DOI: 10.1002/adsc.201500921

# Atmospheric Pressure of $CO_2$ as Protecting Reagent and Reactant: Efficient Synthesis of Oxazolidin-2-ones with Carbamate Salts, Aldehydes and Alkynes

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Received: September 30, 2015; Published online: December 17, 2015

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201500921.

**Abstract:** Carbon dioxide ($CO_2$) has been wildly employed as an environmentally benign $C_1$ resource for organic synthesis in the recent years. The capture of $CO_2$ with primary amines easily provides the corresponding carbamate salts. We described herein that carbamate salts are a useful reactant for the synthesis of oxazolidin-2-ones *via* the reaction with aromatic aldehydes and aromatic terminal alkynes. A variety of oxazolidin-2-ones with different functional groups were synthesized in 68–91% yields with only a 5 mol% amount of CuI as catalyst. It was found that the synergetic effect of iodide is important for the transformation. Notable, the captured $CO_2$ serves not only as a protecting reagent for electron-rich primary amine to avoid catalyst poisoning, but also as a reactant for the construction of oxazolidin-2-ones.

**Keywords:** amines; carbon dioxide fixation; copper catalysis; oxazolidinone

## Introduction

Carbon dioxide ($CO_2$) has gained increasing attention due to its continuous accumulation in the atmosphere which is thought to be causing global warming.[1] A plethora of scientific effort has been devoted to the development of various approaches for reducing $CO_2$ emission, such as $CO_2$ capture and storage/sequestration (CCS).[2] Moreover, $CO_2$ is also regarded as a ubiquitous, abundant, cheap, and non-toxic $C_1$ resource for the production of useful chemicals.[3] One of the most attractive strategies for $CO_2$ fixation is $CO_2$ capture and utilization (CCU), which circumvents the energy consumption of the desorption step in CCS.[4]

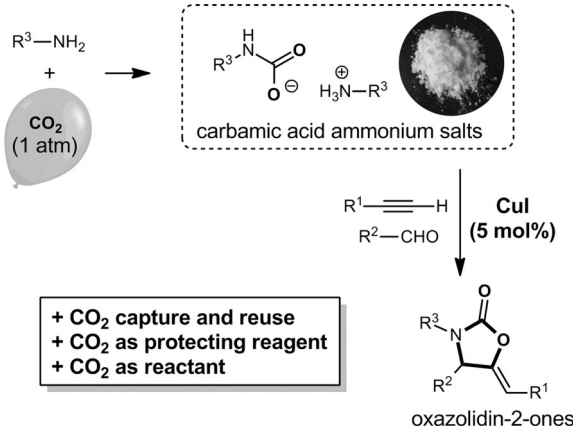
The oxazolidin-2-one framework has continued to capture the interest of chemists worldwide due to its important applications in organic synthesis and pharmaceutical chemistry.[5] Over the past decades, numerous methods have been developed for the synthesis of oxazolidin-2-one and its corresponding derivatives,[6] for example, through the reaction of glycerol carbonate or glycerol with urea,[7] the reaction of amino alcohols and aryl iodides,[8] [2+3] cycloadditions of isocyanates and epoxides.[9] Among the various methods for oxazolidin-2-one synthesis, protocols such as the coupling of $CO_2$ with aziridines,[10] amino alcohols,[11] amines/propargylic alcohols,[12] allenylmethylamines,[13] allylamines,[14] propargylic amines,[15] the utilization of $CO_2$ as a $C_1$ resource with high atom efficiency is highly attractive. However, the substrates or catalyst in those reactions were usually synthesized by tedious reaction procedures. In 2008, Li's group developed the first multicomponent reaction for oxazolidin-2-one synthesis *via* the coupling of a terminal alkyne, an aldehyde, an amine and an atmospheric pressure of $CO_2$.[16] Amine hydrochlorides under basic conditions were also employed for the multicomponent reaction.[17] Subsequently, the tandem decarboxylative/carboxylative cyclization using propiolic acid as $CO_2$ source was proven to be efficient for the synthesis of oxazolidin-2-ones by Eycken et al.[18] Jiang et al. developed a $CuI/SnCl_2$ catalytic system for the similar reaction using a ketone instead of an aldehyde as reactant under 1.5 MPa of $CO_2$.[19] Notably, all of these methodologies required a large amount of catalyst and additives (20–30 mol%), probably due to the fact

that electron-rich primary amines poison the catalyst and lead to deactivation.

In our continuing study on $CO_2$ utilization,[20] it is easy to find that nitrogen-containing compounds are potential absorbents for $CO_2$ capture. For instance, aliphatic primary amines easily trap $CO_2$ under mild conditions generating the corresponding carbamate salts, which are stable and easily handled. Carbamate salts have been employed as an organocatalyst for the Knoevenagel condensation. After reaction, the organocatalyst could be removed under vacuum to give the desired product without extraction, washing, or chromatography steps.[21] Carbamate salts were also used as stable alternatives for toxic liquid amines in the reaction with aldehydes to produce imines.[22] Additionally, compressed $CO_2$ can be applied as a temporary protecting group for the ring closing metathesis of an amine-containing diene[23] and hydroaminomethylation of *N*-ethylmethallylamine.[24] In the selective Michael additions and acylations, an atmospheric pressure of $CO_2$ was also used as a protecting group to inhibit the reaction of primary amines.[25] In the previous reports, however, the protecting reagent $CO_2$ was released as waste after the reaction. Inspired by these achievements, we envisioned that the employment of $CO_2$ as a protecting group and also as a reactant for the synthesis should be feasible, which avoids the emission of $CO_2$.

Herein, we describe our results on the synthesis of oxazolidin-2-ones *via* the CuI-catalyzed multicomponent reaction of carbamate salts, aldehydes and terminal alkynes (Scheme 1). The easily handled solid carbamate salts were generated from $CO_2$ and primary amines. In this procedure, the captured $CO_2$ not only acts as a reactant, but also acts as a protecting reagent for the amine to avoid poisoning of the copper catalyst under the reaction conditions. Importantly, a synergistic cooperation of copper and iodide was observed in the reaction.



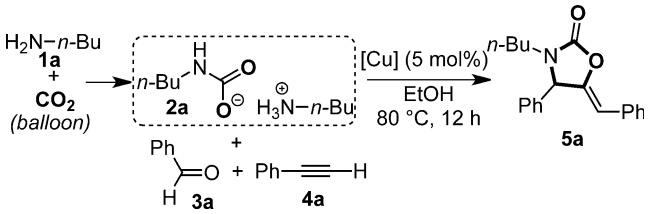

**Scheme 1.** Procedure for the construction of oxazolidin-2-ones from carbamates.

## Results and Discussion

We initiated our studies using *n*-butylamine (**1a**) as a model amine for the optimization of the reaction conditions. Firstly, the primary amine **1a** was treated with $CO_2$ from a balloon, easily affording butan-1-aminium butylcarbamate (**2a**) as a white solid. This solid compound **2a** was stable for months in a screw cap tube on a shelf at ambient temperature without any other protection. The multicomponent reaction of **2a**, benzaldehyde (**3a**), and phenylacetylene (**4a**) was performed in a screw cap vial with a Teflon seal using EtOH as solvent. Screening of various copper catalysts showed that the nature of the catalyst markedly affected the reaction (Table 1). A number of copper catalysts (5 mol%), including CuI, CuCl, CuBr, CuSCN, $Cu_2O$, $Cu(OTf)_2$, CuBr·DMS, CuTC, and $CuCl_2·2H_2O$ etc. were tested (entries 1–15). However, they displayed rather poor catalytic activity in the reaction except for CuI, which provided the product oxazolidin-2-one **5a** in 69% yield.

To improve the performance of the reaction, ligands[26] and Lewis acidic additives[19,27] were surveyed with CuI as catalyst (Table 2). In this reaction, however, $Ph_3P$, L-proline, $Ti(OEt)_4$, $H_3PW_{12}O_{40}$ were proven

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




| Entry | Catalyst | Yield [%][b] |
|---|---|---|
| 1 | CuI | 69 |
| 2 | CuBr | 19 |
| 3 | CuCl | 5 |
| 4 | CuSCN | 8 |
| 5 | $Cu_2O$ | <1 |
| 6 | $Cu(OTf)_2$ | 0 |
| 7 | $(CuOTf)_2$·toluene | 0 |
| 8 | CuBr·DMS | 2 |
| 9 | CuTC | <1 |
| 10 | $CuCl_2·2H_2O$ | 2 |
| 11 | $CuSO_4$ | <1 |
| 12 | $CuSO_4·5H_2O$ | <1 |
| 13 | $CuCO_3·Cu(OH)_2$ | <1 |
| 14 | $Cu(NO_3)_2·3H_2O$ | <1 |
| 15 | $Cu(OAc)_2·H_2O$ | <1 |

[a] *Reaction conditions:* carbamic acid ammonium salt (1 mmol), aldehyde (2 mmol), alkyne (2 mmol), EtOH (0.4 mL), Cu catalyst (5 mol% based on Cu), 80 °C, 12 h.
[b] The yields were determined by GC with biphenyl as the internal standard. DMS = dimethyl sulfide, CuTC = copper(I) thiophene-2-carboxylate.

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

| Entry | Solvent/Additives | Yield [%][b] |
|---|---|---|
| 1 | EtOH/$Ph_3P$ | 70 |
| 2 | EtOH/L-Proline | 49 |
| 3 | EtOH/$Ti(OEt)_4$ | 59 |
| 4 | EtOH/$H_3PW_{12}O_{40}$ | 27 |
| 5 | $CH_3OH$ | 55 |
| 6 | glycol | 54 |
| 7 | diethylene glycol | 53 |
| 8 | PhCl | 20 |
| 9 | DMF | 59 |
| 10 | EtOAc | 19 |
| 11 | $PhCH_3$ | 7 |
| 12 | PhCN | 27 |
| 13 | THF | 30 |
| 14 | $CH_2Cl_2$ | 9 |
| 15 | *i*-PrOH | 79 |
| 16[c] | *i*-PrOH | 89 |

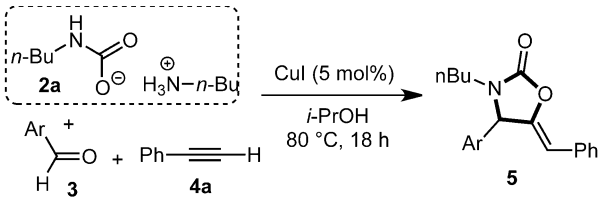
[a] *Reaction conditions unless otherwise specified:* carbamic acid ammonium salt (1 mmol), aldehyde (2 mmol), alkyne (2 mmol), solvent (0.4 mL), CuI (5 mol%), 80 °C, 12 h.
[b] The yields were determined by GC with biphenyl as the internal standard.
[c] 18 h

to be ineffective (Table 2, entries 1–4). Further examination of solvents revealed that *i*-PrOH exhibits somewhat higher performance (79%) than EtOH and other solvents under identical conditions for the reaction (Table 2, entries 5–15). In addition, an improved yield (89%) was then observed when the reaction time was extended to 18 h using *i*-PrOH as solvent (Table 2, entry 16).

Having established the optimal conditions, we then converted a variety of commercially available aldehydes **3** into the corresponding oxazolidin-2-ones **5** to further explore the scope of this $CO_2$ transformation procedure. As showed in Table 3, aromatic aldehydes bearing either electron-donating or electron-withdrawing groups, including 4-Me, 4-MeO, 3-MeO, 2-MeO, 4-Cl, 2-Cl, 4-OH, and 4-CN on the phenyl ring were found to be reactive affording the isolated products **5a**–**5i** with moderate to excellent yields (68–91%). Substrate **3i** was poorly soluble in *i*-PrOH and thus gave the corresponding products **5i** in lower yield (entry 9). Unfortunately, aliphatic aldehydes, for example, 1-octanal gave the corresponding oxazolidin-2-one in poor yield (results not shown).

After having demonstrated that the protocol is compatible with a wide range of aldehydes, an investigation of the scope with respect to the primary amines and terminal alkynes was undertaken (Table 4). Primary amines such as cyclopentylamine **1b**, cyclohexylamine **1c**, and benzylamine **1d** were easily converted into the corresponding carbamate salts as white solids by bubbling $CO_2$ gas into the liquid amines. The carbamate salts were effective substrates for reaction with benzaldehyde **3a** and phenylacetylene **4a** to smoothly provide the products **5j**–**5l** in 74–85% yields under the standard conditions. How-

**Table 3.** Scope of aldehydes for the multicomponent reaction.[a]



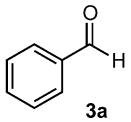
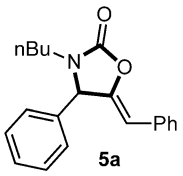
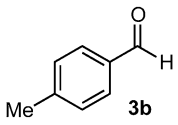
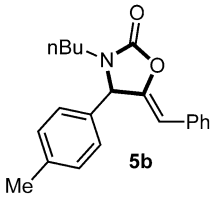
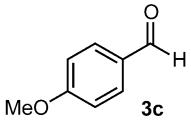
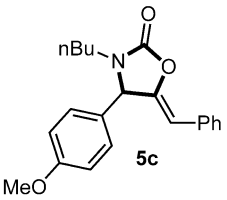
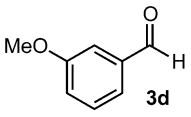
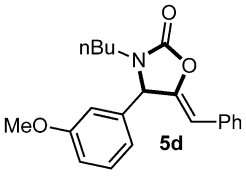
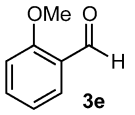
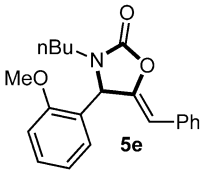
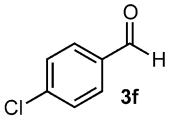
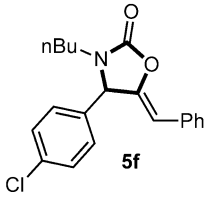
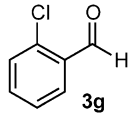
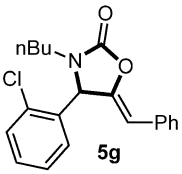
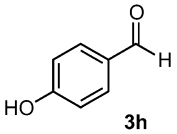
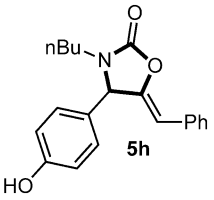
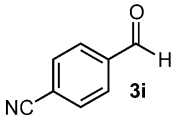
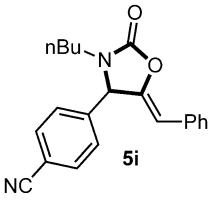

| Entry | 3 | 5 | Yield [%][b] |
|---|---|---|---|
| 1 |  |  | 84 |
| 2 |  |  | 88 |
| 3 |  |  | 91 |
| 4 |  |  | 86 |
| 5 |  |  | 87 |
| 6 |  |  | 82 |

**Table 3.** (Continued)

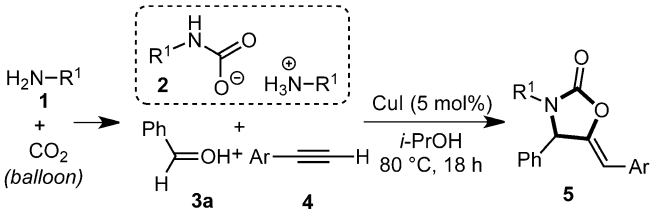
| Entry | 3 | 5 | Yield [%][b] |
|---|---|---|---|
| 7 |  **3g** |  **5g** | 74 |
| 8 |  **3h** |  **5h** | 81 |
| 9 |  **3i** |  **5i** | 68 |

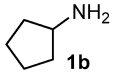
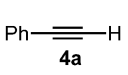
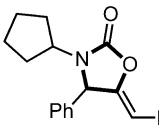
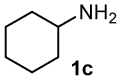
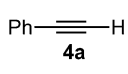
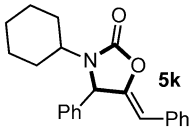
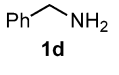
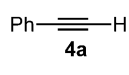
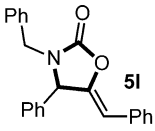
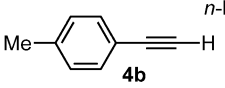
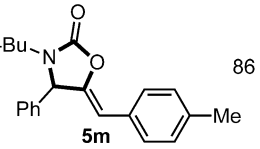
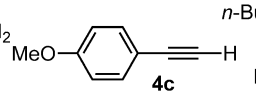
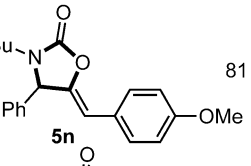
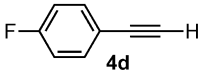
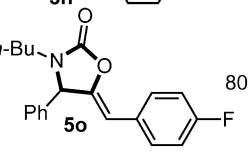
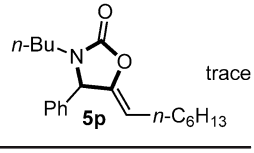
[a] *Reaction conditions:* carbamic acid ammonium salt **2a** (1 mmol), aldehyde **3** (2 mmol), alkyne **4a** (2 mmol), *i*-PrOH (0.4 mL), CuI (5 mol%), 80 °C, 18 h.
[b] Isolated yields were given.

ever, phenylamine failed to afford the desired carbamate salt after bubbling $CO_2$, which revealed that the electron-rich amine is beneficial to our protocol (results not shown). Subsequently, the substituted phenylacetylenes **4b**–**4d** were briefly screened for the construction of oxazolidin-2-ones. It was found that phenylacetylenes with electron-withdrawing substituents and electron-donating substituents at the *para*-position, including Me, MeO, F groups, showed good reactivity, and the corresponding products **5m**–**5o** were obtained in 80–86% yields. However, only a trace amount of **5p** was detected by GC-MS when the aliphatic alkyne **4e** was used. A density functional theory calculation [B3LYP/6–31G(d,p) level] indicated that the negative charge on the C-1 carbon of phenylacetylene is −0.533 and that of 1-octyne is −0.468, which suggested that the nucleophilicity of 1-octyne is weaker.[28]

To gain insight into the effect of the unique CuI catalysis, we performed some control experiments using 5 mol% of CuBr as catalyst, 5 mol% of KI as external iodide under otherwise identical conditions. To our surprise, the product **5a** was obtained in 84% yield (Table 5, entry 1). However, 5 mol% of KI alone does not catalyze this transformation (entry 2). On the other hand, the reaction catalyzed by $ZnBr_2$/KI failed under the given reaction conditions, demonstrating the importance of copper (entry 3). Although

**Table 4.** Scope of amines and alkynes for the multicomponent reaction.[a]




| Entry | 1 | 4 | 5 | Yield {%}[b] |
|---|---|---|---|---|
| 1 |  **1b** |  **4a** |  **5j** | 74 |
| 2 |  **1c** |  **4a** |  **5k** | 78 |
| 3 |  **1d** |  **4a** |  **5l** | 85 |
| 4 | *n*-Bu−NH$_2$ **1a** |  **4b** |  **5m** | 86 |
| 5 | *n*-Bu−NH$_2$ **1a** |  **4c** |  **5n** | 81 |
| 6 | *n*-Bu−NH$_2$ **1a** |  **4d** |  **5o** | 80 |
| 7 | *n*-Bu−NH$_2$ **1a** | $C_6H_{13}$-*n* **4e** |  **5p** | trace |

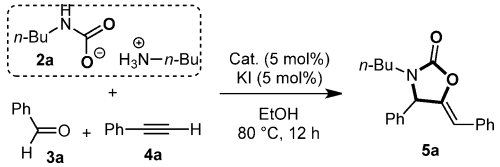
[a] *Reaction conditions:* carbamic acid ammonium salt **2** (1 mmol), aldehyde **3a** (2 mmol), alkyne **4** (2 mmol), *i*-PrOH (0.4 mL), CuI (5 mol%), 80 °C, 18 h.
[b] Isolated yields were given.

further studies are required to clarify the precise mechanism of this CuI catalysis, it was revealed that iodide has an excellent synergistic effect for promoting this copper-catalyzed reaction (Table 5, entry 1 *vs.* Table 1, entry 2).

Based on the above experimental results, we propose a reaction pathway for this copper-catalyzed

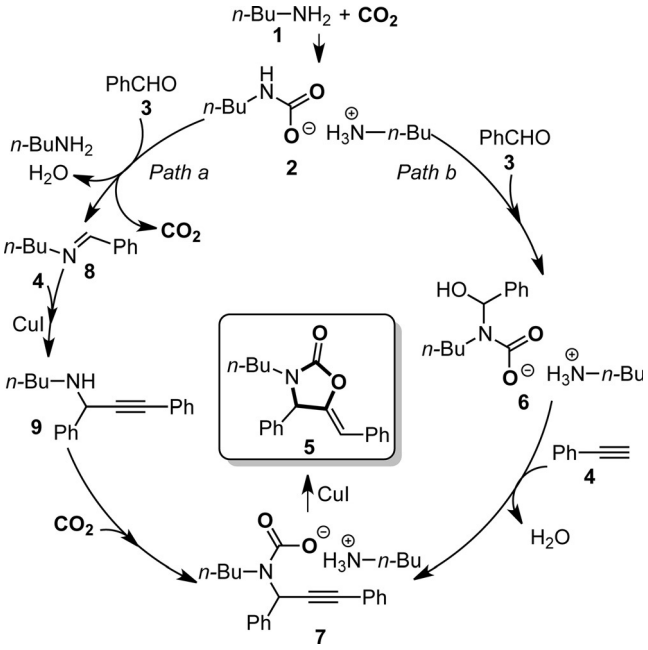
**Table 5.** Control experiments.[a]




| Entry | Catalyst/Additive | Yield [%][b] |
|---|---|---|
| 1 | CuBr/KI | 84 |
| 2 | –/KI | 0 |
| 3 | $ZnBr_2$/KI | 0 |

[a] *Reaction conditions:* carbamic acid ammonium salt (1 mmol), aldehyde (2 mmol), alkyne (2 mmol), catalyst (5 mol%), KI (5 mol%), 80 °C, 12 h in EtOH (0.4 mL).
[b] The yields were determined by GC with biphenyl as the internal standard.

transformation (Scheme 2). The carbamic acid ammonium salt **2** was easily formed by the capture of $CO_2$ with primary amine **1**. Then two plausible pathways were postulated for the subsequent conversion. For path *a*: carbamate salt **2** reacted with aldehyde **3** affording imine **8** with the release of one equivalent of water and $CO_2$. The imine **8** was attacked by the nucleophilic terminal alkyne **4** under catalysis of CuI giving propargylic amine **9** which then trapped the *in situ* released $CO_2$ and was followed by an intramolecular cyclization to generate the heterocycle product **5**. For path *b*: as an alternative, the formation of **7** may proceed by an addition of **2** and **3**, followed by a nucleophilic addition of **4** without the decarboxylation




**Scheme 2.** Proposed reaction pathway for the reaction.

of **2**. To corroborate the reaction pathways outlined in Scheme 2, we carried out a mass spectrometric (MS) study. The GC-mass spectrum for the reaction shows peaks of intermediates **8** and **9**, in agreement with the mechanism proposed by Li.[16] On the other hand, the weak signal of a negative ion at $m/z = 222$ was observed in the ESI-MS, suggesting that the intermediate **6** was probably generated.

## Conclusions

In summary, we have described an efficient catalyic protocol using only 5 mol% of CuI as catalyst for the reaction of carbamate salts, aromatic aldehydes, and aromatic terminal alkynes to produce the important oxazolidin-2-ones. In this work, $CO_2$ captured by primary amines served as a protecting reagent to avoid poisoning of the transition metal catalyst and simultaneously as a reactant for the construction of the heterocycles. By using this strategy, the multicomponent reaction can proceed smoothly without any other protection. In addition, a series of oxazolidin-2-one derivatives bearing different functional groups was synthesized in moderate to good yields. Further studies to expand the application of this concept are ongoing in our laboratory.

## Experimental Section

### General Information

The starting materials are commercially available and were used without further purification. The products were isolated by column chromatography on silica gel (200–300 mesh) using petroleum ether (60–90 °C) and ethyl acetate. All compounds were characterized by $^1$H NMR, $^{13}$C NMR and mass spectroscopy (MS), and the results are consistent with those reported in the literature. NMR spectra were determined on a Bruker 400 MHz instrument in $CDCl_3$. $^1$H NMR chemical shifts were referenced to residual solvent as determined relative to $CDCl_3$ (7.26 ppm). The $^{13}$C NMR chemical shifts were reported in ppm relative to the carbon resonance of $CDCl_3$ (central peak is 77.0 ppm). $^1$H NMR peaks are labeled as singlet (s), doublet (d), triplet (t), and multiplet (m). The coupling constants, *J*, are reported in Hertz (Hz). GC-MS data were obtained on an Agilent 7890A. GC analyses were performed on a Shimadzu GC-2014 equipped with a capillary column (HP-5 30 m × 0.25 μm) using a flame ionization detector.

### Synthesis of Carbamate Salts from $CO_2$ and Primary Amines

To a reaction tube, liquid amine (10 mmol) was added. Then $CO_2$ gas was bubbled into the amine using a balloon. The reaction is strongly exothermic. After about 5 min, the corresponding carbamate salt was generated as white solid.

### Typical Procedure for the Synthesis of Oxazolidin-2-ones

To a 10-mL reaction tube, the copper catalyst (5 mol%), solvent (0.4 mL), alkyne (2 mmol), aldehyde (2 mmol), and carbamate salt (1 mmol) were added. The reactions were carried out in screw cap vials with a Teflon seal at 80 °C for 18 h. The reaction mixture was allowed to cool to room temperature and the crude reaction mixture was further purified by column chromatography (silica gel, petroleum ether/EtOAc) to afford the desired product oxazolidinones.

### Characterization Data of Oxazolidin-2-ones

**(*Z*)-5-Benzylidene-3-butyl-4-phenyloxazolidin-2-one (5a):** $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.53–7.51 (m, 2H), 7.44–7.42 (m, 3H), 7.35–7.28 (m, 4H), 7.20–7.17 (m, 1H), 5.38 (d, 1H, $J$ = 2.0 Hz), 5.25 (d, 1H, $J$ = 2.0 Hz), 3.55–3.48 (m, 1H,), 2.86–2.80 (m, 1H), 1.46–1.44 (m, 2H), 1.29–1.25 (m, 2H), 0.88 (t, 3H, $J$ = 7.4 Hz); $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ = 155.1, 147.7, 137.3, 133.5, 129.4, 129.3, 128.4, 128.3, 127.8, 126.9, 104.5, 63.9, 41.6, 29.0, 19.8, 13.6; HR-MS (ESI): $m/z$ = 330.1471, calcd. for $C_{20}H_{21}NO_2Na$ $[M+Na]^+$: 330.1465; EI-MS: $m/z$ (%) = 180.10 (100), 307.20 (41) $[M^+]$.

**(*Z*)-5-Benzylidene-3-butyl-4-(*p*-tolyl)oxazolidin-2-one (5b):** $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.50–7.48 (m, 2H), 7.24–7.11 (m, 7H), 5.29 (s, 1H), 5.21 (s, 1H), 3.47–3.44 (m, 1H), 2.81–2.77 (m, 1H), 2.33 (s, 3H), 1.43–1.38 (m, 2H), 1.28–1.21 (m, 2H), 0.87 (t, 3H, $J$ = 7.6 Hz); $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ = 154.7, 147.8, 139.0, 134.0, 133.3, 129.7, 128.1, 128.0, 127.5, 126.5, 104.0, 63.3, 41.2, 28.6, 20.9, 19.5, 13.3; HR-MS (ESI): $m/z$ = 344.1636, calcd. for $C_{21}H_{23}NO_2Na$ $[M+Na]^+$: 344.1621; EI-MS: $m/z$ (%) = 194.10 (100), 321.20 (34) $[M^+]$.

**(*Z*)-5-Benzylidene-3-butyl-4-(4-methoxyphenyl)oxazolidin-2-one (5c):** $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.52–7.50 (m, 2H), 7.30–7.28 (m, 3H), 7.23–7.18 (m, 1H), 7.17–7.15 (m, 1H), 6.94–6.92 (m, 2H), 5.34 (d, 1H, $J$ = 2.0), 5.24 (d, 1H, $J$ = 2.0), 3.81 (s, 1H), 3.48–3.43 (m, 1H), 2.83–2.79 (m, 1H), 1.46–1.42 (m, 2H), 1.29–1.25 (m, 2H), 0.87 (t, 3H, $J$ = 7.8 Hz); $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ = 160.2, 154.8, 148.0, 133.4, 129.1, 129.0, 128.3, 128.2, 126.7, 114.5, 104.2, 63.3, 55.2, 41.4, 28.8, 19.7, 13.5; HR-MS (ESI): $m/z$ = 360.1595, calcd. for $C_{21}H_{23}NO_3Na$ $[M+Na]^+$: 360.1570; EI-MS: $m/z$ (%) = 210.10 (100), 337.20 (18) $[M^+]$.

**(*Z*)-5-Benzylidene-3-butyl-4-(3-methoxyphenyl)oxazolidin-2-one (5d):** $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.53–7.51 (m, 2H), 7.36–7.26 (m, 3H), 7.20–7.18 (m, 1H), 6.95–6.91 (m, 2H), 6.84–6.83 (m, 1H), 5.35 (d, 1H, $J$ = 2.0), 5.28 (d, 1H, $J$ = 2.0), 3.82 (s, 3H), 3.55–3.51 (m, 1H), 2.86–2.82 (m, 1H), 1.49–1.45 (m, 2H), 1.33–1.26 (m, 2H), 0.89 (t, 3H, $J$ = 7.8 Hz); $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ = 160.3, 155.0, 147.4, 138.8, 133.4, 130.3, 128.4, 128.3, 126.9, 120.0, 114.6, 113.1, 104.4, 63.7, 55.3, 41.6, 28.9, 19.8, 13.6; HR-MS (ESI): $m/z$ = 360.1595, calcd. for $C_{21}H_{23}NO_3Na$ f$[M+Na]^+$: 360.1570; EI-MS: $m/z$ (%) = 210.10 (100), 337.20 (18) $[M^+]$.

**(*Z*)-5-Benzylidene-3-butyl-4-(2-methoxyphenyl)oxazolidin-2-one (5e):** $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.54–7.52 (m, 2H), 7.38–7.34 (m, 1H), 7.29–7.22 (m, 3H), 7.17–7.14 (m, 1H), 7.00–6.93 (m, 2H), 5.71 (s, 1H), 5.31 (s, 1H), 3.84 (s, 1H), 3.54–3.46 (m, 1H), 2.77–2.73 (m, 1H), 1.46–1.45 (m, 2H), 1.30–1.26 (m, 2H), 0.87 (t, 3H, $J$ = 7.8 Hz); $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ = 157.8, 155.4, 147.6, 133.8, 130.4, 128.3, 128.1, 126.4, 125.1, 120.9, 111.3, 102.6, 55.6, 41.4, 29.0, 19.7, 13.5; HR-MS (ESI): $m/z$ = 360.1593, calcd. for $C_{21}H_{23}NO_3Na$ $[M+Na]^+$: 360.1570; EI-MS: $m/z$ (%) = 210.10 (100), 337.20 (47) $[M^+]$.

**(*Z*)-5-Benzylidene-3-butyl-4-(4-chlorophenyl)oxazolidin-2-one (5f):** $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.55–7.50 (m, 2H), 7.40–7.38 (m, 2H), 7.33–7.25 (m, 4H), 7.20–7.16 (m, 1H), 5.35 (s, 1H), 5.22 (s, 1H), 3.51–3.47 (m, 1H), 2.82–2.79 (m, 1H), 1.46–1.40 (m, 2H), 1.29–1.26 (m, 2H), 0.88 (t, 3H, $J$ = 7.6 Hz); $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ = 154.7, 147.1, 135.8, 135.2, 133.1, 131.6, 129.4, 129.0, 128.2, 126.9, 104.7, 63.0, 41.5, 28.8, 19.6, 13.5; HR-MS (ESI): $m/z$ = 364.1095, calcd. for $C_{20}H_{20}ClNO_2Na$ $[M+Na]^+$: 364.1075; EI-MS: $m/z$ (%) = 214.10 (100), 341.20 (36) $[M^+]$.

**(*Z*)-5-Benzylidene-3-butyl-4-(2-chlorophenyl)oxazolidin-2-one (5g):** $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.78–7.76 (m, 1H), 7.51–7.25 (m, 8H), 5.25 (s, 1H), 5.07 (s, 1H), 3.37–3.33 (m, 1H), 2.63–2.61 (m, 1H), 1.44–1.40 (m, 2H), 1.29–1.26 (m, 2H), 0.89 (t, 3H, $J$ = 7.8 Hz); $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ = 155.03, 146.28, 137.87, 133.16, 131.64, 129.67, 129.21, 128.92, 128.34, 128.29, 127.03, 122.92, 104.06, 51.74, 41.65, 31.90, 19.71, 13.52; HR-MS (ESI): $m/z$ = 364.1104, calcd. for $C_{20}H_{20}ClNO_2Na$ $[M+Na]^+$: 364.1075; EI-MS: $m/z$ (%) = 179.10 (100), 341.10 (43) $[M^+]$.

**(*Z*)-5-Benzylidene-3-butyl-4-(4-hydroxyphenyl)oxazolidin-2-one (5h):** $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 9.84 (s, 1H), 7.81–7.79 (m, 2H), 7.50–7.48 (m, 2H), 7.29–7.20 (m, 2H), 7.18–7.17 (m, 3H), 5.36 (s, 1H), 5.27 (s, 1H), 3.49–3.44 (m, 1H), 2.85–2.81 (m, 1H), 1.29–1.27 (m, 2H), 1.26–1.25 (m, 2H), 0.87 (t, 3H, $J$ = 7.4 Hz); $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ = 156.9, 155.5, 147.8, 132.5, 129.4, 128.4, 128.3, 127.0, 116.1, 116.2, 104.7, 63.5, 41.5, 28.9, 19.7, 13.6; HR-MS (ESI): $m/z$ = 346.1433, calcd. for $C_{20}H_{21}NO_3Na$ $[M+Na]^+$: 346.1414; EI-MS: $m/z$ (%) = 196.10 (100), 323.20 (21) $[M^+]$.

**(*Z*)-4-(5-Benzylidene-3-butyl-2-oxooxazolidin-4-yl)-benzonitrile (5i):** $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.78–7.77 (m, 2H), 7.48–7.45 (m, 4H), 7.29–7.24 (m, 2H), 7.18–7.16 (m, 1H), 5.43 (s, 1H), 5.20 (s, 1H), 3.54–3.52 (m, 1H), 2.80–2.81 (m, 1H), 1.46–1.40 (m, 2H), 1.29–1.26 (m, 2H), 0.87 (t, 3H, $J$ = 7.4 Hz); $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ = 154.9, 146.1, 142.4, 133.5, 132.4, 128.4, 128.3, 128.3, 127.0, 117.7, 113.2, 104.7, 63.5, 41.5, 28.9, 19.7, 13.6; HR-MS (ESI): $m/z$ = 355.1426, calcd. for $C_{21}H_{21}NO_2Na$ $[M+Na]^+$: 355.1418; EI-MS: $m/z$ (%) = 205.10 (100), 332.20 (56) $[M^+]$.

**(*Z*)-5-Benzylidene-3-cyclopentyl-4-phenyloxazolidin-2-one (5j):** $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.59–7.57 (m, 1H), 7.48–7.35 (m, 2H), 7.29–7.24 (m, 6H), 7.18–7.16 (m, 1H), 5.38 (s, 1H), 5.17 (s, 1H), 3.83–3.79 (m, 1H), 1.90–1.88 (m, 2H), 1.76–1.71 (m, 2H), 1.47–1.43 (m, 4H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ = 154.5, 148.0, 139.1, 133.5, 131.6, 129.1, 128.3, 128.2, 127.5, 126.7, 104.1, 64.2, 55.9, 29.6, 24.1; HR-MS (ESI): $m/z$ = 342.1482, calcd. for $C_{21}H_{21}NO_2Na$ $[M+Na]^+$: 342.1465; EI-MS: $m/z$ (%) = 180.10 (100), 319.10 (42) $[M^+]$.

**(*Z*)-5-Benzylidene-3-cyclohexyl-4-phenyloxazolidin-2-one (5k):** $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.56–7.54 (m, 2H), 7.42–7.39 (m, 3H), 7.36–7.31 (m, 5H), 7.22–7.19 (m, 1H), 5.43 (s, 1H), 5.20 (s, 1H), 3.61–3.55 (m, 1H), 1.82–1.75 (m, 3H), 1.71–1.66 (m, 3H), 1.36–1.23 (m, 5H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ = 154.5, 148.2, 139.4, 133.4, 131.6, 129.0, 128.4, 128.1, 127.6, 126.6, 104.0, 63.0, 54.5, 31.0, 25.5, 24.9; HR-MS (ESI): $m/z$ = 356.1642, calcd. for $C_{22}H_{23}NO_2Na$

$[M+Na]^+$: 356.1621; EI-MS: *m/z* (%) = 180.10 (100), 333.20 (39) $[M^+]$.

**(*Z*)-3-Benzyl-5-benzylidene-4-phenyloxazolidin-2-one (5l):** $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.61–7.60 (m, 2H), 7.41–7.39 (m, 3H), 7.32–7.29 (m, 8H), 7.26–7.24 (m, 2H), 5.17 (s, 1H), 5.12 (s, 1H), 3.99 (s, 2H); $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ = 155.0, 147.4, 140.2, 139.7, 136.7, 134.7, 133.3, 131.7, 129.3, 128.8, 128.4, 127.6, 127.0, 123.0, 104.7, 62.7, 45.4; HR-MS (ESI): *m/z* = 364.1335, calcd. for $C_{23}H_{19}NO_2Na$ $[M+Na]^+$: 364.1308; EI-MS: *m/z* (%) = 91.10 (100), 341.10 (36) $[M^+]$.

**(*Z*)-3-Butyl-5-(4-methylbenzylidene)-4-phenyloxazolidin-2-one (5m):** $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.42–7.25 (m, 7H), 7.11–7.09 (m, 2H), 5.37 (s, 1H), 5.21 (s, 1H), 3.54–3.47 (m, 1H), 2.85–2.80 (m, 1H), 2.31 (s, 3H), 1.47–1.43 (m, 2H), 1.31–1.25 (m, 2H), 0.87 (t, 3H, *J* = 7.4 Hz); $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ = 155.1, 146.9, 137.4, 136.7, 130.6, 129.3, 129.2, 129.1, 128.2, 127.8, 104.4, 63.8, 41.6, 28.9, 21.2, 19.8, 13.6; HR-MS (ESI): *m/z* = 344.1666, calcd. for $C_{21}H_{23}NO_2Na$ $[M+Na]^+$: 344.1621; EI-MS: *m/z* (%) = 194.10 (100), 321.20 (49) $[M^+]$.

**(*Z*)-3-Butyl-5-(4-methoxybenzylidene)-4-phenyloxazolidin-2-one (5n):** $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.59–7.57 (m, 1H), 7.47–7.36 (m, 3H), 7.33–7.31 (m, 2H), 6.84–6.82 (m, 3H), 5.36 (s, 1H), 5.19 (s, 1H), 3.78 (s, 1H), 3.52–3.46 (m, 1H), 2.85–2.79 (m, 1H), 1.46–1.43 (m, 2H), 1.30–1.26 (m, 2H), 0.87 (t, 3H, *J* = 7.8 Hz); $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ = 158.4, 155.1, 145.9, 137.5, 133.0, 129.6, 129.2, 127.7, 126.2, 113.8, 104.0, 63.7, 55.2, 41.5, 28.9, 19.7, 13.6; HR-MS (ESI): *m/z* = 360.1587, calcd. for $C_{21}H_{23}NO_3Na$ for $[M+Na]^+$: 360.1570; EI-MS: *m/z* (%) = 210.10 (100), 337.20 (38) $[M^+]$.

**(*Z*)-3-Butyl-5-(4-fluorobenzylidene)-4-phenyloxazolidin-2-one (5o):** $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.50–7.42 (m, 5H), 7.39–7.31 (m, 2H), 6.98–6.94 (m, 2H), 5.37 (s, 1H), 5.21 (s, 1H), 3.52–3.47 (m, 1H), 2.86–2.81 (m, 1H), 1.48–1.40 (m, 2H), 1.30–1.22 (m, 2H), 0.87 (t, 3H, *J* = 7.8 Hz); $^{13}$C NMR ($CDCl_3$, 100.6 MHz): $\delta$ = 162.7, 160.2, 154.8, 147.3, 137.1, 133.5, 129.9, 129.3, 128.5, 127.7, 115.3, 103.3, 63.7, 41.5, 28.8, 19.7, 13.5; HR-MS (ESI): *m/z* = 348.1383, calcd. for $C_{20}H_{20}FNO_2Na$ $[M+Na]^+$: 348.1370; EI-MS: *m/z* (%) = 198.10 (100), 325.10 (39) $[M^+]$.

## Acknowledgements

*We thank the Natural Science Foundation of China (21173021, 21231002, 21276026, 21501010), 973 Program (2014CB932103) for financial support. B.Y. is grateful for the financial support from China Postdoctoral Science Foundation funded project (2015M570939) and BIT Basic Research Foundation (20141942004).*

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