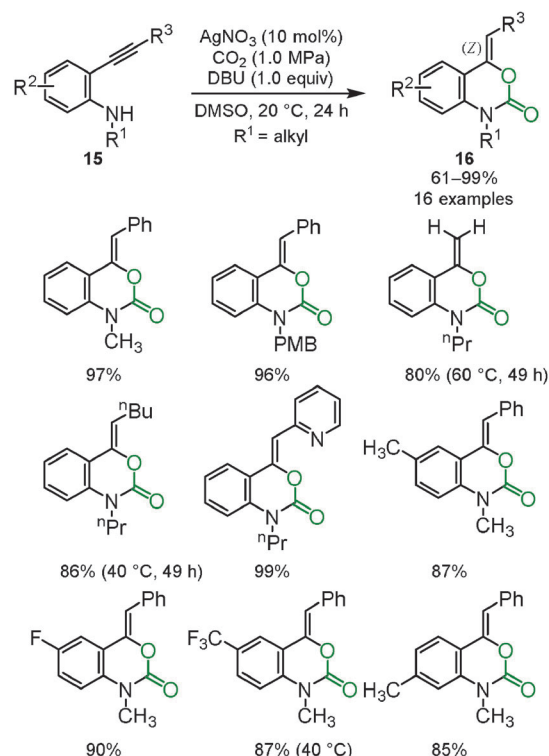
**Scheme 8** Carboxylation and cyclization of propargyl amines and carbon dioxide for the synthesis of oxazolidinone derivatives.

In some cases, toxic reagents, such as phosgene or carbon monoxide, were required. We reported that the silver/DBU system promoted the incorporation of carbon dioxide into *o*-alkynylanilines **15** to afford the corresponding benzoxazine-2-ones **16** bearing the *Z* *exo*-olefin *via* 6-*exo*-dig cyclization. Some variations in the substituents on benzoxazine-2-ones are shown (Scheme 9).<sup>25</sup> The detailed reaction mechanism was studied using DFT calculations by Wang, Yan and co-workers.<sup>26</sup>

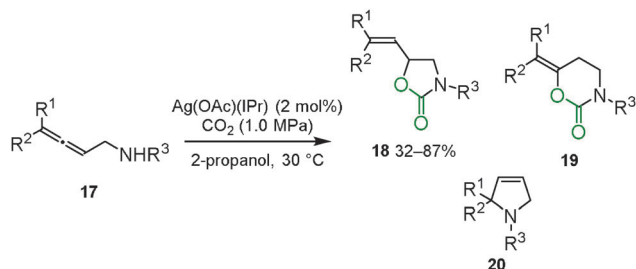
## 2.3 Allenylamine

Ikariya and co-workers reported that Ag(OAc)(IPr) [IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene] effectively catalyzed the carboxylation and cyclization of allenylamines **17** (Scheme 10).<sup>27</sup> Though an intramolecular hydroamination **20** and a 6-membered ring formation **19** were competitive reactions, a 5-membered ring formation highly selectively proceeded to give the corresponding cyclic urethane 3-benzyl-5-vinyl-1,3-oxazolidin-2-one **18**.

In this reaction, catalytic amounts of the gold complex Au(OAc)(IPr) and the copper complex Cu(OAc)(IPr) were found to be much less effective. DFT calculations supported the difference in electronic structures between the alkenylsilver complex and the alkenylgold complex. The silver–carbon bond was suggested to be more polarized than the gold–carbon bond. This result implied that the polarization of the metal–carbon bond could be crucial to regenerate the metal cation for complete turnover of the catalytic cycle.



**Scheme 9** Silver-catalyzed reactions of *o*-alkynylanilines and carbon dioxide for the synthesis of benzoxazine-2-ones.

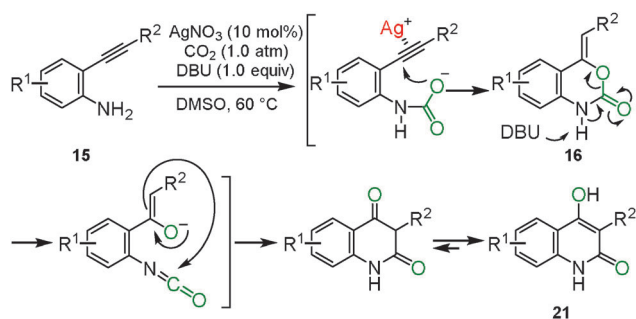


**Scheme 10** Silver-catalyzed carboxylation and cyclization of allenyl-methylamines.

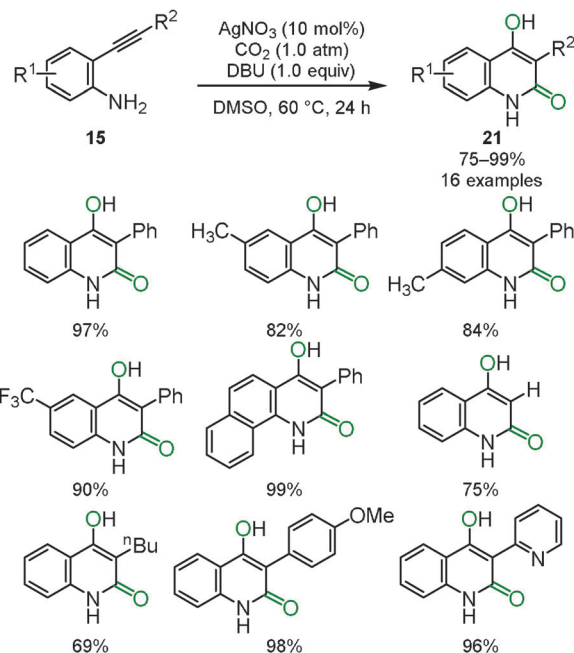
## 2.4 Rearrangement for hydroxyquinolin-2-one and tetramic acid

When the optimized reaction conditions as mentioned in Section 2.2 were applied to the primary *o*-alkynylaniline **15**, a side-product was detected. Based on several analytical results, such as X-ray single crystal structure analysis,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and mass spectrometry, the side-product was identified to be 4-hydroxyquinolin-2(1*H*)-one **21**. The possible reaction mechanism is shown in Scheme 11. First, the corresponding benzoxazin-2-one **16** would be generated from the *o*-alkynylaniline **15** and carbon dioxide catalyzed by the silver catalyst. In the second step, the benzoxazine **16** would immediately be deprotonated by the DBU base to generate the isocyanate and the enolate from the C–O bond cleavage of the carbamate functionality. The enolate would then attack the carbon atom of the isocyanate to afford the 1,3-diketone intermediate, which would produce the corresponding 4-hydroxyquinolin-2(1*H*)-one **21** after enolization. The results of isotopic labeling experiments with  $\text{C}^{18}\text{O}_2$  and *in situ* IR measurements also supported this proposed reaction mechanism. The scope of the reaction system is described in Scheme 12.<sup>28</sup>

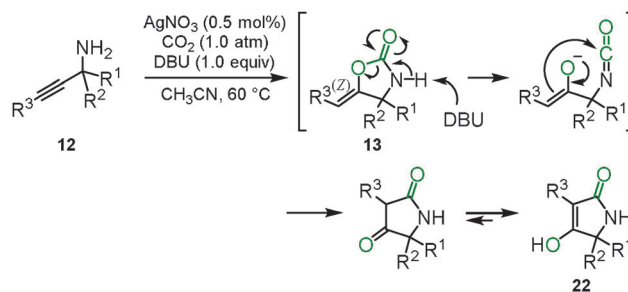
The cyclization and rearrangement system was applied to propargyl amines **12** for the synthesis of tetramic acid derivatives **22** which have been studied as biologically active heterocyclic structures for pharmaceutical and agricultural chemicals (Scheme 13). The silver/DBU system provided various multi-substituted tetramic acid derivatives **22** from easily available primary propargyl amines **12** under mild conditions, though conventional preparative approaches often required highly functionalized starting materials and harsh heating conditions in basic media (Scheme 14).<sup>29</sup>



**Scheme 11** Hypothetical reaction mechanism of intramolecular rearrangement.



**Scheme 12** Preparation of 4-hydroxyquinolin-2(1*H*)-one derivatives.



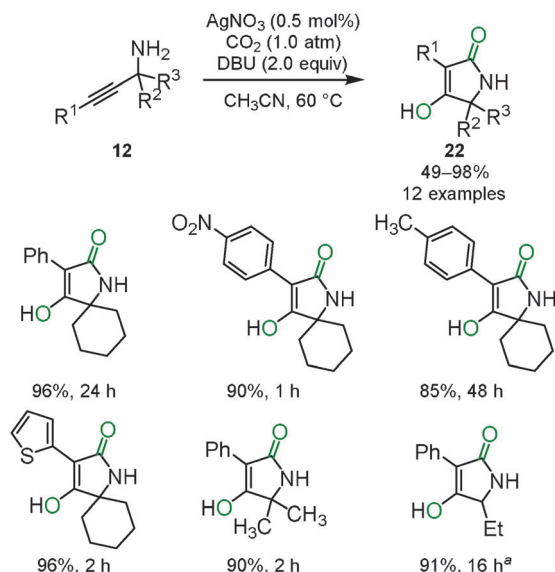
**Scheme 13** New approach for tetramic acids.

## 3. Sequential carboxylation and cyclization with C–C bond formation

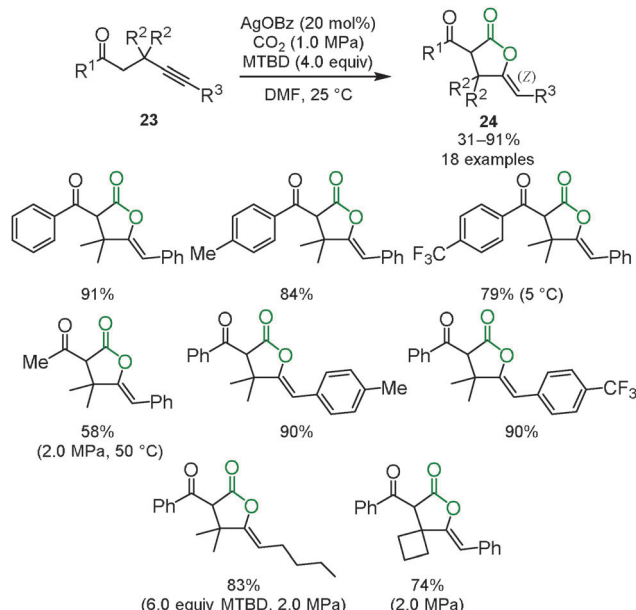
Propargyl alcohols and propargyl amines were converted to the corresponding cyclic carbonates and oxazolidinones in the presence of a transition metal, organic base, phosphine, or carbene catalyst. Though cyclic carbonates and oxazolidinones are important structures in the materials and pharmaceutical sciences, their hydrolysis would readily promote decarboxylation. To incorporate carbon dioxide into organic molecules, the formation of C–C bonds between the substrate and carbon dioxide is important. Cyclization following C–C bond forming carboxylation can afford the corresponding lactones that are not easily decarboxylated. In this chapter, the silver-catalyzed C–C bond forming carboxylation and cyclization reactions are described.

### 3.1 Enolate

Enolate has been a promising reagent for the C–C bond forming reactions in organic chemistry. The reactions of an enolate with carbon dioxide produce the corresponding  $\beta$ -ketocarboxylic acids.



**Scheme 14** Synthesis of tetramic acids by carbon dioxide incorporation and intramolecular rearrangement.



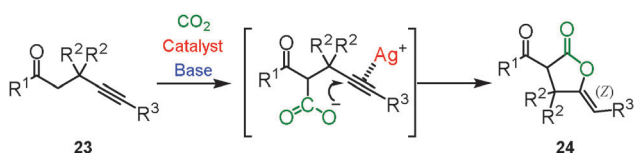
**Scheme 16** C–C bond formation with carbon dioxide for lactone derivatives.

Due to its thermodynamic instability, however,  $\beta$ -ketocarboxylic acid would easily revert to the starting material. Therefore, careful treatment or subsequent reduction of the product was required. A tandem reaction for the conversion of  $\beta$ -ketocarboxylic acid into a stable compound is one of the most reasonable methods for the reaction of an enolate and carbon dioxide. We reported that  $\beta$ -ketocarboxylate was trapped by the silver-activated C–C triple bond to afford the corresponding stable 5-membered lactone **24** in a one-pot synthesis (Scheme 15).<sup>30</sup> A good scope of substrates under the optimized reaction conditions was indicated (Scheme 16). Both aromatic and aliphatic ketones were suitable for this reaction.

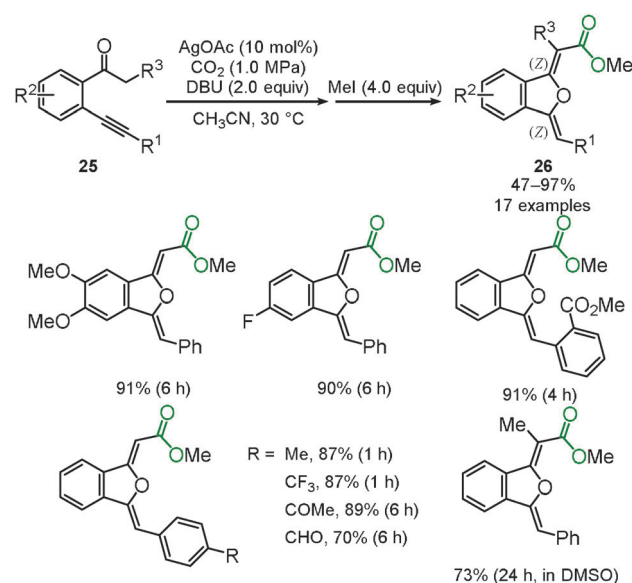
We and Lu's group achieved the transformation of  $\beta$ -ketocarboxylic acid to the dihydroisobenzofuran derivatives **26** at almost the same time (Schemes 17 and 18). The dihydroisobenzofurans bearing a carboxyl group were obtained by the 5-*exo*-dig cyclization of *o*-alkynylacetophenone **25** and carbon dioxide. The geometries of the two C–C double bonds were suggested to be *Z* isomers by NOE. The catalytic system showed the wide-range scope of the substrates; aldehydes and ketones were tolerable (Scheme 17).<sup>31</sup> DFT calculations suggested the plausible reaction mechanism (Scheme 18).<sup>32</sup> After the keto-enol tautomerism of the  $\beta$ -ketocarboxylic acid, the oxygen atom was trapped on the C–C triple bond activated by the silver catalyst. It was assumed that the geometry of the C–C double bond adjacent to the carbonyl group should be determined on the basis of the 6-membered enol form.

### 3.2 Allylsilane

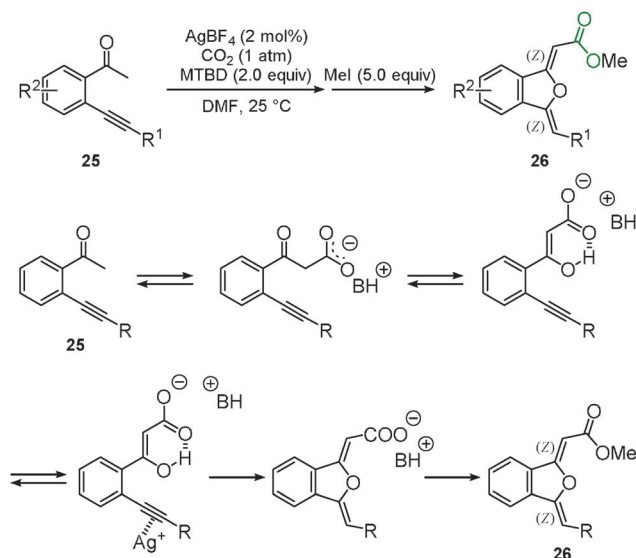
Recently, the silver-catalyzed cascade carboxylation and cyclization of the trimethyl(2-methylenebut-3-yn-1-yl)silane derivatives **27** were developed.<sup>33</sup> The allylsilane compound is one of the useful reagents for new C–C bond formation. For example, Hosomi-Sakurai allylation has been used to provide homoallyl alcohols, which are an important framework for the total synthesis of natural products and medicinal compounds. Though allylsilane compounds have the additional potential for carbon dioxide incorporation, few systems involving the Lewis acid mediated carboxylation have been reported.



**Scheme 15** Postulated reaction pathway.



**Scheme 17** Silver-catalyzed carboxylation and cyclization of *o*-alkynylacetophenones.



Scheme 18 Possible reaction mechanism.

The present reaction was promoted by a silver salt and CsF to afford the corresponding 2-furanones **28** and 2-pyrones **29** in good-to-high yields (Scheme 19). When aromatic ring-substituted alkynes were used, 2-furanone derivatives were selectively obtained *via* 5-*exo*-dig cyclization, whereas the reaction of the alkyl-substituted alkynes produced 2-pyrone derivatives with high selectivity.

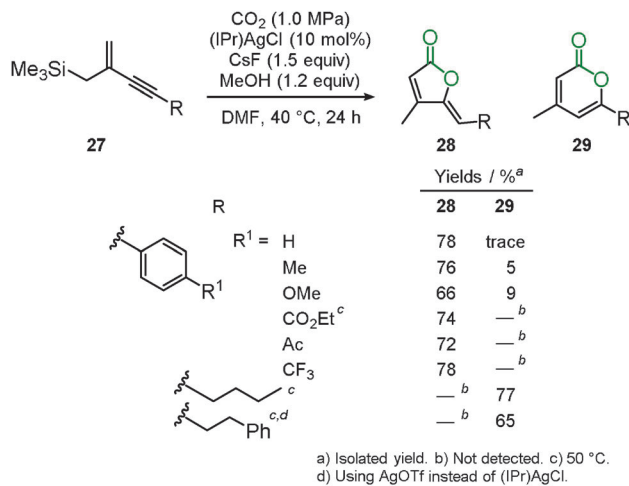
## 4. Other reactions

### 4.1 Carboxylation of terminal alkynes

The fundamental study of the carboxylation of terminal alkyne was reported by Saegusa's group. At this stage, it was found that silver acetylide **30** reacted with carbon dioxide using the appropriate ligand,  $n\text{Bu}_3\text{P}$ , to produce the corresponding propiolic acid methyl ester **31** after methylation (Scheme 20).<sup>34</sup>

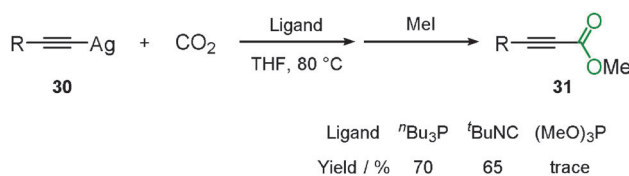
Lu and co-workers reported the silver-catalyzed carboxylation of terminal alkynes **32** using  $\text{Cs}_2\text{CO}_3$  under 0.2 MPa of carbon dioxide in DMF to afford the corresponding propiolic acids **33** (Scheme 21(a)).<sup>35</sup> In addition, Gooßen and co-workers found that the same reaction proceeded at the lower catalyst loading of  $\text{AgBF}_4$  (0.05–0.25 mol%) in DMSO (Scheme 21(b)).<sup>36,37</sup> Zhang's group developed a highly efficient and reusable N-heterocyclic carbene polymer-supported silver nanoparticle catalyst (poly-NHC-Ag). They found that the carboxylation of terminal alkynes was effectively promoted using 0.3 mol% of poly-NHC-Ag and 1.2 equiv. of  $\text{Cs}_2\text{CO}_3$  in DMSO even under 1 atm of carbon dioxide.<sup>38</sup>

Anastas's group reported that the three-component reaction between phenyl acetylene **32**, carbon dioxide and 3-bromo-1-phenyl-propyne **34** successfully proceeded in the presence of silver iodide and potassium carbonate in DMA to produce two isomers of the aryl naphthalene lactones **35** and **36** (Scheme 22).<sup>39</sup> During the first stage of the reaction, propiolic acid was produced by the carboxylation of the terminal alkyne. Propiolic acid then reacted with 3-bromo-1-phenyl-propyne to afford the corresponding



a) Isolated yield. b) Not detected. c) 50 °C. d) Using AgOTf instead of (IPr)AgCl.

Scheme 19 Silver-catalyzed reaction for the synthesis of 2-furanone and 2-pyrone.

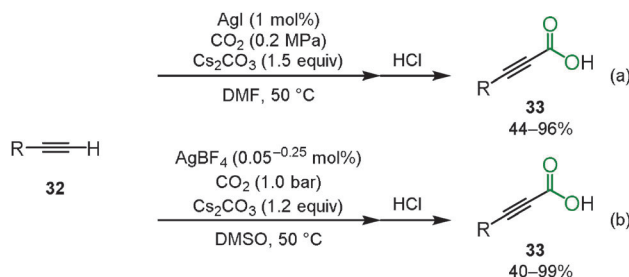


Scheme 20 Reaction of silver acetylide and carbon dioxide.

1,6-diyne compound. Finally, the [2+2+2] cyclization of the 1,6-diyne occurred to provide the two isomers of the aryl naphthalene lactones. The selectivity depended on the electronic properties of the aromatics of the terminal alkyne. Interestingly, in the case of gold iodide, no aryl naphthalene lactone was detected, but a 1,6-diyne compound was obtained. Copper iodide was ineffective in this reaction, though the 1,4-diyne compound was obtained from phenyl acetylene and 3-bromo-1-phenyl-propyne.

### 4.2 Carboxylation of arylboronic esters

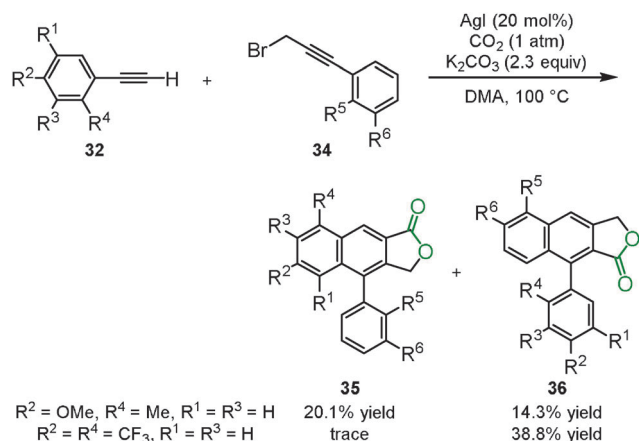
Lu, Zhang and co-workers reported the silver-catalyzed carboxylation of the arylboronic ester **37** with carbon dioxide (Scheme 23).<sup>40</sup> They hypothesized that based on the reaction mechanism of the rhodium- or copper-catalyzed carboxylation of organoboronic esters, carbon dioxide could insert into the silver-carbon bond which was generated by the transmetalation of the silver catalyst



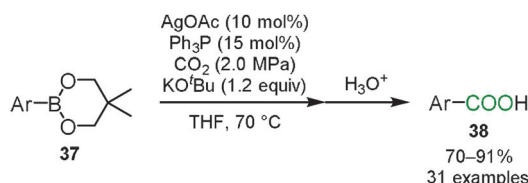
Scheme 21 Silver-catalyzed carboxylation of terminal alkynes.







Scheme 22 Silver-catalyzed one-pot synthesis of aryl naphthalene lactones.



Scheme 23 Carboxylation of arylboronic esters by silver catalysts.

with the arylboronic ester. The  $\text{Ph}_3\text{P}$  ligand played a key role in increasing the yield of the corresponding benzoic acids **38**.

## Conclusions

Recent developments in silver-catalyzed carboxylation chemistry using carbon dioxide were described. In some cases, silver catalysts showed an effective reactivity unlike other transition metals, including the coinage metals. The sequential carboxylation and cyclization of propargyl alcohols and amines were promoted by a simple silver salt or a highly efficient silver catalyst. Silver-catalyzed C–C bond forming reactions with carbon dioxide were also described.

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