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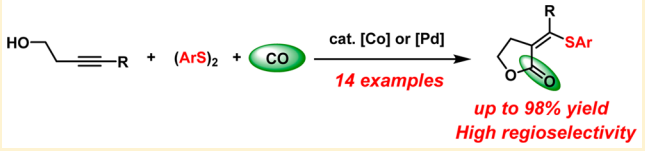
# Selective Thiolative Lactonization of Internal Alkynes Bearing a Hydroxyl Group with Carbon Monoxide and Organic Disulfides Catalyzed by Transition-Metal Complexes

Shinya Higashimae, Taichi Tamai, Akihiro Nomoto, and Akiya Ogawa*

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Nakaku, Sakai, Osaka 599-8531, Japan

Supporting Information

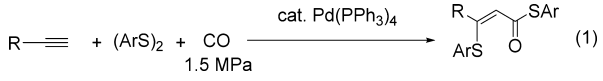
**ABSTRACT:** Although many transition-metal catalysts are ineffective for the addition and carbonylative addition of organic disulfides to internal alkynes, dicobalt octacarbonyl and palladium complexes such as $Pd(PPh_3)_4$ and $Pd(OAc)_2$ were found to exhibit excellent catalytic activity for the thiolative lactonization of internal alkynes bearing a hydroxyl group. In the presence of the cobalt or palladium catalyst, internal alkynes bearing a hydroxy group, such as homopropargyl alcohol derivatives, successfully undergo thiolative carbonylation with carbon monoxide and an organic disulfide regio- and stereoselectively to afford the corresponding thio group bearing-lactones in good yields. In the Co-catalyzed reaction, the cobalt−alkyne complex from dicobalt octacarbonyl and internal alkyne acts as a key species, making it possible to attain thiolative lactonization of internal alkynes with a hydroxyl group. In the Pd-catalyzed reaction, the coordination of the hydroxy group to the palladium catalyst plays an important role for the thiolative lactonization.




## 1. INTRODUCTION

Transition-metal-catalyzed simultaneous introduction of heteroatom functional groups and carbon monoxide into organic molecules is one of the most important tools for the direct synthesis of heteroatom-functionalized carbonyl compounds.[1] Organosilicon compounds, such as hydrosilanes, are widely employed for this purpose.[2]

Organosulfur compounds are useful synthetic intermediates; however, only a very limited number of examples of transition-metal-catalyzed carbonylation with concurrent introduction of sulfur functional groups have been reported.[3,4] We previously reported a series of transition-metal-catalyzed carbonylations of terminal alkynes with CO and organosulfur compounds, such as thiols and disulfides. For example, the palladium-catalyzed reaction of terminal alkynes with CO and $(ArS)_2$ affords the corresponding $\beta$-(arylthio)-$\alpha,\beta$-unsaturated thioesters regio- and stereoselectively (eq 1).[5] Rhodium complexes catalyze the regio- and stereoselective thioformylation of terminal alkynes with CO and ArSH (eq 2),[6] whereas platinum complexes catalyze the hydrothioesterification of terminal alkynes with CO and R'SH regioselectively (eq 3).[7] However, these thiolative carbonylation reactions could not be applied to internal alkynes, most probably due to the increased steric hindrance around them.

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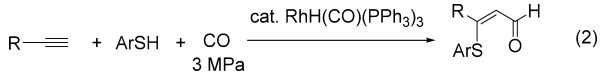


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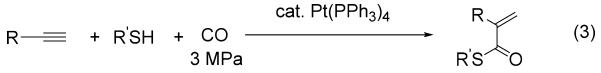
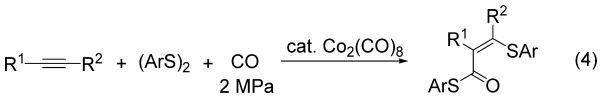



(3)

These reactions (eqs 1−3) are assumed to proceed via the initial formation of metal−sulfide complexes, followed by their coordination by alkynes. In contrast to Pd or Rh complexes, cobalt carbonyl ($Co_2(CO)_8$) easily complexes internal alkynes to give cobalt−alkyne complexes. This coordination property of $Co_2(CO)_8$ may make it possible to attain novel thiolative carbonylation of internal alkynes. On the basis of this idea, we have recently developed a method for the cobalt-catalyzed thiolative mono- and double carbonylation of internal alkynes with CO and disulfides or thiols. (eqs 4 and 5).[8,9] During the course of this study, we also found that, in the case of internal alkynes bearing a hydroxyl group, novel thiolative carbonylation took place regioselectively to afford the corresponding thiolated lactone derivatives bearing an *exo*-methylene group.

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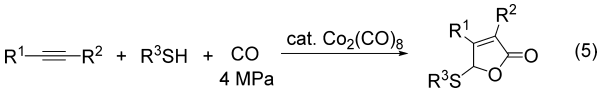


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In this paper, we report the cobalt-catalyzed thiolative lactonization of internal alkynes bearing a hydroxyl group with CO and disulfides. In addition, a comparison of this thiolative

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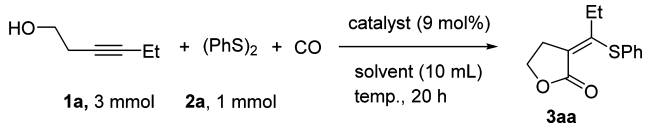
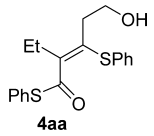
**Table 1. $Co_2(CO)_8$-Catalyzed Thiolative Lactonization of 3-Hexyn-1-ol with Diphenyl Disulfide**



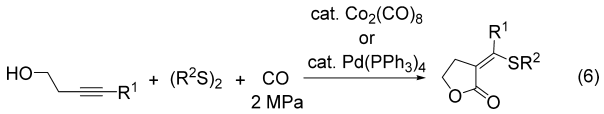

| entry | catalyst | CO, MPa | solvent | temp, °C | yield, %[a] |
|---|---|---|---|---|---|
| 1[b] | $Co_2(CO)_8$ | 2 | toluene | 140 | 30 |
| 2[c] | $Co_2(CO)_8$ | 2 | toluene | 140 | 52 |
| 3 | $Co_2(CO)_8$ | 2 | toluene | 140 | 82 (71) |
| 4 | $Co_2(CO)_8$ | 3 | toluene | 140 | 80 |
| 5 | $Co_2(CO)_8$ | 1 | toluene | 140 | 68 |
| 6 | $Co_2(CO)_8$ | 0.1 | toluene | 140 | 6 |
| 7 | $Co_2(CO)_8$ | 2 | toluene | 120 | 62 |
| 8 | $Co_2(CO)_8$ | 2 | toluene | 110 | 54 |
| 9 | $Co_2(CO)_8$ | 2 | toluene | 100 | 30 |
| 10[d] | $Co_2(CO)_8$ | 2 | toluene | 140 | 80 |
| 11[e] | $Co_2(CO)_8$ | 2 | toluene | 140 | 78 |
| 12 | $Co_2(CO)_8$ | 2 | $CH_3CN$ | 140 | 60 |
| 13[f] | $Co_2(CO)_8$ | 2 | toluene | 140 | 50 |
| 14[g,h] | $Co(acac)_2{\cdot}2H_2O$ | 2 | toluene | 140 | 64 |
| 15[i] | $CoCl_2{\cdot}6H_2O$ | 2 | toluene | 140 | trace |
| 16[i] | $Co(OAc)_2{\cdot}4H_2O$ | 2 | toluene | 140 | N.R. |

[a]Determined by $^1$H NMR (isolated). [b]3-Hexyn-1-ol (1.0 mmol) was used. [c]3-Hexyn-1-ol (1.5 mmol) was used. [d]Reaction time (40 h). [e]Catalyst (3 mol %). [f]1,2-Bis(diphenylphosphino)ethane (dppe, 18 mol %) was added. [g]Catalyst (5 mol %). [h]Regioisomeric carbonylation byproduct **4aa** was obtained.




[i]Catalyst (18 mol %).

lactonization to the corresponding palladium-catalyzed carbonylation is reported (eq 6).




(6)

## 2. RESULTS AND DISCUSSION

**2.1. Cobalt-Catalyzed Thiolative Lactonization of Internal Alkynes Bearing a Hydroxy Group with CO and Disulfides.** When the reaction of 3-hexyn-1-ol **1a** (1 mmol) with diphenyl disulfide **2a** (1 mmol) under carbon monoxide (2 MPa) in toluene (10 mL) is conducted using 9 mol % of $Co_2(CO)_8$ at 140 °C for 20 h, thiolative lactonization occurs to give the corresponding $\gamma$-lactone derivative **3aa** bearing an *exo*-methylene group in 30% yield (Table 1, entry 1). The structure of **3aa** was determined unambiguously by X-ray structural analysis (see the Supporting Information, Figure S1). As can be seen from the ORTEP representation of **3aa**, carbon monoxide is introduced regioselectively to the acetylenic carbon bonded to the hydroxyethyl group, and the thio group is located at the *cis* position of the carbonyl group. Therefore, the present thiolative carbonylation of **1a** apparently proceeds regio- and stereoselectively. The yield of **3aa** is dramatically improved with the use of excess **1a** (Table 1, entries 2 and 3). Higher CO pressure (3 MPa) does not increase the yield of **3aa** (Table 1, entry 4); however, lower CO pressure (1 MPa, 0.1 MPa) decreases the yield (Table 1, entries 5 and 6). With decreasing temperature, the yields of **3aa** decrease (Table 1, entries 7–9). Prolonging the reaction time to 40 h does not influence the yield (Table 1, entry 10). Decreasing the amount of the catalyst to 3 mol % results in a decrease of the yield of **3aa** (Table 1, entry 11). With a polar solvent ($CH_3CN$), the yield of **3aa** slightly decreases (Table 1, entry 12). Addition of 1,2-bis(diphenylphosphino)-ethane (dppe) decreases the yield (Table 1, entry 13). Some other cobalt catalysts were investigated, and $Co(acac)_2$ also shows catalytic activity in this thiolative lactonization (Table 1, entry 14). However, with this catalyst, a regioisomeric carbonylation derivative **4aa** is also obtained. The optimum result is obtained when the thiolative carbonylation is performed under 2 MPa of CO in toluene at 140 °C for 20 h (Table 1, entry 3).

Next, the thiolative lactonization was examined using several hydroxyalkynes and diaryl disulfides under the optimized reaction conditions (Table 1, entry 3), and the results are shown in Table 2. In the cases of diaryl disulfides having an electron-donating (**2b**, **2c**) or electron-withdrawing group (**2d**), the thiolative lactonization proceeded successfully to give the corresponding $\gamma$-lactone derivatives **3ab**, **3ac**, and **3ad** in good yields (Table 2, entries 2–4). Substituted hydroxyalkynes **1b** and **1c** also underwent the thiolative lactonization regio- and stereoselectively in high yields (Table 2, entries 5 and 6). The thiolative lactonization of **1d** took place to give thiolated lactone **3da** in 27% yield along with some byproducts (the conversion of disulfide was 78%) (Table 2, entry 7). The thiolative lactonization of terminal alkynes **1e** and **1f** was also attempted, and the corresponding $\gamma$- and $\delta$-lactone derivatives **3ea** and **3fa** were obtained, respectively, although the yield of **3fa** was low



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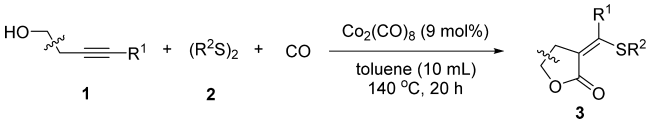
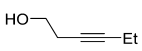
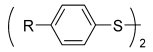
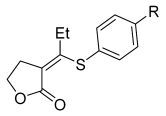
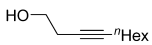
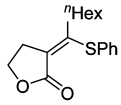
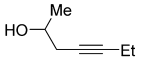
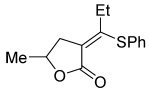
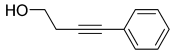
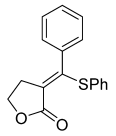
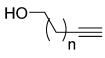
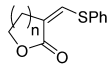
**Table 2. $Co_2(CO)_8$-Catalyzed Thiolative Lactonization of Acetylenic Alcohols with Various Disulfides[a]**




| entry | alkyne | disulfide | yield,%[b] |
|---|---|---|---|
| |  |  |  |
| 1 | **1a** | R = H (**2a**) | **3aa**, 82 (71) |
| 2 | | Me (**2b**) | **3ab**, 71 (64) |
| 3 | | OMe (**2c**) | **3ac**, 73 (65) |
| 4 | | Cl (**2d**) | **3ad**, 81 (75) |
| 5 |  | $(PhS)_2$ |  |
| | **1b** | **2a** | **3ba**, 93 |
| 6 |  | $(PhS)_2$ |  |
| | **1c** | **2a** | **3ca**, 90 (76) |
| 7 |  | $(PhS)_2$ |  |
| | **1d** | **2a** | **3da**, 27 |
| |  | $(PhS)_2$ |  |
| 8 | n = 1 (**1e**) | **2a** | **3ea**, 82 (51) |
| 9 | 2 (**1f**) | | **3fa**, 39 (19) |

[a]Alkyne (3 mmol), disulfide (1 mmol), CO (2 MPa), toluene (10 mL), $Co_2(CO)_8$ (9 mol %), 140 °C, 20 h. [b]Determined by $^1H$ NMR (isolated).

(Table 2, entries 8 and 9). In the case of **1f**, the (*E*)-isomer of **3fa** was also obtained in 23% yield.

To gain insight into the reaction pathway for this thiolative lactonization, the same reaction was examined using a cobalt−alkyne complex as catalyst (eq 7). As a result, the thiolative lactonization of **1a** proceeded successfully to give **3aa** in 81% yield. The result suggests that the cobalt−alkyne complex is a key species in this thiolative lactonization. In this $Co_2(CO)_8$-catalyzed thiolative lactonization, most of the catalyst was soluble in solution (toluene), and therefore, the reaction may proceed by homogeneous catalysis.[10] Although the precise mechanism for this cobalt-catalyzed thiolative lactonization requires further detailed mechanistic experiments, an outline of a possible pathway is shown in Scheme 1. Initially, $Co_2(CO)_8$ reacts with acetylenic alcohol **1** to form cobalt−alkyne complex **A**. Intramolecular coordination of the hydroxyl group of **1** to the cobalt atom of complex **A** and reaction with disulfide **2** leads to complex **B** with concomitant formation of the thiol. The formation of the thiol was confirmed by monitoring the reaction mixture by $^1H$ NMR. CO insertion gives complex **C**, followed by reductive elimination to form complex **D**. The subsequent ligand-exchange reaction with substrate **1** affords the desired thiolated lactone derivative **3** with regeneration of complex **A**.

**Scheme 1. A Possible Pathway for the $Co_2(CO)_8$-Catalyzed Thiolative Lactonization**

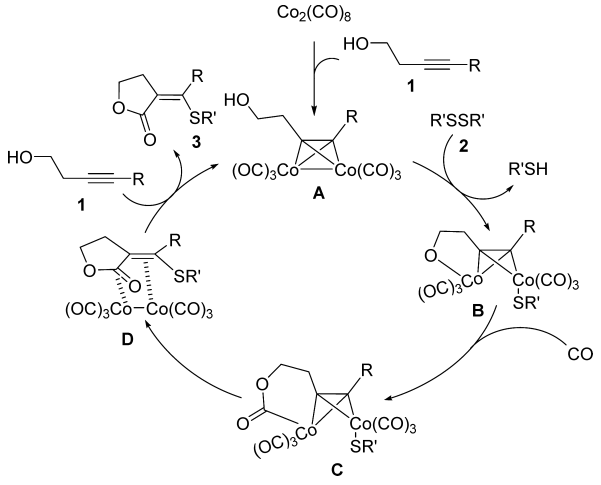
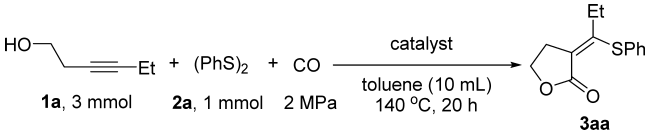
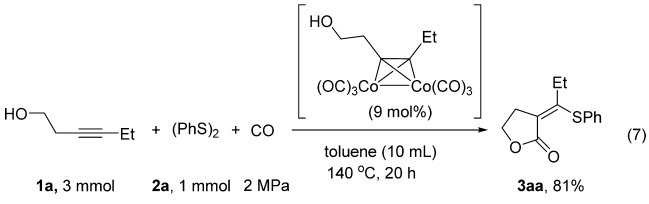



**Table 3. Transition-Metal-Catalyzed Thiolative Lactonization of 3-Hexyn-1-ol**




| entry | catalyst | | yield, %[a] |
|---|---|---|---|
| 1 | none | | N.R. |
| 2 | $Co_2(CO)_8$ | 9 mol % | 82 |
| 3 | $RuHCl(CO)(PPh_3)_3$ | 5 mol % | 38 |
| 4 | $Rh_2Cl_2(cod)_2$ | 2.5 mol % | 30 |
| 5 | $NiCl_2$ | 5 mol % | 24 |
| 6 | $Ni(acac)_2{\cdot}2H_2O$ | 5 mol % | 32 |
| 7 | $(PPh_3)AuNTf_2$ | 5 mol % | N.D. |
| 8 | $PdCl_2$ | 5 mol % | 68 |
| 9 | $Pd(OAc)_2$ | 5 mol % | 58 |
| 10 | $Pd(OAc)_2$ | 18 mol % | 76 |
| 11[b] | $PdCl_2$ | 5 mol % | 78 |
| 12[b] | $Pd(OAc)_2$ | 5 mol % | 82 |
| 13 | $Pd_2(dba)_3{\cdot}CHCl_3$ | 2.5 mol % | 66 |
| 14 | $Pd(PPh_3)_4$ | 5 mol % | 95 |
| 15 | $Pd(PPh_3)_4$ | 2 mol % | 78 |
| 16 | $Pd(PPh_3)_4$ | 18 mol % | 98 |

[a]Determined by $^1H$ NMR. [b]$PPh_3$ (10 mol %) was added.



(7)



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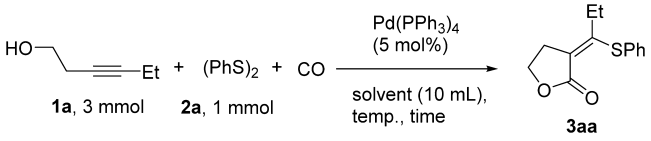
**Table 4. Palladium-Catalyzed Thiolative Lactonization of 3-Hexyn-1-ol with Diphenyl Disulfide**




1a, 3 mmol 2a, 1 mmol 3aa

| entry | CO, MPa | solvent | temp, °C | time, h | yield, %[a] |
|---|---|---|---|---|---|
| 1 | 0.5 | toluene | 140 | 20 | 78 |
| 2 | 1 | toluene | 140 | 20 | 88 (83) |
| 3 | 2 | toluene | 140 | 20 | 95 |
| 4 | 3 | toluene | 140 | 20 | 87 |
| 5 | 2 | toluene | 120 | 20 | 71 |
| 6 | 2 | toluene | 100 | 20 | 8 |
| 7[b] | 2 | toluene | 140 | 20 | 48 |
| 8 | 2 | $CH_3CN$ | 140 | 20 | 76 |
| 9 | 1 | PhCN | 140 | 20 | 98 |
| 10 | 2 | toluene | 140 | 10 | 91 |
| 11 | 2 | toluene | 140 | 40 | 84 |

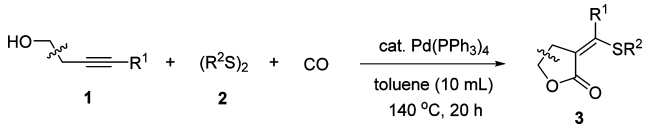
[a]Determined by $^1$H NMR (isolated). [b]3-Hexyn-1-ol (1.2 mmol).

**2.2. Palladium-Catalyzed Thiolative Lactonization of Internal Alkynes Bearing a Hydroxy Group.** To clarify the catalyst scope of the thiolative lactonization, we next examined the carbonylation of 3-hexyn-1-ol **1a** with CO and diphenyl disulfide **2a** by varying the catalysts, and the results are shown in Table 3. Among the catalysts examined, ruthenium (Table 3, entry 3), rhodium (Table 3, entry 4), nickel (Table 3, entries 5 and 6), and palladium (Table 3, entries 8–16) complexes exhibit catalytic activity in the thiolative carbonylation. Among them, $Pd(PPh_3)_4$ is the best catalyst. Interestingly, increasing the amount of the catalyst leads to exclusive formation of the desired **3aa** (Table 3, entry 16). In the absence of catalyst, no reaction is observed (Table 3, entry 1).

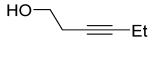
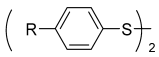
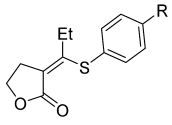
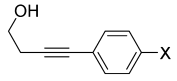
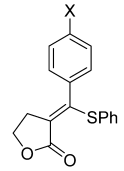
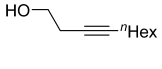
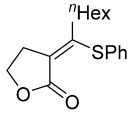
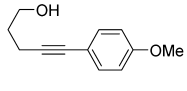
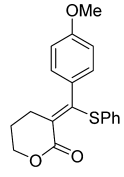
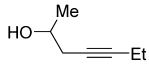
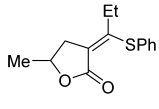
Further detailed optimization of the thiolative lactonization conditions was investigated using 5 mol % of $Pd(PPh_3)_4$, and the results are shown in Table 4. Both lower and higher CO pressures slightly decrease the yield of **3aa** (Table 4, entries 1, 2, and 4), A decrease in the temperature (Table 4, entries 5 and 6) or the amount of **1a** (Table 4, entry 7) dramatically decreases the yield of **3aa**. The thiolative lactonization also proceeds in $CH_3CN$ or PhCN as solvent (Table 4, entries 8 and 9). Even in 10 h, the thiolative lactonization proceeds well (Table 4, entry 10).

To investigate the scope and limitation of substrates, thiolative lactonization using a variety of acetylenic alcohols **1** and organic disulfides **2** was examined, and the results are shown in Table 5.

**Table 5. Palladium-Catalyzed Thiolative Lactonization of Acetylenic Alcohols with Various Disulfides[a]**




1 2 3

| entry | alkyne | disulfide | yield, %[b] | entry | alkyne | disulfide | yield, %[b] |
|---|---|---|---|---|---|---|---|
| |  |  |  | |  | $(PhS)_2$ |  |
| 1 | **1a** | R = H (**2a**) | **3aa**, 88 (83) | 8[c] | X = H (**1d**) | **2a** | **3da**, 46 (20) |
| 2 | | Me (**2b**) | **3ab**, 93 (81) | 9 | Me (**1g**) | | **3ga**, 74 (62) |
| 3 | | OMe (**2c**) | **3ac**, 90 (80) | 10 | OMe (**1h**) | | **3ha**, 98 (83) |
| 4 | | Cl (**2d**) | **3ad**, 80 (68) | 11[c] | $CF_3$ (**1i**) | | **3ia**, 40 (27) |
| 5 | | $NO_2$ (**2e**) | **3ae**, 83 (74) | | | | |
| 6 |  | $(PhS)_2$ |  | 12[c] |  | $(PhS)_2$ |  |
| | **1b** | **2a** | **3ba**, 87 (65) | | **1j** | **2a** | **3ja**, 72 (55) |
| 7 |  | $(PhS)_2$ |  | | | | |
| | **1c** | **2a** | **3ca**, 71 (66) | | | | |

[a]Alkyne (3 mmol), disulfide (1 mmol), CO (1 MPa), toluene (10 mL), $Pd(PPh_3)_4$ (5 mol %), 140 °C, 20 h. [b]Determined by $^1$H NMR (isolated). [c]CO (2 MPa).



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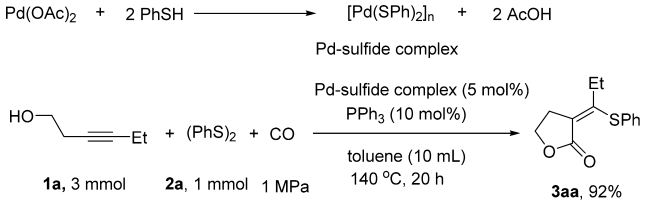
When the reaction of hydroxyalkyne **1** (3 mmol) with diphenyl disulfide (1 mmol) was conducted in the presence of $Pd(PPh_3)_4$ (5 mol %) in toluene (10 mL) at 140 °C for 20 h, the corresponding γ-lactone **3** is obtained. Methoxy, chloro, and nitro groups on the para position of disulfides **2c**, **2d**, and **2e** are tolerant to the thiolative lactonization (Table 5, entries 3−5). Similarly, both electron-donating (Table 5, entries 9 and 10) and electron-withdrawing (Table 5, entry 11) groups on the para position of acetylenic alcohols **1g**, **1h**, and **1i** are also tolerant to the reaction conditions. In the case of **1d**, the conversion of disulfide was 56%, and some byproducts were obtained. A similar result was obtained from **1i**. Not only γ-lactones, but also δ-lactone **3ja**, can be synthesized by this thiolative lactonization, although the yield of **3ja** is lower compared with those of the γ-lactones (Table 5, entry 12).

To obtain insight into the present Pd-catalyzed thiolative lactonization, we examined the catalytic thiolative lactonization of acetylenic alcohols using a preformed Pd−sulfide complex (Scheme 2). Initially, the Pd−sulfide complex was prepared by

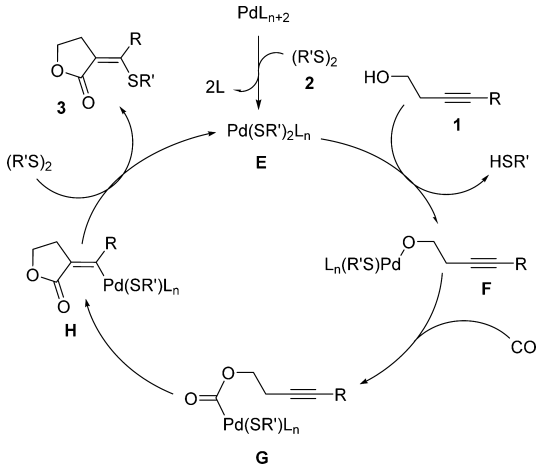
**Scheme 2. Pd−Sulfide Complex Catalyzed Thiolative Lactonization**



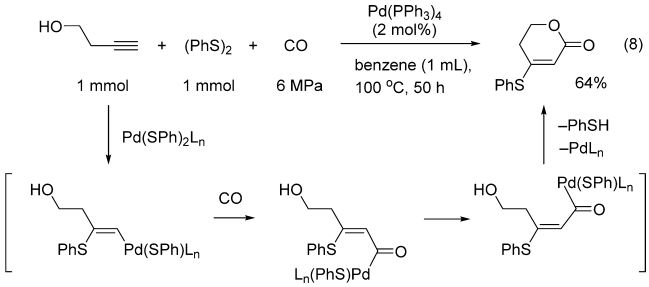

reaction of $Pd(OAc)_2$ with benzenethiol according to the literature.[11] The reaction of 3-hexyn-1-ol (**1a**) with diphenyl disulfide (**2a**), triphenylphosphine, and CO in the presence of 5 mol % of Pd−sulfide complex as a catalyst afforded the corresponding γ-lactone derivative (**3aa**) in 92% yield. This result suggests that the Pd−sulfide complex is a highly effective catalyst for the thiolative lactonization of acetylenic alcohols. In this $Pd(PPh_3)_4$-catalyzed thiolative lactonization, large amounts of a reddish brown solid (most probably Pd−sulfide cluster) were formed during the reaction. Therefore, the Pd-catalyzed reaction may proceed by heterogeneous catalysis.[12]

We have previously reported a similar thiolative lactonization of terminal alkynes having a hydroxy group using palladium catalysts such as $Pd(PPh_3)_4$ (eq 8).[13] This thiolative lactonization is assumed to proceed via the oxidative addition of $(PhS)_2$ to the Pd(0) complex to generate the palladium sulfide complex, which adds regioselectively to the alkyne, followed by CO insertion, leading to the (*Z*)-isomer of the corresponding thiolative carbonylation product. Finally, *Z*-to-*E* isomerization, followed by cyclization, affords the thiolated lactone derivative. The *Z*-to-*E* isomerization gradually proceeded *in situ* in the presence of a hydroxyl group, and therefore, this thiolative lactonization requires a longer reaction time (50 h). The regioselectivity of this reaction is determined in the thiopalladation stage, where the more bulky palladium moiety is located at the terminal position. In the case of internal alkynes, it is reasonable to assume that a regioisomeric mixture of the thiolated lactone derivatives will be formed because of the similar bulkiness surrounding both alkyne carbons. However, the present thiolative lactonization proceeds regioselectively. This suggests that, in the thiolative lactonization of internal alkynes, coordination of the hydroxy group to the palladium catalyst plays an important role. Thus, we propose a possible pathway for the palladium-catalyzed thiolative lactonization of internal alkynes bearing a hydroxy group, as shown in Scheme 3. In contrast to $Co_2(CO)_8$, which forms the alkyne

**Scheme 3. A Possible Pathway for $Pd(PPh_3)_4$-Catalyzed Thiolative Lactonization**




complex initially, in the palladium-catalyzed reaction, oxidative addition of disulfide **2** to the low-valence palladium complex may occur initially to form palladium sulfide complex **E**. Then, the hydroxyl group of acetylenic alcohol **1** coordinates to the palladium species **E** with release of a thiol (R'SH), generating complex **F**. The subsequent CO insertion to give complex **G**, followed by intramolecular acylpalladation to the carbon−carbon triple bond of complex **G**, leads to complex **H**. Reductive elimination of the thiolative lactonization product **3** and oxidative addition of disulfide **2** regenerate the palladium sulfide complex **E**.




## 3. CONCLUSION

In summary, we have developed a novel transition-metal-catalyzed thiolative lactonization of internal alkynes bearing a hydroxyl group with CO and disulfides, which successfully affords γ-lactone derivatives bearing *exo*-methylene and thio groups with excellent regio- and stereoselectivities. The procedure can also be applied to δ-lactone synthesis. The obtained thiolated lactone derivatives are promising as synthetic intermediates, as the thio group can be displaced by a variety of nucleophiles, and *exo*-methylene groups make them a possible substrate for Michael addition. The mechanistic details and scope of this thiolative carbonylation are currently under investigation.

## 4. EXPERIMENTAL SECTION

**4.1. General Information.** $Co_2(CO)_8$ was obtained from commercial suppliers. $Pd(PPh_3)_4$ was synthesized according to the literature.[14] All disulfides and aliphatic alkynes (**1a**−**1c**, **1e**, and **1f**) were



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purchased from a commercial source and used without further purification. Aromatic alkynes (**1d** and **1g**−**1j**) were synthesized according to the literature.[15] Toluene was used as solvent after distillation using $CaH_2$. $^1H$ NMR spectra (400 MHz) and $^{13}C$ NMR spectra (100 MHz) were taken in $CDCl_3$ with $Me_4Si$ as an internal standard. Chemical shifts in $^1H$ NMR were measured relative to $CDCl_3$ and converted to $\delta$ ($Me_4Si$) values by using $\delta$ ($CDCl_3$) 7.26 ppm. Chemical shifts in $^{13}C$ NMR were measured relative to $CDCl_3$ and converted to $\delta$ ($Me_4Si$) values by using $\delta$ ($CDCl_3$) 77.0 ppm. The use of broadband decoupling is indicated with braces. IR spectra are reported in wavenumbers ($cm^{-1}$). FAB mass spectra were obtained by employing double focusing mass spectrometers.

**4.2. General Procedure for the Synthesis of (*Z*)-3-{1-(Phenylthio)propylidene}dihydrofuran-2-one (3aa).** In a 50 mL stainless steel autoclave with a magnetic stirring bar under a $N_2$ atmosphere were sequentially placed catalyst (0.05−0.09 mmol), distilled toluene (10 mL), alkyne (3.0 mmol), and disulfide (1.0 mmol). The vessel was purged three times with carbon monoxide and then charged with the same gas to achieve a pressure of 1−2 MPa. The reaction was conducted with magnetic stirring for 20 h at 140 °C. After removal of the unreacted carbon monoxide, the resulting mixture was filtered through Celite with diethyl ether and concentrated *in vacuo* to give the crude products. Purification was performed by silica gel column chromatography (hexanes:AcOEt, 2:1) followed by recrystallization or recycling preparative HPLC employing GPC columns with $CHCl_3$ as eluent.

*4.2.1. (Z)-3-{1-(Phenylthio)propylidene}dihydrofuran-2-one (**3aa**).* In the presence of $Co_2(CO)_8$ (30.8 mg, 0.09 mmol), compound **3aa** was obtained in 71% yield (167.6 mg) following the general procedure. In the presence of $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol), compound **3aa** was obtained in 83% yield (195.2 mg) following the general procedure. Isolated as a white solid; mp 111−113 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 7.5 Hz, 3H), 2.18 (q, $J$ = 7.5 Hz, 2H), 2.98 (t, $J$ = 7.5 Hz, 2H), 4.39 (t, $J$ = 7.5 Hz, 2H), 7.35−7.44 (m, 3H), 7.54−7.58 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 12.5, 27.5, 28.3, 64.9, 114.9, 129.1, 129.4, 130.4, 136.0, 156.3, 169.9; IR (KBr) 3058, 2973, 2936, 1724, 1598, 1475, 1452, 1439, 1375, 1231, 1144, 1063, 1021, 965, 931, 853, 754, 708, 695, 672, 526 $cm^{-1}$; HRMS (FAB) calcd for $C_{13}H_{15}O_2S$ $[M + H]^+$: 235.0787; found: 235.0784. Anal. Calcd for $C_{13}H_{14}O_2S$: C, 66.64; H, 6.02. found: C, 66.52; H, 5.96.

*4.2.2. (Z)-3-{1-(p-Tolylthio)propylidene}dihydrofuran-2-one (**3ab**).* In the presence of $Co_2(CO)_8$ (30.8 mg, 0.09 mmol), compound **3ab** was obtained in 64% yield (159.7 mg) following the general procedure. In the presence of $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol), compound **3ab** was obtained in 81% yield (201.4 mg) following the general procedure. Isolated as a white solid; mp 126−128 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 0.90 (t, $J$ = 7.5 Hz, 3H), 2.17 (q, $J$ = 7.5 Hz, 2H), 2.38 (s, 3H), 2.97 (t, $J$ = 7.5 Hz, 2H), 4.38 (t, $J$ = 7.5 Hz, 2H), 7.18 (d, $J$ = 7.8 Hz, 2H), 7.44 (d, $J$ = 7.8 Hz, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 12.6, 21.3 27.4, 28.3, 64.9, 114.3, 126.7, 129.9, 136.0, 139.7, 157.0, 170.0; IR (KBr) 2977, 2934, 2872, 1721, 1597, 1492, 1461, 1444, 1369, 1243, 1147, 1030, 1019, 970, 856, 812, 750, 679, 541, 517 $cm^{-1}$; HRMS (FAB) calcd for $C_{14}H_{17}O_2S$ $[M + H]^+$: 249.0944; found: 249.0933. Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.71; H, 6.49. found: C, 67.62; H, 6.48.

*4.2.3. (Z)-3-{1-(4-Methoxyphenylthio)propylidene}dihydrofuran-2-one (**3ac**).* In the presence of $Co_2(CO)_8$ (30.8 mg, 0.09 mmol), compound **3ac** was obtained in 65% yield (171.0 mg) following the general procedure. In the presence of $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol), compound **3ac** was obtained in 80% yield (212.3 mg) following the general procedure. Isolated as a white solid; mp 139−140 °C; $^1H$ NMR (400 MHz, CDCl3): $\delta$ 0.90 (t, $J$ = 7.5 Hz, 3H), 2.15 (q, $J$ = 7.5 Hz, 2H), 2.96 (t, $J$ = 7.5 Hz, 2H), 3.84 (s, 3H), 4.38 (t, $J$ = 7.6 Hz, 2H), 6.89−6.93 (m, 2H), 7.46−7.50 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, CDCl$^3$): $\delta$ 12.5, 27.2, 28.2, 55.3, 65.0, 113.9, 114.6, 120.6, 137.6, 157.5, 160.7, 170.0; IR (KBr) 2977, 2935, 2873, 2842, 1719, 1597, 1568, 1492, 1459, 1438, 1375, 1288, 1246, 1148, 1031, 1020, 970, 855, 837, 811, 799, 748, 674, 619, 531 $cm^{-1}$; HRMS (FAB) calcd for $C_{14}H_{17}O_3S$ $[M + H]^+$: 265.0893; found: 265.0905. Anal. Calcd for $C_{14}H_{16}O_3S$: C, 63.61; H, 6.10. found: C, 63.51; H, 6.06.

*4.2.4. (Z)-3-{1-(4-Chlorophenylthio)propylidene}dihydrofuran-2-one (**3ad**).* In the presence of $Co_2(CO)_8$ (30.8 mg, 0.09 mmol), compound **3ad** was obtained in 75% yield (200.8 mg) following the general procedure. In the presence of $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol), compound **3ad** was obtained in 68% yield (182.8 mg) following the general procedure. Isolated as a white solid; mp 109−110 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 0.91 (t, $J$ = 7.6 Hz, 3H), 2.18 (q, $J$ = 7.5 Hz, 2H), 2.98 (t, $J$ = 7.6 Hz, 2H), 4.40 (t, $J$ = 7.3 Hz, 2H), 7.34−7.38 (m, 2H), 7.47−7.50 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 12.4, 27.4, 28.2, 64.9, 115.6, 129.0, 129.3, 135.8, 137.0, 155.1, 169.8; IR (KBr) 3075, 2978, 2935, 2909, 2874, 1723, 1599, 1477, 1465, 1452, 1440, 1373, 1287, 1232, 1146, 1095, 1012, 832, 746, 515 $cm^{-1}$; HRMS (FAB) calcd for $C_{13}H_{14}O_2ClS$ $[M + H]^+$: 269.0398; found: 269.0382. Anal. Calcd for $C_{13}H_{13}O_2ClS$: C, 58.10; H, 4.88. found: C, 57.94; H, 4.78.

*4.2.5. (Z)-3-{1-(4-Nitrophenylthio)propylidene}dihydrofuran-2-one (**3ae**).* In the presence of $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol), compound **3ae** was obtained in 74% yield (205.3 mg) following the general procedure. Isolated as a yellow solid; mp 141−143 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 0.95 (t, $J$ = 7.5 Hz, 3H), 2.25 (q, $J$ = 7.5 Hz, 2H), 3.02 (t, $J$ = 7.4 Hz, 2H), 4.39 (t, $J$ = 7.5 Hz, 2H), 7.58−7.63 (m, 2H), 8.15−8.20 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 12.4, 28.1, 28.4, 64.8, 120.1, 123.9, 134.3, 140.8, 147.6, 151.2, 169.1; IR (KBr) 3091, 2980, 2935, 2917, 1873, 1715, 1598, 1576, 1441, 1379, 1344, 1301, 1279, 1257, 1235, 1225, 1175, 1148, 1065, 1033, 1011, 962, 861, 850, 747, 730, 690, 668, 572, 503 $cm^{-1}$; HRMS (FAB) calcd for $C_{13}H_{14}O_4NS$ $[M + H]^+$: 280.0638; found: 280.0641. Anal. Calcd for $C_{13}H_{13}O_4NS$: C, 55.90; H, 4.69; N, 5.01 found: C, 55.80; H, 4.61; N, 5.08.

*4.2.6. (Z)-3-{1-(Phenylthio)heptylidene}dihydrofuran-2-one (**3ba**).* In the presence of $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol), compound **3ba** was obtained in 65% yield (188.2 mg) following the general procedure. Isolated as a colorless oil; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 0.80 (t, $J$ = 7.3 Hz, 3H), 0.98−1.03 (m, 4H), 1.10−1.18 (m, 2H), 1.26−1.34 (m, 2H), 2.10−2.16 (m, 2H), 2.97 (t, $J$ = 7.6 Hz, 2H), 4.38 (t, $J$ = 7.6 Hz, 2H), 7.35−7.44 (m, 3H), 7.53−7.56 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 13.8, 22.2, 27.7, 28.4, 28.7, 30.9, 34.0, 64.9, 115.0, 128.9, 129.2, 130.2, 135.9, 155.0, 169.8; IR (NaCl) 2955, 2927, 2856, 1734, 1600, 1475, 1457, 1440, 1373, 1239, 1140, 1038, 1024, 967, 831, 751, 705, 692 $cm^{-1}$; HRMS (EI) calcd for $C_{17}H_{22}O_2S$ $[M]^+$: 290.1341; found: 290.1350.

*4.2.7. (Z)-5-Methyl-3-{1-(phenylthio)propylidene}dihydrofuran-2-one (**3ca**).* In the presence of $Co_2(CO)_8$ (30.8 mg, 0.09 mmol), compound **3ca** was obtained in 76% yield (189.7 mg) following the general procedure. In the presence of $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol), compound **3ca** was obtained in 66% yield (164.8 mg) following the general procedure. Isolated as a white solid; mp 95−96 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 0.89 (t, $J$ = 7.5 Hz, 3H), 1.43 (d, $J$ = 6.2 Hz, 3H), 2.15 (q, $J$ = 7.4 Hz, 2H), 2.53 (dd, $J$ = 6.1, 16.2 Hz, 1H), 3.10 (dd, $J$ = 7.8, 16.2 Hz, 1H), 4.63−4.73 (m, 1H), 7.35−7.44 (m, 3H), 7.53−7.58 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 12.5, 22.2, 27.4, 36.0, 73.3, 116.1, 129.1, 129.3, 130.4, 135.9, 155.8, 169.5; IR (KBr) 3057, 2973, 2935, 2871, 1718, 1595, 1475, 1438, 1338, 1239, 1148, 1158, 1114, 1027, 955, 934, 912, 889, 826, 753, 708, 664 $cm^{-1}$; HRMS (FAB) calcd for $C_{14}H_{17}O_2S$ $[M + H]^+$: 249.0944; found: 249.0956.

*4.2.8. (Z)-3-{1-Phenyl-1-(phenylthio)methylene}dihydrofuran-2-one (**3da**).* In the presence of $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol), compound **3da** was obtained in 20% yield (56.4 mg) following the general procedure. Isolated as a white solid; mp 139−141 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.77 (t, $J$ = 7.4 Hz, 2H), 4.33 (t, $J$ = 7.4 Hz, 2H), 6.95−7.14 (m, 8H), 7.16−7.20 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 29.9, 65.3, 117.4, 127.9, 128.0, 128.1, 128.2, 130.9, 135.3, 136.8, 153.0, 169.7; IR (KBr) 3055, 2982, 2905,1738, 1729, 1607, 1581, 1588 1473, 1440, 1367, 1214, 1160, 1080, 1028, 967, 897, 749, 699, 684 $cm^{-1}$; HRMS (FAB) calcd for $C_{17}H_{15}O_2S$ $[M + H]^+$: 283.0787; found: 283.0786.

*4.2.9. (Z)-3-{(Phenylthio)methylene}dihydrofuran-2-one (**3ea**).* In the presence of $Co_2(CO)_8$ (30.8 mg, 0.09 mmol), compound **3ea** was obtained in 51% yield (107.3 mg) following the general procedure. Isolated as a white solid; mp 125−126 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 3.00 (td, $J$ = 2.3, 7.6 Hz, 2H), 4.42 (t, $J$ = 7.5 Hz, 2H), 7.12 (t, $J$ = 2.0 Hz, 1H), 7.32−7.41 (m, 3H), 7.47−7.51 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 28.7, 66.6, 118.2, 128.3, 129.4, 131.1, 135.5,



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141.1, 170.2; IR (KBr) 2994, 2978, 2919, 1729, 1610, 1478, 1443, 1434, 1373, 1318, 1260, 1188, 1176, 1164, 1095, 1018, 963, 850, 835, 762, 745, 693, 664 $cm^{-1}$; HRMS (EI) calcd for $C_{11}H_{10}O_2S$ $[M]^+$: 206.0402; found: 206.0390.

*4.2.10. (Z)-3-{(Phenylthio)methylene}tetrahydropyran-2-one (**3fa**).* In the presence of $Co_2(CO)_8$ (30.8 mg, 0.09 mmol), compound **3fa** was obtained in 19% yield (40.9 mg) following the general procedure. Isolated as a white solid; mp 148−150 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 1.91−1.98 (m, 2H), 2.65 (dt, $J$ = 1.4, 6.3 Hz, 2H), 4.37 (t, $J$ = 5.5 Hz, 2H), 7.12 (t, $J$ = 1.6 Hz, 1H), 7.33−7.40 (m, 3H), 7.48−7.53 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 23.0, 28.9, 69.3, 117.8, 128.2, 129.3, 131.2, 137.0, 148.5, 165.2; IR (KBr) 2970, 2937, 2898, 1683, 1558, 1472, 1439, 1432, 1398, 1341, 1314, 1274, 1228, 1189, 1176, 1132, 1071, 980, 959, 882, 835, 828, 756, 693, 502 $cm^{-1}$; HRMS (FAB) calcd for $C_{12}H_{13}O_2S$ $[M + H]^+$: 221.0631; found: 221.0612.

*4.2.11. (Z)-3-{1-(Phenylthio)-1-(p-tolyl)methylene}dihydrofuran-2-one (**3ga**).* In the presence of $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol), compound **3ga** was obtained in 62% yield (185.2 mg) following the general procedure. Isolated as a pale yellow solid; mp 107−109 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.20 (s, 3H), 2.78 (t, $J$ = 7.5 Hz, 2H), 4.31 (t, $J$ = 7.5 Hz, 2H), 6.85−6.94 (m, 4H), 7.00−7.11 (m, 3H), 7.16−7.19 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 21.1, 30.0, 65.2, 117.5, 128.0, 128.1, 128.2, 128.7, 131.2, 133.9, 135.1, 137.9, 153.2, 169.7; IR (KBr) 3034, 2974, 2914, 1736, 1601, 1508, 1478, 1438, 1376, 1220, 1208, 1194, 1083, 1029, 968, 906, 810, 747, 691, 678, 538 $cm^{-1}$; HRMS (EI) calcd for $C_{18}H_{16}O_2S$ $[M]^+$: 296.0871; found: 296.0867.

*4.2.12. (Z)-3-{1-(4-Methoxyphenyl)-1-(phenylthio)methylene}-dihydrofuran-2-one (**3ha**).* In the presence of $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol), compound **3ha** was obtained in 83% yield (258.3 mg) following the general procedure. Isolated as a yellow solid; mp 117−119 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.81 (t, $J$ = 7.4 Hz, 2H), 3.70 (s, 3H), 4.31 (t, $J$ = 7.4 Hz, 2H), 6.65 (d, $J$ = 6.8 Hz, 2H), 6.94 (d, $J$ = 6.8 Hz, 2H), 7.01−7.11 (m, 3H), 7.15−7.19 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 30.0, 55.1, 65.1, 113.3, 117.6, 127.9, 128.2, 129.1, 129.7, 131.4, 134.8, 152.7, 159.1, 169.7; IR (KBr) 3058, 2978, 2959, 2909, 2831, 1723, 1606, 1591, 1506, 1462, 1440, 1413, 1369, 1293, 1246, 1216, 1175, 1088, 1032, 972, 905, 835, 815, 744, 702, 683, 643, 590, 544, 525 $cm^{-1}$; HRMS (FAB) calcd for $C_{18}H_{17}O_3S$ $[M + H]^+$: 313.0893; found: 313.0884.

*4.2.13. (Z)-3-[1-(Phenylthio)-1-{4-(trifluoromethyl)phenyl}methylene]dihydrofuran-2-one (**3ia**).* In the presence of $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol), compound **3ia** was obtained in 27% yield (94.1 mg) following the general procedure. Isolated as a white solid; mp 130−132 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.75 (t, $J$ = 7.5 Hz, 2H), 4.35 (t, $J$ = 7.5, 2H), 7.01−7.07 (m, 2H), 7.08−7.13 (m, 3H), 7.15−7.19 (m, 2H), 7.36−7.41 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): $\delta$ 29.8, 65.3, 118.2, 123.6 (q, $J_{C-F}$ = 272 Hz), 125.1 (q, $J_{C-F}$ = 3.8 Hz), 128.5, 128.6, 128.7, 130.0 (q, $J_{C-F}$ = 32.7 Hz), 130.2, 135.5, 140.5, 151.3, 169.4; $^{19}F\{^1H\}$NMR (376 MHz, $CDCl_3$): $\delta$ −62.8; IR (KBr) 3073, 3056, 2977, 2918, 1733, 1605, 1473, 1442, 1434, 1408, 1376, 1329, 1223, 1165, 1156, 1115, 1092, 1067, 1034, 1022, 977, 827, 745, 690, 664 $cm^{-1}$; HRMS (FAB) calcd for $C_{18}H_{14}O_2F_3S$ $[M + H]^+$: 351.0661; found: 351.0683.

*4.2.14. (Z)-3-{1-(4-Methoxyphenyl)-1-(phenylthio)methylene}-tetrahydropyran-2-one (**3ja**).* In the presence of $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol), compound **3ja** was obtained in 55% yield (178.6 mg) following the general procedure. Isolated as a white solid; mp 115−117 °C; $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 1.79−1.86 (m, 2H), 2.30 (t, $J$ = 6.6 Hz, 2H), 3.68 (s, 3H), 4.32 (t, $J$ = 5.2 Hz, 2H), 6.58−6.63 (m, 2H), 6.74−6.79 (m, 2H), 6.98−7.10 (m, 3H), 7.13−7.17 (m, 2H); $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): $\delta$ 23.1, 28.6, 55.1, 68.6, 113.3, 116.8, 128.0, 128.1, 129.1, 129.6, 132.6, 135.8, 158.7, 159.5, 165.8; IR (KBr) 2945, 2910, 2832, 1682, 1606, 1547, 1503, 1440, 1395, 1331, 1283 1267, 1245, 1174, 1129, 1110, 1073, 1032, 917, 839, 803, 742, 691, 585, 547, 539 $cm^{-1}$; HRMS (EI) calcd for $C_{19}H_{18}O_3S$ $[M]^+$: 326.0977; found: 326.0964.

**4.3. Preparation of Cobalt Alkyne Complex.** In a flask (30 mL) equipped with a magnetic stirring bar were placed $Co_2(CO)_8$ (1.0 mmol), distilled toluene (1 mL), and 3-hexyn-1-ol (1.0 mmol). The mixture was stirred for 24 h at room temperature under a $N_2$ atmosphere. The resulting mixture was concentrated *in vacuo*. The purification was performed by silica gel column chromatography (hexanes:AcOEt, 2:1).

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

X-ray crystal structures (ORTEP) of **3aa**, the details of the experiment about the catalytic system, characterization data for all new compounds, and a CIF file giving crystallographic data for **3aa**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00977.

## ■ AUTHOR INFORMATION


### Corresponding Author

*Tel.: +81-72-254-9290. Fax: +81-72-254-9910. E-mail: ogawa@chem.osakafu-u.ac.jp.


### Notes

The authors declare no competing financial interest.

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