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Gold-Catalyzed Oxidative Reactions of Propargylic Carbonates Involving 1,2-Carbonate Migration: Stereoselective Synthesis of Functionalized Alkenes

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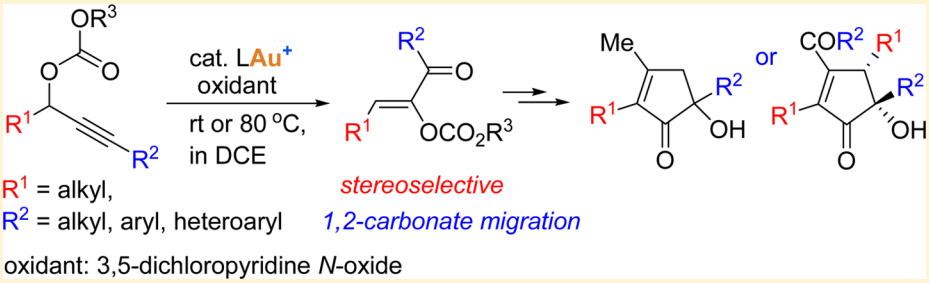
Supporting Information



ABSTRACT: A gold-catalyzed oxidative reaction of propargylic carbonates or acetates using 3,5-dichloropyridine as the oxidant has been developed. The reaction provides efficient access to α-functionalized-α,β-unsaturated ketones with excellent regio- and diastereocontrol via a regioselective attack of the *N*-oxide to the gold-activated alkyne followed by a 1,2-carbonate migration. In addition, the alkene products could be further transformed into the valuable 5-hydroxycyclopent-2-enones via cyclocondensation with acetone or cyclodimerization under basic conditions.

INTRODUCTION

Gold-catalyzed rearrangement reactions of propargylic carboxylates have been proved as useful strategies for rapid access to a wide range of functionalized structural motifs.[1] Two main competitive processes, namely 1,2-acyloxy migration[2] and 3,3-rearrangement[3] via intermediate **A**, are usually involved, leading to the formation of vinyl gold-carbenoid **B** or gold-coordinated carboxyallene **C**, respectively (Scheme 1). The reaction patterns are highly dependent on the substituents on either end of the propargyl moiety. It is widely accepted that terminal or electron-poor alkynes undergo 1,2-acyloxy migration, while internal alkynes prefer 3,3-rearrangement, although there are some exceptions.[4] It is noted that compared with the intensive development of propargyl esters, little attention has been paid to the gold-catalyzed transformations of propargyl carbonates.[5] On the other hand, gold-catalyzed oxidative reactions of alkynes in the presence of pyridine or quinoline *N*-oxides provide new possibilities in the development of novel transformation reactions.[6] During our ongoing project on gold-catalyzed rearrangement reactions of propargylic carbonates[7] and oxidative reactions of propargylic alcohols,[8] we envisioned that the presence of an oxidant in the reaction system of the internal propargylic carbonates may hamper the normal 3,3-rerrangement reaction and trigger a new reaction pathway. That is, gold catalyzes regioselective generation of α-carbonyl gold carbenoid **E** followed by nucleophilic attack of the adjacent carbonyl group of the carbonate (Scheme 2). This would result in a formal 1,2-carbonate migration of the internal propargylic carbonates, leading to functionalized alkenes.[9] In this study, we report the gold-catalyzed oxidative reaction of propargylic carbonates using 3,5-dichloropyridine *N*-oxide as the oxidant, which provides α-functionalized-α,β-unsaturated ketones with excellent stereoselectivity. In addition, these alkene products are also applied successfully as diketone equivalents for the diastereoselective synthesis of cyclopentenones.

RESULTS AND DISCUSSION

To test the feasibility of our hypothesis, methyl (1-phenylhept-1-yn-3-yl) carbonate **1a** was chosen as a model substrate for optimization of the reaction conditions. The results are shown in Table 1. In light of the efficient performance of 8-methyl quinoline *N*-oxide (**2a**) in various gold-catalyzed oxidative reactions,[6q−t] we first investigated the reaction of **1a** with **2a** in the presence of 5 mol % of Johnphos(MeCN)AuSbF$_6$ (**A**) (Table 1, entry 1). It was found that α-functionalized-α,β-unsaturated ketone **3a** could be obtained in 70% NMR yield at 50 °C for 4 h in DCE as a mixture of geometric isomers (Z/E = 3.7:1).[10] The results indicated that 1,2-carbonate migration indeed occurred during the reaction process. Switching the oxidant to 3,5-dichloropyridine *N*-oxide **2b** allowed the formation of **3a** in higher yield of 88% with high Z/E ratio (28:1, entry 2). Decreasing the amount of **2b** to 1.2 equiv

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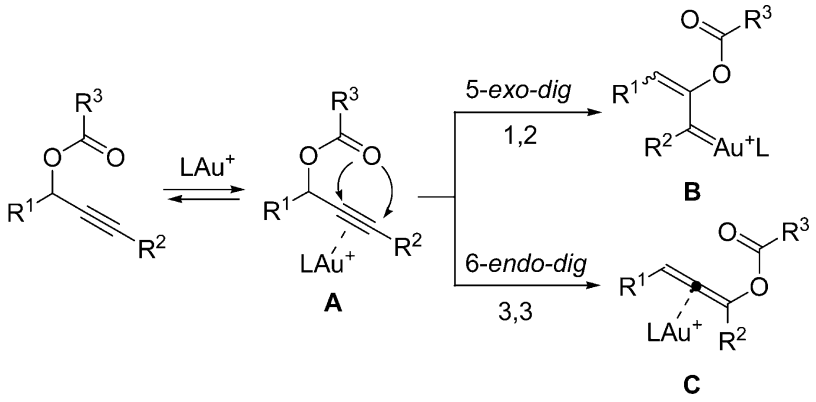
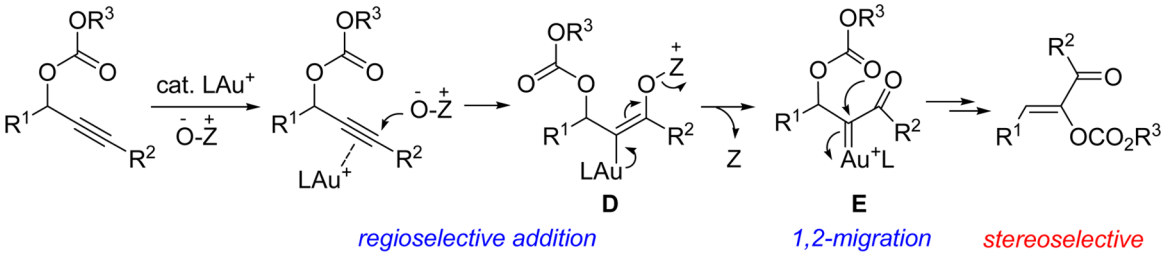
Scheme 1

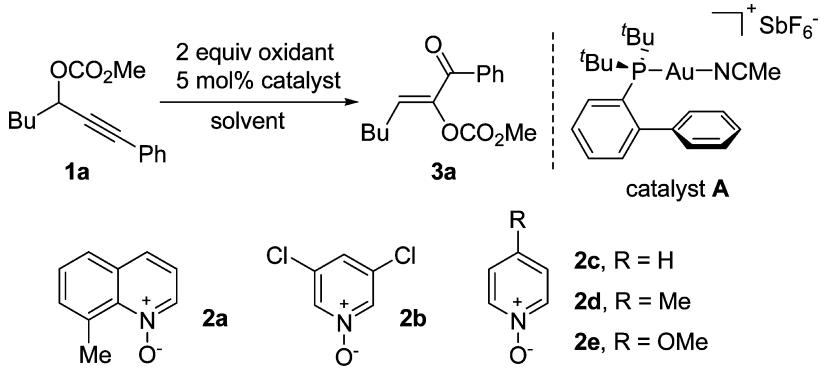


Scheme 2



$^{-}O\text{-}Z^{+}$ = pyridine *N*-oxide, quinoline *N*-oxide

Table 1. Optimization Studies for the Formation of Alkene 3a



entry	oxidant	catalyst	solvent	temp (°C)	time (h)	yield (%) (*Z*/*E* ratio)[a]
1	**2a**	**A**	DCE	50	4	70 (3.7:1)
2	**2b**	**A**	DCE	50	3	88 (28:1)
3	**2b**	**A**	DCE	50	5	88 (21:1)[b]
4	**2c**	**A**	DCE	50	10	45 (76:1)
5	**2d**	**A**	DCE	50	10	29 (>200:1)
6	**2e**	**A**	DCE	50	10	14 (>300:1)
7	**2b**	**A**	DCM	50	5	93 (22:1)[c]
8	**2b**	**A**	THF	50	3	93 (46:1)
9	**2b**	**A**	Toluene	50	3	88 (21:1)
10	**2b**	$PPh_3AuCl/AgSbF_6$	DCE	50	2	89 (59:1)
11	**2b**	$PPh_3AuCl/AgOTf$	DCE	50	3	89 (52:1)
12	**2b**	PPh_3AuNTf_2	DCE	50	2	85 (65:1)
13	**2b**	$IPrAuCl/AgSbF_6$	DCE	50	2	97 (74:1)
14	**2b**	$IPrAuCl/AgSbF_6$	DCE	rt	1.5	96 (69:1)[d]
15	**2b**	PPh_3AuCl	DCE	50	5	–[e]
16	**2b**	$AgSbF_6$	DCE	50	5	–[e]

[a]Combined NMR yields. Determined by ^1H NMR using CH_2Br_2 as an internal standard of the crude reaction mixture. [b]A 1.2 equiv of **2b** was used. [c]In a sealed tube. [d]Isolated yield was 95%. [e]Compound **1a** was recovered in 99% yield.

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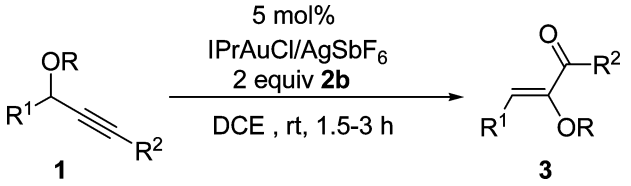
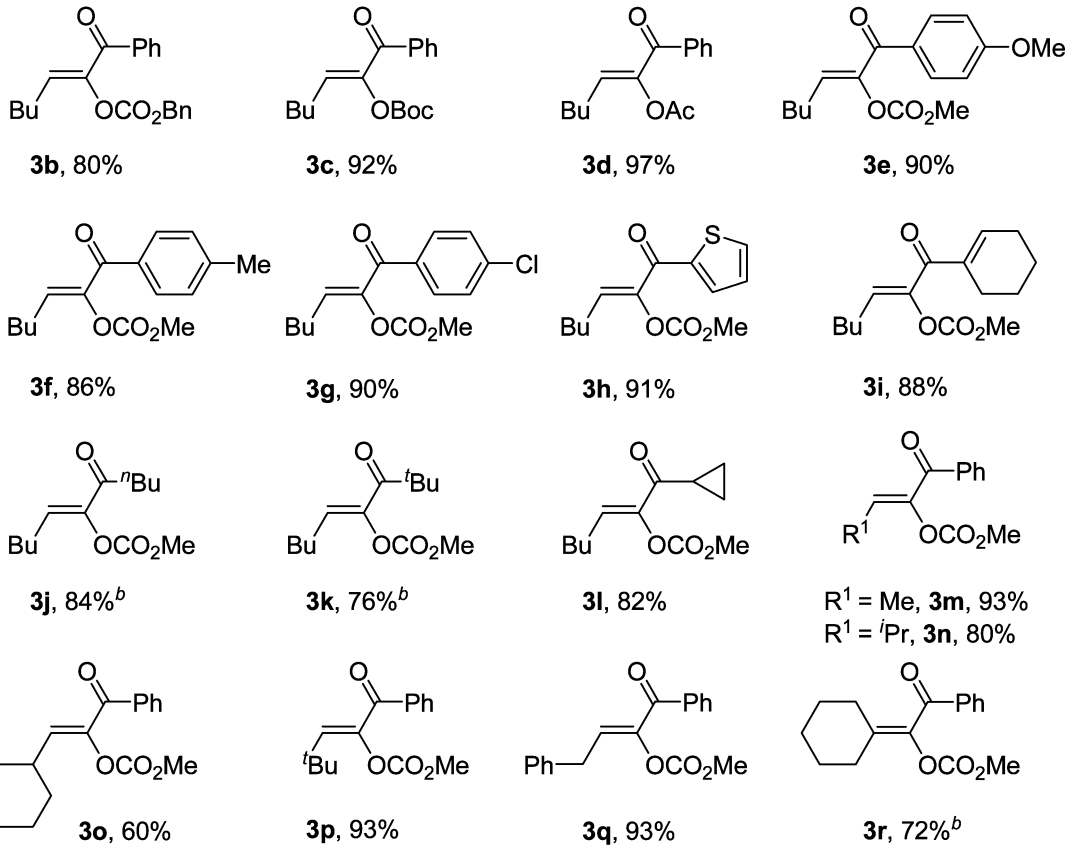
Table 2. Synthesis of Functionalized Alkenes 3 through Gold-Catalyzed Oxidative Reactions of 1[a]





[a]Isolated yields. [b]At 80 °C, 2−5 h.

resulted in a longer reaction time and lower *Z*/*E* ratio (entry 3). Employment of other oxidants such as pyridine *N*-oxide, 4-methylpyridine *N*-oxide, or 4-methoxypyridine *N*-oxide resulted in lower yields of **3a** (14−45%, entries 4−6), possibly due to the competitive coordination of the released pyridine derivatives, which decreased the reactivity of the gold catalyst.[11] The solvent effects were also examined. The reactions proceeded well also in DCM, THF, and toluene, providing **3a** in 88−93% yields with the *Z*/*E* ratio ranging from 21:1 to 46:1 (entries 7−9). Next, a series of gold catalysts were screened with the use of 3,5-dichloropyridine *N*-oxide **2b** as the oxidant. The frequently employed gold(I) complexes such as PPh_3AuCl with different counterions of SbF_6^-, OTf^-, or NTf_2^- catalyzed the reaction efficiently to deliver **3a** in 85−89% yields with high stereoselectivity (entries 10−12). To our delight, the reaction of **1a** with IPrAuCl/$AgSbF_6$ [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] as the catalyst in DCE led to 97% yield (*Z*/*E* = 74:1) at 50 °C or 96% yield (*Z*/*E* = 69:1) of **3a** at the room temperature (entries 13−14). Control experiments with PPh_3AuCl or $AgSbF_6$ alone did not give the desired product, and the starting material **1a** was recovered in high yields (entries 15−16).

Having the optimized reaction conditions in hand, we next examined the substrate scope using various substituted propargylic carbonates under the reaction conditions shown in Table 1, entry 14. The results are shown in Table 2. In all cases, the desired alkene products **3** were obtained as a single *Z*-isomer. We first investigated the effect of the protecting groups (R) on the carbonate moiety. It was found that in addition to methyl carbonate, benzyl or *tert*-butyl carbonates were all compatible under the catalytic reaction conditions, furnishing **3b** and **3c** in 80 and 92% yields, respectively. Propargylic acetate also underwent the reaction smoothly to afford **3d** in 97% yield. We next examined the substituent effect (R^2) on the alkyne terminus. Both electron-rich and electron-deficient aryl substituents (*p*-OMe, *p*-Me, *p*-Cl) were tolerated well during the reaction, providing the corresponding products **3e**−**3g** in high yields of 86−90%. A thienyl-substituted alkyne was also suited, producing **3h** in 91% yield. Alkenyl-substituted alkyne such as a cyclohexenyl-substituted one could also be used in this reaction, and the desired **3i** was obtained in 88% yield. A range of alkyl-substituted alkynes such as *n*-butyl, *tert*-butyl, or cyclopropyl-substituted ones were efficiently transformed into alkenes **3j**−**3l** in good yields of 76−84%. It should be noted

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Scheme 3

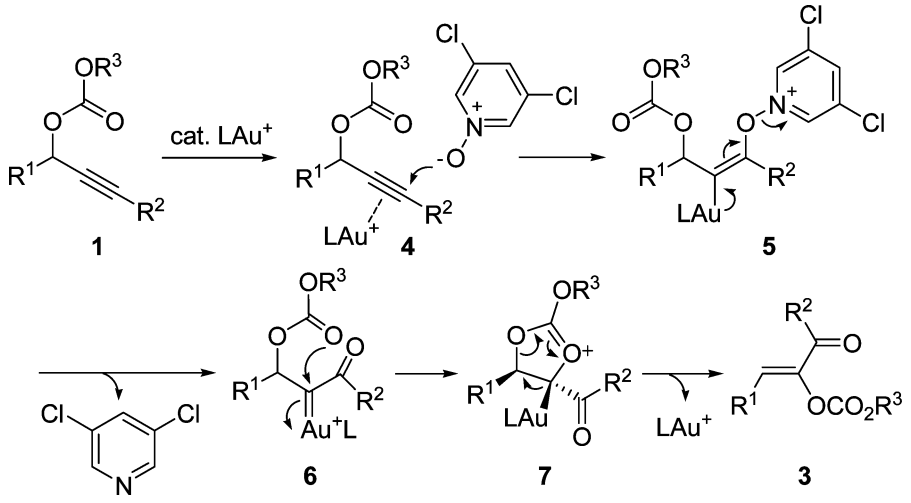
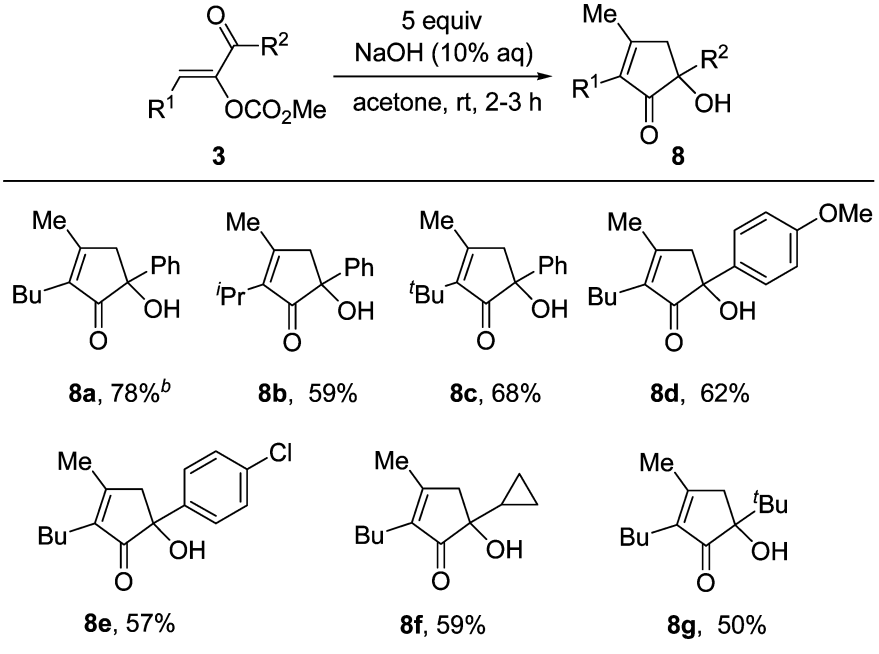


Table 3. Cyclocondensation of 3 with Acetone to Cyclopentenones 8[a]



[a]Isolated yields. [b]A 1.2 equiv of NaOH (10% aq) was used.

that in the cases of *n*-butyl or *tert*-butyl-substituted alkynes higher reaction temperature (80 °C) was required in order to complete the reaction (for **3j** and **3k**). We also investigated the substituent effect at the propargylic position (R^1). When R^1 is a methyl group, the reaction proceeded smoothly to give **3m** in 93% yield. Sterically more demanding alkyl substitutents such as isopropyl, cyclohexyl, and even *tert*-butyl groups at this position were accommodated well to afford **3n**−**3p** in 60−93% yields. Benzyl-substituted propargyl carbonate afforded **3q** in a high yield of 93%. Tertiary propargyl carbonate bearing a cyclic ring at C-1 also participated in this reaction, leading to **3r** in 72% yield. When substrate bearing a phenyl group at the propargylic position such as 1,3-diphenylprop-2-ynyl methyl carbonate was employed, two major products were isolated in a high combined yield. However, because these two products could not be separated from each other by column chromatography, their exact structures have not been defined yet. The structure and the geometric configuration of the functionalized alkenes **3** was unambiguously confirmed by X-ray crystallographic analysis of **3p**.[12]

A mechanistic proposal for this gold-catalyzed oxidative reaction of propargylic carbonates is depicted in Scheme 3. Initially, regioselective attack of 3,5-dichloropyridine *N*-oxide to the gold-activated alkyne affords the alkenylgold intermediate **5**. The regioselectivity might be due to the inductive effect of the carbonate group,[9] rendering the *β*-carbon of the propargylic carbonate more electrophilic. Fragmentation of **5** gives *α*-carbonyl gold carbenoid **6**. Subsequent nucleophilic attack of the carbonyl group on the gold carbenoid[13] followed by elimination of the cationic gold catalyst affords the *α*-functionalized-*α*,*β*-unsaturated ketone **3**.[14] In cyclic transition state **7**, R^1 and COR^2 groups may prefer to be orientated trans to avoid the large steric effect, while due to the longer Au−$C(sp^3)$ bond,[15] the cis orientation of R^1 and LAu moiety might

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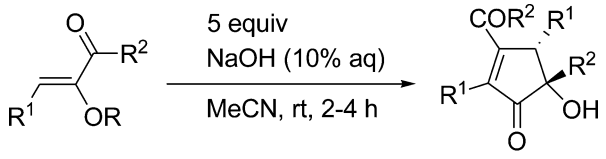
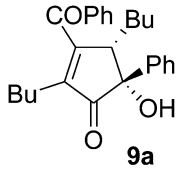
Table 4. Cyclodimerization of 3 Under Basic Conditions[a]

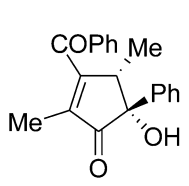


3 → **9**

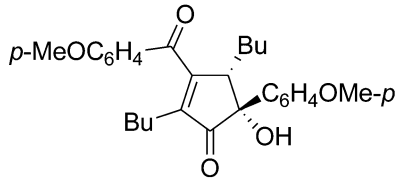


9a

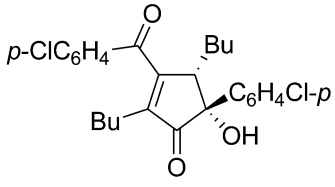
64%[b] (when R = CO_2Me)
64% (when R = Boc)
60% (when R = Ac)



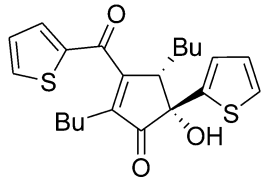
9b, 59%



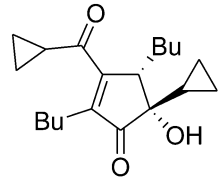
9c, 45%



9d, 46%



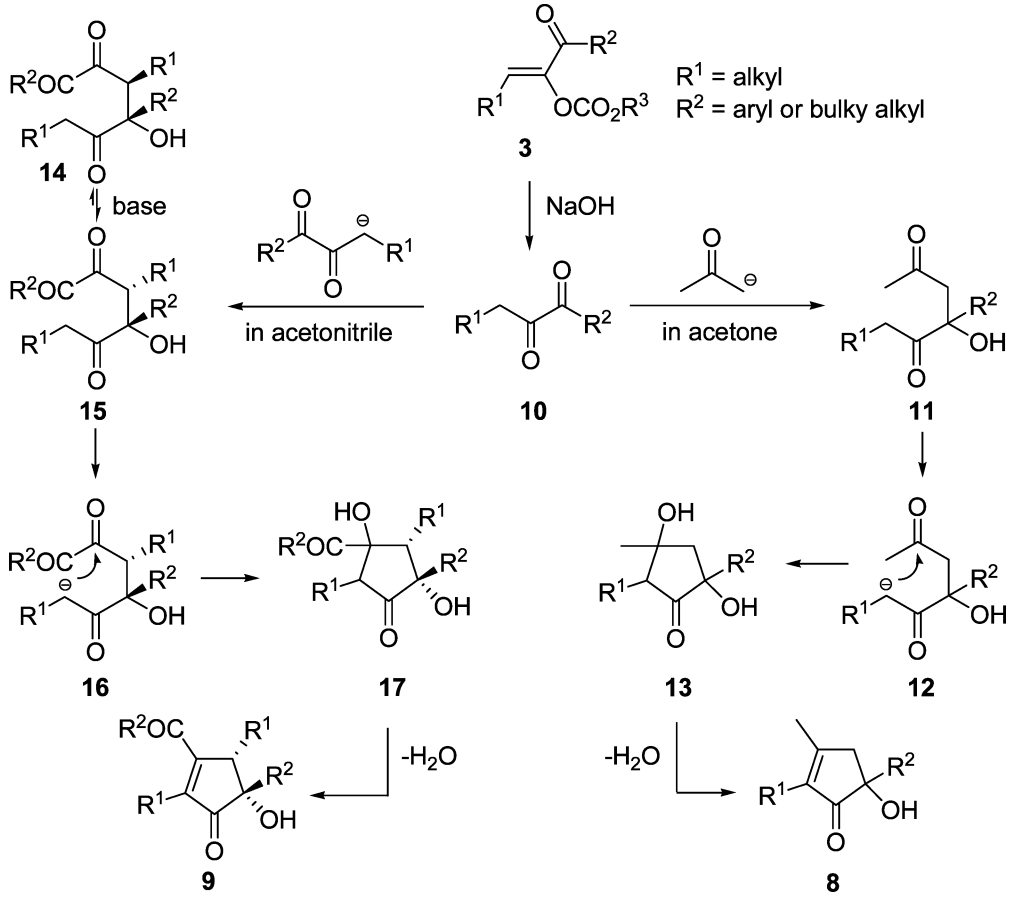
9e, 53%



9f, 64%

[a]Isolated yields. [b]A 1.2 equiv of NaOH (10% aq) was used.

Scheme 4



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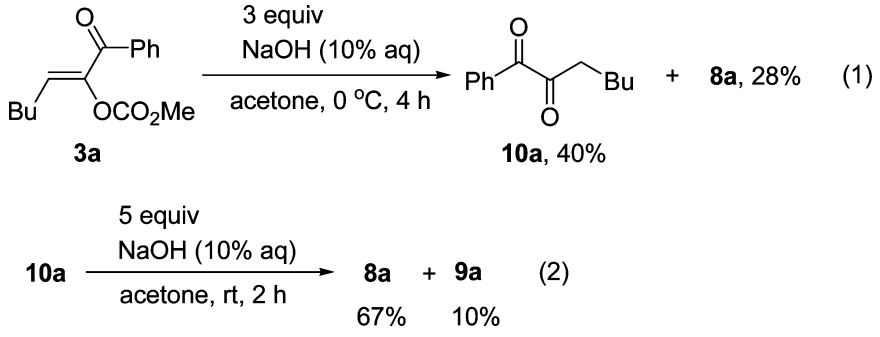
Scheme 5



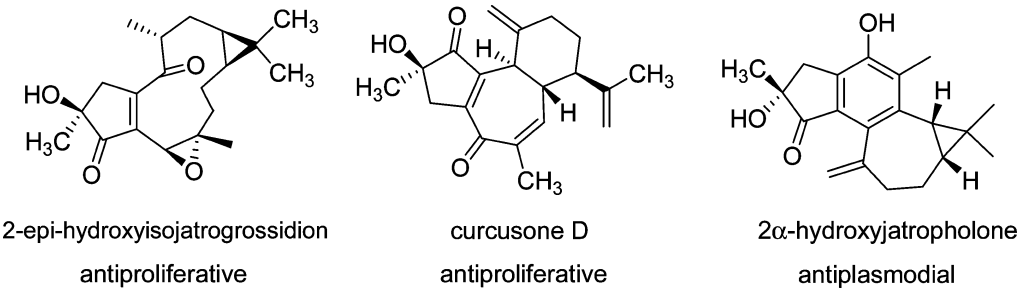


Figure 1. Biologically active cyclopentenones with a 5-hydroxy-bearing quaternary stereocenter.

be less steric hindrance, thus leading to the stereoselective formation of the *Z*-isomer of **3**.

Interestingly, when deprotection of the carbonate group on functionalized alkene **3** was carried out in acetone using NaOH as a base, cyclocondensation of **3** with acetone occurred efficiently to afford 5-hydroxycyclopent-2-enone **8**[12] bearing a quaternary stereocenter in moderate to good yields. Typical results are shown in Table 3. Substrates with alkyl groups as R^1 and aryl groups as R^2 cyclized smoothly, providing **8a**−**8e** in 57−78% yields. Satisfactory results were also obtained when R^1 is a normal alkyl group and R^2 is a sterically demanding group such as isopropyl or *tert*-butyl group, leading to **8f** and **8g** regioselectively in 59 and 50% yields, respectively.

To our surprise, when the reaction was carried out in CH_3CN, a cyclodimerization of **3** occurred smoothly to afford cyclopentenone **9** with an acyl functional group at the C-3 position (Table 4). The reaction is highly stereoselective, as only trans- diastereomer was obtained in all cases. The stereochemistry of cyclopentenones **9** was verified unambiguously by X-ray crystallography of **9b**.[12] The method is applicable to a range of suitably substituted alkene **3**, resulting in 45−64% yields of **9a**−**9f**.

A possible reaction mechanism for the formation of cyclopentenones **8** and **9** is shown in Scheme 4. The reaction starts with hydrolysis of the carbonate moiety of **3** to give 1,2-diketone **10**. Nucleophilic attack of the carboanion derived from acetone on the COR^2 moiety produces the intermediate **11**, which can be deprotonated by base to generate a stable enough carboanion **12** due to the presence of an adjacent carbonyl group. This is followed by intramolecular nucleophilic addition and dehydration to afford cyclopentenone **8**. Similarly, in the absence of acetone, attack of carboanion derived from diketone **10** gives intermediate **14** or its diastereomer **15**. Fast epimerization of **14** to more stable **15** under basic conditions might occur, which undergoes intramolecular nucleophilic addition and dehydration leading to cyclopentenone **9** as a single diastereomer. To isolate the possible intermediate, we carried out the reaction of **3a** with 3.0 equiv of NaOH in acetone at 0 °C. It was found that 1,2-diketone **10a** was formed in 40% yields, together with 28% of **8a** (Scheme 5, eq 1). Subjection of **10a** to the basic conditions in acetone afforded **8a** and **9a** in 67 and 10% yields, respectively (Scheme 5, eq 2). These results well supported our proposed reaction mechanism. 1,2-Diketones are versatile building blocks in organic synthesis;[16] however, the cyclizations of 1,2-diketones to cyclopentenones are quite rare.[17] In an earlier report, upon acid-promoted reaction of butan-2,3-dione, cyclopentenone of type **9** via dimerization of butan-2,3-dione was isolated in only a trace amount.[18] In addition, cyclopentenones with a 5-hydroxy-bearing quaternary stereocenter represent an important structural motif frequently found in a variety of bioactive compounds.[19] For example, 2-epi-hydroxyisojatrogrossidion and curcusone D are diterpenoids with carbon skeleton from *Jatropha curcas*, which show a potent antiproliferative activity against L5178Y (mouse lymphoma) cell line.[19a] 2α-Hydroxyjatropholone exhibits an in vitro activity against *Plasmodium falciparum*[19b] (Figure 1). Our method provides an attractive new route for diverse substituted cyclopentenones in a regio- and stereoselective manner.

■ CONCLUSION

In summary, we have developed a gold-catalyzed oxidative reaction of propargylic carbonates or acetates using 3,5-dichloropyridine *N*-oxide as the oxidant. The reaction provides efficient access to α-functionalized-α,β-unsaturated ketones with excellent regio- and diastereocontrol via a regioselective attack of the *N*-oxide followed by a 1,2-carbonate migration. In addition, the alkene products could be further transformed into valuable cyclopentenones bearing a quaternary stereocenter via cyclocondensation with acetone or cyclodimerization under basic conditions.

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EXPERIMENTAL SECTION

General Methods. All reactions were carried out under argon unless noted. DCM and DCE were distilled from CaH_2. Toluene was distilled from sodium and benzophenone. THF was distilled from sodium and benzophenone or purified using solvent purification system (for the synthesis of substrates). MeCN was purified using a solvent purification system. Unless noted, all commercial reagents were used without further purification. 1,3-Bis(2,6-di-isopropylphenyl)imidazole-2-ylidene gold(I) chloride and (acetonitrile)[(2-biphenyl)di-*tert*-butylphosphine]gold(I) hexafluoroantimonate were purchased from Chemical Company. PPh_3PAuCl[20] and PPh_3AuNTf_2[21] were prepared according to the published methods. 8-Methylquinoline *N*-oxide was prepared according to the published method.[22]

^1H NMR spectra were recorded at 400 MHz, and ^{13}C NMR spectra were recorded at 100 MHz, in $CDCl_3$ (containing 0.03% TMS). ^1H NMR spectra were recorded with tetramethylsilane (δ = 0.00 ppm) as internal reference; ^{13}C NMR spectra were recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference. High-resolution mass spectrometry was performed on a mass spectrometer with a TOF (for EI or ESI) analyzer. The single crystals of **3p** and **8b** were obtained after recrystallization from the mixed solvent of hexane and dichloromethane, and the single crystal of **9b** was obtained after recrystallization from the mixed solvent of toluene and hexane.

Synthesis of Propargyl Carbonates 1. *Typical Procedure for the Synthesis of Methyl(1-phenylhept-1-yn-3-yl)carbonate (**1a**).* To a solution of ethynylbenzene (1.43 mL, 13 mmol) in THF (35.0 mL) was added *n*-BuLi (4.8 mL, 12 mmol, 2.5 M in hexanes) at −78 °C. After the solution stirred at the same temperature for 15 min, valeraldehyde (1.06 mL, 10 mmol, dissolved in 5 mL THF) was added at −78 °C. The dry ice/acetone bath was then removed. The reaction mixture was warmed to room temperature and stirred for 2 h. Then, the resulting mixture was quenched with saturated ammonium chloride solution, extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure, and the residue was used directly for the next step.

To a solution of the above alcohol in DCM (40 mL) were added pyridine (8 mL, 100 mmol) and DMAP (122 mg, 1 mmol). Methyl chloroformate (3.85 mL, 50 mmol) was added to the mixture at 0 °C. The resulting solution was warmed to room temperature and stirred for 2 h. Then, the mixture was quenched with saturated ammonium chloride solution, extracted with dichloromethane, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1) to afford propargyl carbonate **1a** in 90% isolated yield (2.228 g) over two steps as a light yellow oil.

*Methyl(1-phenylhept-1-yn-3-yl)carbonate (**1a**).* ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.45−7.42 (m, 2H), 7.30−7.27 (m, 3H), 5.46 (t, J = 6.8 Hz, 1H), 3.79 (s, 3H), 1.93−1.87 (m, 2H), 1.53−1.47 (m, 2H), 1.41−1.35 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 131.7, 128.5, 128.1, 122.0, 85.9, 85.7, 68.5, 54.6, 34.5, 26.9, 22.1, 13.7; IR (neat) 2957, 2863, 2231, 2198, 1748, 1490, 1442, 1342, 1254, 1114, 1070, 1027, 1004, 948, 933, 875, 790, 756, 690 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{18}O_3$, 246.1256; found, 246.1257.

*Benzyl(1-phenylhept-1-yn-3-yl)carbonate (**1b**).* Three equivalent of $ClCO_2Bn$ was used. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1) afforded the title product as a yellow liquid in 93% (2 mmol scale, 600 mg) isolated yield from 1-phenylhept-1-yn-3-ol. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.48−7.32 (m, 10H), 5.52 (t, J = 6.4 Hz, 1H), 5.23 (s, 2H), 1.98−1.92 (m, 2H), 1.59−1.51 (m, 2H), 1.46−1.37 (m, 2H), 0.97 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 135.0, 131.7, 128.54, 128.45, 128.4, 128.2, 128.1, 122.1, 86.0, 85.8, 69.7, 68.7, 34.5, 27.0, 22.1, 13.8; IR (neat) 3033, 2956, 2863, 2231, 1952, 1744, 1598, 1490, 1456, 1383, 1235, 1113, 1070, 1027, 1003, 940, 909, 881, 788, 755, 691 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{26}NO_3$ $[M + NH_4]^+$, 340.1907; found, 340.1908.

*tert-Butyl (1-Phenylhept-1-yn-3-yl) Carbonate (**1c**).* Three equivalent of Et_3N and 2 equiv of $(Boc)_2O$ were used. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1) afforded the title product as a yellow liquid in 94% (2 mmol scale, 542 mg) isolated yield from 1-phenylhept-1-yn-3-ol. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.44−7.42 (m, 2H), 7.29−7.26 (m, 3H), 5.41 (t, J = 6.8 Hz, 1H), 1.92−1.84 (m, 2H), 1.54−1.47 (m, 11H), 1.43−1.34 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 131.7, 128.4, 128.1, 122.3, 86.2, 85.5, 82.3, 67.4, 34.6, 27.6, 27.1, 22.1, 13.8; IR (neat) 2957, 2932, 2864, 2227, 1740, 1490, 1458, 1444, 1394, 1369, 1271, 1251, 1158, 1112, 1083, 1034, 986, 965, 844, 791, 755, 690 cm^{-1}. HRMS (EI) calcd for $C_{18}H_{24}O_3$, 288.1725; found, 288.1730.

*1-Phenylhept-1-yn-3-yl Acetate (**1d**).* Three equivalent of Et_3N and 2 equiv of $(Ac)_2O$ were used. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1) afforded the title product as a light yellow liquid in 93% (2 mmol scale, 428 mg) isolated yield from 1-phenylhept-1-yn-3-ol. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.45−7.42 (m, 2H), 7.30−7.26 (m, 3H), 5.60 (t, J = 6.8 Hz, 1H), 2.10 (s, 3H), 1.88−1.82 (m, 2H), 1.52−1.45 (m, 2H), 1.43−1.34 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 131.7, 128.4, 128.1, 122.2, 86.6, 85.0, 64.4, 34.5, 27.1, 22.2, 20.9, 13.8; IR (neat) 3056, 2957, 2863, 2227, 2198, 1741, 1668, 1598, 1490, 1465, 1443, 1370, 1225, 1112, 1070, 1047, 1016, 994, 953, 915, 862, 798, 755, 690 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{22}NO_2$ $[M + NH_4]^+$, 248.1645; found, 248.1650. **1d** is a known compound.[23]

*1-(4-Methoxyphenyl)hept-1-yn-3-yl Methyl Carbonate (**1e**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1) afforded the title product as a yellow liquid in 91% (5 mmol scale, 1.257 g) isolated yield over two steps. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.37−7.35 (m, 2H), 6.82−6.79 (m, 2H), 5.44 (t, J = 6.4 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 1.93−1.83 (m, 2H), 1.53−1.46 (m, 2H), 1.42−1.33 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 154.8, 133.0, 113.9, 113.6, 85.7, 84.3, 68.5, 54.8, 54.4, 34.4, 26.8, 21.9, 13.6; IR (neat) 2956, 2863, 2227, 1747, 1606, 1571, 1509, 1441, 1342, 1244, 1172, 1108, 1030, 992, 933, 874, 831, 805, 789 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{20}O_4$, 276.1362; found, 276.1365.

*Methyl (1-(p-Tolyl)hept-1-yn-3-yl) Carbonate (**1f**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1) afforded the title product as a yellow liquid in 89% (5 mmol scale, 1.158 g) isolated yield over two steps. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.33 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 5.45 (t, J = 6.4 Hz, 1H), 3.80 (d, J = 1.2 Hz, 3H), 2.32 (s, 3H), 1.96−1.83 (m, 2H), 1.54−1.47 (m, 2H), 1.43−1.34 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 138.7, 131.6, 128.9, 119.0, 86.1, 85.1, 68.7, 54.7, 34.6, 27.0, 22.1, 21.3, 13.8; IR (neat) 2956, 2864, 2229, 1748, 1510, 1441, 1353, 1254, 1114, 1045, 1021, 994, 946, 933, 882, 816, 789, 735 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{20}O_3$, 260.1412; found, 260.1413.

*1-(4-Chlorophenyl)hept-1-yn-3-yl Methyl Carbonate (**1g**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1) afforded the title product as a yellow liquid in 88% (5 mmol scale, 1.235 g) isolated yield over two steps. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.37−7.35 (m, 2H), 7.28−7.25 (m, 2H), 5.45 (t, J = 6.8 Hz, 1H), 3.81 (s, 3H), 1.93−1.85 (m, 2H), 1.54−1.46 (m, 2H), 1.42−1.33 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 134.4, 132.8, 128.3, 120.4, 86.7, 84.6, 68.2, 54.5, 34.3, 26.8, 22.0, 13.6; IR (neat) 2957, 2863, 2231, 1899, 1748, 1489, 1441, 1343, 1253, 1114, 1091, 1046, 1015, 993, 948, 933, 882, 827, 789, 763 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{17}O_3Cl$, 280.0866; found, 280.0864.

*Methyl (1-(Thiophen-2-yl)hept-1-yn-3-yl) Carbonate (**1h**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1) afforded the title product as a yellow liquid in 92% (5 mmol scale, 1.16 g) isolated yield over two steps. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.26 (dd, J = 5.2, 1.2 Hz, 1H), 7.22 (dd, J = 3.6, 1.2 Hz, 1H), 6.95 (dd, J = 5.2, 3.6 Hz, 1H), 5.45 (t, J = 6.8 Hz, 1H), 3.81 (s, 3H), 1.95−1.85 (m, 2H), 1.53−1.45 (m, 2H), 1.43−1.34 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 132.7,

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127.6, 126.8, 121.9, 89.7, 79.3, 68.6, 54.8, 34.4, 26.9, 22.1, 13.8; IR (neat) 3106, 2956, 2863, 2225, 1747, 1440, 1360, 1340, 1256, 1192, 1113, 1038, 946, 895, 848, 789, 701 cm^{-1}. HRMS (EI) calcd for $C_{13}H_{16}O_3S$, 252.0820; found, 252.0821.

*1-(Cyclohex-1-en-1-yl)hept-1-yn-3-yl Methyl Carbonate (**1i**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1) afforded the title product as a yellow liquid in 93% (5 mmol scale, 1.162 g) isolated yield over two steps. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 6.13−6.11 (m, 1H), 5.33 (t, J = 6.8 Hz, 1H), 3.79 (s, 3H), 2.12−2.06 (m, 4H), 1.88−1.74 (m, 2H), 1.65−1.54 (m, 4H), 1.48−1.41 (m, 2H), 1.38−1.31 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 135.8, 119.7, 87.7, 83.0, 68.7, 54.6, 34.6, 28.8, 26.9, 25.4, 22.1, 22.0, 21.2, 13.7; IR (neat) 3483, 2934, 2864, 2212, 1748, 1679, 1442, 1345 1259, 1113, 1039, 933, 889, 845, 789 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{22}O_3$, 250.1569; found, 250.1572.

*Methyl Undec-6-yn-5-yl Carbonate (**1j**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1) afforded the title product as a yellow liquid in 91% (5 mmol scale, 1.028 g) isolated yield over two steps. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 5.20 (tt, J = 6.4, 2.0 Hz, 1H), 3.79 (s, 3H), 2.21 (td, J = 7.2, 2.0 Hz, 2H), 1.85−1.71 (m, 2H), 1.52−1.30 (m, 8H), 0.93−0.89 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 86.9, 76.9, 68.6, 54.5, 34.7, 30.4, 26.9, 22.1, 21.7, 18.2, 13.7, 13.4; IR (neat) 2957, 2933, 2864, 2238, 1749, 1442, 1343, 1258, 1161, 1108, 1030, 937, 887, 790, 737 cm^{-1}. HRMS (EI) calcd for $C_{13}H_{22}O_3$, 226.1569; found, 226.1572.

*2,2-Dimethylnon-3-yn-5-yl Methyl Carbonate (**1k**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1) afforded the title product as a yellow liquid in 96% (5 mmol scale, 1.087 g) isolated yield over two steps. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 5.22 (t, J = 6.8 Hz, 1H), 3.79 (s, 3H), 1.83−1.69 (m, 2H), 1.46−1.31 (m, 4H), 1.21 (s, 9H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 94.9, 75.3, 68.5, 54.5, 34.8, 30.6, 27.2, 26.9, 22.0, 13.7; IR (neat) 2958, 2866, 2242, 1749, 1442, 1363, 1253, 1117, 1007, 935, 879, 791 cm^{-1}. HRMS (EI) calcd for $C_{13}H_{22}O_3$, 226.1569; found, 226.1565.

*1-Cyclopropylhept-1-yn-3-yl Methyl Carbonate (**1l**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1) afforded the title product as a light yellow liquid in 97% (5 mmol scale, 1.018 g) isolated yield over two steps. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 5.16 (td, J = 6.8, 2.0 Hz, 1H), 3.78 (s, 3H), 1.82−1.68 (m, 2H), 1.45−1.31 (m, 4H), 1.29−1.22 (m, 1H), 0.91 (t, J = 7.2 Hz, 3H), 0.80−0.75 (m, 2H), 0.69−0.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 89.7, 71.9, 68.3, 54.3, 34.5, 26.8, 21.9, 13.5, 7.94, 7.92, −0.9; IR (neat) 3011, 2957, 2864, 2246, 1747, 1441, 1364, 1342, 1256, 1164, 1112, 1054, 1028, 935, 887, 813, 790 cm^{-1}. HRMS (EI) calcd for $C_{12}H_{18}O_3$, 210.1256; found, 210.1251.

*Methyl 4-Phenylbut-3-yn-2-yl Carbonate (**1m**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 10:1) afforded the title product as a light yellow liquid in 99% (10 mmol scale, 2.026 g) isolated yield over two steps. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.45−7.43 (m, 2H), 7.32−7.27 (m, 3H), 5.56 (q, J = 6.8 Hz, 1H), 3.81 (s, 3H), 1.63 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 131.8, 128.6, 128.2, 122.0, 86.5, 85.3, 64.8, 54.8, 21.4; IR (neat) 3057, 2992, 2957, 2236, 1746, 1598, 1490, 1441, 1377, 1346, 1314, 1250, 1108, 1080, 1020, 940, 916, 858, 790, 756, 690 cm^{-1}. HRMS (EI) calcd for $C_{12}H_{12}O_3$, 204.0786; found, 204.0788.

*Methyl (4-Methyl-1-phenylpent-1-yn-3-yl) Carbonate (**1n**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 30:1) afforded the title product as a yellow liquid in 91% (5 mmol scale, 1.057 g) isolated yield over two steps. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.45−7.43 (m, 2H), 7.31−7.28 (m, 3H), 5.31 (d, J = 5.2 Hz, 1H), 3.81 (d, J = 0.8 Hz, 3H), 2.19−2.10 (m, 1H), 1.10 (dd, J = 12.4, 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 131.8, 128.5, 128.1, 122.1, 86.6, 84.4, 73.5, 54.8, 32.6, 18.1, 17.4. The spectroscopic data are in agreement with that previously reported.[24]

*1-Cyclohexyl-3-phenylprop-2-yn-1-yl Methyl Carbonate (**1o**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 30:1) afforded the title product as a yellow liquid in 89% (5 mmol scale, 1.212 g) isolated yield over two steps. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.45−7.42 (m, 2H), 7.31−7.28 (m, 3H), 5.30 (d, J = 5.6 Hz, 1H), 3.80 (s, 3H), 1.95−1.67 (m, 7H), 1.29−1.16 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 131.7, 128.4, 128.0, 122.1, 86.6, 84.7, 72.7, 54.7, 42.0, 28.3, 27.9, 26.0, 25.55, 25.49. The spectroscopic data are in agreement with that previously reported.[24]

*4,4-Dimethyl-1-phenylpent-1-yn-3-yl Methyl Carbonate (**1p**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1) afforded the title product as a light yellow solid in 82% (5 mmol scale, 1.011 g) isolated yield over two steps; mp 64−66 °C; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.45−7.43 (m, 2H), 7.30−7.27 (m, 3H), 5.19 (s, 1H), 3.81 (s, 3H), 1.10 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 131.7, 128.5, 128.1, 122.2, 86.5, 84.7, 76.5, 54.8, 35.5, 25.4. IR (neat): 2966, 2931, 2866, 2198, 1748, 1664, 1598, 1490, 1476, 1435, 1396, 1367, 1343, 1309, 1254, 1190, 1099, 1072, 1049, 1028, 994, 953, 933, 891, 791, 761, 693 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{19}O_3$ $[M + H]^+$, 247.1329; found, 247.1332. **1p** is a known compound.[25]

*1,4-Diphenylbut-3-yn-2-yl Methyl Carbonate (**1q**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1) afforded the title product as a yellow liquid in 86% (5 mmol scale, 1.211 g) isolated yield over two steps. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.40−7.38 (m, 2H), 7.33−7.26 (m, 8H), 5.62 (t, J = 6.8 Hz, 1H), 3.78 (s, 3H), 3.15−3.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 135.6, 131.8, 129.7, 128.7, 128.4, 128.2, 127.0, 122.0, 87.0, 85.3, 69.1, 54.9, 41.3; IR (neat) 3031, 2956, 2854, 2228, 1747, 1598, 1491, 1441, 1355, 1249, 1192, 1104, 1081, 1070, 1028, 1009, 995, 955, 931, 851, 789, 755, 690 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{20}NO_3$ $[M + NH_4]^+$, 298.1438; found, 298.1437.

*Synthesis of Methyl 1-(Phenylethynyl)cyclohexyl Carbonate (**1r**).* To a solution of ethynylbenzene (0.71 mL, 6.5 mmol) in THF (15.0 mL) was added *n*-BuLi (2.4 mL, 6 mmol, 2.5 M in hexanes) at −78 °C. After the solution stirred at the same temperature for 15 min, cyclohexanone (0.52 mL, 5 mmol, dissolved in 5 mL of THF) was added at −78 °C and stirred at the same temperature for 2 h. Then, methyl chloroformate (1.15 mL, 15 mmol) was added at −78 °C. The dry ice/acetone bath was then removed. The reaction mixture was warmed to room temperature and stirred for 2 h. The resulting mixture was quenched with saturated ammonium chloride solution at 0 °C, extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 30:1) to afford **1r** in 81% isolated yield (1.05 g) over two steps as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.46−7.42 (m, 2H), 7.30−7.26 (m, 3H), 3.75 (s, 3H), 2.28−2.25 (m, 2H), 1.97−1.89 (m, 2H), 1.73−1.52 (m, 5H), 1.39−1.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 131.6, 128.2, 128.0, 122.4, 88.2, 86.5, 77.9, 54.0, 36.9, 24.9, 22.6. The spectroscopic data are in agreement with that previously reported.[26]

Typical Procedure for the Synthesis of α-Functionalized-α,β-Unsaturated Ketones 3a. In a glovebox, to a Schlenk tube was added $AgSbF_6$ (5.2 mg, 0.015 mmol). The Schlenk tube was then removed from the glovebox, IPrAuCl (9.3 mg, 0.015 mmol) and DCE (1 mL) were added successively, and the mixture was stirred at room temperature for 10 min. Then 3,5-dichloropyridine *N*-oxide **2b** (98 mg, 0.6 mmol) was added, followed by the addition of a DCE solution of **1a** (74 mg, 0.3 mmol in 2 mL of DCE). After the reaction mixture was stirred at room temperature for 1.5 h, the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 30:1) to afford **3a** (74.7 mg, 95%) as a yellow oil.

*(Z)-Methyl (1-Oxo-1-phenylhept-2-en-2-yl) Carbonate (**3a**).* ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.77 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 6.16 (t, J = 7.6 Hz, 1H), 3.85 (s, 3H), 2.34 (q, J = 7.2 Hz, 2H), 1.49−1.41 (m, 2H), 1.40−1.31 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.5, 153.3, 145.4, 136.7, 134.8, 132.3, 129.2, 128.2, 55.5, 30.2, 25.7, 22.3, 13.6. IR (neat): 3059, 2958, 2930, 2860, 1760, 1663, 1598, 1579, 1441, 1320, 1250, 1163, 1027, 1001, 940, 799, 781, 746, 698, 660 cm^{-1};

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HRMS (ESI) calcd for $C_{15}H_{19}O_4$ $[M + H]^+$ 263.1278; found, 263.1278.

*Synthesis of the (E)-Isomer of **3a**.* To a solution of **1a** (148 mg, 0.6 mmol) in DCE (6 mL) was added 8-methylquinoline *N*-oxide (115 mg, 0.72 mmol) and catalyst **A** (23.2 mg, 0.03 mmol). After the reaction mixture was stirred at 50 °C for 4 h, the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 35:1) to afford *E*-**3a** (21 mg, 13%) and *Z*-**3a** (89 mg, 57%) as a yellow oil. For the characterization data of *E*-**3a**: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.90−7.87 (m, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 6.01 (t, J = 8.4 Hz, 1H), 3.71 (s, 3H), 2.15 (q, J = 7.6 Hz, 2H), 1.42−1.35 (m, 2H), 1.30−1.21 (m, 2H), 0.82 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 153.9, 143.7, 137.0, 133.1, 129.2, 129.0, 128.5, 55.4, 31.2, 26.4, 22.1, 13.7. HRMS (ESI) calcd for $C_{15}H_{19}O_4$ $[M + H]^+$, 263.1278; found, 263.1276.

*(Z)-Benzyl (1-Oxo-1-phenylhept-2-en-2-yl) Carbonate (**3b**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 30:1) afforded the title product as a yellow liquid in 80% (81.6 mg) isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.76−7.74 (m, 2H), 7.55−7.52 (m, 1H), 7.44−7.40 (m, 2H), 7.36−7.32 (m, 5H), 6.16 (t, J = 7.6 Hz, 1H), 5.20 (s, 2H), 2.31 (q, J = 7.6 Hz, 2H), 1.46−1.40 (m, 2H), 1.38−1.30 (m, 2H), 0.88 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.4, 152.7, 145.6, 136.7, 134.59, 134.56, 132.3, 129.1, 128.53, 128.50, 128.2, 128.1, 70.4, 30.2, 25.7, 22.3, 13.6; IR (neat) 3062, 3033, 2958, 2929, 2872, 1758, 1664, 1598, 1498, 1449, 1380, 1319, 1226, 1165, 1112, 1026, 1001, 937, 908, 779, 745, 696, 662 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{26}NO_4$ $[M + NH_4]^+$, 356.1856; found, 356.1854.

*(Z)-tert-Butyl (1-Oxo-1-phenylhept-2-en-2-yl) Carbonate (**3c**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 30:1) afforded the title product as a yellow liquid in 92% (84 mg) isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.79−7.76 (m, 2H), 7.56−7.52 (m, 1H), 7.46−7.42 (m, 2H), 6.11 (t, J = 7.6 Hz, 1H), 2.34 (q, J = 7.2 Hz, 2H), 1.46−1.30 (m, 13H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 150.8, 145.6, 136.9, 133.6, 132.2, 129.1, 128.2, 83.8, 30.3, 27.4, 25.6, 22.3, 13.7; IR (neat) 2960, 2932, 2873, 1753, 1693, 1667, 1599, 1581, 1450, 1396, 1371, 1318, 1270, 1251, 1143, 1070, 1024, 1001, 945, 856, 783, 761, 702 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{28}NO_4$ $[M + NH_4]^+$, 322.2013; found, 322.2017.

*(Z)-1-Oxo-1-phenylhept-2-en-2-yl Acetate (**3d**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 30:1) afforded the title product as a yellow liquid in 97% (72 mg) isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.77−7.75 (m, 2H), 7.56−7.52 (m, 1H), 7.45−7.42 (m, 2H), 6.15 (t, J = 7.6 Hz, 1H), 2.28 (q, J = 7.6 Hz, 2H), 2.26 (s, 3H), 1.48−1.40 (m, 2H), 1.40−1.31 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 168.7, 145.6, 136.9, 134.9, 132.2, 129.2, 128.1, 30.2, 25.8, 22.3, 20.2, 13.6; IR (neat) 3055, 2957, 2930, 2861, 1758, 1663, 1598, 1578, 1447, 1370, 1319, 1272, 1199, 1159, 1105, 1076, 1044, 1013, 961, 930, 899, 762, 707, 667 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{19}O_3$ $[M + H]^+$, 247.1329; found, 247.1330.

*(Z)-1-(4-Methoxyphenyl)-1-oxohept-2-en-2-yl Methyl Carbonate (**3e**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 30:1) afforded the title product as a yellow liquid in 90% (79.3 mg) isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.82−7.80 (m, 2H), 6.95−6.93 (m, 2H), 6.10 (t, J = 7.6 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 2.33 (q, J = 7.6 Hz, 2H), 1.50−1.44 (m, 2H), 1.39−1.32 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 163.2, 153.3, 145.3, 133.0, 131.6, 129.1, 113.5, 55.5, 55.3, 30.3, 25.5, 22.3, 13.6; IR (neat) 2958, 2930, 2860, 1760, 1655, 1599, 1574, 1509, 1441, 1420, 1306, 1249, 1157, 1114, 1026, 930, 843, 816, 774, 685 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{21}O_5$ $[M + H]^+$, 293.1384; found, 293.1380.

*(Z)-Methyl (1-Oxo-1-(p-tolyl)hept-2-en-2-yl) Carbonate (**3f**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 30:1) afforded the title product as a yellow liquid in 86% (71 mg) isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.69 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 6.14 (t, J = 7.6 Hz, 1H), 3.84 (s, 3H), 2.41 (s, 3H), 2.33 (q, J = 7.2 Hz, 2H), 1.48−1.41 (m, 2H), 1.40−1.31 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 153.3, 145.4, 143.2, 134.0, 133.9, 129.4, 128.9, 55.5, 30.2, 25.6, 22.3, 21.5, 13.6; IR (neat) 2958, 2929, 2861, 1761, 1660, 1607, 1441, 1380, 1314, 1251, 1181, 1163, 1114, 1037, 988, 935, 833, 781, 766, 685 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{21}O_4$ $[M + H]^+$, 277.1434; found, 277.1435.

*(Z)-1-(4-Chlorophenyl)-1-oxohept-2-en-2-yl Methyl Carbonate (**3g**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 30:1) afforded the title product as a light yellow solid in 90% (80 mg) isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.74−7.72 (m, 2H), 7.45−7.42 (m, 2H), 6.13 (t, J = 7.6 Hz, 1H), 3.85 (s, 3H), 2.34 (q, J = 7.2 Hz, 2H), 1.49−1.42 (m, 2H), 1.40−1.31 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.3, 153.3, 145.2, 138.8, 135.0, 134.7, 130.6, 128.6, 55.6, 30.2, 25.7, 22.3, 13.6; IR (neat) 2959, 2931, 2873, 1761, 1667, 1589, 1488, 1441, 1400, 1252, 1165, 1090, 1014, 988, 935, 842, 775, 735, 703, 680 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{18}ClO_4$ $[M + H]^+$, 297.0888; found, 297.0887.

*(Z)-Methyl (1-Oxo-1-(thiophen-2-yl)hept-2-en-2-yl) Carbonate (**3h**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 30:1) afforded the title product as a yellow liquid in 91% (73.5 mg) isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.80 (dd, J = 3.6, 0.8 Hz, 1H), 7.68 (dd, J = 4.8, 0.8 Hz, 1H), 7.14 (dd, J = 4.8 Hz, 4.0 Hz, 1H), 6.44 (t, J = 7.6 Hz, 1H), 3.85 (s, 3H), 2.33 (q, J = 7.6 Hz, 2H), 1.53−1.47 (m, 2H), 1.45−1.34 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1, 153.2, 144.9, 141.3, 134.0, 133.5, 132.3, 127.9, 55.6, 30.2, 25.6, 22.2, 13.6; IR (neat) 2958, 2930, 2860, 1761, 1638, 1514, 1440, 1412, 1356, 1251, 1228, 1158, 1083, 1039, 946, 905, 853, 782, 768, 726, 702, 666 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{17}O_4S$ $[M + H]^+$, 269.0842; found, 269.0843.

*(Z)-1-(Cyclohex-1-en-1-yl)-1-oxohept-2-en-2-yl Methyl Carbonate (**3i**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 30:1) afforded the title product as a yellow liquid in 88% (70.2 mg) isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 6.73−6.71 (m, 1H), 6.07 (t, J = 8.0 Hz, 1H), 3.84 (s, 3H), 2.30−2.24 (m, 6H), 1.70−1.62 (m, 4H), 1.49−1.42 (m, 2H), 1.41−1.31 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 153.4, 145.0, 140.7, 137.4, 131.3, 55.4, 30.3, 25.7, 25.4, 23.8, 22.3, 21.7, 21.4, 13.6; IR (neat) 3514, 2933, 2872, 1760, 1715, 1652, 1442, 1379, 1251, 1145, 1038, 947, 781 cm^{-1}.; HRMS (ESI) calcd for $C_{15}H_{23}O_4$ $[M + H]^+$, 267.1591; found, 267.1587.

*(Z)-Methyl (7-Oxoundec-5-en-6-yl) Carbonate (**3j**).* Reactions were carried out on a 0.3 mmol scale. The reaction was carried out at 80 °C. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 30:1) afforded the title product as a yellow liquid in 84% (61.3 mg) isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 6.45 (t, J = 7.6 Hz, 1H), 3.86 (s, 3H), 2.63 (t, J = 7.2 Hz, 2H), 2.26 (q, J = 7.2 Hz, 2H), 1.66−1.59 (m, 2H), 1.50−1.42 (m, 2H), 1.39−1.31 (m, 4H), 0.92 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 153.3, 145.8, 131.9, 55.5, 36.7, 30.2, 26.2, 25.6, 22.3, 22.2, 13.7, 13.6; IR (neat) 2959, 2933, 2873, 1764, 1688, 1442, 1380, 1250, 1129, 1004, 947, 781 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{23}O_4$ $[M + H]^+$, 243.1591; found, 243.1591.

*(Z)-2,2-Dimethyl-3-oxonon-4-en-4-yl Methyl Carbonate (**3k**).* Reactions were carried out on a 0.3 mmol scale. The reaction was carried out at 80 °C. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 30:1) afforded the title product as a yellow liquid in 76% (55 mg) isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 6.38 (t, J = 7.2 Hz, 1H), 3.86 (s, 3H), 2.22 (q, J = 7.2 Hz, 2H), 1.49−1.42 (m, 2H), 1.40−1.31 (m, 2H), 1.27 (s, 9H), 0.92 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 153.3, 144.1, 131.4, 55.4, 42.8, 30.2, 27.5, 25.5, 22.3, 13.7; IR (neat) 2960, 2933, 2874, 1763, 1680, 1479, 1442, 1397, 1368, 1250, 1178, 1091,

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1030, 948, 781 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{23}O_4$ $[M + H]^+$, 243.1591; found, 243.1592.

*(Z)-1-Cyclopropyl-1-oxohept-2-en-2-yl Methyl Carbonate (**3l**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 30:1) afforded the title product as a yellow liquid in 82% (56 mg) isolated yield. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 6.58 (t, J = 7.6 Hz, 1H), 3.86 (s, 3H), 2.32−2.25 (m, 3H), 1.51−1.45 (m, 2H), 1.42−1.33 (m, 2H), 1.15−1.11 (m, 2H), 0.99−0.91 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 153.3, 146.3, 131.6, 55.5, 30.2, 25.6, 22.3, 16.0, 13.6, 11.3; IR (neat) 2959, 2932, 2874, 1765, 1713, 1672, 1442, 1394, 1239, 1086, 1033, 984, 945, 875, 779, 674 cm^{-1}. HRMS (ESI) calcd for $C_{12}H_{19}O_4$ $[M + H]^+$, 227.1278; found, 227.1276.

*(Z)-Methyl 1-Oxo-1-phenylbut-2-en-2-yl Carbonate (**3m**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1) afforded the title product as a yellow liquid in 93% (61.4 mg) isolated yield. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.78−7.75 (m, 2H), 7.57−7.53 (m, 1H), 7.46−7.42 (m, 2H), 6.25 (q, J = 7.2 Hz, 1H), 3.85 (s, 3H), 1.90 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 153.2, 146.4, 136.6, 132.3, 129.9, 129,1, 128.2, 55.5, 11.6; IR (neat) 3061, 2959, 2850, 1759, 1658, 1598, 1579, 1442, 1380, 1334, 1276, 1240, 1164, 1065, 984, 941, 923, 847, 799, 781, 743, 697, 660 cm^{-1}. HRMS (ESI) calcd for $C_{12}H_{13}O_4$ $[M + H]^+$, 221.0808; found, 221.0808.

*(Z)-Methyl (4-Methyl-1-oxo-1-phenylpent-2-en-2-yl) Carbonate (**3n**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 30:1) afforded the title product as a yellow liquid in 80% (60 mg) isolated yield. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.78−7.76 (m, 2H), 7.58−7.54 (m, 1H), 7.46 (t, J = 7.6 Hz, 2H), 5.99 (d, J = 10.0 Hz, 1H), 3.85 (s, 3H), 2.96−2.87 (m, 1H), 1.08 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 153.4, 143.6, 140.8, 136.7, 132.4, 129.3, 128.3, 55.6, 26.1, 21.8; IR (neat) 2962, 2872, 1760, 1663, 1598, 1578, 1441, 1320, 1270, 1238, 1166, 1119, 1066, 1027, 964, 925, 798, 779, 747, 699, 666 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{17}O_4$ $[M + H]^+$, 249.1121; found, 249.1121.

*(Z)-1-Cyclohexyl-3-oxo-3-phenylprop-1-en-2-yl Methyl Carbonate (**3o**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 30:1) afforded the title product as a yellow liquid in 60% (51.9 mg) isolated yield. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.77−7.75 (m, 2H), 7.58−7.54 (m, 1H), 7.45 (t, J = 8.0 Hz, 2H), 6.00 (d, J = 9.6 Hz, 1H), 3.86 (s, 3H), 2.67−2.58 (m, 1H), 1.77−1.66 (m, 5H), 1.38−1.26 (m, 2H), 1.23−1.10 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 153.4, 143.8, 139.4, 136.8, 132.4, 129.3, 128.2, 55.6, 35.5, 31.7, 25.6, 25.2; IR (neat) 2928, 2854, 1744, 1491, 1441, 1349, 1259, 1185, 965, 926, 891, 790, 756, 691 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{21}O_4$ $[M + H]^{+1}$, 289.1434; found, 289.1438.

*(Z)-4,4-Dimethyl-1-oxo-1-phenylpent-2-en-2-yl Methyl Carbonate (**3p**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1) afforded the title product as a white solid in 93% (73 mg) isolated yield; mp 86−88 °C. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.78−7.76 (m, 2H), 7.57−7.53 (m, 1H), 7.45 (t, J = 7.6 Hz, 2H), 6.06 (s, 1H), 3.84 (s, 3H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 153.2, 143.9, 142.2, 136.8, 132.3, 129.3, 128.2, 55.6, 33.1, 29.5; IR (neat) 2959, 2864, 1761, 1665, 1598, 1441, 1366, 1317, 1249, 1201, 1138, 1072, 1026, 963, 945, 916, 800, 780, 748, 698, 669, 653 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{19}O_4$ $[M + H]^+$, 263.1278; found, 263.1281.

*(Z)-Methyl (1-Oxo-1,4-diphenylbut-2-en-2-yl) Carbonate (**3q**).* Reactions were carried out on a 0.5 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1) afforded the title product as a yellow liquid in 93% (138 mg) isolated yield. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.77 (d, J = 7.6 Hz, 2H), 7.52−7.48 (m, 1H), 7.41−7.37 (m, 2H), 7.30−7.26 (m, 2H), 7.22−7.18 (m, 3H), 6.28 (t, J = 8.0 Hz, 1H), 3.84 (s, 3H), 3.66 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 153.2, 145.3, 137.3, 136.3, 132.4, 132.1, 129.1, 128.6, 128.4, 128.20, 128.15, 126.6, 55.6, 32.1; IR (neat) 3053, 3028, 2958, 2850, 1760, 1662, 1598, 1578, 1496, 1441, 1320, 1239, 1197, 1178, 1142, 1069, 1028, 1001, 990, 941, 781, 745, 696, 659 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{17}O_4$ $[M + H]^+$, 297.1121; found, 297.1124.

*1-Cyclohexylidene-2-oxo-2-phenylethyl Methyl Carbonate (**3r**).* Reactions were carried out on a 0.3 mmol scale. The reaction was carried out at 80 °C. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 30:1) afforded the title product as a yellow liquid in 72% (59 mg) isolated yield. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.90−7.88 (m, 2H), 7.56−7.53 (m, 1H), 7.44 (t, J = 7.6 Hz, 2H), 3.72 (s, 3H), 2.42−2.39 (m, 2H), 2.22−2.19 (m, 2H), 1.72−1.66 (m, 2H), 1.61−1.51 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 154.0, 140.3, 137.8, 137.1, 132.8, 129.1, 128.4, 55.4, 29.7, 28.5, 27.4, 27.2, 25.9; IR (neat) 2931, 2855, 1755, 1660, 1597, 1580, 1441, 1318, 1277, 1248, 1223, 1150, 1059, 1027, 1003, 945, 874, 849, 817, 784, 738, 697 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{19}O_4$ $[M + H]^+$, 275.1278; found, 275.1280.

General Procedure for the Synthesis of 8. For the synthesis of **8**, there is no need to exclude the air. The reactions were carried out on 0.2 or 0.3 mmol scale. To a solution of **3** (0.3 mmol) in acetone (3 mL) was added 10% sodium hydroxide solution (1.5 mmol, 0.55 mL). The resulting mixture was stirred at room temperature until the reaction was complete as monitored by thin-layer chromatography. Then the mixture was quenched with water, extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel to afford the product **8**.

*2-Butyl-5-hydroxy-3-methyl-5-phenylcyclopent-2-enone (**8a**).* Reactions were carried out on a 0.2 mmol scale. A 1.2 equiv 10% sodium hydroxide solution was used. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 8:1) afforded the title product in 78% (38 mg) isolated yield as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.33−7.22 (m, 5H), 3.35 (s, 1H), 2.97 (d, J = 18.4 Hz, 1H), 2.87 (d, J = 18.8 Hz, 1H), 2.34−2.20 (m, 2H), 2.12 (s, 3H), 1.46−1.38 (m, 2H), 1.36−1.27 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 169.5, 143.0, 138.3, 128.4, 127.4, 124.4, 78.4, 49.9, 30.2, 22.9, 22.6, 17.2, 13.8; IR (neat) 3432, 3059, 3022, 2956, 2929, 2858, 1698, 1636, 1600, 1494, 1447, 1385, 1344, 1232, 1185, 1103, 1058, 1033, 967, 928, 876, 769, 729, 697 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{21}O_2$ $[M + H]^+$, 245.1535; found, 245.1536.

*5-Hydroxy-2-isopropyl-3-methyl-5-phenylcyclopent-2-enone (**8b**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 7:1) afforded the title product as a white solid in 59% (41 mg) isolated yield; mp 115−117 °C. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.32−7.22 (m, 5H), 3.32 (s, 1H), 2.95 (d, J = 18.0 Hz, 1H), 2.83 (d, J = 18.0 Hz, 1H), 2.90−2.83 (m, 1H), 2.12 (s, 3H), 1.23−1.20 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.0, 168.1, 143.1, 142.4, 128.4, 127.3, 124.3, 78.2, 49.9, 25.1, 20.4, 19.8, 17.4; IR (neat) 3426, 2956, 2914, 2872, 1688, 1628, 1601, 1490, 1450, 1419, 1386, 1342, 1237, 1102, 1073, 828, 783, 745, 701, 684, 656 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{18}O_2Na$ $[M + Na]^+$, 253.1199; found, 253.1208.

*2-tert-Butyl-5-hydroxy-3-methyl-5-phenylcyclopent-2-enone (**8c**).* Reactions were carried out on a 0.2 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 7:1) afforded the title product as a white solid in 68% (33 mg) isolated yield; mp 118−120 °C. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.31−7.22 (m, 5H), 3.29 (s, 1H), 2.95 (dd, J = 18.0 Hz, 0.8 Hz, 1H), 2.82 (d, J = 18.0 Hz, 1H), 2.27 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.5, 166.6, 143.4, 143.0, 128.4, 127.4, 124.3, 78.0, 51.3, 33.6, 29.4, 19.6; IR (neat) 3709, 3422, 2956, 2916, 2851, 1687, 1607, 1486, 1449, 1422, 1360, 1327, 1236, 1154, 1119, 1106, 1071, 883, 839, 778, 742, 701, 578, 655 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{20}O_2Na$ $[M + Na]^+$, 267.1356; found, 267.1357.

*2-Butyl-5-hydroxy-5-(4-methoxyphenyl)-3-methylcyclopent-2-enone (**8d**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 7:1) afforded the title product as a yellow oil in 62% (51 mg) isolated yield. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.22−7.20 (m, 2H), 6.84−6.82 (m, 2H), 3.77 (s, 3H), 3.31 (s, 1H), 2.96 (d, J = 18.0 Hz,

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1H), 2.86 (d, J = 18.0 Hz, 1H), 2.31−2.19 (m, 2H), 2.11 (s, 3H), 1.41−1.28 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 169.1, 158.8, 138.2, 135.0, 113.7, 78.0, 55.2, 49.7, 30.3, 22.9, 22.6, 17.2, 13.8; IR (neat) 3439, 2955, 2931, 2858, 1699, 1637, 1609, 1582, 1509, 1637, 1609, 1582, 1509, 1464, 1441, 1385, 1344, 1293, 1249, 1178, 1101, 1031, 924, 876, 831, 796, 734 cm^{-1}. HRMS (ESI) calcd for $C_{17}H_{22}O_3Na$ [M + Na]$^+$, 297.1461; found, 297.1465.

*2-Butyl-5-(4-chlorophenyl)-5-hydroxy-3-methylcyclopent-2-enone (**8e**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 7:1) afforded the title product as a white solid in 57% (47.6 mg) isolated yield; mp 76−78 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.27−7.25 (m, 2H), 7.21−7.19 (m, 2H), 3.50 (s, 1H), 2.96 (d, J = 18.0 Hz, 1H), 2.82 (s, J = 18.4 Hz, 1H), 2.31−2.21 (m, 2H), 2.13 (s, 3H), 1.43−1.25 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 169.7, 141.5, 138.4, 133.2, 128.5, 125.9, 78.0, 49.9, 30.2, 22.9, 22.6, 17.3, 13.8; IR (neat) 3431, 2956, 2929, 2859, 1697, 1635, 1489, 1466, 1433, 1385, 1343, 1233, 1185, 1156, 1091, 1057, 1013, 966, 925, 876, 830, 758, 725 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{19}O_2ClNa$ [M + Na]$^+$, 301. 0966; found, 301. 0978.

*2-Butyl-5-cyclopropyl-5-hydroxy-3-methylcyclopent-2-enone (**8f**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 8:1) afforded the title product as a yellow oil in 59% (37 mg) isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 2.57 (d, J = 17.6 Hz, 1H), 2.45 (d, J = 18.0 Hz, 1H), 2.48 (s, 1H), 2.25−2.12 (m, 2H), 2.04 (s, 3H), 1.39−1.26 (m, 4H), 1.08−1.01 (m, 1H), 0.90 (t, J = 7.2, 3H), 0.49−0.44 (m, 1H), 0.40−0.35 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.1, 167.9, 137.7, 76.2, 45.1, 30.4, 22.7, 22.6, 18.1, 17.1, 13.9, 0.9, 0.1; IR (neat) 3452, 2956, 2928, 2858, 1698, 1639, 1466, 1430, 1386, 1343, 1187, 1098, 1069, 1041, 1020, 984, 946, 918, 893, 869, 831 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{20}O_2Na$ [M + Na]$^+$, 231.1356; found, 231.1356.

*5-tert-Butyl-2-butyl-5-hydroxy-3-methylcyclopent-2-enone (**8g**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 7:1) afforded the title product as a yellow oil in 50% (33.7 mg) isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 2.73 (d, J = 18.0 Hz, 1H), 2.41 (d, J = 18.4 Hz, 1H), 2.56 (s, 1H), 2.23−2.09 (m, 2H), 2.04 (s, 3H), 1.39−1.26 (m, 4H), 0.93 (s, 9H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.2, 167.9, 138.8, 80.7, 43.5, 36.7, 30.3, 24.5, 22.8, 22.7, 16.9, 13.8; IR (neat) 3484, 2956, 2933, 2872, 1697, 1644, 1467, 1386, 1366, 1341, 1215, 1182, 1107, 1067, 1039, 1010, 980, 930, 875, 848, 811, 729 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{24}O_2Na$ [M + Na]$^+$, 247.1669; found, 247.1670.

General Procedure for the Synthesis of 9. For the synthesis of **9**, there is no need to exclude the air. The reactions were carried out on 0.2 or 0.3 mmol scale. To a solution of **3** (0.3 mmol) in acetonitrile (3 mL) was added 10% sodium hydroxide solution (1.5 mmol, 0.55 mL). The resulting mixture was stirred at room temperature until the reaction was complete as monitored by thin-layer chromatography. Then the mixture was quenched with water, extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel to afford the product **9**.

(4S, 5R*)-3-Benzoyl-2,4-dibutyl-5-hydroxy-5-phenylcyclopent-2-enone (**9a**).* Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 10:1) afforded the product **9a** in 64% isolated yield (25 mg) as a light yellow oil (0.2 mmol scale, and when **3a** and 1.2 equiv of 10% sodium hydroxide solution were used). **9a** was obtained in 64% yield (0.3 mmol scale, 37.5 mg) when **3c** was used, or 60% yield (0.3 mmol scale, 35 mg) when **3d** was used. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.85−7.83 (m, 2H), 7.66−7.63 (m, 1H), 7.50 (t, J = 8.0 Hz, 2H), 7.45−7.42 (m, 2H), 7.38−7.34 (m, 2H), 7.31−7.27 (m, 1H), 3.54−3.50 (m, 1H), 3.35 (s, 1H), 2.29−2.22 (m, 1H), 2.08−2.00 (m, 1H), 1.87−1.83 (m, 1H), 1.52−1.43 (m, 2H), 1.35−1.26 (m, 2H), 1.22−1.14 (m, 3H), 1.13−1.05 (m, 2H), 0.77−0.69 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 196.5, 168.5, 143.1, 140.8, 135.7, 134.4, 129.1, 129.0, 128.6, 127.8, 124.7, 80.7, 55.3, 30.2, 29.9, 29.6, 24.1, 22.6, 22.3, 13.7, 13.4; IR (neat) 3465, 3062, 2956, 2930, 2860, 1713, 1660, 1596, 1579, 1494, 1448, 1379, 1343, 1315, 1241, 1209, 1176, 1151, 1123, 1073, 1053, 1018, 1001, 923, 890, 804, 721, 697, 673 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{34}NO_3$ [M + NH_4]$^+$, 408.2533; found, 408.2537.

(4S, 5R*)-3-Benzoyl-5-hydroxy-2,4-dimethyl-5-phenylcyclopent-2-enone (**9b**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 5:1) afforded the title product as a light yellow solid in 59% (27.0 mg) isolated yield; mp 116−118 °C. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.87−7.85 (m, 2H), 7.67−7.63 (m, 1H), 7.54−7.50 (m, 2H), 7.44−7.40 (m, 2H), 7.39−7.33 (m, 2H), 7.32−7.27 (m, 1H), 3.60−3.54 (m, 1H), 3.47 (s, 1H), 1.71 (d, J = 2.0 Hz, 3H), 1.23 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.0, 196.1, 168.9, 142.4, 136.0, 135.6, 134.5, 129.09, 129.07, 128.6, 127.7, 124.7, 79.9, 49.8, 14.0, 9.7; IR (neat) 3447, 3059, 2976, 2927, 2850, 1714, 1689, 1596, 1579, 1495, 1448, 1377, 1343, 1314, 1265, 1240, 1177, 1119, 1074, 1014, 952, 918, 894, 848, 733, 697 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{19}O_3$ [M + H]$^+$, 307.1329; found, 307.1329.

(4S, 5R*)-2,4-Dibutyl-5-hydroxy-3-(4-methoxybenzoyl)-5-(4-methoxyphenyl) Cyclopent-2-enone (**9c**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 10:1) afforded the title product as a yellow oil in 45% (30.3 mg) isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.82−7.80 (m, 2H), 7.37−7.35 (m, 2H), 6.98−6.96 (m, 2H), 6.90−6.88 (m, 2H), 3.90 (s, 3H), 3.81 (s, 3H), 3.48 (dd, J = 7.6, 4.0 Hz, 1H), 3.13 (s, 1H), 2.28−2.23 (m, 1H), 2.07−2.20 (m, 1H), 1.85−1.78 (m, 1H), 1.47−1.43 (m, 2H), 1.33−1.05 (m, 7H), 0.77−0.70 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 194.8, 168.8, 164.6, 159.0, 139.9, 135.1, 131.6, 128.7, 126.1, 114.3, 113.9, 80.5, 55.6, 55.25, 55.16, 30.3, 30.0, 29.6, 24.1, 22.7, 22.4, 13.8, 13.5; IR (neat) 3465, 2956, 2930, 2859, 1712, 1651, 1594, 1572, 1509, 1463, 1442, 1422, 1379, 1313, 1248, 1166, 1111, 1026, 925, 892, 847, 831, 798, 735, 703 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{34}O_5Na$ [M + Na]$^+$, 473.2298; found, 473.2304.

(4S, 5R*)-2,4-Dibutyl-3-(4-chlorobenzoyl)-5-(4-chlorophenyl)-5-hydroxycyclopent-2-enone (**9d**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 10:1) afforded the title product as a yellow oil in 46% (32 mg) isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.79−7.77 (m, 2H), 7.52−7.50 (m, 2H), 7.37−7.32 (m, 4H), 3.45 (dd, J = 8.0, 4.4 Hz, 1H), 3.18 (s, 1H), 2.28−2.21 (m, 1H), 2.04−1.96 (m, 1H), 1.86−1.79 (m, 1H), 1.64 (s, 1H), 1.42−1.07 (m, 8H), 0.77−0.71 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.6, 195.1, 167.9, 141.4, 141.3, 140.8, 133.9, 133.7, 130.5, 129.6, 128.8, 126.2, 80.3, 55.2, 30.3, 30.0, 29.6, 24.2, 22.6, 22.4, 13.7, 13.5; IR (neat) 3457, 2957, 2929, 2860, 1713, 1660, 1585, 1570, 1489, 1465, 1401, 1379, 1247, 1209, 1171, 1152, 1091, 1053, 1012, 925, 890, 848, 828, 799, 768, 738, 676 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{28}O_3Cl_2Na$ [M + Na]$^+$, 481.1292; found, 481.1308.

(4S,5R*)-2,4-Dibutyl-5-hydroxy-5-(thiophen-2-yl)-3-(thiophene-2-carbonyl)-cyclopent-2-enone (**9e**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 10:1) afforded the title product as a light yellow solid in 53% (32 mg) isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.82 (d, J = 4.8 Hz, 1H), 7.55 (d, J = 4.0 Hz, 1H), 7.26 (d, J = 4.8 Hz, 1H), 7.18 (t, J = 4.0 Hz, 1H), 7.02−7.01 (m, 1H), 6.98−6.96 (m, 1H), 3.63−3.60 (m, 1H), 3.39 (s, 1H), 2.36−2.29 (m, 1H), 2.24−2.17 (m, 1H), 1.81−1.78 (m, 1H), 1.59−1.13 (m, 9H), 0.81−0.74 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.6, 187.7, 166.8, 147.0, 142.8, 140.1, 136.3, 134.7, 128.7, 127.0, 125.2, 123.7, 79.2, 55.5, 30.2, 29.9, 29.6, 24.3, 22.7, 22.4, 13.8, 13.5; IR (neat) 3455, 3105, 2956, 2930, 2861, 1716, 1638, 1512, 1465, 1409, 1353, 1257, 1208, 1164, 1121, 1050, 1013, 1050, 1013, 897, 853, 839, 788, 730, 701, 668 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{26}O_3S_2Na$ [M + Na]$^+$, 425.1216; found, 425.1230.

(4S, 5S*)-2,4-Dibutyl-3-(cyclopropanecarbonyl)-5-cyclopropyl-5-hydroxycyclopent-2-enone (**9f**).* Reactions were carried out on a 0.3 mmol scale. Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 10:1) afforded the title product as a

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yellow oil in 64% (30.4 mg) isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 3.10−3.07 (m, 1H), 2.44 (t, J = 7.6 Hz, 2H), 2.36 (s, 1H), 2.27−2.21 (m, 1H), 1.63−1.55 (m, 1H), 1.47−1.40 (m, 3H), 1.38−1.07 (m, 10H), 1.02−0.95 (m, 1H), 0.91−0.84 (m, 6H), 0.53−0.48 (m, 1H), 0.44−0.37 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.1, 204.2, 166.6, 141.1, 78.6, 50.5, 30.5, 30.4, 30.0, 23.9, 22.8, 22.6, 21.2, 19.9, 13.9, 13.7, 13.6, 12.7, 0.8, 0.2; IR (neat) 3478, 3009, 2957, 2929, 2860, 1711, 1671, 1466, 1383, 1338, 1190, 1162, 1050, 1022, 960, 933, 878, 824, 734, 679 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{30}O_3Na$ [M + Na]$^+$, 341.2087; found, 341.2089.

Isolation of the Intermediate of 1,2-Diketone 10a. To a solution of **3a** (0.2 mmol, 52.5 mg) in acetone (2 mL) was added 10% sodium hydroxide solution (0.6 mmol, 0.22 mL). The resulting mixture was stirred at 0 °C until the reaction was complete as monitored by thin-layer chromatography. Then the mixture was quenched with water, extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1 to 8:1) to afford **10a** in 40% (16.3 mg) yield as a yellow liquid and **8a** in 28% (13.7 mg) yield as a light yellow liquid.

*1-Phenylheptane-1,2-dione (**10a**).* ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 7.97 (d, J = 7.6 Hz, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 2.87 (t, J = 7.2 Hz, 2H), 1.73−1.66 (m, 2H), 1.35−1.34 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.4, 192.4, 134.4, 131.9, 130.0, 128.7, 38.6, 31.2, 22.4, 22.3, 13.8; IR (neat) 3061, 2957, 2931, 2872, 1710, 1671, 1596, 1580, 1449, 1401, 1378, 1319, 1268, 1235, 1201, 1181, 1159, 1128, 1086, 1001, 935, 911, 881, 845, 786, 689, 658 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{17}O_2$ [M + H]$^+$, 205.1223; found, 205.1225. The spectroscopic data are in agreement with those previously reported.[27]

*Transformation of 1,2-Diketone **10a** to Cyclopentenones.* To a solution of **10a** (0.2 mmol, 40.9 mg) in acetone (2 mL) was added 10% sodium hydroxide solution (1.0 mmol, 0.36 mL). The resulting mixture was stirred at room temperature until the reaction was complete as monitored by thin-layer chromatography. Then the mixture was quenched with water, extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 10:1) to afford **8a** in 67% (33 mg) yield as a light yellow liquid and **9a** in 10% (4 mg) yield as a light yellow liquid.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallography and the crystal data of compounds **3p**, **8b**, and **9b**, spectroscopic characterization of all substrates and products, and CIF files giving crystal data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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