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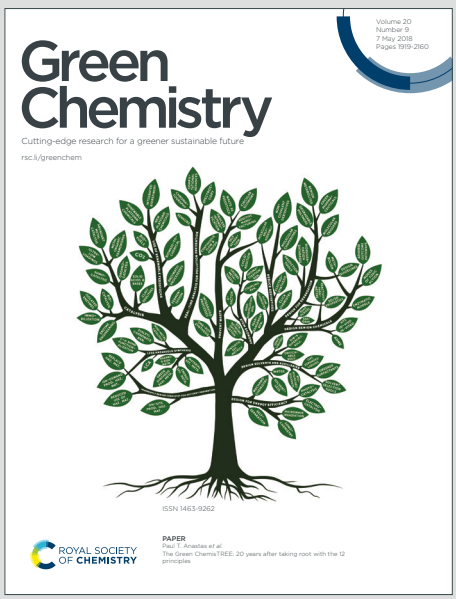

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# Silver(I)-catalysed carboxylative cyclisation of primary propargylic amines in neat water using potassium bicarbonate as the carboxyl source: environment-friendly synthesis of Z-5-alkylidene-1,3-oxazolidin-2-ones

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

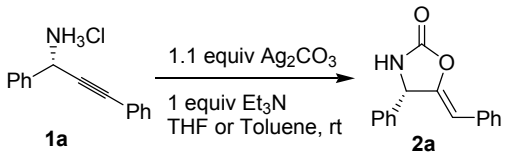
www.rsc.org/

Jian-Feng Qin, [a] Bing Wang*[b] and Guo-Qiang Lin [a,b]

Herein we report a mild and environment-friendly synthesis of Z-5-alkylidene-2-oxazolidinones in neat water, using a low loading (2 mol%) of silver carbonate as the catalyst. Instead of pressurised gaseous carbon dioxide, potassium bicarbonate was used as the source of carboxyl. An interesting solvent effect and a C–N cleavage side reaction with a 6-endo-dig mechanism is also discussed.

## Introduction

Oxazolidinone is the key structural motif of Evans-type chiral auxiliaries which have found tremendously wide applications in asymmetric synthesis.[1] Meanwhile, it is also present in many biologically active compounds including the antibiotic drug Linezolid.[2] The incorporation of an enol functionality in 5-alkylidene-2-oxazolidinone enables further molecular decoration, providing access to value-added chemicals. Typically, the synthesis of 5-alkylidene-2-oxazolidinones involves a metal-catalysed carboxylative cyclisation of propargylic amines with carbon dioxide, which was reported by Mitsudo and Watanabe in 1987.[3] Li and co-worker developed a Cu-catalysed four-component reaction[4] based on $A^3$-coupling.[5] Yamada's group extended the scope of substrate to primary propargylic amines with a silver-catalysed protocol in 2009.[6] Later, the groups of Ikariya and Fujita independently reported procedures using gold(I)-NHC complexes as the catalyst.[7, 8] Very recently, Bourissou and co-workers achieved carboxylative cyclisation of multiple types of propargylic amines using a Pd SCS pincer complex.[9] Superbases and triethanolamine were also found to effect this transformation, however the scope was rather limited.[10] Spontaneous cyclisation of certain type of propargylic amines was also observed in supercritical carbon dioxide.[11] Alternatively, N-Boc propargylic amines also underwent cyclisation by using gold-catalysis.[12] Nevado's group developed a Pd-catalysed tandem cyclisation-cross-coupling sequence which enabled introduction of an additional substituent on the alkylidene side chain.[13] It should be noted that these previous works require either expensive and exotic catalysts, organic solvents such as toluene or DMSO, specialised equipment, or harsh conditions. Only a few are reported to be applicable to primary propargylic amines due to their lower nucleophilicity.[6,9] Regarding the alkyne moiety, alkyl-substituted internal triple bond remains a class of difficult substrate. Last but not least, no protocol that uses water or aqueous media as the solvent has been reported so far.[14] Therefore, developing a synthetic method that is general in substrate scope, economic in reagent and catalyst, while at the same time meeting the requirements of green and sustainable chemistry, is still a challenge.




**Scheme 1.** $Ag_2CO_3$ promoted carboxylative cyclisation of propargylic amine.

As our continued interest in the chemistry of propargylic amines,[15] we incidentally found that they gave 5-alkylidene-2-oxazolidinones **2** in high yields upon treatment with 1.1 equiv of silver carbonate in common organic solvents such as toluene and THF, in the absence of a $CO_2$ atmosphere (Scheme 1). The carboxyl in the product was apparently derived from $Ag_2CO_3$ which was used in a stoichiomeric amount.[16] Since $Ag_2CO_3$ is relatively expensive and light-sensitive, we set out to develop a catalytic system for this transformation, with environment awareness in mind.

## Results and discussion

[a] Institutes of Biomedical Sciences, Fudan University, 131 Dongan Road, Shanghai 200032, China.
[b] Department of Chemistry, Fudan University, 2005 Songhu Road, Shanghai 200438, China.
E-mail: wangbing@fudan.edu.cn
† Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: ee DOI: 10.1039/x0xx00000x

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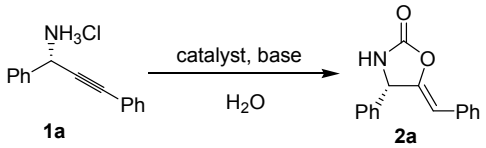
**Table 1.** Condition optimisation.[a]




| Entry | catalyst | base | T [°C] | time [h] | Conversion [%] | Yield [%][b] |
|---|---|---|---|---|---|---|
| 1 | 10 mol% $Ag_2CO_3$ | 10 equiv. $Na_2CO_3$ | 70 | 6 | <5 | nd |
| 2 | 10 mol% $Ag_2CO_3$ | 10 equiv. $NaHCO_3$ | 70 | 6 | 72 | 86 |
| 3 | 10 mol% $Ag_2CO_3$ | 10 equiv. $KHCO_3$ | 70 | 6 | 89 | 86 |
| 4 | 10 mol% $Ag_2CO_3$ | 10 equiv. $NH_4HCO_3$ | 70 | 6 | 57 | 45 |
| 5 | 10 mol% $Ag_2CO_3$ | 6 equiv. $Bu_4NHCO_3$ | 70 | 6 | 71 | 89 |
| 6 | 10 mol% $Ag_2CO_3$ | 6 equiv. $KHCO_3$ | 70 | 6 | 89 | 86 |
| 7 | 10 mol% $Ag_2CO_3$ | 4 equiv. $KHCO_3$ | 70 | 12 | 73 | 86 |
| 8 | 10 mol% $Ag_2CO_3$ | 6 equiv. $KHCO_3$ | 50 | 18 | 88 | 90 |
| 9 | 10 mol% $Ag_2CO_3$ | 6 equiv. $KHCO_3$ | 30 | 30 | 62 | 90 |
| 10[c] | 10 mol% $Ag_2CO_3$ | 6 equiv. $KHCO_3$ | 50 | 18 | 95 | 95 |
| 11[d] | 10 mol% $Ag_2CO_3$ | 6 equiv. $KHCO_3$ | 50 | 18 | 90 | 86 |
| 12[e] | 10 mol% $Ag_2CO_3$ | 6 equiv. $KHCO_3$ | 50 | 18 | 95 | 53 |
| 13[f] | 10 mol% $Ag_2CO_3$ | 6 equiv. $KHCO_3$ | 50 | 18 | 75 | 35 |
| 14[c] | 2 mol% $Ag_2CO_3$ | 6 equiv. $KHCO_3$ | 50 | 18 | 95 | 95 |
| 15[c] | 1 mol% $Ag_2CO_3$ | 6 equiv. $KHCO_3$ | 50 | 18 | 91 | 92 |
| 16[c] | 2 mol% $AgOCOCF_3$ | 6 equiv. $KHCO_3$ | 50 | 18 | 86 | 95 |
| 17[c] | 2 mol% AgOAc | 6 equiv. $KHCO_3$ | 50 | 18 | 78 | 90 |
| 18[c] | 2 mol% $AgNO_3$ | 6 equiv. $KHCO_3$ | 50 | 18 | 90 | 95 |
| 19[c] | 2 mol% CuI | 6 equiv. $KHCO_3$ | 50 | 18 | 0 | nd |
| 20[c] | 2 mol% $CuCl_2$ | 6 equiv. $KHCO_3$ | 50 | 18 | 0 | nd |
| 21[c] | 2 mol% $Pd(PPh_3)_4$ | 6 equiv. $KHCO_3$ | 50 | 18 | 0 | nd |
| 22[c] | 2 mol% $Pd(OAc)_2$ | 6 equiv. $KHCO_3$ | 50 | 18 | 0 | nd |

[a] Reaction conditions: 1.0 mmol substrate **1a**, catalyst, and base in 5 ml water. [b] Isolated yields of pure product **2** after column chromatography, based on reacted starting material. [c] Dropwise addition of **1** in water to the reaction mixture. [d] In 4:1 $H_2O$-EtOH (v/v). [e] In 4:1 $H_2O$-THF (v/v). [f] In 4:1 $H_2O$-$CH_2Cl_2$ (v/v).

Initially, we expected that using a catalytic amount of Ag(I) salt with an aqueous solution of alkali carbonate would suffice to complete the catalytic cycle of silver, and bring the environmental benefit as well. Indeed, $Ag_2CO_3$ can be readily prepared from a simple inorganic metathesis reaction of $AgNO_3$ with $Na_2CO_3$.[17] The hydrochloride of compound **1a** was chosen as the standard substrate for optimisation for its water solubility and ease of handling (Table 1). However, to our disappointment, the reaction showed virtually no progress. We reasoned that unlike reactions using gaseous or $scCO_2$ which are Lewis acidic, the carbonate anion in water or the mixed salt $AgNaCO_3$ may not be sufficiently electrophilic for amine, so the key carbamate intermediate was not formed efficiently. Hydrogen-bonding may also be crucial to the formation of carbamate intermediate.[10b] Thus we turned our attention to the less basic bicarbonate salts. Gratifyingly, with 10 mol% Ag(I) as the catalyst, the reaction proceeded smoothly to 72% conversion‡ and 86% yield (based on reacted starting material) under 70 °C when 10 equivalents of $NaHCO_3$ was used (entry 2). The olefin in the product **2a** was determined to be of Z-configuration exclusively by comparison of its NMR with that reported previously.[12] Potassium bicarbonate improved the

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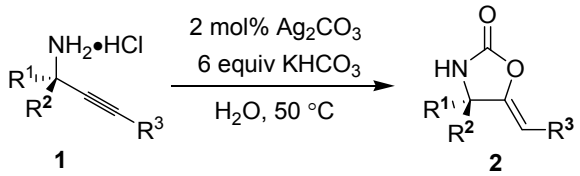
**Table 2.** Ag-catalysed carboxylative cyclysation of propargylic amines in water.[a]




| Entry | 1 | $R^1$ | $R^2$ | $R^3$ | time [h] | Conversion [%] | Yield [%][b] |
|---|---|---|---|---|---|---|---|
| 1 | **1a** | Ph | H | Ph | 18 | 95 | 95 |
| 2 | **1b** | Ph | H | cyclopropyl | 18 | 93 | 81 |
| 3 | **1c** | Ph | H | *n*-Bu | 18 | 92 | 74 |
| 4 | **1d** | Ph | H | *t*-Bu | 18 | 87 | 86 |
| 5 | **1e** | Ph | H | TMS | 18 | 89 | 86[d] |
| 6 | **1f** | Ph | H | H | 24 | 82 | 80 |
| 7 | **1g** | 3-hydoxy propyl | H | Ph | 12 | 93 | 95 |
| 8 | **1h** | *n*-Pr | H | Ph | 48 | 88 | 95 |
| 9 | **1i** | 4-$ClC_6H_4$ | H | Ph | 12 | 95 | 90 |
| 10 | **1j** | *E*-cinnamyl | H | Ph | 18 | 85 | 95 |
| 11[c] | **1k** | *t*-Bu | H | Ph | 72 | 89 | 98 |
| 12[c] | **1l** | cyclohexyl | Me | TMS | 72 | 81 | 88[d] |
| 13 | **1m** | Ph | Me | H | 18 | 70 | 95 |
| 14 | **1n** | 2-thienyl | H | Ph | 10 | 95 | 75 |
| 15 | **1o** | Ph | H | *p*-$MeOC_6H_4$ | 16 | 86 | 90 |

[a] Reaction conditions: 1.0 mmol substrate **1** dissolved in minimum water was added dropwise to 2 mol% $Ag_2CO_3$, 6 mmol $KHCO_3$ in 5 ml water at 50 °C. [b] Isolated yields of pure product **2** after column chromatography, based on reacted starting material. [c] 5 mol% catalyst. [d] Desilylated product ($R^3$ = H).





conversion to 89%. In contrast, the more acidic $NH_4HCO_3$ gave inferior results under the same conditions, while the analogous quaternary ammonium bicarbonate restored good yield (entries 4 and 5). The high yield was maintained when the amount of $KHCO_3$ of was reduced to 6 equiv, on a 1 mmol scale (entry 6). Further decreasing the amount of $KHCO_3$ to 4 equiv resulted in incomplete conversion (73%) after prolonged reaction time. Lowering the temperature to 50 °C minimised side reactions and enhanced the yield to 90%, while under rt the conversion reached only 62% even after 30 h (entries 8 and 9). It was found that if the substrate was added in one portion, the free amine quickly emulsified, which might be deleterious for heterogeneous catalysis. Importantly, by gradual addition of an aqueous solution of **1a**, the conversion and yield were both improved to 95% (entry 10). On the contrary, when the free amine **1a-fb** was employed and an organic solvent such as EtOH or THF were used to dissolve the substrate, the yield decreased significantly due to side reactions. Water-immiscible solvent like $CH_2Cl_2$ gave an even worse yield (entries 11–13). For the gradual addition protocol in neat water, it was determined that the amount of $Ag_2CO_3$ could be further decreased to as low as 1–2 mol% without sacrificing the yield and conversion (entry 14). A control experiment proved that silver(I) is necessary. Other silver(I) salts gave similar results with slightly eroded conversion (entries 16–18). It is interesting that the reaction was not inhibited by the presence of a large excess of chloride anion with regard to silver. The reaction proceeded smoothly in tap water as well, demonstrating its robustness. Common copper(I/II) salts and Pd(0/II) species were inactive under the same conditions.

With the optimal condition in hand, the scope of this protocol was explored (Table 2). All primary propargylic amine hydrochlorides were obtained directly from removal of N-*tert*-

butanesulfinyl by HCl in MeOH. We were pleased that substrates with various patterns of substitution all gave good to excellent results. Substrates with an aryl group at the γ-position ($R^3$) generally exhibited higher yields and reaction rates (entries 1 and 7–11) than their alkyl counterparts (entries 2–4). Terminal alkynes were also suitable substrate (entry 6). However, TMS-capped alkynes were desilylated under the basic condition,[18] and furnished the same product as the analogous terminal alkyne substrate did (entries 5 and 12). The presence of free hydroxyl, halogen, alkene, and cyclopropyl group did not interfere with the reaction. The hydroxyl had even a beneficial rate-enhancing effect, probably through hydrogen-bonding with the carbamate intermediate (entry 7). Highly hindered substrates with *tert*-butyl substituent adjacent to the triple bond such as **1d** and **1k** both reacted smoothly in very good yields (entries 4 and 11). It is interesting that increasing the steric hindrance at the α-position of amine ($R^1$ or $R^2$) retarded the reaction more significantly, thus 5 mol% catalyst was used to ensure good conversion (entries 11 and 12). α,α-Disubstituted propargylic amines also cyclised in good yields, albeit at diminished conversion (entries 12 and 13). The sulfur-containing thienyl group posed no difficulty either (entry 14). Finally, an alkyne with a terminal electron-rich aryl group furnished the desired product uneventfully (entry 15).

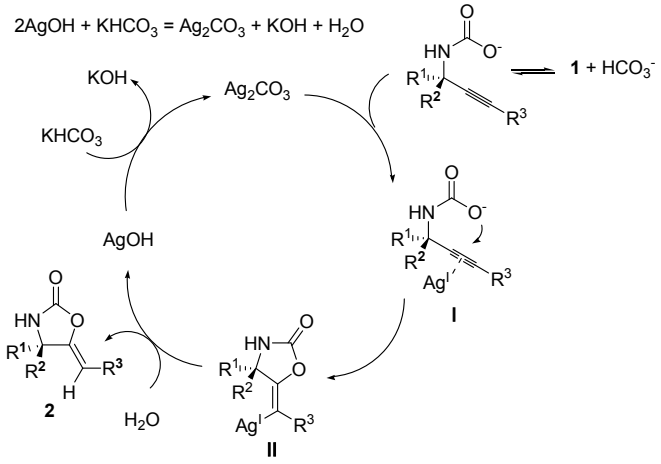
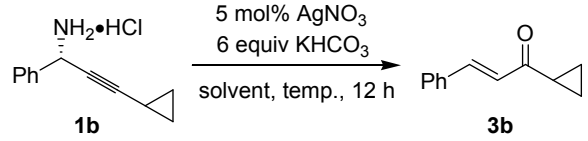



**Figure 1.** Plausible catalytic cycle.

The mechanism of this protocol is in part reminiscent of other metal-catalysed carboxylative cyclisation.[7,12,19] Silver(I) coordinated with alkyne, and the carbamate oxygen attacked the triple bond from the back in a predominant 5-exo-dig manner (Fig. 1). This process is stereospecific regarding the double bond geometry, with the silver atom *trans*- to the oxygen atom in the resulting intermediate **II**. Protolysis of **II** with water formed the product and silver hydroxide, the latter was subsequently transformed back to $Ag_2CO_3$ via $AgHCO_3$ which is reportedly unstable.[20] It should be noted that 1 equiv of KOH is generated as a byproduct which also consumed bicarbonate, therefore an excess of the latter must be used as a buffer, as elevated pH may be detrimental to the protolysis of C–Ag bond. Moreover, we speculate that under our conditions the formation of the carbamate intermediate **(I)** may be assisted by another bicarbonate anion through hydrogen bonding.[21] On the other hand, the possibility that the substrate reacted with $CO_2$ generated from thermal decomposition of bicarbonate to form carbamate **I** cannot be ruled out.

As mentioned above, it is also possible that the carbamate oxygen of **I** attacks the triple bond in a 6-endo-dig way. In fact, this occurs in some Ag- or Pd-catalysed cyclisation protocols.[6b, 9] After careful purification of the reaction mixture of **1b**, we isolated a minor (~10%) nonpolar byproduct **3b**. Interestingly, spectral analysis revealed that instead of the six-membered cyclic carbamate, it was an α,β-unsaturated ketone, whose carbonyl carbon was derived from the distal alkyne (γ-) carbon of propargylic amine **1b**. As this side reaction involved a formal C–N cleavage with double bond transposition under a mild condition, and the mechanism is not apparent, it prompted some further investigation.[22]

**Table 3.** Ag-catalysed C–N cleavage of propargylic amines.



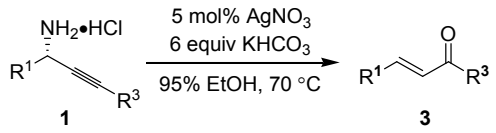

| Entry | Deviation from initial conditions[a] | Yield [%][b] |
|---|---|---|
| 1 | none | ~10 |
| 2 | abs. EtOH | 33 |
| 3 | 95% EtOH | 59 |
| 4 | 50% EtOH | 26 |
| 5 | 95% MeOH | 40 |
| 6 | THF : $H_2O$ (95:5) | ~10 |
| 7 | 95% EtOH, NaOH instead of $KHCO_3$ | 0 |
| 8 | 95% EtOH, DBU instead of $KHCO_3$ | 0 |
| 9 | 95% EtOH, 50 °C | 44 |
| 10 | 95% EtOH, 3 mol% $AgNO_3$ | 47 |
| 11 | CuI, or $CuCl_2$, or $Pd(OAc)_2$ instead of $AgNO_3$ | 0 |

[a] Initial conditions: 1.0 mmol substrate **1b**, 5 mol% $AgNO_3$, 6 mmol $KHCO_3$ in 5 ml water at 70 °C. [b] Isolated yields of pure product **3b** after column chromatography.

As the source of Ag(I) has virtually little effect on this reaction, $AgNO_3$ (5 mol%) was employed as it is the most readily available silver salt. It turned out that this reaction is highly solvent-dependent (Table 3). In neat water, the extent of this side reaction is very limited, and **2b** was obtained in high yield. However, when the solvent is shifted to ethanol, the yield of **3b** increased significantly. It was determined that 95% aqueous ethanol was the optimal solvent for the formation of **3b** (entries 2–6). It is notable that under this condition, the yield for oxazolidinone **2b** was low. Bicarbonate proved essential, as other common inorganic or organic bases failed to afford **3b**, no matter the basicity was strong or weak (entries 7

and 8). The optimal temperature is 70 °C, and a catalyst loading of 5 mol% should be used. A few Cu(I/II) and Pd(II) salts were also tested and proved inactive (entry 11).

**Table 4.** The scope of Ag-catalysed C–N cleavage of propargylic amines.[a]




| Entry | $R^1$ | $R^3$ | 3 | Time [h] | Yield [%][b] |
|---|---|---|---|---|---|
| 1 | Ph | *c*-propyl | **3b** | 12 | 59 |
| 2 | Ph | *t*-Bu | **3d** | 14 | 61 |
| 3 | Ph | Me | **3y** | 8 | 72 |
| 4 | Ph | H | **3f** | 6 | 66 |
| 5 | Ph | Ph | **3a** | 12 | 0 |
| 6 | *t*-Bu | *n*-Bu | **3z** | 12 | 0 |
| 7 | *t*-Bu | Ph | **3k** | 12 | 0 |

[a] Reaction conditions: 1.0 mmol substrate **1**, 5 mol% $AgNO_3$, 6 mmol $KHCO_3$ in 5 ml 95% EtOH at 70 °C. [b] Isolated yields of pure product **3** after column chromatography.

Subsequently, the scope of this C–N cleavage reaction is scrutinized. Substrates bearing a terminal alkyl substituent (or H) afforded **3** in moderate yields§ (Table 4, entries 1–4). However, alkynes conjugated with an aryl group yielded the normal product **2** exclusively, presumably due to the electron-withdrawing effect of the aromatic ring (entry 5). In addition, bulky substituent on the $\alpha$-position of the amino group inhibited this reaction too, as steric hindrance strongly disfavored the formation of an Ag–C bond at the adjacent $\beta$-carbon (entries 6 and 7).

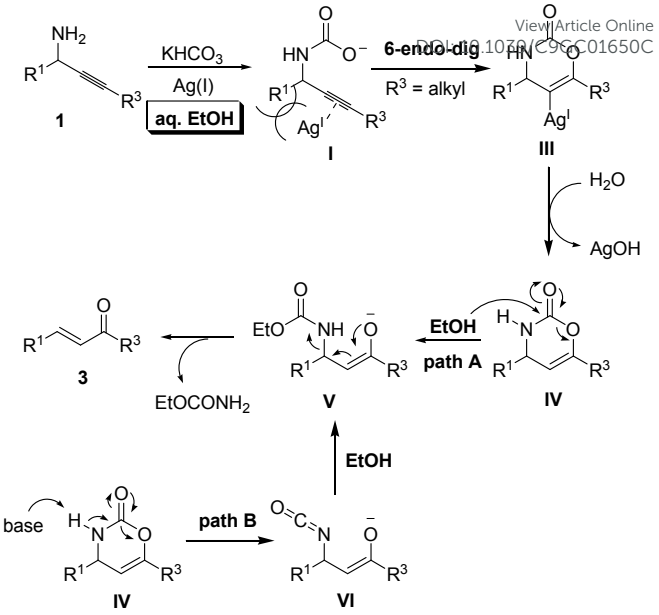



**Figure 2.** Proposed mechanism for the C–N cleavage side reaction.

We believe that the mechanism outlined in Figure 2 serves to elucidate this side reaction. Intermediate **III** was formed when the carbamate oxygen of **I** attacked alkyne in a 6-endo-dig manner. Subsequent protonation led to compound **IV**. The cyclic carbamate could either undergo alcoholysis to form **V** (path A) or ring-opening to form an isocyanate **VI** (path B). Trapping of **VI** by ethanol afforded **V** also, which eventually eliminated urethane to form the product **3**. Although isocyanate is generally regarded as very reactive and moisture-sensitive, its formation from cyclic carbamate upon treatment with a base has been documented.[23,24]

## Experimental

Typical procedure for carboxylative cyclisation: To a stirred solution of $KHCO_3$ (600 mg, 6.0 mmol) in water (5 ml) at 50 °C was added $Ag_2CO_3$ (5.5 mg, 0.02 mmol) in one portion followed by dropwise addition of a solution of **1a** (244 mg, 1.0 mmol) in water (5 ml). The dropping was kept at a rate that no excessive emulsion was formed. The mixture was stirred at 50 °C until completion of reaction (TLC), cooled to rt, and extracted with MTBE or EtOAc. The organic phase was washed successively with 1 M HCl, water and brine, dried over $Na_2SO_4$, and concentrated. The residue was purified by flash column chromatography (EA/PE = 1/6) or recrystallization. Compound **2a**: 95% yield (borsm), white solid, mp 170–171 °C; $[\alpha]_D^{20}$ +96.5 (*c* 0.10, $CHCl_3$); $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.53–7.20 (m, 10H), 5.71 (s, 1H), 5.55 (s, 1H), 5.31 (s, 1H); $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 155.8, 148.8, 138.7, 133.2, 129.3, 129.2, 128.4, 128.3, 127.1, 127.0, 104.9, 60.6. HR-MS-ESI [M+H$^+$] Calcd: 252.1019, Found: 252.1018.

Typical procedure for C–N cleavage: To a stirred solution of $KHCO_3$ (600 mg, 6.0 mmol) in 95% EtOH (5 ml) was added $AgNO_3$ (8.5 mg, 0.05 mmol) followed by **1b** (208 mg, 1.0 mmol) in one portion. The mixture was stirred at 70 °C until

completion of reaction (TLC), cooled, and concentrated under reduced pressure. The residue was partitioned between MTBE and 1 M HCl, the organic phase was separated and washed successively with water and brine, dried over $Na_2SO_4$, and purified by flash column chromatography (EA/PE = 1/30). Compound **3b**: 59% yield, $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.69–7.54 (m, 3H), 7.47 – 7.37 (m, 3H), 6.90 (d, $J$ = 16.1 Hz, 1H), 2.34 – 2.21 (m, 1H), 1.18 (dt, $J$ = 6.8, 3.4 Hz, 2H), 1.00 (dt, $J$ = 7.3, 3.7 Hz, 2H).

## Conclusions

In summary, we have developed an environment-friendly synthesis of *Z*-5-alkylidene-2-oxazolidinones, which is carried out in neat water under gas-free conditions. This protocol is amenable to primary propargylic amines with a wide variety of substitution patterns. It is notable that potassium bicarbonate is used as a low cost $CO_2$ surrogate. We have also investigated the associated C–N cleavage side reaction for substrates with an alkyl $\gamma$-substituent and identified an interesting solvent effect. In neat water this side reaction is negligible, while in 95% aqueous ethanol it becomes the major pathway. Mechanistically, it involved a 6-endo-dig cyclisation and subsequent base-induced ring-opening and elimination of urethane.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

Financial support from the National Natural Science Foundation (No. 21272039) is gratefully acknowledged.

## Notes and references

‡ Unreacted amine was easily separated and recovered during workup by simple acid-base workup.
§ Compounds **3** may be volatile.

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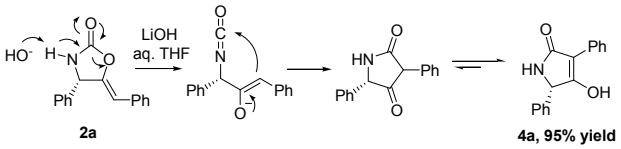


**Scheme 2.** Formation of tetramic acid **4a** in attempted hydrolysis of oxazolidinone.

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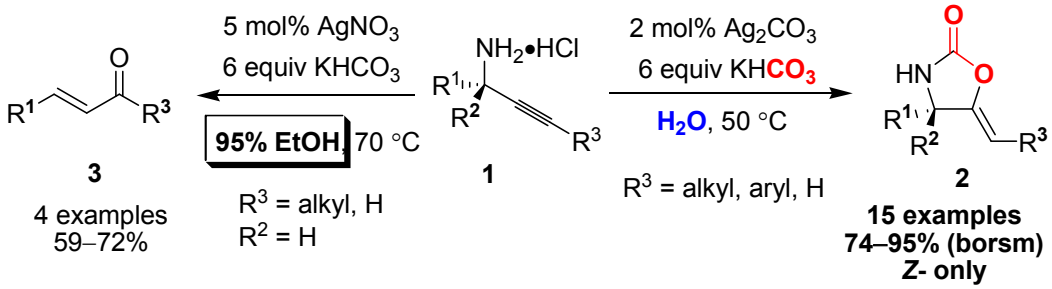
DOI: 10.1039/C9GC01650C

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