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Gold and platinum catalyzed cascade reaction of propargyl acetates bearing terminal alkynes or methyl ketones

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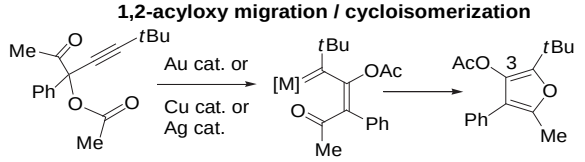
ABSTRACT

A gold (III)-catalyzed cascade reaction of propargyl acetates bearing an extra terminal alkyne (**1**) afforded γ-keto esters **3** and lactones **4**. These products should be generated through allenyl ketone intermediate **B** via a 1,2-acyloxy cyclization/fragmentation/cycloisomerization/hydrolysis sequence. On the other hand, the cascade reaction of α-acetoxy ketones bearing terminal alkynes **5** afforded lactone **6** via allenyl ketone intermediate **A**. This reaction involves a [3,3]-sigmatropic acyloxy rearrangement/cycloisomerization/hydrolysis sequence.

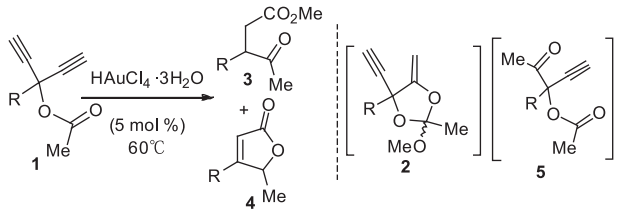
1. Introduction

2(5*H*)-Furanones and 2(3*H*)-furanones are well known as basic components of natural products, some of which display a wide range of characteristic physiological properties.[1] Gold and platinum catalyzed transformations of propargyl esters have been widely used for the construction of a variety of carbo- and heterocycles.[2] An appropriately situated O-ester group undergoes an internal 1,2- or [3,3]-sigmatropic acyloxy rearrangement upon electrophilic activation of the alkyne moiety to give rearranged products or reactive intermediates. More specifically, the reactions of propargyl esters possessing a 1,4-diyne structure provide cyclopentanones,[3a] furans,[3b] pyrroles,[3c] and pyrazoles.[3d] Gevorgyan's group extensively studied the formation of furan rings from α-acetoxy ketones bearing internal alkynes. The oxygen atom of the acetate was introduced in the C3 position of the furan ring via a 1,2-acyloxy migration/cycloisomerization sequence (Scheme 1).[4]

In a preliminary communication, we reported that cascade reactions of propargyl acetates bearing an extra terminal alkyne **1** afforded γ-keto esters **3** and lactones **4** (Scheme 2).[3e] In the process of investigating the mechanism of the reaction, control experiments were performed using compounds **2**–**6** as the substrates. During the course of this study, we found a [3,3]-sigmatropic acyloxy rearrangement/cycloisomerzation/hydrolysis sequence for α-acetoxy ketones bearing terminal alkynes **5** catalyzed by $PtCl_4$. In contrast with the reaction of internal alkynes (Scheme 1), in the case of terminal alkynes, the oxygen atom of the acetate is introduced in the C2 position of the furan ring (Scheme 3).



Scheme 1. V. Gevorgyan et al. Reaction of α-acetoxy ketones bearing internal alkynes.



Scheme 2. This work (1).

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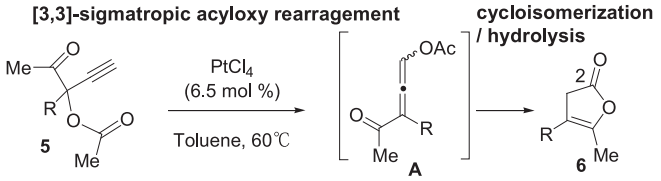
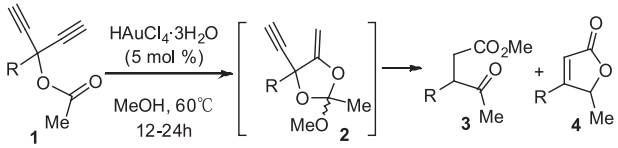


Scheme 3. This work (2). Reaction of α-acetoxy ketones bearing terminal alkynes.

2. Results and discussion

The reaction of **1a** with $HAuCl_4 \cdot 3H_2O$ (5 mol %) in methanol at 60 °C afforded γ-keto ester **3a** and lactone **4a** in 51% and 39% yields, respectively (Table 1, entry 1).

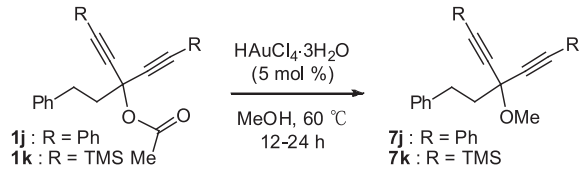
Table 1
Cascade reaction of 1,1-diethynyl acetate **1**



Entry	R	Yield of **3** (%)	Yield of **4** (%)
1	$Ph(CH_2)_2$	51:**3a**	39:**4a**
2[a]	$Ph(CH_2)_2$	52:**3b**	26:**4a**
3[b]	$Ph(CH_2)_2$	Complex mixture	
4	$PhCH_2$	53:**3c**	27:**4c**
5	1-Naphthyl–CH_2	46:**3d**	18:**4d**
6	4-Methylphenyl–CH_2	50:**3e**	20:**4e**
7	Octyl	46:**3f**	47:**4f**
8	Pentyl	46:**3g**	40:**4g**
9	Cyclohexyl–CH_2	36:**3h**	38:**4h**
10	Cyclohexyl	31:**3i**	51:**4i**

[a] Carried out in ^{i}BuOH; ^{i}Butyl ester **3b** was obtained together with **4a**.
[b] Carried out in toluene.

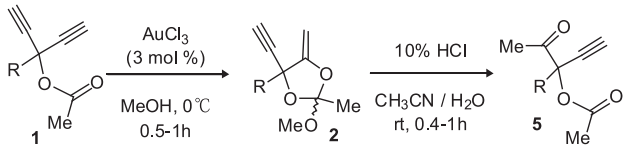
Although commercially available AuCl, $HAuCl_4 \cdot 3H_2O$, $PtCl_4$, $PtCl_2$, $AuCl_3$, and cationic $Ph_3PAuCl/AgSbF_6$ exhibited nearly the same catalytic activity (**3a**: 40–54%, **4a**: 19–30%), the use of $HAuCl_4 \cdot 3H_2O$ provided a better total yield. When ^{i}BuOH was used as the solvent, ^{i}butyl ester **3b** and lactone **4a** were obtained in similar yields (entry 2). A complex mixture was obtained, however, when toluene was used as the solvent (entry 3). With the optimized conditions in hand (entry 1), the scope of the reaction was explored. For substrates **1a**–**e** containing an arylmethylene chain, the reaction proceeded well (entries 1, 2, 4–6). Alkyl-substituted substrates **1f**–**i** provided **3f**–**i** (31–46%) and **4f**–**i** (38–51%) in good combined yields (entries 7–10). In the case of internal alkynes **1i** and **1j**, methyl ether **7i** and **7j** were obtained in 91 and 80% yields, respectively (Scheme 4).



Scheme 4. Reaction of internal alkynes **1j** and **1k**.

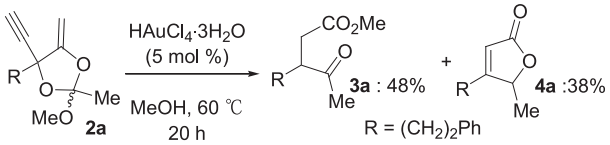
Thin-layer chromatography suggested that the orthoester **2** is the first intermediate in the transformation **1**→**3** and **4**. In general, orthoesters are easily converted to the corresponding ketones under acidic conditions. We expected that the orthoester **2** and ketone **5** are the possible intermediates in this cascade reaction, and thus substrates **1** were converted to corresponding compounds **2** and **5** (Table 2). The reaction of **1** with $AuCl_3$ (3 mol %) in methanol at 0 °C afforded **2** in 56–98% yield. Treatment of **2** with 10% HCl(aq) in CH_3CN/H_2O at room temperature gave the corresponding ketone **5** in 79–99% yield.

Table 2
Preparation of **2** and **5**

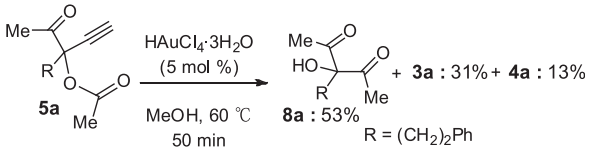


Entry	R	Yield of **2** (%)	Yield of **5** (%)
1	$Ph(CH_2)_2$	86:**2a**	99:**5a**
2	$PhCH_2$	88:**2c**	92:**5c**
3	1-Naphthyl–CH_2	68:**2d**	81:**5d**
4	4-Methylphenyl–CH_2	56:**2e**	79:**5e**
5	Octyl	93:**2f**	85:**5f**
6	Pentyl	71:**2g**	84:**5g**
7	Cyclohexyl–CH_2	63:**2h**	99:**5h**
8	Cyclohexyl	98:**2i**	97:**5i**

To investigate the mechanism of the present reaction (Table 1), some control experiments were performed. As expected, the reaction of **2a** gave similar results to that of **1a** (Scheme 5). On the other hand, the reaction of **5a** afforded diketone **8a** as a major product (53%) together with **3a** (31%) and **4a** (13%) (Scheme 6). Compound **8a** is likely produced by neighboring group participation in the hydration of the terminal alkyne.[5] These results indicated that **2a** is the first intermediate of the reaction.

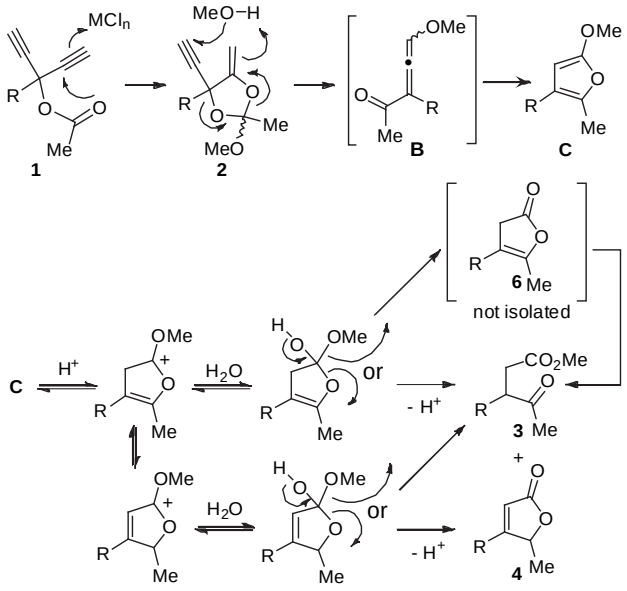


Scheme 5. Reaction of orthoester **2a**.



Scheme 6. Reaction of ketone **5a**.

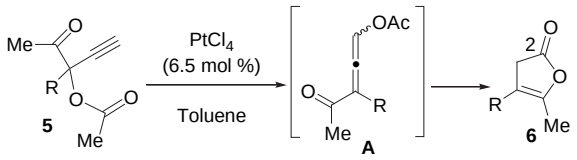
Next, the products **3a** and **4a** were independently treated under the reaction conditions depicted in Table 1. Interconversion between **3a** and **4a** was not observed. These results indicated that the products **3a** and **4a** were produced by independent pathways. In general, 2-methoxyfurans are unstable in the presence of acid and afford hydrolyzed 2-furanones or γ-keto esters.[6] For example, 2-methoxy-5-pentylfuran[7a] was treated with $HAuCl_4 \cdot 3H_2O$ (5 mol %) in methanol at room temperature for 0.5 h to give methyl 4-oxononanoate[7b] (83%) by acid hydrolysis. Based on these control experiments, a plausible mechanism for the present reaction is shown in Scheme 7. 5-*exo*-*dig* Cyclization of 1,1-diethynyl acetate **1** via nucleophilic attack of the first alkyne by a carbonyl oxygen in accordance with Markovnikov's rule, followed by protonolysis, generates the intermediate **2**. Elimination of AcOMe should induce a nucleophilic attack of the second alkyne by methanol with *anti*-



Scheme 7. Proposed mechanism for the reaction of propargyl acetate with terminal aklynes.

Markovnikov regioselectivity to give allenyl ketone intermediate **B**, followed by cyclization to produce the 2-methoxyfuran intermediate **C**. Hydrolysis of the 2-methoxyfuran intermediate **C** gives the products **3** and **4**. In this situation, we could not explain why lactone **6** was not isolated. It was purely by chance that lactone **6** was obtained from the reaction of ketone **5** (Table 3). Treatment of **6a** under the present reaction conditions gave γ-keto ester **3a** in 47% yield along with an unidentified mixture of compounds.[8] Thus lactone **6** could be converted to **3** if it is produced in the reaction mixture.

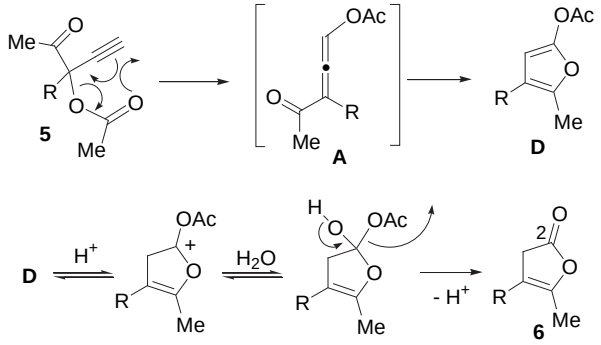
Table 3
Cascade reaction of ketone **5** with terminal alkynes



Entry	R	Condition	Yield of **6** (%)
1	$Ph(CH_2)_2$	rt, 5.5h	68:**6a**
2	$PhCH_2$	rt −60 °C, 75 min	76:**6c**
3	1-Naphthyl−CH_2	rt −60 °C, 75 min	60:**6d**
4	*p*-Tolyl−CH_2	rt −60 °C, 75 min	71:**6e**
5	Octyl	rt −60 °C, 75 min	63:**6f**
6	Pentyl	rt −60 °C, 2 h	55:**6g**
7	Cyclohexyl−CH_2	rt −60 °C, 45 min	51:**6h**
8	Cyclohexyl	rt −60 °C, 75 min	46:**6i**

Although **5a** was not an intermediate for the reaction, we were interested in the reaction of terminal alkyne **5a** depicted in Scheme 6, because the reaction sequence was different from that of internal alkynes reported by Gevorgyan's group[4] (Scheme 1). Thus, we investigated the gold and platinum catalyzed reaction of **5a** in detail.

The reaction of **5a** with $PtCl_4$ (6.5 mol %) in toluene afforded the lactone **6a** in 68% yield (Table 3, entry 1). Although AuCl, $HAuCl_4 \cdot 3H_2O$, and $PtCl_2$ exhibited nearly the same catalytic activity (**6a**: 53–66%), the use of $PtCl_4$ gave better yields. The use of CH_2Cl_2 and CH_3CN reduced yields. Substrates bearing an arylmethylene chain or long alkyl chain gave moderate yields (Table 3, entries 1–6), whereas the presence of a cyclohexyl side chain resulted in decreased yields (Table 3, entries 7 and 8). A plausible mechanism of the reaction is proposed as shown in Scheme 8. [3,3]-Sigmatropic acyloxy rearrangement of **5** provides allenyl ketone intermediate **A**, which undergoes cycloisomerization to produce the furan intermediate **D**. Hydrolysis of the furan intermediate **D** gives the product **6**, which is an olefinic isomer of **4**. In this step, the acetoxy group acts as a preferential leaving group. In contrast with the reaction of internal alkynes (Scheme 1), in the case of terminal alkynes, the oxygen atom of the acetate is introduced at the C2 position of the furan ring.



Scheme 8. .Proposed mechanism for the reaction of propargyl acetate with methyl ketones.

3. Conclusion

We have reported two kinds of cascade reactions of propargyl acetates catalyzed by gold or platinium. The reaction of propargyl acetates bearing an extra terminal alkyne (**1**) afforded γ-keto esters **3** and lactones **4** through allenyl ketone intermediate **B** via a 1,2-acyloxy cyclization/fragmentation/cycloisomerization/hydrolysis sequence. On the other hand, the reaction of α-acetoxy ketones bearing terminal alkynes (**5**) afforded lactones **6** through allenyl ketone intermediate **A** via a [3,3]-sigmatropic acyloxy rearrangement/cycloisomerization/hydrolysis sequence.

4. Experimental section

4.1. General

All melting points were measured on a Yanaco MP-3S micro melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on JEOL AL 400 and JEOL Lambda 500 spectrometers in $CDCl_3$ with Me_4Si as an internal reference. ^{13}C NMR spectra were recorded at 100 MHz. High-resolution mass spectra (HR-MS) and fast atom bombardment mass spectra (FAB-MS) were obtained with JEOL GC Mate II, JMS-SX102, and JEOL JMS 600H spectrometers. IR spectra were recorded with a JASCO FT/IR-300 spectrometer. All reagents were purchased from commercial sources and used without purification. All evaporations were performed under reduced pressure. For column chromatography, silica-gel (Kieselgel 60) was employed.

4.2. Preparation of substrates 1

Substrates **1** were prepared as we already described. **1a**,[3e] **1c**,[3e] **1d**,[3a] **1e**,[3a] **1f**,[3e] **1g**,[3e] and **1h**[3a] were known compounds.

*4.2.1. α,α-Diethynylcyclohexanemethanol-1-acetate (**1i**).* Colorless needles; mp 75–76 °C (heptane); ^1H NMR (400 MHz, $CDCl_3$) δ 1.19–1.32 (5H, m), 1.76 (1H, br d, *J*=11.6 Hz), 1.83–1.94 (3H, m), 2.04–2.12 (2H, m), 2.09 (3H, s), 2.63 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 25.8, 26.1, 26.9, 47.7, 70.4, 74.1, 79.4, 168.3; IR (KBr)

3267, 2932, 2855, 2120, 1738, 1376, 1244, 989, 689 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{13}H_{16}O_2$ 204.1150; found 204.1146.

*4.2.2. α,α-Bis(2-phenylethynyl)benzenepropanol-1-acetate (**1j**).* Pale yellow needles; mp 82–83 °C; ^1H NMR ($CDCl_3$) δ 2.12 (3H, s), 2.55–2.60 (2H, m), 3.07–3.11 (2H, m), 7.21–7.24 (1H, m), 7.27–7.33 (10H, m), 7.49–7.52 (4H, m); ^{13}C NMR ($CDCl_3$) δ 21.5, 30.9, 44.5, 68.1, 85.3, 85.9, 122.0, 126.1, 128.2, 128.5, 128.6, 128.8, 132.1, 141.0, 168.3; IR (ATR) 2925, 2244, 1744, 1489, 1227 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{27}H_{22}O_2$ 378.1620; found 378.1611.

*4.2.3. α,α-Bis(2-trimethylsilylethynyl)benzenepropanol-1-acetate (**1k**).* Colorless solid; mp 92–93 °C; ^1H NMR ($CDCl_3$) δ 0.20 (18H, s), 2.06 (3H, s), 2.33–2.37 (2H, m), 2.89–2.93 (2H, m), 7.18–7.32 (5H, m); ^{13}C NMR ($CDCl_3$) δ 0.2, 21.7, 31.1, 44.9, 67.8, 90.7, 101.5, 126.3, 128.7, 128.8, 141.4, 168.1; IR (ATR) 2968, 2171, 1746, 1366, 1227, 1130, 1023 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{21}H_{30}O_2Si_2$ 370.1784; found 370.1788.

4.3. General procedure for the reaction of 1 (Table 1)

A 20 mL round-bottom flask, containing a magnetic stirring bar, catalyst (0.015 mmol), **1** (0.3 mmol), and MeOH (5 mL) was fitted with a Dimroth condenser capped with a rubber septum. After being stirred for 12–24 h at 60 °C, the mixture was diluted with EtOAc (20 mL) and washed with 3% $NaHCO_3$ aq (20 mL). The organic layers were separated and the aqueous layer extracted with EtOAc (30 mL). The combined organic layers were then dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by column chromatography on silica-gel. The fraction eluted with hexane/ethyl acetate (100/1 to 50/1) and (10/1) afforded **3** and **4**, respectively. **3a**, **3b**, **3c**, **3f**, **3g**, **4a**, **4c**, **4f**, and **4g** were known compounds.[3e]

*4.3.1. β-Acetyl-1-naphthalenebutanoic acid methyl ester (**3d**).* Pale yellow oil; ^1H NMR ($CDCl_3$) δ 2.04 (3H, s), 2.39 (1H, dd, *J*=17.2, 4.4 Hz), 2.85 (1H, dd, *J*=17.2, 9.6 Hz), 3.07 (1H, dd, *J*=13.6, 8.0 Hz), 3.36 (1H, dd, *J*=13.6, 7.4 Hz), 3.47–3.50 (1H, m), 3.59 (3H, s), 7.26 (1H, d, *J*=6.0 Hz), 7.38 (1H, dd, *J*=8.0, 7.0 Hz), 7.49–7.59 (2H, m), 7.75 (1H, d, *J*=8.4 Hz), 7.87 (1H, dd, *J*=8.0, 0.8 Hz), 8.04 (1H, d, *J*=8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 30.7, 35.0, 35.6, 48.4, 51.7, 123.3, 125.4, 125.8, 126.4, 127.5, 127.7, 129.0, 131.6, 134.0, 134.2, 172.6, 211.0; IR (ATR) 1739, 1712, 1436, 1355, 1162 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{17}H_{18}O_3$ 270.1256; found 270.1258.

*4.3.2. 4-(1-Naphthylmethyl)-5-methyl-2(5H)-furanone (**4d**).* Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.55 (3H, d, *J*=6.8 Hz), 3.97 (1H, dd, *J*=18.0, 1.6 Hz), 4.18 (1H, d, *J*=18.0 Hz), 4.98 (1H, q, *J*=6.8 Hz), 5.49–5.50 (1H, m), 7.35 (1H, d, *J*=6.8 Hz), 7.44 (1H, dd, *J*=6.8, 8.4 Hz), 7.49–7.53 (2H, m), 7.76–7.79 (1H, m), 7.83 (1H, d, *J*=8.4 Hz), 7.88–7.91 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.5, 32.3, 80.1, 117.2, 123.3, 125.5, 126.1, 126.7, 127.5, 128.5, 129.1, 131.5, 131.7, 134.0, 172.5, 172.6; IR (ATR) 1739, 1639, 1169 cm^{-1}; HRMS-EI *m/z*: [M+] calcd for $C_{16}H_{14}O_2$ 238.0994; found 238.0994.

*4.3.3. β-Acetyl-4-methylphenylbutanoic acid methyl ester (**3e**).* Pale yellow oil; ^1H NMR ($CDCl_3$) δ 2.12 (3H, s), 2.32 (3H, s), 2.35 (1H, dd, *J*=17.0, 4.4 Hz), 2.56 (1H, dd, *J*=13.6, 8.4 Hz), 2.74 (1H, dd, *J*=17.0, 10.0 Hz), 2.89 (1H, dd, *J*=13.6, 6.8 Hz), 3.22–3.26 (1H, m), 7.04 (2H, d, *J*=8.0 Hz), 7.10 (2H, d, *J*=8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 21.0, 30.3, 35.0, 37.3, 49.8, 51.7, 128.8, 129.4, 135.1, 136.3, 172.8, 210.8; IR (ATR) 1734, 1713, 1515, 1437, 1356, 1162 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{14}H_{18}O_3$ 234.1256; found 234.1259.

*4.3.4. 5-Methyl-4-[(4-methylphenyl)methyl]-2(5H)-furanone (**4e**).* Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.45 (3H, d, *J*=6.8 Hz), 2.34 (3H, s), 3.51 (1H, d, *J*=16.6 Hz), 3.71 (1H, d, *J*=16.6 Hz), 4.91 (1H, q, *J*=6.8 Hz), 5.67 (1H, d, *J*=6.8 Hz), 7.06 (2H, d, *J*=8.0 Hz), 7.15 (2H, d, *J*=8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.3, 21.1, 34.2, 79.9, 116.6, 128.8, 129.7, 132.5, 137.1, 172.7, 173.1; IR (ATR) 1744, 1638, 1514, 1167, 1062, 948 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{13}H_{14}O_2$ 202.0994; found 202.0998.

*4.3.5. β-Acetyl-cyclohexanebutanoic acid methyl ester (**3h**).* Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.86–0.92 (2H, m), 1.18–1.22 (5H, m), 1.46–1.49 (1H, m), 1.60–1.72 (5H, m), 2.23 (3H, s), 2.35 (1H, dd, *J*=16.8, 4.0 Hz), 2.71 (1H, dd, *J*=16.8, 10.0 Hz), 3.06–3.08 (1H, m), 3.65 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.1, 26.2, 26.4, 29.4, 32.9, 33.7, 35.3, 35.4, 39.0, 45.3, 51.7, 173.0, 211.3; IR (ATR) 2923, 2851, 1737, 1713, 1437, 1354, 1159 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{13}H_{22}O_3$ 226.1569; found 226.1570.

*4.3.6. 4-Cyclohexylmethyl-5-methyl-2(5H)-furanone (**4h**).* Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88–1.04 (2H, m), 1.15–1.29 (3H, m), 1.42 (3H, d, *J*=6.8 Hz), 1.54–1.56 (1H, m), 1.71–1.75 (5H, m), 2.14–2.30 (2H, m), 4.92 (1H, q, *J*=6.8 Hz), 5.76 (1H, d, *J*=1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.3, 26.0, 26.1, 26.2, 33.0, 33.6, 35.8, 36.4, 80.5, 115.9, 173.1, 173.1; IR (ATR) 2924, 2851, 1745, 1636, 1448, 1320, 1170, 947,cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{12}H_{18}O_2$ 194.1307; found 194.1309.

*4.3.7. β-Acetyl-cyclohexanepropanoic acid methyl ester (**3i**).* Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89–0.98 (1H, m), 1.05–1.32 (5H, m), 1.55–1.67 (3H, m), 1.72–1.82 (2H, m), 2.24 (3H, s), 2.37 (1H, dd, *J*=16.8, 3.2 Hz), 2.76 (1H, dd, *J*=16.8, 11.4 Hz), 2.89–2.94 (1H, m), 3.64 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.2, 26.4, 26.5, 29.4, 30.9, 31.4, 32.4, 39.5, 51.7, 53.5, 173.5, 211.2; IR (KBr) 2929, 2854, 1738, 1712, 1449, 1438, 1359, 1162 cm^{-1}; HRMS-FAB *m/z*:[M^++H] calcd for $C_{12}H_{21}O_3$ 213.1491; found 213.1519.

*4.3.8. 4-Cyclohexyl-5-methyl-2(5H)-furanone (**4i**).* Colorless oil; ^1H NMR ($CDCl_3$) δ 0.92–1.04 (1H, m), 1.16–1.40 (5H, m), 1.44 (3H, d, *J*=6.8 Hz), 1.65–1.93 (3H, m), 2.11–2.26 (2H, m), 5.02 (1H, qd, *J*=6.8, 1.2 Hz), 5.73 (1H, s); ^{13}C NMR ($CDCl_3$) δ 18.4, 25.6, 25.8, 26.1, 30.7, 32.3, 37.0, 79.4, 113.6, 173.3, 179.0; IR (KBr) 2928, 2855, 1757, 1631, 1449, 1175 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{11}H_{16}O_2$ 180.1150; found 180.1151.

*4.3.9. Methyl ether (**7j**).* Yellow solid; mp 53–56 °C; ^1H NMR ($CDCl_3$) δ 2.40–2.44 (2H, m), 3.04–3.08 (2H, m), 3.66 (3H, s), 7.17–7.28 (1H, m), 7.26–7.34 (10H, m), 7.49–7.51 (4H, m); ^{13}C NMR ($CDCl_3$) δ 31.0, 44.7, 53.3, 71.0, 85.3, 86.8, 122.2, 125.9, 128.3, 128.4, 128.5, 128.7, 131.9, 141.6; IR (ATR) 2943, 2214, 1598, 1489, 1454, 1289, 1102, 1061 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{26}H_{22}O$ 350.1671; found 350.1664.

*4.3.10. Methyl ether (**7k**).* Yellow solid; mp 48–51 °C; ^1H NMR ($CDCl_3$) δ 0.2 (18H, s), 2.16–2.21 (2H, m), 2.87–2.91 (2H, m), 3.49 (3H, s), 7.16–7.30 (5H, m); ^{13}C NMR ($CDCl_3$) δ 0.2, 31.0, 44.8, 53.2, 70.8, 90.1, 102.7, 126.0, 128.6, 128.7, 141.9; IR (ATR) 2963, 2163, 1738, 1456, 1251, 1099, 1058 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{20}H_{30}OSi_2$ 342.1835; found 342.1824.

4.4. General procedure for the preparation of 2 (Table 2)

A mixture of $AuCl_3$ (4.2 mg, 0.014 mmol) and **1** (0.47 mmol) in MeOH (5 mL) was stirred for 0.5–1 h at 0 °C. The reaction was quenched with powdered $NaHCO_3$ (50 mg), and the mixture was then diluted with EtOAc (20 mL) and washed with 5% $NaHCO_3$ aq (40 mL). The organic layers were separated and the aqueous layer extracted with EtOAc (30 mL). The combined organic layers were then dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by column chromatography on silica-gel. The

fraction eluted with hexane/ethyl acetate (50/1 to 10/1) afforded orthoester **2**.

*4.4.1. 4-Ethynyl-2-methoxy-2-methyl-5-methylene-4-(2-phenylethyl)-1,3-dioxolane (**2a**)*[3e]. Colorless oil, inseparable mixture of diastereomers, ratio=2.3:1; ^{1}H NMR ($CDCl_3$) (major diastereomer) δ 1.66 (3H, s), 2.05–2.25 (2H, m), 2.66 (1H, s), 2.79–2.96 (2H, m), 3.40 (3H, s), 4.18 (1H, d, J=2.8 Hz), 4.50 (1H, d, J=2.8 Hz), 7.18–7.32 (5H, m); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 24.0, 30.3, 44.4, 50.1, 73.9, 78.8, 80.8, 82.4, 123.1, 126.1, 128.4, 128.5, 141.0, 159.8; IR (KBr) 3287, 2117, 1687, 1052 cm^{-1}; HRMS-EI m/z: [M$^+$] calcd for $C_{16}H_{18}O_3$ 258.1256; found 258.1258.

*4.4.2. 4-Ethynyl-2-methoxy-2-methyl-5-methylene-4-(phenylmethyl)-1,3-dioxolane (**2c**).* Colorless oil, inseparable mixture of diastereomers, ratio=3:1; ^{1}H NMR ($CDCl_3$) (major diastereomer) δ 1.31 (3H, s), 2.64 (1H, s), 3.15 (1H, d, J=14.0 Hz), 3.19 (1H, d, J=14.0 Hz), 3.34 (3H, s), 4.17 (1H, d, J=3.0 Hz), 4.52 (1H, d, J=3.0 Hz), 7.27–7.30 (5H, m); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 23.9, 48.0, 50.0, 74.6, 79.3, 81.4, 82.8, 123.4, 127.3, 127.9, 131.2, 134.4, 159.3; IR (ATR) 3286, 2110, 1685, 1387, 1151, 1101, 1046 cm^{-1}; HRMS-EI m/z: [M$^+$] calcd for $C_{15}H_{16}O_3$ 244.1100; found 244.1109.

*4.4.3. 4-Ethynyl-2-methoxy-2-methyl-5-methylene-4-(1-naphthylmethyl)-1,3-dioxolane (**2d**).* Colorless oil, inseparable mixture of diastereomers, ratio=8:1; ^{1}H NMR ($CDCl_3$) (major diastereomer) δ 0.94 (3H, s), 2.64 (1H, s), 3.32 (3H, s), 3.48 (1H, d, J=14.4 Hz), 3.94 (1H, d, J=14.4 Hz), 4.29 (1H, d, J=3.0 Hz), 4.57 (1H, d, J=3.0 Hz), 7.41–7.51 (4H, m), 7.76–7.80 (2H, m), 8.18 (1H, d, J=8.1 Hz); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 23.3, 44.0, 50.0, 74.7, 79.8, 81.7, 83.2, 123.5, 125.0, 125.2, 125.4, 125.5, 128.1, 128.4, 129.5, 130.8, 133.4, 133.7, 159.5; IR (ATR) 3287, 2105, 1685, 1386, 1151, 1099, 1048 cm^{-1}; HRMS-EI m/z: [M$^+$] calcd for $C_{19}H_{18}O_3$ 294.1256; found 294.1261.

*4.4.4. 4-Ethynyl-2-methoxy-2-methyl-5-methylene-4-[(4-methylphenyl)methyl]-1,3-dioxolane (**2e**).* Colorless oil, inseparable mixture of diastereomers, ratio=4:1; ^{1}H NMR ($CDCl_3$) (major diastereomer) δ 1.34 (3H, s), 2.32 (3H, s), 2.64 (1H, s), 3.10 (1H, d, J=13.6 Hz), 3.15 (1H, d, J=13.6 Hz), 3.34 (3H, s), 4.16 (1H, d, J=2.8 Hz), 4.52 (1H, d, J=2.8 Hz), 7.10 (2H, d, J=8.0 Hz), 7.20 (2H, d, J=8.0 Hz); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 21.1, 24.0, 47.7, 50.0, 74.6, 79.4, 81.3, 82.8, 123.4, 128.6, 131.1, 131.3, 136.9, 159.4; IR (ATR) 3286, 2110, 1685, 1387, 1152, 1047 cm^{-1}; HRMS-EI m/z: [M$^+$] calcd for $C_{16}H_{18}O_3$ 258.1256; found 258.1254.

*4.4.5. 4-Ethynyl-2-methoxy-2-methyl-5-methylene-4-(1-octyl)-1,3-dioxolane (**2f**).* Colorless oil, inseparable mixture of diastereomers, ratio=2:1; ^{1}H NMR ($CDCl_3$) (major diastereomer) δ 0.88 (3H, t, J=6.4 Hz), 1.23–1.36 (10H, m), 1.54–1.61 (2H, m), 1.63 (3H, s), 1.78–1.90 (2H, m), 2.60 (1H, s), 3.37 (3H, s), 4.12 (1H, d, J=2.8 Hz), 4.45 (1H, d, J=2.8 Hz); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 14.1, 22.7, 23.8, 24.0, 24.1, 29.2, 29.4, 31.9, 42.5, 50.1, 73.5, 79.3, 80.4, 82.9, 123.0, 160.2; IR (ATR) 3310, 2925, 2855, 2136, 1686, 1465, 1386, 1154, 1053 cm^{-1}; HRMS-EI m/z: [M$^+$] calcd for $C_{16}H_{26}O_3$ 266.1882; found 266.1883.

*4.4.6. 4-Ethynyl-2-methoxy-2-methyl-5-methylene-4-(1-pentyl)-1,3-dioxolane (**2g**).* Colorless oil, inseparable mixture of diastereomers, ratio=1.4:1; ^{1}H NMR ($CDCl_3$) (major diastereomer) δ 0.90–0.92 (3H, m), 1.32–1.36 (4H, m), 1.54–1.61 (2H, m), 1.63 (3H, s), 1.78–1.90 (2H, m), 2.60 (1H, s), 3.37 (3H, s), 4.12 (1H, d, J=2.8 Hz), 4.45 (1H, d, J=2.8 Hz); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 14.0, 23.5, 24.0, 24.1, 31.5, 42.5, 50.1, 73.5, 79.3, 80.4, 82.9, 123.1, 160.2; IR (ATR) 3294, 2951, 2872, 2124, 1210, 1154, 1052, 979 cm^{-1}; HRMS-EI m/z: [M$^+$] calcd for $C_{13}H_{20}O_3$ 224.1413; found 224.1410.

*4.4.7. 4-Cyclohexylmethyl-4-ethynyl-2-methoxy-2-methyl-5-methylene-1,3-dioxolane (**2h**).* Colorless oil, inseparable mixture of diastereomers, ratio=1.5:1; ^{1}H NMR ($CDCl_3$) (major diastereomer) δ 0.96–1.34 (6H, m), 1.66–1.84 (7H, m), 1.62 (3H, s), 2.61 (1H, s), 3.36 (3H, s), 4.10 (1H, d, J=2.9 Hz), 4.42 (1H, d, J=2.9 Hz); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 24.4, 26.2, 26.3, 26.3, 34.1, 34.4, 34.6, 49.7, 50.0, 73.7, 79.3, 80.3, 83.1, 123.1, 161.1; IR (ATR) 3290, 2922, 2851, 2116, 1685, 1448, 1385, 1152, 1052 cm^{-1}; HRMS-EI m/z: [M$^+$] calcd for $C_{15}H_{22}O_3$ 250.1569; found 250.1567.

*4.4.8. 4-Cyclohexyl-4-ethynyl-2-methoxy-2-methyl-5-methylene-1,3-dioxolane (**2i**).* Colorless oil, inseparable mixture of diastereomers, ratio=4:1; ^{1}H NMR ($CDCl_3$) (major diastereomer) δ 1.13–1.30 (5H, m), 1.64 (3H, s), 1.54–2.10 (6H, m), 2.59 (1H, s), 3.38 (3H, s), 4.13 (1H, d, J=2.8 Hz), 4.51 (1H, d, J=2.8 Hz); ^{13}C NMR ($CDCl_3$) (major diastereomer) δ 23.2, 26.1, 26.1, 26.2, 26.5, 27.3, 47.7, 50.3, 74.1, 81.7, 82.3, 82.6, 122.7, 159.0; IR (KBr) 3283, 2935, 2855, 2111, 1686, 1453, 1387, 1285, 1153, 1043 cm^{-1}; HRMS-EI m/z: [M$^+$] calcd for $C_{14}H_{20}O_3$ 236.1413; found 236.1407.

4.5. General procedure for the preparation of 5 (Table 2)

To a solution of **2** (0.46 mmol) in CH_3CN (4 mL)/H_2O (1.5 mL) was added 10% HCl (0.5 mL), and the mixture stirred for 0.4–1 h at room temperature. The reaction was quenched with powdered $NaHCO_3$ (50 mg), and the mixture was then diluted with EtOAc (20 mL) and 5% $NaHCO_3$ aq (20 mL). The organic layers were separated and the aqueous layer extracted with EtOAc (30 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by column chromatography on silica-gel. The fraction eluted with hexane/ethyl acetate (30/1 to 10/1) afforded α-acetoxy ketone **5**.

*4.5.1. 3-Acetyloxy-3-(2-phenylethyl)-4-pentyn-2-one (**5a**).* Colorless oil; ^{1}H NMR ($CDCl_3$) δ 2.11 (3H, s), 2.16–2.19 (2H, m), 2.41 (3H, s), 2.78 (1H, s), 2.86 (2H, t, J=8.6 Hz), 7.19–7.31 (5H, m); ^{13}C NMR ($CDCl_3$) δ 20.6, 25.1, 30.1, 39.1, 77.0, 79.3, 79.7, 126.3, 128.4, 128.6, 140.5, 169.3, 201.0; IR (ATR) 3274, 2129, 1730, 1369, 1236, 699 cm^{-1}; HRMS-EI m/z: [M$^+$] calcd for $C_{15}H_{16}O_3$ 244.1099; found 244.1101.

*4.5.2. 3-Acetyloxy-3-phenylmethyl-4-pentyn-2-one (**5c**).* Colorless oil; ^{1}H NMR ($CDCl_3$) δ 2.11 (3H, s), 2.19 (3H, s), 2.73 (1H, s), 3.15 (1H, d, J=13.2 Hz), 3.23 (1H, d, J=13.2 Hz), 7.30–7.31 (5H, m); ^{13}C NMR ($CDCl_3$) δ 20.6, 27.2, 43.5, 77.8, 79.2, 79.8, 127.6, 128.2, 130.8, 133.2, 169.2, 201.8; IR (ATR) 3277, 3032, 2118, 1731, 1369, 1224, 699 cm^{-1}; HRMS-EI m/z: [M$^+$] calcd for $C_{14}H_{14}O_3$ 230.0943; found 230.0946.

*4.5.3. 3-Acetyloxy-3-(1-naphthylmethyl)-4-pentyn-2-one (**5d**).* Colorless oil; ^{1}H NMR ($CDCl_3$) δ 2.03 (3H, s), 2.23 (3H, s), 2.64 (1H, s), 3.61 (1H, d, J=14.0 Hz), 3.76 (1H, d, J=14.0 Hz), 7.43–7.50 (4H, m), 7.80–7.84 (2H, m), 8.17 (1H, d, J=8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 20.7, 27.0, 39.3, 78.2, 79.6, 79.9, 124.8, 125.0, 125.6, 125.7, 128.5, 128.6, 129.6, 129.7, 132.9, 133.8, 169.2, 201.8; IR (ATR) 3274, 2121, 1721, 1354, 1227 cm^{-1}; HRMS-EI m/z: [M$^+$] calcd for $C_{18}H_{16}O_3$ 280.1100; found 280.1103.

*4.5.4. 3-Acetyloxy-3-[(4-methylphenyl)methyl]-4-pentyn-2-one (**5e**).* Pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 2.10 (3H, s), 2.19 (3H, s), 2.34 (3H, s), 2.72 (1H, s), 3.11 (1H, d, J=13.3 Hz), 3.18 (1H, d, J=13.3 Hz), 7.11 (2H, d, J=8.1 Hz), 7.17 (2H, d, J=8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 20.7, 21.1, 27.3, 43.2, 77.7, 79.3, 80.0, 128.9, 130.0, 130.6, 137.3, 169.3, 201.9; IR (ATR) 3278, 2926, 2111, 1729, 1516, 1368, 1224 cm^{-1}; HRMS-EI m/z: [M$^+$] calcd for $C_{15}H_{16}O_3$ 244.1100; found 244.1098.

*4.5.5. 3-Acetyloxy-3-ethynyl-undecan-2-one (**5f**).* Colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.88 (3H, t, J=6.8 Hz), 1.27–1.30 (10H, m), 1.48–1.54 (2H, m), 1.82–1.87 (2H, m), 2.11 (3H, s), 2.39 (3H, s), 2.69 (1H, s); ^{13}C

NMR ($CDCl_3$) δ 14.1, 20.7, 22.6, 23.6, 26.1, 29.2, 29.3, 29.4, 31.8, 37.6, 76.4, 79.6, 80.1, 169.4, 201.5; IR (ATR) 3274, 2925, 2855, 2117, 1732, 1369, 1233 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{15}H_{24}O_3$ 252.1726; found 252.1730.

*4.5.6. 3-Acetyloxy-3-ethynyl-octan-2-one (**5g**).* Colorless oil; ^1H NMR ($CDCl_3$) δ 0.90 (3H, t, *J*=7.2 Hz), 1.31–1.34 (4H, m), 1.49–1.55 (2H, m), 1.82–1.86 (2H, m), 2.11 (3H, s), 2.39 (3H, s), 2.71 (1H, s); ^{13}C NMR ($CDCl_3$) δ 13.9, 20.7, 22.4, 23.2, 26.1, 31.5, 37.6, 76.4, 79.6, 80.1, 169.4, 201.5; IR (ATR) 3273, 2956, 2932, 2871, 2117, 1732, 1369, 1237 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{12}H_{18}O_3$ 210.1256; found 210.1262.

*4.5.7. 3-Acetyloxy-3-[(cyclohexyl)methyl]-4-pentyn-2-one (**5h**).* Colorless oil; ^1H NMR ($CDCl_3$) δ 0.97–1.05 (2H, m), 1.13–1.19 (1H, m), 1.24–1.30 (2H, m), 1.61–1.76 (7H, m), 1.87–1.90 (1H, m), 2.10 (3H, s), 2.38 (3H, s), 2.72 (1H, s); ^{13}C NMR ($CDCl_3$) δ 20.8, 25.7 (2C), 26.1, 26.1, 26.2, 34.0, 34.4, 44.0, 76.7, 79.7, 80.2, 169.2, 201.2; IR (ATR) 3269, 2923, 2851, 2121, 1731, 1448, 1368, 1226 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{14}H_{20}O_3$ 236.1413; found 236.1409.

*4.5.8. 3-Acetyloxy-3-cyclohexyl-4-pentyn-2-one (**5i**).* Colorless oil; ^1H NMR ($CDCl_3$) δ 1.12–1.35 (5H, m), 1.57–1.92 (6H, m), 2.08 (3H, s), 2.41 (3H, s), 2.68 (1H, s); ^{13}C NMR ($CDCl_3$) δ 20.6, 25.8, 25.8, 25.9, 26.7, 26.9, 28.1, 45.1, 76.8, 79.4, 82.3, 169.6, 202.7; IR (KBr) 3293, 2929, 2860, 2116, 1740, 1373, 1354, 1241 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{13}H_{18}O_3$ 222.1256; found 222.1257.

4.6. Control experiment (Scheme 6)

*4.6.1. 3-Hydroxy-3-(2-phenylethyl)-pentan-2,4-dione (**8a**).* Colorless oil; ^1H NMR ($CDCl_3$) δ 2.22 (6H, s), 2.26–2.29 (2H, m), 2.53–2.57 (2H, m), 4.79 (1H, s), 7.15–7.29 (5H, m); ^{13}C NMR ($CDCl_3$) δ 25.2, 29.6, 38.2, 90.8, 126.3, 128.5, 128.5, 140.8, 207.2; IR (ATR) 3446, 1702, 1355, 1125, 700 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{13}H_{16}O_3$ 220.1100; found 220.1109.

4.6.2. 4-Oxononanoate. To a solution of 2-methoxy-5-pentylfuran (50.5 mg, 0.3 mmol) in MeOH (5 mL) was added $HAuCl_4 \cdot 3H_2O$ (5.9 mg, 0.015 mmol) and the mixture stirred at room temperature for 0.5 h. The reaction mixture was then quenched with powdered $NaHCO_3$ (100 mg), diluted with CH_2Cl_2 (30 mL) and washed with satd $NaHCO_3$(aq) (20 mL). The layers were separated and the aqueous layer extracted with CH_2Cl_2 (30 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by column chromatography on silica-gel with hexane/ethyl acetate (10/1) as eluent to afford 4-oxononanoate[7b] as a colorless oil (46.5 mg, 83%).

4.7. General procedure for the reaction of 5 (Table 3)

A 20 mL round-bottomed flask containing a magnetic stirring bar, $PtCl_4$ (2.6 mg, 0.007 mmol), **5** (0.11 mmol), and toluene (5 mL) was fitted with a Dimroth condenser capped with a rubber septum. The mixture was stirred for a period of time at an appropriate temperature. The reaction was quenched with powdered $NaHCO_3$ (50 mg), and the mixture was then diluted with EtOAc (20 mL) and washed with 5% $NaHCO_3$ aq (40 mL). The organic layers were separated, and the aqueous layer was then extracted with EtOAc (30 mL). The combined organic layers were dried over $MgSO_4$ and then concentrated in vacuo. The crude product was purified by column chromatography on silica-gel. The fraction eluted with hexane/ethyl acetate (50/1 to 30/1) afforded lactone **6**.

*4.7.1. 5-Methyl-4-(2-phenylethyl)-2(3H)-furanone (**6a**).* Pale yellow oil; ^1H NMR ($CDCl_3$) δ 1.77 (3H, dd, *J*=2.4, 0.4 Hz), 2.43 (2H, t, *J*=7.6 Hz), 2.71 (2H, t, *J*=7.6 Hz), 3.03–3.04 (2H, m), 7.13 (2H, d, *J*=6.8 Hz), 7.19–7.22 (1H, m), 7.06–7.31 (2H, m); ^{13}C NMR ($CDCl_3$) δ 10.9, 27.4, 34.7, 36.0, 111.1, 126.3, 128.3, 128.6, 140.8, 147.1, 176.1; IR (KBr) 2923, 1790, 1496, 1454, 1234 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{13}H_{14}O_2$ 202.0994; found 202.0995.

*4.7.2. 5-Methyl-4-phenylmethyl-2(3H)-furanone (**6c**).* Colorless oil; ^1H NMR ($CDCl_3$) δ 2.05 (3H, t, *J*=2.4 Hz), 2.99–3.00 (2H, m), 3.44 (2H, br s), 7.12 (2H, d, *J*=6.8 Hz), 7.21–7.26 (1H, m), 7.29–7.33 (2H, m); ^{13}C NMR ($CDCl_3$) δ 11.2, 32.0, 35.8, 111.4, 126.7, 128.2, 128.8, 138.3, 147.1, 175.8; IR (KBr) 2912, 1795, 1704, 1495, 1455, 1388, 1243 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{12}H_{12}O_2$ 188.0837; found 188.0836.

*4.7.3. 4-(1-Naphtylmethyl)-5-methyl-2(3H)-furanone (**6d**).* Colorless oil; ^1H NMR ($CDCl_3$) δ 2.09 (3H, br s), 2.95–2.97 (2H, m), 3.89 (2H, br s), 7.27 (1H, d, *J*=7.7 Hz), 7.41 (1H, dd, *J*=8.2, 7.1 Hz), 7.49–7.55 (2H, m), 7.77 (1H, d, *J*=8.2 Hz), 7.87–7.94 (2H, m); ^{13}C NMR ($CDCl_3$) δ 11.4, 29.3, 36.2, 111.0, 123.1, 125.6, 125.9, 126.2, 126.3, 127.7, 129.0, 131.7, 133.9, 134.1, 147.0, 175.8; IR (ATR) 2929, 1790, 1597, 1510, 1386, 1218, 1134 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{16}H_{14}O_2$ 238.0994; found 238.0995.

*4.7.4. 5-Methyl-4-[(4-methylphenyl)methyl]-2(3H)-furanone (**6e**).* Pale yellow oil; ^1H NMR ($CDCl_3$) δ 2.04 (3H, br s), 2.33 (3H, s), 2.98–3.00 (2H, m), 3.39 (2H, s), 7.01 (2H, d, *J*=8.0 Hz), 7.11 (2H, d, *J*=8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 11.2, 21.0, 31.6, 35.8, 111.6, 128.1, 129.4, 135.2, 136.3, 146.9, 175.9; IR (ATR) 2923, 1793, 1514, 1386, 1240, 1126 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{13}H_{14}O_2$ 202.0994; found 202.0992.

*4.7.5. 5-Methyl-4-(1-octyl)-2(3H)-furanone (**6f**).* Colorless oil; ^1H NMR ($CDCl_3$) δ 0.89 (3H, t, *J*=6.8 Hz), 1.27–1.40 (12H, m), 1.93 (3H, t, *J*=2.4 Hz), 2.09 (2H, t, *J*=7.4 Hz), 3.07–3.09 (2H, m); ^{13}C NMR ($CDCl_3$) δ 11.1, 14.1, 22.6, 25.4, 28.3, 29.2, 29.2, 29.3, 31.8, 35.9, 112.3, 146.2, 176.4; IR (ATR) 2925, 2855, 1740, 1707, 1461, 1377, 1163 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{13}H_{22}O_2$ 210.1620; found 210.1620.

*4.7.6. 5-Methyl-4-(1-pentyl)-2(3H)-furanone (**6g**).* Colorless oil; ^1H NMR ($CDCl_3$) δ 0.90 (3H, t, *J*=7.2 Hz), 1.24–1.41 (6H, m), 1.93 (3H, t, *J*=2.8 Hz), 2.10 (2H, t, *J*=7.6 Hz), 3.07–3.09 (2H, m); ^{13}C NMR ($CDCl_3$) δ 11.1, 14.0, 22.4, 25.4, 28.0, 31.3, 35.9, 112.3, 146.2, 176.4; IR (ATR) 2955, 2931, 2867, 1740, 1717, 1387, 1251, 1157 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{10}H_{16}O_2$ 168.1150; found 168.1145.

*4.7.7. 4-[(Cyclohexyl)methyl]-5-methyl-2(3H)-furanone (**6h**).* Colorless oil; ^1H NMR ($CDCl_3$) δ 0.84–0.93 (2H, m), 1.09–1.38 (4H, m), 1.60–1.74 (5H, m), 1.92 (3H, t, *J*=2.4 Hz), 1.97 (2H, d, *J*=7.2 Hz), 3.07–3.08 (2H, m); ^{13}C NMR ($CDCl_3$) δ 11.2, 26.1(2C), 26.4, 33.2(2C), 33.4, 36.5, 36.9, 111.1, 147.0, 176.4; IR (KBr) 2926, 2852, 1798, 1449, 1386, 1241, 1165 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{12}H_{18}O_2$ 194.1307; found 194.1304.

*4.7.8. 4-Cyclohexyl-5-methyl-2(3H)-furanone (**6i**).* Pale yellow oil; ^1H NMR ($CDCl_3$) δ 1.10–1.22 (3H, m), 1.26–1.36 (2H, m), 1.61–1.79 (5H, m), 1.94 (3H, t, *J*=2.4 Hz), 2.22–2.29 (1H, m), 3.07 (2H, dd, *J*=2.0, 2.4 Hz); ^{13}C NMR ($CDCl_3$) δ 11.2, 25.8, 26.2(2C), 32.2(2C), 33.5, 35.2, 117.3, 144.9, 176.5; IR (KBr) 2925, 2850, 1794, 1711, 1451, 1389, 1250, 1220, 1166 cm^{-1}; HRMS-EI *m/z*: [M^+] calcd for $C_{11}H_{16}O_2$ 180.1150; found 180.1153.

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References and notes

1. (a) Rao, Y. S. *Chem. Rev.* **1976**, *76*, 625; (b) Marshal, P. G.; *Rodd's Chemistry of Carbon Compounds*, 2nd ed.; Elsevier: New York, NY, 1970; Vol. II, Part D, p 369; (c) Tanabe, Y.; Ohno, N. *J. Org. Chem.* **1988**, *53*, 1560; (d) Lorimer, S. D.; Mawson, S. D.; Perry, N. B.; Weavers, R. T. *Tetrahedron* **1995**, *51*, 7287; (e) Carter, N. B.; Mabon, R.; Richecoeur, A. M. E.; Sweeney, J. B. *Tetrahedron* **2002**, *58*, 9117; (f) Bellina, F.; Falchi, E.; Rossi, R. *Tetrahedron* **2003**, *59*, 9091; (g) Padakanti, S.; Pal, M.; Yeleswarapu, K. R. *Tetrahedron* **2003**, *59*, 7915; (h) Boukouvalas, J.; Wang, J.-X.; Marion, O. *Tetrahedron Lett.* **2007**, *48*, 7747; (i) Fernández-Rodríguez, E.; Manso, J.; Pérez-Prior, M. T.; García-Santos, M. D. P.; Calle, E.; Casado, J. *Int. J. Chem. Kinet.* **2007**, 591; (j) Husain, A.; Alam, M. M.; Hasan, S. M.; Yar, M. S. *Acta Pol. Pharm.* **2009**, *66*, 173; (k) Alam, M. M.; Husain, A.; Hasan, S. M.; Suruchi; Anwer, T. *Eur. J. Med. Chem.* **2009**, *44*, 2636.
2. Reviews: (a) Bruneau, C. *Angew. Chem., Int. Ed.* **2005**, *44*, 2328; (b) Zhang, L.; Sun, J.; Kozmin, S. A. *Adv. Synth. Catal.* **2006**, *348*, 2271; (c) Jiménez-Núñez, E.; Echavarren, A. M. *Chem. Commun.* **2007**, 333; (d) Marion, N.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2750; (e) Hashimi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180; (f) Marco-Contelles, J.; Sariano, E. *Chem.—Eur. J.* **2007**, *13*, 1350; (g) Belmont, P.; Parker, E. *Eur. J. Org. Chem.* **2009**, 6075; (h) Marion, N.; Lemière, G.; Correa, A.; Costabile, C.; Ramón, R.; Moreau, X.; de Frémont, P.; Dahmane, R.; Hours, A.; Lesage, D.; Tabet, J.-C.; Goddard, J.-P.; Gandon, V.; Cavallo, L.; Fensterbank, L.; Malacria, M.; Nolan, S. P. *Chem.—Eur. J.* **2009**, *15*, 3243; (i) Hashimi, A. S. K. *Angew. Chem., Int. Ed.* **2010**, *49*, 5232; (j) Wang, S.; Zhang, G.; Zhang, L. *Synlett* **2010**, 692.
3. (a) Oh, C. H.; Karmakar, S. *J. Org. Chem.* **2009**, *74*, 370; (b) Barluenga, J.; Riesgo, L.; Vicente, R.; López, L. A.; Tomás, M. *J. Am. Chem. Soc.* **2008**, *130*, 13528; (c) Tejedor, D.; López-Tosco, S.; González-Platas, J.; García-Tellado, F. *Chem.—Eur. J.* **2009**, *15*, 838; (d) Tejedor, D.; López-Tosco, S.; González-Platas, J.; García-Tellado, F. *Chem.—Eur. J.* **2010**, *16*, 3276; (e) Kato, K.; Teraguchi, R.; Kusakabe, T.; Motodate, S.; Yamamura, S.; Mochida, T.; Akita, H. *Synlett* **2007**, 63.
4. Schwier, T.; Sromek, A. W.; Yap, D. M. L.; Chernyak, D.; Gevorgyan, V. *J. Am. Chem. Soc.* **2007**, *129*, 9868.
5. Kato, K.; Yamamoto, Y.; Akita, H. *Tetrahedron Lett.* **2002**, *43*, 6587.
6. (a) Chang, K.-H.; Gung, H.-L.; Lin, Y.-C. *Eur. J. Inorg. Chem.* **2006**, 649; (b) Semmelhack, M. F.; Bozell, J. J.; Keller, L.; Sato, T.; Spiess, E. J.; Wulff, W.; Zask, A. *Tetrahedron* **1985**, *41*, 5803.
7. (a) Maras, A.; Altay, A.; Ballini, R. *Synth. Commun.* **2008**, *38*, 212; (b) Ballini, R.; Petrini, M.; Rosini, G. *Synthesis* **1987**, 711.
8. Guntrum, E.; Kuhn, W.; Spönlein, W.; Jäger, V. *Synthesis* **1986**, 921.