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Copper-Catalyzed Ring-Expansion/Thiolactonization *via* Azidation of Internal Olefinic C–H Bond under Mild Conditions

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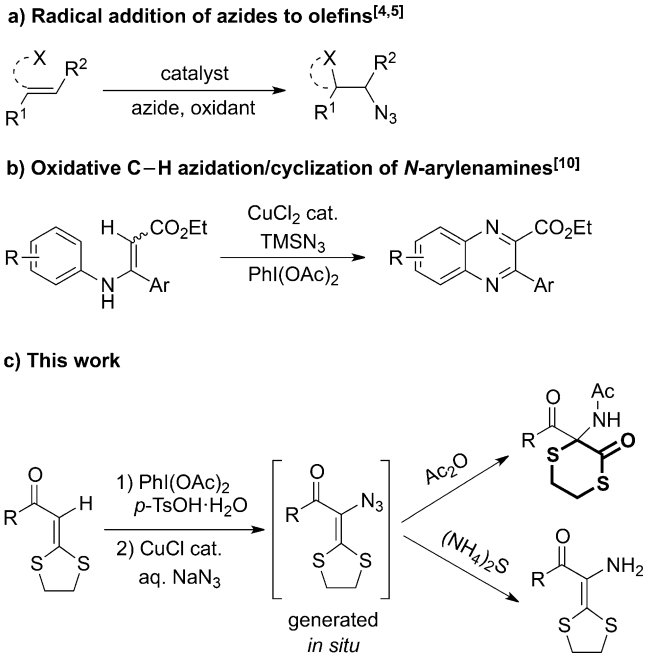
Abstract: A copper(I)-catalyzed, (diacetoxyiodo)-benzene [$PhI(OAc)_2$]-mediated ring-expansion/thiolactonization of α-oxo ketene dithioacetals was efficiently realized *via* azidation of the internal olefinic C–H bond with sodium azide under mild conditions. Sequential amination, ring-expansion rearrangement, and thiolactonization occurred to form aminated thiolactones in the presence of acetic anhydride as the additive, while only C–H amination to afford the unprotected enamines occurred when using ammonium sulfide as a reducing additive. The *in situ* generated vinyl azides were confirmed as the reactive intermediates, which were captured by phenylacetylene to produce triazoles. This protocol provides a concise route to thiolactone derivatives and unprotected enamines.

Keywords: C–H functionalization; copper; enamines; internal olefins; thiolactones

Functionalization of olefins is essential for functional group interconversions in organic synthesis.[1] Owing to their versatile reactivities, azides have been widely used to functionalize olefins for the synthesis of valuable organic azides as building blocks.[2,3] By means of azide reagents such as NaN_3, TfN_3, $TMSN_3$, or azido iodine(III) reagents as well as nucleophiles elegant work on intermolecular three-component azidoselenenylation,[4a] diazidation,[4b] aminoazidation,[4c] azidocyanation,[4d] azidofluorination,[4e] trifluoromethylazidation,[4f] azidophosphonation,[4g] and oxyazidation[4h–j] of olefins has been documented for the simultaneous formation of both C–N and C–X bonds. Oxidative azidation of olefins followed by a ring closure has also been well developed. In this regard, azido-substituted tetrahydropyrroles,[5a] morpholines,[5b] indolines,[5c–e] oxindoles,[5f] and isoxazolines[5g] were synthesized. These reactions are believed to proceed by the addition of radicals to the olefinic C=C bond followed by trapping with another heteroatom (Scheme 1a). Unfortunately, other straightforward and efficient approaches for olefin functionalization with azides have been scarcely reported.

Recently, transition metal-catalyzed C–H functionalization has emerged as an effective tool for constructing substituted arenes and olefins.[6] Azidation and amination of arenes and heteroarenes with azides *via* C–H activation have been successfully achieved to yield the corresponding azide and amine products.[7,8] However, direct C–H azidation of olefins is very challenging due to the easy addition of the azide function-



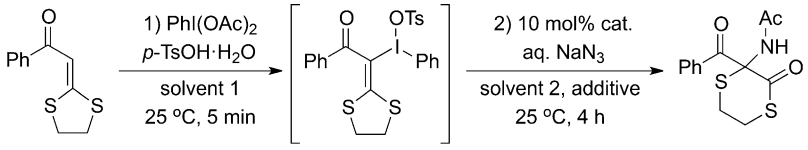
Scheme 1. Functionalization of olefins with azides.

ality to olefinic C=C bonds (Scheme 1a).[4,5] Meanwhile, the low reactivity of internal olefinic C–H bonds and the huge steric hindrance around such bonds make direct C–H functionalization of internal olefins very difficult.[9] The first tandem C–H azidation/cyclization of internal olefins, that is, *N*-arylenamines, with $TMSN_3$ was just recently reported, forming quinoxaline derivatives (Scheme 1b).[10]

Internal olefins such as α-oxo ketene dithioacetals have recently been used as versatile reagents in organic synthesis.[11] Our group reported a transition metal-catalyzed direct alkenylation,[12a,b] allylation,[12c] alkylation,[12d] and trifluoromethylation[12e] of their olefinic C–H bonds. However, the further transformations of the stable five-membered thiocycles of cyclic α-oxo ketene dithioacetals are very limited. Based on the structural features, cyclic α-oxo ketene dithioacetals can be reasonably envisioned to undergo ring expansion to form cyclic organosulfur compounds such as thiolactones, an important class of skeletal motifs in organic synthesis,[13] polymer science,[14] and pharmaceuticals.[15] Traditionally, thiolactones are prepared through intramolecular cyclization of thiocarboxylic acids and derivatives.[16] The relevant synthetic procedures suffer from prefunctionalization of the substrates and limited substrate scopes. To develop simple and efficient approaches to access thiolactones from readily available substrates has been strongly desired. At the outset of our investigation of C–H functionalization of α-oxo ketene dithioacetals with sodium azide, we envisioned that such internal olefinic C–H bonds might undergo transition metal-catalyzed azidation. Unexpectedly, our preliminary trial using CuCl-catalyzed, $PhI(OAc)_2$-mediated reaction of cyclic α-oxo ketene dithioacetal (**1a**) with NaN_3 afforded an aminated thiolactone product. Herein, we disclose the copper-catalyzed functionalization of α-oxo ketene dithioacetals with NaN_3 for the synthesis of thiolactone derivatives (Scheme 1c).

Initially, the reaction of benzoylketene dithioacetal (**1a**) with aqueous NaN_3 was conducted to screen the reaction conditions (Table 1). Using 10 mol% CuCl as the catalyst, $PhI(OAc)_2$ as the oxidant in the presence of *p*-TsOH·H_2O, the target product **2a** was obtained in 27% yield from the one-pot, two-step reaction in a mixed solvent of MeCN/DMSO (1/2, v/v) at ambient temperature (Table 1, entry 1). The reaction hardly proceeded by employing $BF_3{\cdot}OEt_2$ and K_2CO_3 as the additives (Table 1, entries 2 and 3). Surprisingly, use of Ac_2O (2.0 equiv.) remarkably enhanced the yield of **2a** to 65% (Table 1, entry 4). Among the screened copper sources, CuCl, $Cu(OTf)_2$, CuBr, and CuI, the copper(I) salt CuCl acted as the most efficient catalyst (Table 1, entries 4–7). The MeCN/DMF (1/2, v/v) combination was the most effective solvent for the desired reaction, leading to **2a** in 72–73% yield (Table 1, entry 11). Elevating the reaction temperature was detrimental to the reaction due to de-

Table 1. Optimization of conditions for the synthesis of thiolactones.[a]



1a **A1** **2a**

Entry	Catalyst	Solvent 1/Solvent 2	Additive (equiv.)	Yield[b] of **2a** [%]
1	CuCl	MeCN/DMSO		27
2	CuCl	MeCN/DMSO	$BF_3{\cdot}OEt_2$ (1.0)	trace
3	CuCl	MeCN/DMSO	K_2CO_3 (1.0)	0
4	CuCl	MeCN/DMSO	Ac_2O (2.0)	65 (65)[c]
5	$Cu(OTf)_2$	MeCN/DMSO	Ac_2O (2.0)	56
6	CuBr	MeCN/DMSO	Ac_2O (2.0)	60
7	CuI	MeCN/DMSO	Ac_2O (2.0)	47
8	CuCl	MeCN	Ac_2O (2.0)	45
9	CuCl	DMSO	Ac_2O (2.0)	0
10	CuCl	DMF	Ac_2O (2.0)	trace
11	CuCl	MeCN/DMF	Ac_2O (2.0)	73 (72)[c]
12	CuCl	MeCN/dioxane	Ac_2O (2.0)	58
13	CuCl	MeCN/toluene	Ac_2O (2.0)	59

[a] *Reaction conditions:* 1) **1a** (0.20 mmol), $PhI(OAc)_2$ (1.05 equiv.), *p*-TsOH·H_2O (1.2 equiv.), solvent 1 (0.5 mL), 25 °C, 5 min, 0.1 MPa N_2; 2) aq. NaN_3 (1.5 equiv., 1.0 M in 0.3 mL H_2O), catalyst (0.10 equiv.), solvent 2 (1.0 mL), additive (1.0–2.0 equiv.), 25 °C, 4 h, 0.1 MPa N_2.

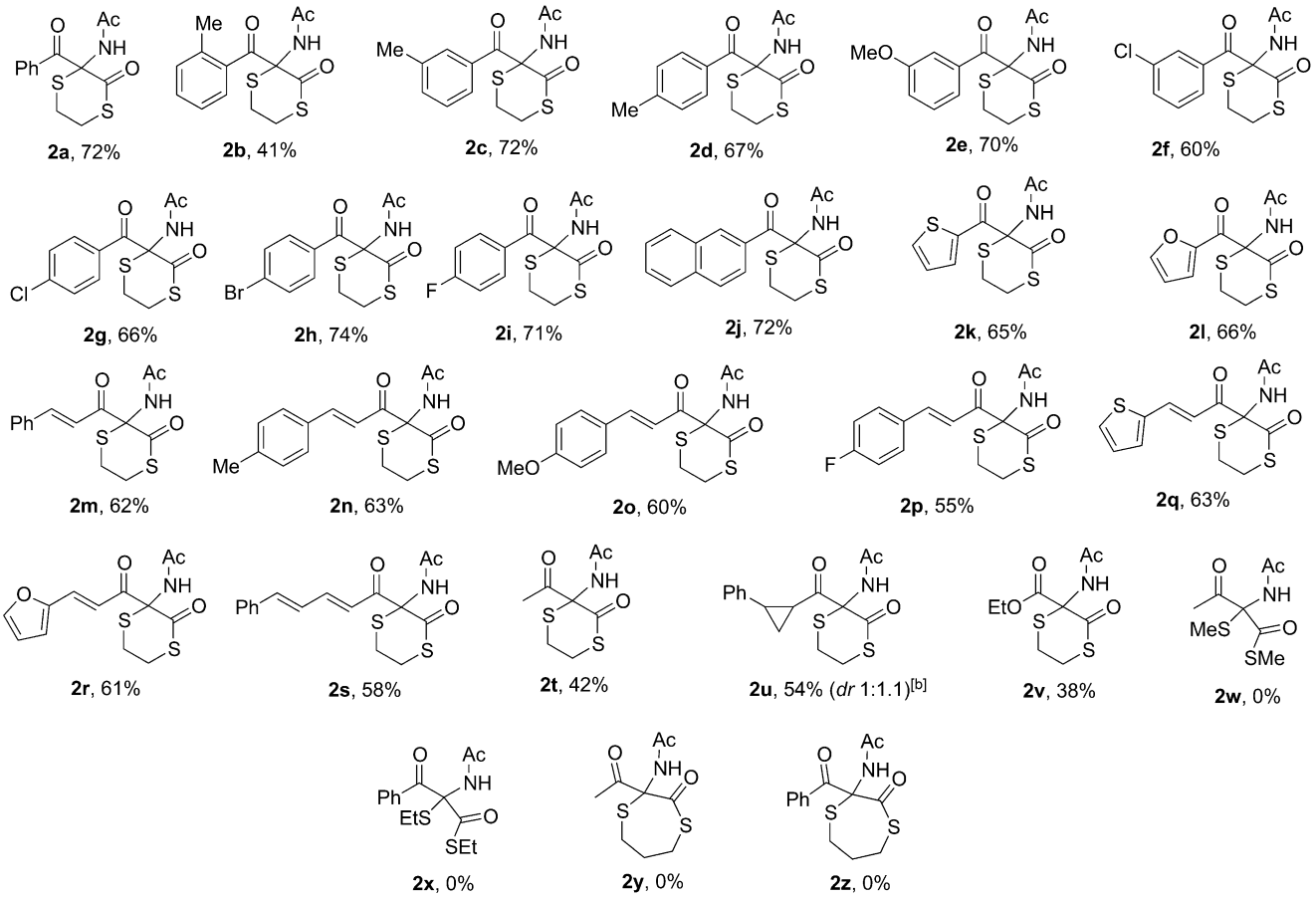
[b] Isolated yield.

[c] Using 0.3 mmol **1a**.

composition of the target product at higher temperatures (see the Supporting Information for details). It should be noted that no reaction occurred without preactivation of the olefinic C–H bond by the first step – the iodination reaction, and the hypervalent idodine(III) intermediate **A1** was speculated to readily form by treatment of **1a** with $PhI(OAc)_2$ and *p*-$TsOH{\cdot}H_2O$ at ambient temperature.

Under the optimal conditions, the generality of the protocol was explored by using various α-oxo ketene dithioacetals (**1**) as the substrates (Table 2). Benzoylketene dithioacetals bearing an electron-donating or withdrawing group on the phenyl ring could tolerate the reaction conditions, forming the target products **2a** and **2c**–**2i** in 60–74% yields, revealing no obvious electronic impact from the substituents. However, an *ortho*-methyl group exhibited a remarkable steric effect on the formation of product **2b** (41%) owing to the increased steric hindrance. The 2-naphthyl-bearing substrate reacted to afford the corresponding thiolactone **2j** (72%). Heteroaryl substrates of type **1** also underwent the reaction to give products **2k** (65%) and **2l** (66%), respectively. The reactions of cinnamoyl- or dienoylketene dithioacetals and derivatives formed products **2m**–**2s** in 55–63% yields. Replacement of the aryl group in **1** with methyl or cyclopropyl led to the corresponding products **2t** and **2u** (42–54%). The ester ketene dithioacetal underwent the

Table 2. Synthesis of thiolactones **2**.[a]



[a] *Reaction conditions:* 1) **1** (0.30 mmol), $PhI(OAc)_2$ (1.05 equiv.), *p*-$TsOH{\cdot}H_2O$ (1.2 equiv.), MeCN (0.8 mL), 25 °C, 5 min; 2) aq. NaN_3 (0.45 mmol in 0.45 mL H_2O), CuCl (0.03 mmol), DMF (1.6 mL), Ac_2O (0.60 mmol), 25 °C, 4 h, 0.1 MPa N_2. Yields refer to the isolated products.

[b] The *dr* value was determined by ^1H NMR analysis.

same type of reaction to produce **2v** in 38% yield. However, products **2w–2z** could not be obtained in the cases of using acyclic α-oxo ketene dithioacetals and cyclic α-oxo ketene 1,3-dithioacetal as the internal olefin substrates due to no generation of the corresponding hypervalent idodine(III) intermediates of type **A1** under the stated conditions. The molecular structures of compounds **2** were further confirmed by the X-ray single crystal structural determination of **2a** (Figure 1).[17]

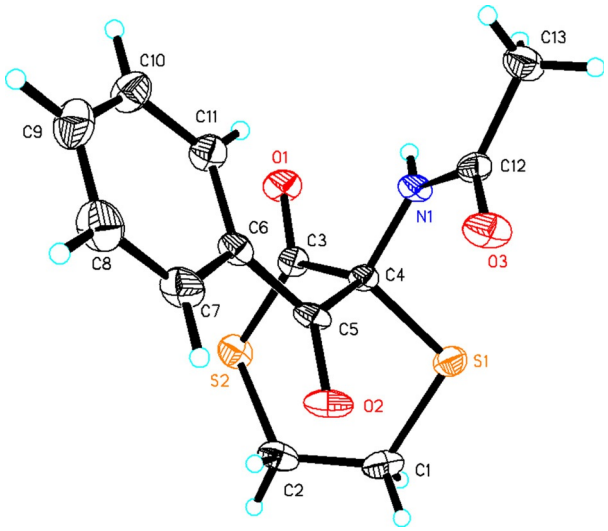
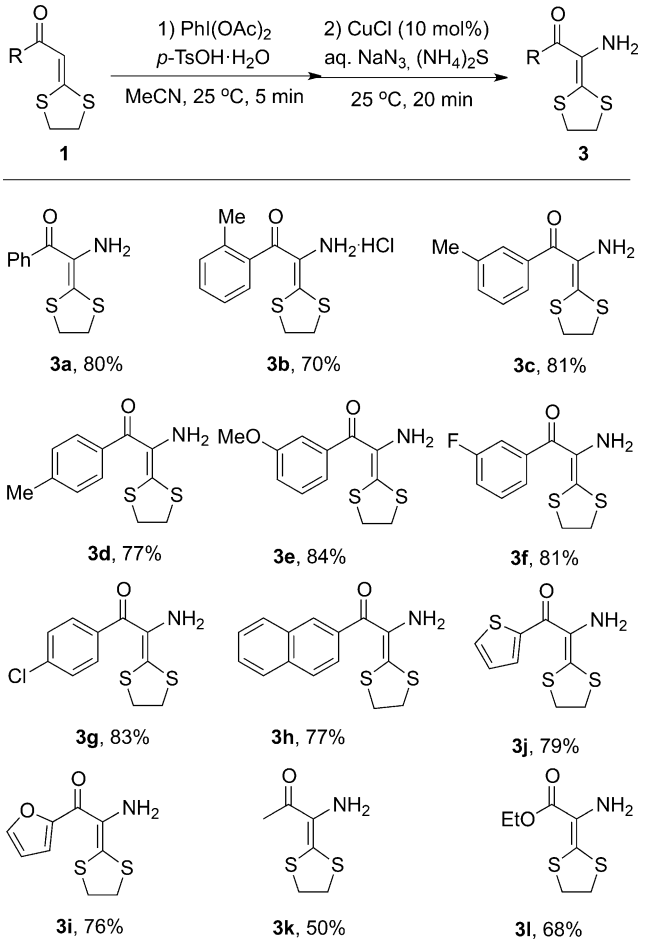


Figure 1. Molecular structure of **2a**.

Due to the occurrence of the ring-expansion rearrangement/aminothiolactonization, we hypothesized that C–H azidation intermediates were formed in the reaction. However, such intermediate compounds could not be successfully isolated. In order to attain the desired azidation products from the reactions of α-oxo ketene dithioacetals (**1**) with NaN_3, aqueous $(NH_4)_2S$ instead of Ac_2O was introduced as a reducing additive in the second step manipulation. To our delight, unprotected enamines **3** were collected as the products (Table 3). Enamine derivatives have been widely applied for the preparation of heterocycles[9,18] and chiral amines.[19] Although transition metal-catalyzed oxidative C–H amination of olefins has become an attractive method to directly access enamines,[20] the relevant internal olefins have been less explored as the substrates,[21] and most of the available approaches require a protecting group attached at the nitrogen atom. Particularly, there have been few examples of oxidative cross-coupling of internal olefins with NaN_3 for the synthesis of unprotected enamines. In our case, the C–H azidation intermediates were reduced *in situ* by $(NH_4)_2S$ to afford the C–H amination products, the unprotected enamines **3a–3l** (50–84%) (Table 3). The scope of the C–H amination reactions

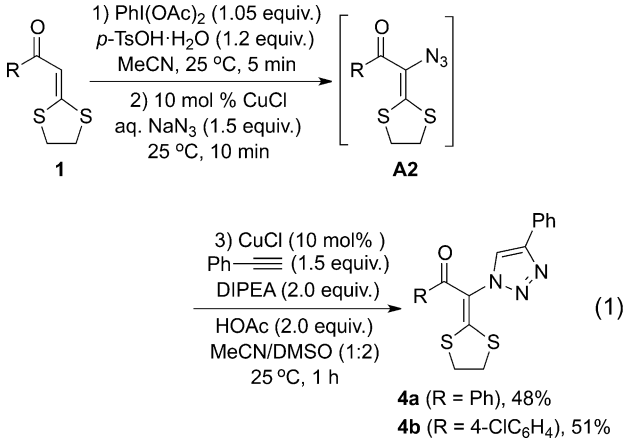
Table 3. C–H Amination of internal olefins **1**.[a]



[a] *Reaction conditions:* 1) **1** (0.30 mmol), $PhI(OAc)_2$ (1.05 equiv.), *p*-TsOH·H_2O (1.2 equiv.), MeCN (2.4 mL), 25 °C, 5 min, 0.1 MPa N_2; 2) aq. NaN_3 (0.45 mmol in 0.45 mL H_2O), CuCl (0.03 mmol), aq. $(NH_4)_2S$ (0.75 mmol in 0.25 mL H_2O), 25 °C, 20 min, 0.1 MPa N_2. Yields refer to the isolated products.

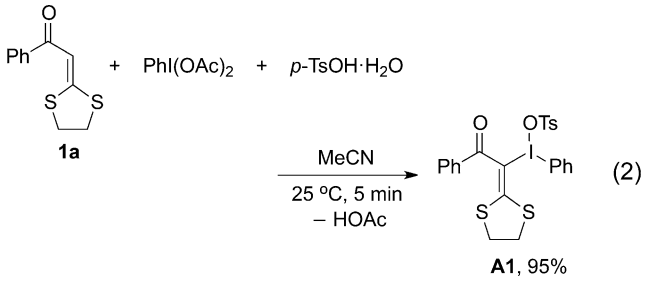
is similar to that for the synthesis of thiolactones (Table 2). Different substituents were well tolerated on the aryl ring of the aroylketene dithioacetals. α-Acetyl and ester ketene dithioacetals exhibited relatively low reactivity, giving **3k** and **3l** in moderate yields (50–68%).

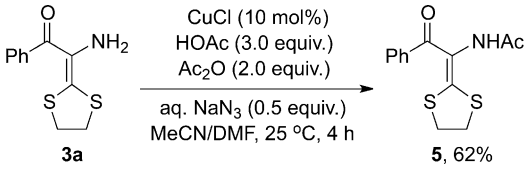
To verify generation of the C–H azidation intermediates, i.e., **A2**, the following click chemistry was performed [Eq. (1)]. After the first step reaction of **1**, $PhI(OAc)_2$, and *p*-TsOH·H_2O was completed, CuCl catalyst and aqueous NaN_3 were introduced to the reactor. The resultant mixture was stirred for 10 min followed by extraction with CH_2Cl_2. Under the typical conditions for click chemistry,[22] the extracted reactive intermediate was used to react with phenylacetylene in the presence of CuCl catalyst. To our delight, the reactions afforded 1,4-disubstituted 1,2,3-triazoles (**4**) in 48–51% yields, revealing formation of vinyl



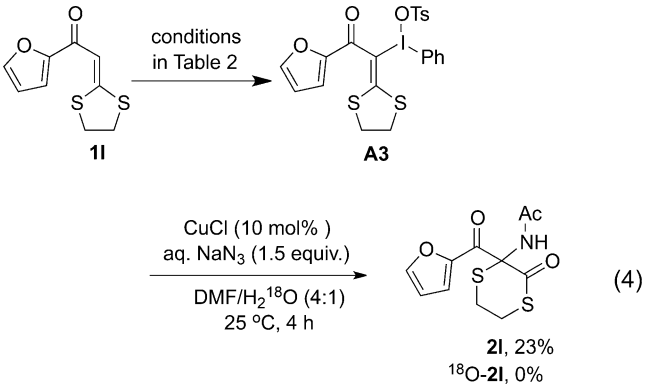
azide **A2** during the reaction (see the Supporting Information for details).

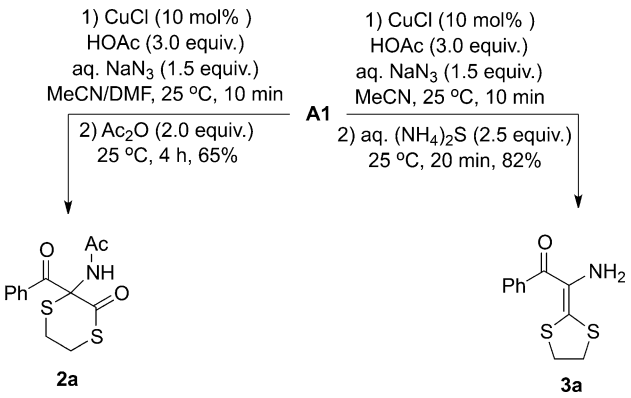
In order to probe the reaction mechanism, control experiments were conducted to identify other reaction intermediates. Under the conditions for the first step reaction[7a,c] iodonium(III) salt **A1** was unambiguously prepared in 95% yield from the reaction of **1a**, $PhI(OAc)_2$, and *p*-TsOH·H_2O [Eq. (2)], and was applied to react with NaN_3 under the standard conditions as shown in Table 2 and Table 3, affording the target products **2a** (65%) and **3a** (82%), respectively (Scheme 2). It should be noted that HOAc was necessary for the formation of both **2a** and **3a**. These results reveal that iodonium(III) salts of type **A1** are the reaction intermediates and act as the activated form of **1**. The enamine products were also tested if they could behave as the reaction intermediates. In the presence of CuCl catalyst, HOAc, Ac_2O, and NaN_3 enamine **3a** could not undergo aminothiolactonization to form **2a**, but was only acetylated to yield **5** (62%) [Eq. (3)], suggesting that the enamine products could not act as the reaction intermediates to generate the thiolactone products.



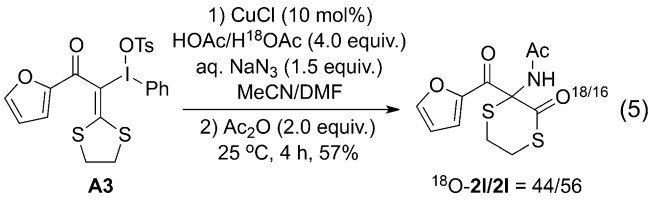


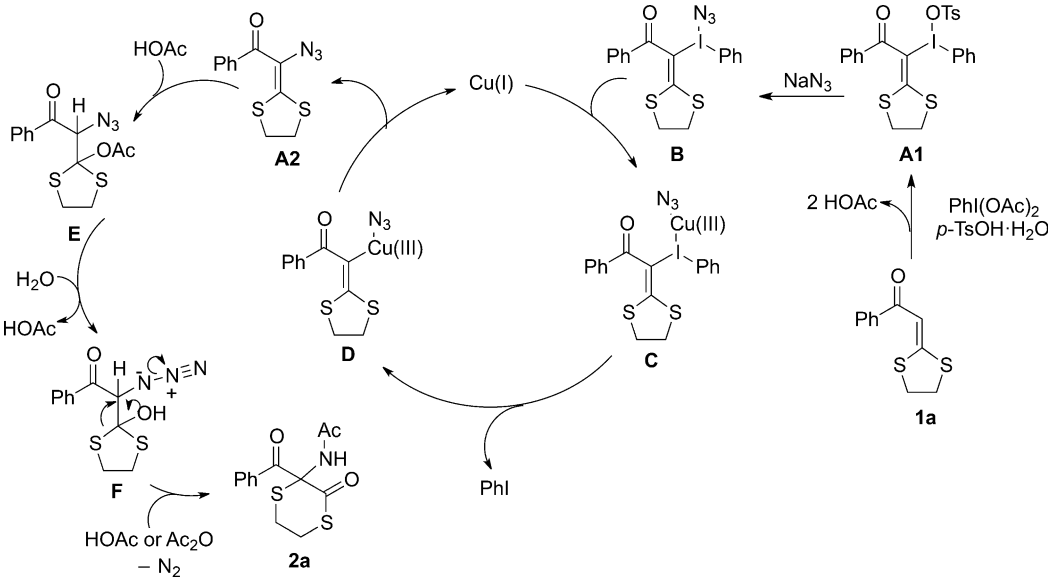
The origin of the incorporated oxygen in the thiolactone products **2** was then investigated. In the one-pot synthesis of thiolactone **2l**, $H_2{}^{18}O$ was added in the second step manipulation and Ac_2O was not introduced to avoid the additive effect [Eq. (4)]. Eventually, **2l** (23%) was obtained without incorporated ^{18}O, suggesting that the incorporated oxygen in **2** was not from water. A mixture of HOAc and $H^{18}OAc$ was prepared (see the Supporting Information) and employed to facilitate transformation of intermediate **A3** with NaN_3 under the aminothiolactonization conditions. Thus, thiolactone **2l** (57%) was obtained with 44% ^{18}O incorporation [Eq. (5)].





Scheme 2. Transformation of intermediate **A1**.





Scheme 3. Proposed mechanism.

A plausible mechanism is proposed in Scheme 3. Iodonium(III) salt **A1** is initially formed by the reaction of **1a**, $PhI(OAc)_2$, and *p*-TsOH·H_2O, followed by the replacement of tosylate with azide anion to generate iodonium(III) azide **B**. Oxidative addition of **B** to Cu(I) catalyst produces Cu(III) species **C**, which releases PhI and forms copper(III) species **D**. Subsequent reductive elimination forms the C–H azidation intermediate **A2** and regenerates the catalyst. Interaction of **A2** with the *in situ* generated HOAc yields species **E** which is then hydrolyzed to form azido alcohol **F**. Sequential ring-expansion rearrangement[23]/thiolactonization, and *N*-acetylation result in aminated thiolactone **2a** with the extrusion of nitrogen. In the reaction sequence, $PhI(OAc)_2$ acts as a trifunctional agent: oxidant, oxygen atom source, and acetylating reagent. In the presence of $(NH_4)_2S$ intermediate **A2** is reduced to *N*-unprotected enamine **3a**.

In summary, the copper-catalyzed functionalization of internal olefins such as α-oxo ketene dithioacetals with NaN_3 has been successfully achieved under mild conditions, in which sequential amination/ring-expansion rearrangement/thiolactonization *via* the C–H azidated intermediates establish new C–N, C=O and C–S bonds in a one-pot style. This protocol provides a facile and straightforward method to access thiolactone and unprotected enamine derivatives.

Experimental Section

Typical Procedure for the Synthesis of Thiolactone (2a) from α-Oxo Ketene Dithioacetal (1)

Under a nitrogen atmosphere, to a solution of $PhI(OAc)_2$ (102 mg, 0.315 mmol) and *p*-TsOH·H_2O (68 mg, 0.36 mmol) in MeCN (0.8 mL) was added benzoylketene dithioacetal (**1a**) (67 mg, 0.30 mmol) and the resulting suspension was stirred for 5 min at ambient temperature, followed by the addition of DMF (1.6 mL), aqueous NaN_3 (0.45 mmol in 0.45 mL H_2O) and CuCl (3 mg, 0.03 mmol). After the resultant mixture was stirred for 10 min, Ac_2O (60 mg, 0.60 mmol) was added, and the stirring was continued for 4 h at 25 °C. Then 10 mL CH_2Cl_2 were added and the resultant mixture was filtered through a short pad of celite, followed by rinsing with 10 mL CH_2Cl_2. The combined filtrate was washed with brine (10 mL) and separated. The organic phase was dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (eluent: CH_2Cl_2/EtOAc = 10:1, v/v) to afford **2a** as a yellow solid; yield: 64 mg (72%).

Typical Procedure for the C–H Amination of α-Oxo Ketene Dithioacetals (1): Synthesis of 3a

Under a nitrogen atmosphere, to a solution of $PhI(OAc)_2$ (102 mg, 0.315 mmol) and *p*-TsOH·H_2O (68 mg, 0.36 mmol) in MeCN (2.4 mL) was added benzoylketene dithioacetal (**1a**) (67 mg, 0.30 mmol) and the resulting suspension was stirred for 5 min at at ambient temperature, followed by the addition of aqueous NaN_3 (0.45 mmol in 0.45 mL H_2O) and CuCl (3 mg, 0.03 mmol). After the resultant mixture was stirred for 10 min, aqueous $(NH_4)_2S$ (0.75 mmol in 0.25 mL H_2O) was added, and the stirring was continued for 20 min at 25 °C. Then 10 mL CH_2Cl_2 were added and the resultant mixture was filtered through a short pad of celite, followed

by rinsing with 10 mL CH_2Cl_2. The combined filtrate was washed with brine (10 mL) and separated. The organic phase was dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography [eluent: petroleum ether (60–90 °C)/EtOAc/CH_2Cl_2 = 15:2:3, v/v/v] to afford **3a** as a yellow liquid; yield: 57 mg (80%).

Acknowledgements

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